ATMOSPHERE-REGOLITH INTERACTIONS WITH A SALTY MARTIAN REGOLITH: THE ROLE OF HYDRATION AND DELIQUESCENCE ON THE MARTIAN WATER CYCLE. E. G. Rivera-Valentín, V. F. Chevrier, R. V. Gough, K. M. Primm, G. M. Martínez, and M. Tolbert; Lunar and Planetary Institute, Universities Space Research Association, Houston, TX (ervalentin@usra.edu), Department of Chemistry and Biochemistry, Univ. of Colorado, Boulder, CO, Department of Climate and Space Sciences and Engineering, Univ. of Michigan, Ann Arbor, MI.

**Introduction:** Perchlorate salts have now been identified in-situ by the Phoenix lander (PHX) [1], potentially at the two Viking sites [2], by the Mars Science Laboratory (MSL) [3], possibly in the form of hydrated calcium perchlorate [4], and from orbit at sites with recurring slope linear activity [5]. Such salts are interesting because of their ability to transition from a solid crystalline form into an aqueous solution given the appropriate environmental conditions (i.e., deliquescence) [6-9]. Were such transitions possible on present-day Mars, which depends on the kinetics of the process [8], deliquescence could act as a sink/source for near-surface water vapor on short timescales.

Hygroscopic salts, such as Ca(ClO₄)₂, could also undergo hydration/dehydration cycles since some have multiple hydration states. For example, calcium perchlorate has the tetrahydrate and octahydrate states [9]. Water uptake to produce the hydrate and subsequent release to produce the anhydrous or a lower hydrate form could potentially be another water vapor sink/source for atmosphere-regolith interactions on present-day Mars. Production of a stable hydrate form (one that does not dehydrate) could also act as a long-term water reservoir in the martian subsurface, potentially forming a perennally “wet” layer at depth [10].

Here we explore the role of a salty martian regolith on the near-surface water cycle on short timescales through either production of transient liquids or hydration/dehydration cycles of salts in the shallow subsurface. Data from MSL’s Rover Environmental Monitoring Station (REMS) along with a heat and mass transfer model [11] is used to investigate these processes in the subsurface. Additionally, the shallow subsurface conditions at PHX are simulated. The locations of these two missions are advantageous because they represent extreme conditions, the polar and equatorial regions, respectively. Thus, we can explore the variation of each process with respect to geography (latitude), terrain (thermal inertia), and availability of atmospheric water vapor.

**REMS Data Analysis:** MSL’s REMS is a suite of sensors recording daily air temperature, relative humidity, wind speed and direction at 1.6 m, along with the ground temperature, pressure, and ultraviolet radiation of the martian surface. Corrections to the data are applied to eliminate the rover’s influence as well as other factors that may be altering the measurement accuracy. Here, we used REMS measured air relative humidity w.r.t. ice (RH冰) and air temperature (T冰) at 1.6 m as well as the ground surface temperature (T地) through sol 1648. Ground relative humidity (RH地) was inferred assuming water vapor pressure is constant through the 1.6 m air column. T地 has a typical systematic error of ±1 K during daytime measurements, up to ±10 K at nighttime, while uncertainty in RH冰 is ±10% for 203 K ≤ T地 ≤ 243 K and ±20% for T地 < 203 K [12]. Propagating error, we found that most low RH地 have large errors that do not preclude the possibility of RH地 < 0%; therefore, this data was not included.

**Results:** In Fig. 1, we show the REMS data in terms of relative humidity w.r.t. liquid along with the Ca(ClO₄)₂ liquid phase diagram. Accounting for updated REMS data calibrations and comparing relative humidity values in consistent phase space, we found that no measured environmental conditions favor deliquescence of calcium perchlorate at the surface. Accounting for error, we found that to the 1-σ level deliquescence is still not favored; however, to the 2-σ level in T地 there are two points on sols 1232 and 1311, Ls 99° and Ls 137° respectively, that could be within the liquid phase. These values, delineated in Fig. 1, occurred while the rover was near active sand dunes during the early morning and late evening.

**Figure 1.** REMS data (cyan) compared to the liquid phase diagram of calcium perchlorate, where blue is DRH, red ERH, and black the ice line. Sol 1232 (magenta) and 1311 (purple) are shown with 2-sigma error.

**Modeling:** We apply a fully coupled, heat and mass transfer model to simulate the subsurface conditions at the PHX and MSL sites [11]. The thermal surface boundary condition is radiative and includes direct...
illumination, along with the scattering and thermal emission atmospheric components. Water vapor diffusion through the regolith is approximately Fickian, undergoes diffusion advection, and follows

\[ J_{DA} = \frac{\varphi}{\mu} \left( \frac{D_{H_2O/CO_2}}{RT} \frac{\partial y}{\partial z} + J_{DA} \right), \]

where \( \varphi = 0.5 \) and \( \tau = 2 \), are porosity and tortuosity respectively, \( \mu \) is the ratio between the molecular weights of \( H_2O \) and \( CO_2 \), \( D_{H_2O/CO_2} \) is the diffusivity of water vapor through \( CO_2 \) gas, \( P \) is air pressure, \( R \) is the ideal gas constant, and \( y \) is water vapor mixing ratio. Perturbations to diffusion, such as adsorption, are not considered.

For MSL, REMS in-situ surface humidity measurements are applied as a surface boundary condition. Various terrain thermal properties are explored as constrained in [13]. For PHX, we include an ice table at a depth of 10 cm and account for diffusion. Soil thermal properties are derived from [14], with an albedo of 0.2 and thermal inertia of \(~300 J m^{-2} K^{-1} s^{1/2}\).

**Results:** Thermal diffusion was simulated to a depth of 4 m with an element thickness of 0.01 m and time step of 370 s. Besides looking for favorable conditions for deliquescence, we also investigated hydrate phases as a function of temperature-humidity.

![Figure 2. Simulated subsurface conditions (gray scale) for the typical terrain encountered by MSL on the hydrate phase diagram of calcium perchlorate, where green is the tetrahydrate boundary and magenta is the 8:4 boundary. Gray scale represents depth from light to dark of 1 cm, 5 cm, 10 cm, 15 cm, and 20 cm.](image)

In Figure 2, we show the hourly temperature and relative humidity throughout a martian year at Gale crater for the typical terrain encountered by MSL (350 J m\(^{-2}\) K\(^{-1}\) s\(^{1/2}\), albedo of 0.2) at various depths, from 1 cm to 20 cm. Environmental conditions are compared to the hydrate phase diagram of calcium perchlorate. Results suggest a hydration cycle may be active in the shallow subsurface, with calcium perchlorate potentially transitioning between the octahydrate, tetrahydrate, and anhydrous; however, recent experimental results demonstrated that dehydration to the anhydrous was only possible at \( T \sim 290 \) K [15], which is not achieved at Gale. This may suggest the hydration cycle is limited to only the hydrated phases. Below some 15 cm, the temperature-humidity wave is dampened sufficiently to limit the time conditions would permit the formation of the tetrahydrate. Therefore for depths below 15 cm, the predicted stable phase of calcium perchlorate is the octahydrate, though depending on the kinetics of the process, an 8:4 transition may be inhibited. An active diurnal hydration/dehydration cycle, thus, may only occur at shallow depths.

**Conclusions:** Results shown in this abstract are for Gale crater, using MSL as constraints; however, results for PHX and a comparison between these contrasting latitudes will be presented at the workshop.

Data analysis suggests the surface environmental conditions of Gale crater as explored by MSL in the first 1648 sols are not favorable to the deliquescence of calcium perchlorate. On the other hand, subsurface simulations suggest that for certain terrains, specifically those with low thermal inertia (e.g., terrains of loose materials and active sand dunes), deliquescence is favored in the shallow subsurface. Assuming typical perchlorate salt concentrations (~0.5 wt% [3]) and that all the salt enters solution, brine abundance is expected to be low, up to ~1 wt% with ~0.5 wt% water in the regolith, and last for only 1 hr for a limited number of sols. Therefore at Gale crater, and potentially at other equatorial regions, deliquescence may not be an efficient sink/source for atmospheric water vapor. At polar regions, such as PHX, deliquescence is expected to play a more active role [9].

Simulations suggest that the shallow subsurface would permit for a diurnal hydration/dehydration cycle between the octahydrate and tetrahydrate. Assuming typical salt concentrations in the regolith, this results in an exchange of some ~0.2 wt% water vapor in the regolith. Salt hydration is thus comparable, in terms of magnitude, to deliquescence at Gale crater; however, hydration may occur throughout the year while deliquescence is limited to a few sols.

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