WATER UPTAKE OF CALCIUM PERCHLORATE: AN INVESTIGATION OF STABLE AQUEOUS SOLUTIONS RELEVANT TO MARS. D. L. Nuding1,2, R. V. Gough1,3, V.F. Chevrier4, M. A. Tolbert1,3, 1Cooperative Institute for Research in Environmental Sciences, 2Department of Atmospheric and Oceanic Sciences, 3Department of Chemistry and Biochemistry; University of Colorado, Boulder, CO 80309. 4W. M. Keck Laboratory for Space and Planetary Simulation. Arkansas Center for Space and Planetary Science, University of Arkansas, Fayetteville, AR, USA.

The Wet Chemistry Laboratory (WCL) aboard the Phoenix Mars Lander identified the presence of 0.5% perchlorate [1]. Reanalysis of the Viking gas chromatography-mass spectrometry results 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 NaClO₄ and Mg(ClO₄)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 (recrystallization) of these salt solutions, expected due to the kinetic inhibition of crystal nucleation. The efflorescence relative humidity (ERH) 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(ClO₄)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.

To understand the likely phase of Ca(ClO₄)₂ on the Martian surface, we have used a Raman microscope equipped with an environmental cell to determine the DRH and ERH as a function of temperature (223 K to 273 K). Figure 1 depicts a typical Ca(ClO₄)₂ deliquescence experiment. Here the experiment begins with dry Ca(ClO₄)₂ at 1.4%. As relative humidity is increased to RH 14%, a hydrate forms as observed by optical microscopy as well as Raman peaks near 3500 cm⁻¹ from the O-H stretch. By 40% RH, both the Raman spectra and optical images suggest deliquescence to an aqueous solution.

Experimental results are compared to the calculated thermodynamic stability diagram for the CaClO₄·2H₂O system (Fig. 2). This figure shows the hydration states that may exist (anhydrous Ca(ClO₄)₂, Ca(ClO₄)₂·4H₂O and Ca(ClO₄)₂·8H₂O). We observe the deliquescence of at least two of these hydration states. Regardless of hydration state, Ca(ClO₄)₂ is highly deliquescent. At 243 K, the DRH is experimentally measured and also thermodynamically predicted to be lower than 40% RH.

Additionally, Ca(ClO₄)₂ efflorescence is found to occur at relative humidity values far below where deliquescence occurs, typically lower than 10% RH. Given that the surface RH on Mars likely varies from 0-100% throughout a diurnal cycle [6], it is likely that Ca(ClO₄)₂ salts could deliquescence, providing a mechanism for brine formation under present day Martian conditions.