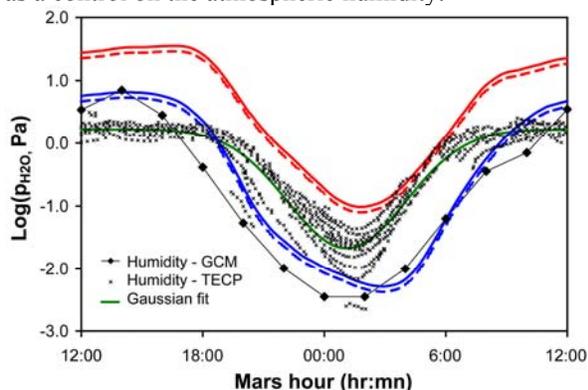


**REGOLITH CONTROL OF ATMOSPHERIC WATER VAPOR ON MARS FROM ANALYSIS OF PHOENIX TECP DATA.** V. F. Chevrier<sup>1</sup>, J. Hanley<sup>1</sup>, E. Rivera-Valentin<sup>1</sup>, <sup>1</sup>Arkansas Center for Space and Planetary Science, MUSE 202, University of Arkansas, Fayetteville, AR 72701, USA. [vchevrie@uark.edu](mailto:vchevrie@uark.edu)

**Introduction:** One of the most important results from Phoenix was the measurement of the atmospheric humidity using the Thermal and Electrical Conductivity Probe TECP [1], which allows studying the water cycle in fine details, especially at the diurnal timescale. During the summer where Phoenix performed its observations, the humidity profiles exhibits a very specific nearly Gaussian shape with a lower amplitude than described by purely atmospheric GCM models (Fig. 1). Alternatively if the humidity in the atmosphere controls possible liquids at the Phoenix landing site [2,3], their evaporation alone does not explain the shape of the pressure profile, suggesting that other controls are effective, especially during the day.

Phoenix showed the presence of ~1% perchlorate in the landing site regolith [4]. This ion is associated to sodium and magnesium [4], making these compounds ideal candidates controlling the water humidity through hydration-dehydration cycles. A second phenomenon is adsorption, which can also control the humidity especially at low temperatures [5,6]. In this abstract we focus on the effect of perchlorate hydrates as a control on the atmospheric humidity.

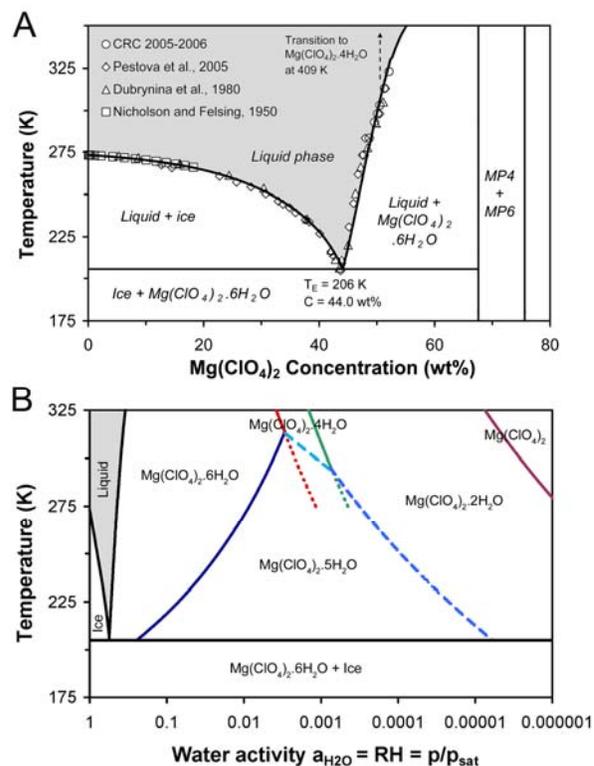


**Figure 1.** Atmospheric water vapor from TECP (crosses) compared to modelled values from the LMD-GCM (diamonds) and equilibrium values above eutectic solutions of NaClO<sub>4</sub> (dashed) and Mg(ClO<sub>4</sub>)<sub>2</sub> (plain) for the coldest (blue) and warmest (red) days.

**Control of humidity by perchlorates:**

*Thermodynamics of perchlorate hydrates:* The two main perchlorates suggested to be present in Phoenix soil are of magnesium Mg(ClO<sub>4</sub>)<sub>2</sub>.nH<sub>2</sub>O (0 ≤ n ≤ 6) and sodium NaClO<sub>4</sub>.nH<sub>2</sub>O (0 ≤ n ≤ 2). Potassium perchlorate has a very low solubility and does not form any hydrate and is therefore highly unlikely to participate in the humidity cycle. Figure 2A shows the thermodynamic diagram for Mg(ClO<sub>4</sub>)<sub>2</sub>, which exhibits a eutectic at 206 K, while NaClO<sub>4</sub> has a eutectic of 236

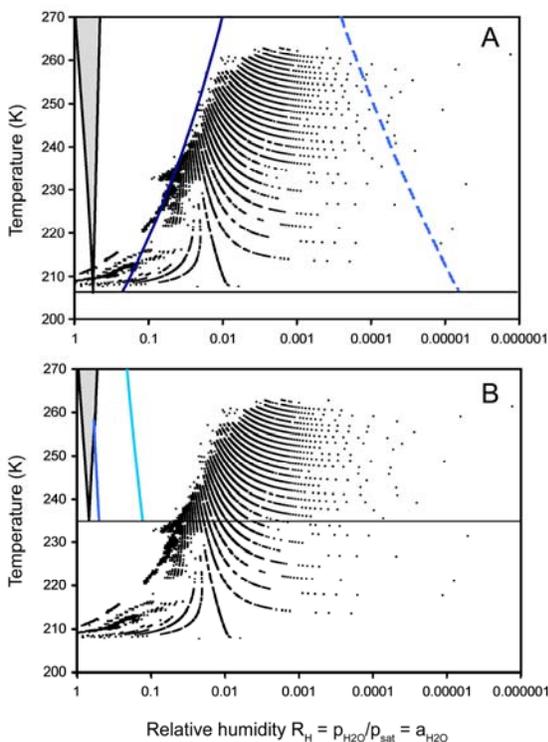
K [2]. Such diagrams represent equilibriums with the liquid phase (represented in shaded grey for reference). However, when equilibriums with the gas phase are also present it is more useful to represent these diagrams as a function of the water activity (in solution), which is equivalent to the relative humidity (in the gas phase, Fig. 2B). From previous experimental data [7], we observe an additional hydrate, which does not equilibrate with the liquid, only with the vapor phase. Various thermodynamic arguments suggest that this is a pentahydrate Mg(ClO<sub>4</sub>)<sub>2</sub>.5H<sub>2</sub>O, mostly stable at low temperature (< 300K) and low relative humidity (R<sub>H</sub> < 0.1-0.01).



**Figure 2.** Phase diagrams for Mg(ClO<sub>4</sub>)<sub>2</sub>. A. Temperature versus concentration from [2] and B. Temperature versus water activity / relative humidity. Solid lines are calculated from the experimental data of [7]. The equilibrium between the penta- (MP5) and the hexahydrate (MP6) has been extrapolated to low temperatures. Dashed lines are theoretical lines supposing a pentahydrate. Dotted lines are the extension of the data from [7] in the stability field of the pentahydrate.

*Humidity Control:* When looking at the activity of water versus temperature as measured by Phoenix (Fig. 3), we notice that the high humidity values are limited by two equilibriums in the Mg(ClO<sub>4</sub>)<sub>2</sub> stability field:

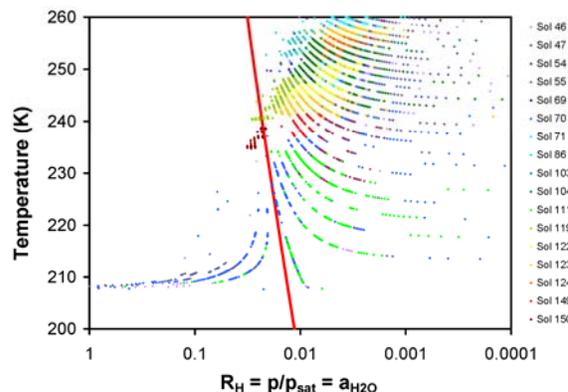
first the MP5-MP6 curve at high temperatures ( $220 < T < 260$  K) and by the eutectic limit at  $T < 220$  K (Fig. 3A). Almost all the data lie in the stability field of  $\text{Mg}(\text{ClO}_4)_2 \cdot 5\text{H}_2\text{O}$ , with only the data at low-T high RH being in the stability field of the hexahydrate. We also notice that the data largely extend beyond the T- $R_{\text{H}}$  limit for liquid (i.e. some data lay in the grey area and in the ice + liquid area at very high humidity). This suggests that liquids should form by possible melting of  $\text{MgClO}_4 \cdot 6\text{H}_2\text{O}$ .



**Figure 2.** Comparison of the temperature versus relative humidity ( $T$ - $R_{\text{H}}$ ) stability diagrams with the Phoenix humidity data for A. Magnesium perchlorate and B. Sodium perchlorate. Lines in Fig. A are identical to Fig. 2B with the solid line being the MP5-MP6 equilibrium and the dashed line the MP5-MP4 theoretical equilibrium. In Fig. B, the darker blue solid line is the sodium perchlorate SP1-SP2 (mono-dihydrate) equilibrium and the light blue is the SP1-SPO (mon-anhydrous) equilibrium.

By comparison, hydrates of  $\text{NaClO}_4$ , i.e. the mono- and dihydrate are stable at much too high  $T$ - $R_{\text{H}}$  ( $T > 236$  K,  $R_{\text{H}} > 0.1$ ) to affect the humidity at the Phoenix landing site (Fig. 3B). However, we observe an indent on the Phoenix humidity data at  $T \sim 233$ - $235$  K and  $R_{\text{H}} \sim 0.08 - 0.1$  which could be explained by the presence of the eutectic of sodium perchlorate at 236 K. However, the extremely low humidity compared to the values typical for sodium perchlorate make this kind of control quite unlikely. It is possible that other species than perchlorates could also control the humidity in this  $T$ - $R_{\text{H}}$  region.

Further experimental investigation into the nature of perchlorate hydration with atmospheric humidity is necessary, and especially to confirm the nature of the hydrate which controls most of the relative humidity.



**Figure 3.** Humidity data taken in the regolith. Each color corresponds to a different day. The thick red line corresponds to adsorption of almost one monolayer of water on the surface of grains calculated using the BET adsorption model. Note how the humidity data converge towards this line.

**Control of humidity by adsorption:** Adsorption has long been thought to be responsible for diurnal variations of atmospheric humidity [5,6]. The evaluation of its significance at the Phoenix landing site is complicated due to the lack of constraints on the exact nature and physical properties of the regolith (mostly specific surface area and adsorption constant) which can largely affect the resulting adsorption properties [8]. However, applying the BET adsorption theory with parameters for a volcanic tuff – sulfate mixture [8], we observe that the data converge towards an equilibrium line corresponding to nearly one adsorbed monolayer (0.85). We are still working on the significance of this observation and if adsorption is indeed responsible for the data behavior in this region of the  $T$ - $R_{\text{H}}$  space.

**Conclusions:** Our preliminary analysis shows that thermodynamic equilibria in the  $\text{Mg}(\text{ClO}_4)_2 - \text{H}_2\text{O}$  system control humidity at high  $R_{\text{H}}$  values. Our calculations suggest that adsorption could also affect humidity in the stability field of  $\text{Mg}(\text{ClO}_4)_2 \cdot 5\text{H}_2\text{O}$ , but further work is still required to confirm this hypothesis.

**References:** [1] Zent A. P. et al. (2009) *J. Geophys. Res.* In press. [2] Chevrier V. et al. (2009) *Geophysical Research Letters* 36. [3] Renno N. O. et al. (2009) *J. Geophys. Res.* 114. [4] Hecht M. H. et al. (2009) *Science* 325, 64-67. [5] Chevrier V. et al. (2008) *Icarus* 196, 459-476. [6] Zent A. P. et al. (2001) *J. Geophys. Res.* 106, 14667-14674. [7] Besley L. M., G. A. Bottomley (1969) *Journal of Chemical Thermodynamics* 1, 13-19. [8] Pommerol A. et al. (2009) *Icarus* 204, 114-136.