

ATMOSPHERE-REGOLITH INTERACTIONS THROUGH DELIQUESCENCE AS SUGGESTED BY THE PHOENIX LANDER AND THE MARS SCIENCE LABORATORY. E. G. Rivera-Valentín¹, D. L. Nuding², J. Hanley³; ¹Arecibo Observatory, Universities Space Research Association, Arecibo, PR (*ed@naic.edu*); ²Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109; ³Lowell Observatory, 1400 Mars Hill Rd, Flagstaff, AZ 86001.

Introduction: Deliquescence is the transition from a solid crystalline salt into an aqueous solution that occurs for hygroscopic salts. These salts, such as perchlorates, deliquesce when the ambient temperature is above the eutectic and when the relative humidity is above the deliquescent relative humidity (DRH). Experiments under Mars-relevant conditions [1-3] and Mars-like diurnal, subsurface conditions [3] have shown that perchlorates undergo hysteresis. The solution effloresces at a relative humidity, termed ERH, much lower than the DRH. For the case of calcium perchlorate, as low as ERH=5% [3]. The DRH and ERH are a function of temperature. Deliquescence has been found to be instantaneous, but the rate of liquescence thereafter is slow [4].

This process has been shown to be relevant to arid, terrestrial regions [5] and could play a role in atmosphere-regolith interactions on present-day Mars. Indeed, the Phoenix lander (PHX), which landed at 68.2°N, 234.4°E, suggested the presence of transient liquids in the subsurface via the observation of the heterogeneous distribution of salts [6] and the measured dielectric signatures [7] in the regolith. Subsurface simulations for PHX-relevant conditions along with experimental results suggest deliquescence could be the cause [3]. Additionally, the Mars Science Laboratory's (MSL) Rover Environmental Monitoring Station (REMS) has found that the near-surface environmental conditions at Gale crater permit the deliquescence of calcium perchlorate [8]. Thermodynamic data from both missions would also suggest active, exothermic reactions, such as liquescence, at these sites [9, 10]. Here we investigate the subsurface conditions at PHX and MSL in search for the appropriate environmental temperature and relative humidity that would allow for deliquescence of calcium perchlorate, a likely component of the regolith at both sites [11-13].

Methods: We apply a fully coupled, heat and mass transfer model to simulate the subsurface conditions at the PHX and MSL sites. The thermal surface boundary condition is radiative and includes direct illumination, along with the scattering and thermal emission atmospheric components [14-16]. Water vapor diffusion through the regolith, which has been shown to be approximately Fickian [17] and undergo diffusion advection [18], follows

$$J_{DA} = \frac{\varphi}{\tau\mu} \left(D_{H_2O/CO_2} \frac{P}{RT} \frac{d\gamma}{dz} + J_{DA} \right), \quad (1)$$

where $\varphi = 0.5$ [19] and $\tau = 2$ [20, 21], are porosity and tortuosity respectively, μ is the ratio between the molecular weights of H₂O and CO₂ and D_{H_2O/CO_2} is the diffusivity of water vapor through CO₂ gas, which is modeled as temperature dependent with nominal values on the order of 10⁻⁴ m² s⁻¹ [22], P is air pressure, R is the ideal gas constant, and γ is the water vapor missing ratio. The instantaneous γ at a given depth z and time t is found by

$$\frac{d\gamma}{dt} = D_{H_2O/CO_2} \frac{d^2\gamma}{dz^2} + \left(\frac{\mu RT}{P} \right) \xi, \quad (2)$$

where ξ is a reaction term that includes phase changes.

Mars Science Laboratory. Atmosphere-regolith water vapor transport is simulated by coupling our model with REMS in-situ humidity measurements as a boundary condition. We assume an albedo of 0.2, and a thermal inertia of ~300 J m⁻² K⁻¹ s^{-1/2}, which are parameters relevant to sandy terrains of Gale crater [23].

Phoenix Lander: For PHX, we include an ice table at a depth of 10 cm and account for diffusion. Soil thermal properties are derived from [19], with an albedo of 0.2 and thermal inertia of ~300 J m⁻² K⁻¹ s^{-1/2}.

Results: We simulated thermal diffusion to a depth of 4 m with an element thickness of 0.01 m and time step of 370 s. Several martian years are simulated until the temperature profile at the vernal equinox from the previous year is nearly identical to that of the current simulation, at which point convergence is reached.

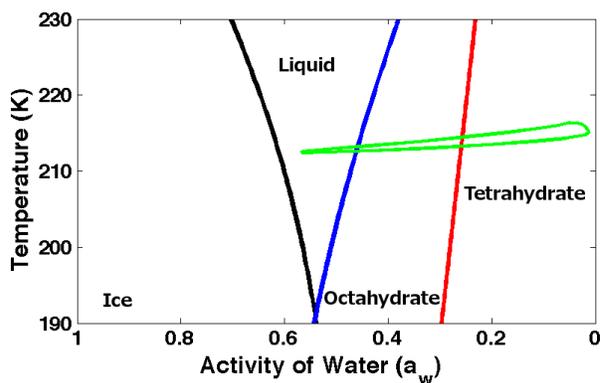


Figure 1. Phase diagram for calcium perchlorate including the simulated diurnal cycle (green) for Ls 141 at 15 cm. The black line is the solidus, blue is DRH, and red is ERH.

Mars Science Laboratory. Though on the surface and near-surface (*i.e.*, within the top ~ 5 cm), the conditions required for deliquescence for calcium perchlorate occur, they are found to only last for less than an hour. Moreover, the conditions quickly enter the solidus, and so any solution formed would transition to ice. However, in the deeper subsurface, the attenuated temperature and resulting relative humidity, avoid the transition to the ice phase. In this scenario, a solution is present for several hours, and can effloresce.

Phoenix Lander: Similar conditions are found at PHX, where solutions transition to ice and are not allowed to effloresce in the near-surface. However, unlike at MSL, an aqueous solution at the near-surface is present for longer time periods.

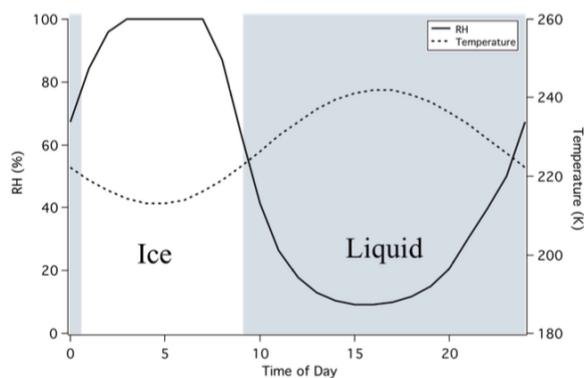


Figure 2. Simulated subsurface conditions for PHX at a depth of 3 cm for temperature (dashed line) and RH (solid line). Liquid here lasts for several hours at depth, but transitions to the ice phase without efflorescing. *Image credit:* Figure 12 [3].

Conclusions: Our results suggest that water vapor can be stored within the regolith via deliquescence of calcium perchlorate. In the top, few meters of soil, the stored water vapor would be released by sublimation after the solution transitions to the ice phase. Deeper in the regolith, though, the attenuation of the diurnal temperature permits solution activity for longer periods until the ERH is met. At these depths, water vapor would instantly be released, and would diffuse through ~15 cm of regolith.

The efficacy of deliquescence as a water vapor sink and source in the regolith is dependent on the amount of perchlorate salts. Both PHX and MSL suggest an abundance of 0.3 – 0.5 wt% [12, 24]. Though the abundance is rather low, perchlorates are suggested to be globally distributed on Mars. Therefore, this process may play an important role in the near-surface water cycle on present-day Mars.

References: [1] Zorzano, M.-P. et al. (2009) *GRL*, 36, L20201. [2] Gough, R. V. et al. (2011) *EPSL*, 312, 371-377. [3] Nuding, D. L. et al. (2014) *Icarus*, 243, 420-428. [4] [5] Davila, A. F. et al. (2010) *Astrobiology*, 10, 617-628. [6] Cull, S. C. et al. (2010) *GRL*, 37, L22203. [7] Stillman, D. E. and Grimm, R. E. (2011) *JGR*, 116, E09005. [8] Martin-Torres, F. J. et al. (2015) *Nat. Geo.*, 8, 357-361. [9] Rivera-Valentin, E. G. and Chevrier, V. F. (2015) *Icarus*, 253, 156-158. [10] Estevez-Galarza, C. A. and Rivera-Valentin, E. G. (2016) *LPSC*, Abstract#1268. [11] Leshin, L. A. et al. (2013) *Science*, 341. [12] Glavin, D. P. et al. (2013) *JGR-Planets*, 118, 1 – 19. [13] Ming, D. W. et al. (2014) *Science*, 343. [14] Applebaum, J. and Flood (1989) *NASA Technical Memorandum* 1 – 34. [15] Aharanson, O. and Schorghofer, N. (2006) *JGR*, 111, E11107. [16] Schmidt, F. et al. (2009) *Icarus*, 200, 374. [17] Clifford, S. M. and Hillel, D. (1986) *Soil Science*, 141, 289-297. [18] Ulrich, R. K. (2009) *Icarus*, 201, 127-134. [19] Zent, A. P. et al. (2010) *JGR*, 115. [20] Hudson, T. and Aharanson, O. (2008) *JGR*, 113. [21] Sizemore, H. G. and Mellon, M. (2008) *Icarus*, 197, 606-620. [22] Chevrier, V. F. et al. (2007) *GRL*, 34. [23] Martinez, G. M. et al. (2014) *JGR Planets*, 119. [24] Hecht, M. H. et al. (2009) *Science*, 325, 64.

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