

DELIQUESCENCE-INDUCED HYDRATION OF SUBSURFACE MINERALS AT GALE CRATER, MARS.

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Introduction: Calcium perchlorate ($\text{Ca}(\text{ClO}_4)_2$) is suggested as a likely component of Gale crater's regolith [1] and has been demonstrated experimentally to be highly deliquescent [2], with an eutectic temperature of $T_e \sim 196$ K and corresponding deliquescent relative humidity of $DRH \sim 0.5$. Recently, the Mars Science Laboratory's (MSL) Rover Environmental Monitoring Station's (REMS) measurements of the near-surface environmental conditions were found to suggest that deliquescence of $\text{Ca}(\text{ClO}_4)_2$ is possible on the surface and shallow subsurface [3], which was a surprise as this process was thought to only be possible polewards of 60° [4]. Brines produced in this manner have been observed not to effloresce until much lower relative humidities of $ERH \sim 3\%$ [2], allowing for transitions into hydrated phases such as $\text{Ca}(\text{ClO}_4)_2 \cdot 8\text{H}_2\text{O}$ and $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ while a liquid is present. Re-transitioning to the anhydrous phase is difficult since it requires relative humidities approaching zero.

MSL's Dynamic Albedo of Neutrons (DAN) instrument has detected a subsurface layer ~ 17 cm deep with an increase in water equivalent hydrogen, indicative of a hydrated region [3]. The temperature (T) and relative humidity (RH) inferred at this depth from REMS would allow for hydrated phases of $\text{Ca}(\text{ClO}_4)_2$. Because of the dampening of T and RH at this depth, which is below the diurnal skin-depth (~ 5 cm), transitions to the anhydrous phase are not expected. A permanently hydrated layer may then be produced. However, hydrated phases are kinetically easier to produce if the system passes through a liquid phase first. Here we use experimental constraints [2] and thermal modeling [5] to simulate the behavior of $\text{Ca}(\text{ClO}_4)_2$ in the subsurface of Gale crater to test if the system deliquesces and transitions into a hydrated phase before it dehydrates into the anhydrous.

Methods: Atmosphere-regolith water vapor transport is simulated by coupling a heat and mass transfer model [5] with REMS in-situ humidity measurements as a boundary condition for the surface. We assume an albedo of 0.2, and a thermal inertia of $\sim 300 \text{ J m}^{-2} \text{ K}^{-1} \text{ s}^{-1/2}$, which are parameters relevant to sandy terrains of Gale crater [6]. The surface boundary condition is radiative and includes direct illumination, along with scattering and thermal emission atmospheric components [7, 8, 9]. Water vapor diffusion through the regolith, which has been shown to be approximately Fick-

ian [10] and undergo diffusion advection [11], follows

$$J_{DA} = \frac{\varphi}{\tau\mu} \left(D_{\text{H}_2\text{O}/\text{CO}_2} \frac{P}{RT} \frac{d\gamma}{dz} + J_{DA} \right), \quad (1)$$

where $\varphi=0.5$ [12] and $\tau=2$ [13, 14], are porosity and tortuosity respectively, μ is the ratio between the molecular weights of H_2O and CO_2 , and $D_{\text{H}_2\text{O}/\text{CO}_2}$ is the diffusivity of water vapor through CO_2 gas, which is modeled as temperature dependent with nominal values on the order of $10^{-4} \text{ m}^2 \text{ s}^{-1}$ [15, 16], P is air pressure, R is the ideal gas constant, and γ is the water vapor mixing ratio. The instantaneous γ at a given depth z and time t is found by,

$$\frac{d\gamma}{dt} = D_{\text{H}_2\text{O}/\text{CO}_2} \frac{d^2\gamma}{dz^2} + \left(\frac{\mu RT}{P} \right) \xi, \quad (2)$$

where ξ is a reaction term that includes phase changes.

Results: We simulate 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.

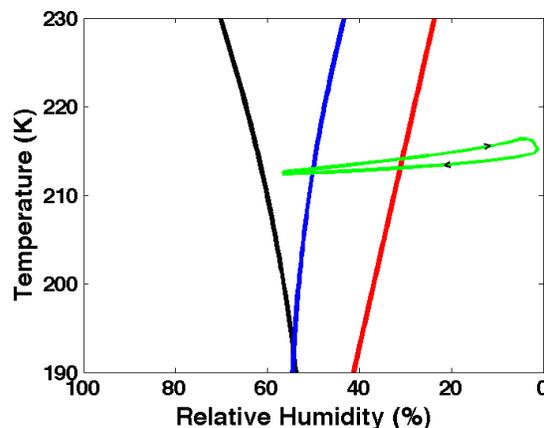


Figure 1: Phase diagram for calcium perchlorate including the simulated diurnal cycle (green) for $\text{Ls } 141^\circ$ at 15 cm. The black line is the solidus, blue is DRH, and red is ERH. The arrows indicate the progression for morning to evening.

In Fig. 1, the diurnal profile at 15 cm deep is plotted against the phase diagram of $\text{Ca}(\text{ClO}_4)_2$ at $\text{Ls } 141^\circ$. On this sol, deliquescence occurs near 1400 LST. This is in contrast to the expected morning and late evening hours from [3], which is due to the thermal diffusion

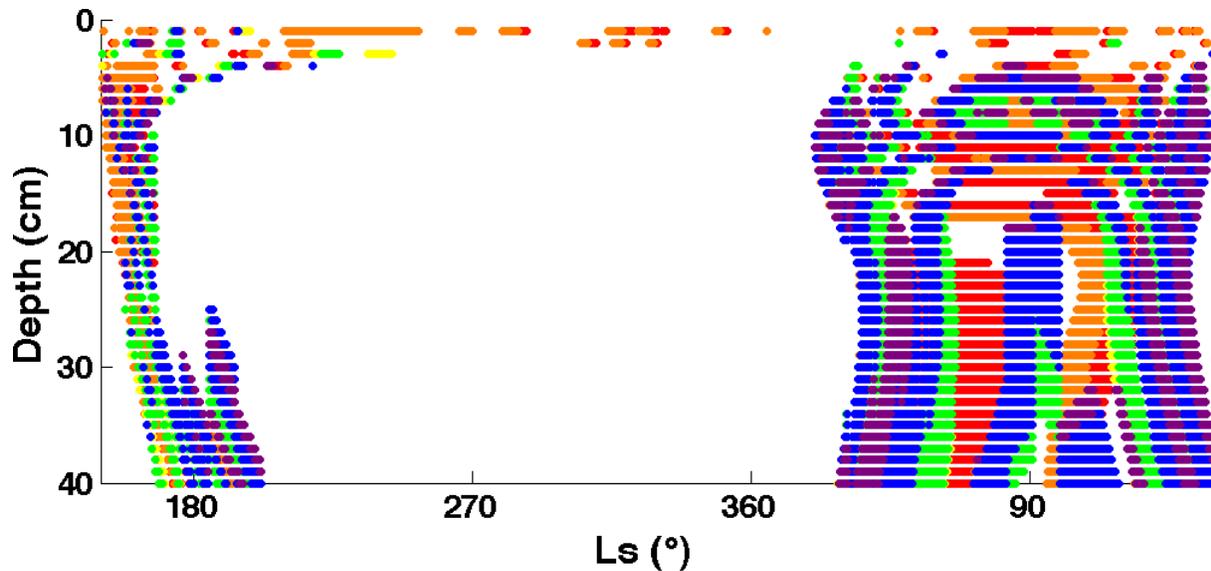


Figure 2: Location in depth (cm) and time (Ls) of the aqueous solution in the subsurface of Gale crater. The colors represent the RH during the presence of the brine, where red = 55%-60%, orange = 50%-55%, yellow = 45%-50%, green = 40%-45%, blue = 35%-40%, and violet is anything <35%.

timescales. An aqueous solution remains until 1900 LST when the ambient conditions induce efflorescence. For the next few sols, the minimum $RH \sim 2\%$, therefore the hydrate is not expected to transition to anhydrous.

In general, we find that deliquescence of calcium perchlorate is possible to depths of 40 cm, assuming the salt is present (Fig. 2). Our results suggest that RH near 0% may occur for depths above ~ 10 cm and so formed hydrates could revert to anhydrous. The minimum annual RH at depths near 15 cm, though, does not permit dehydration; therefore, a permanently hydrated layer may form. Of note, these results are best suited for sandy terrains traversed by the rover with thermal inertias close to $\sim 300 \text{ J m}^{-2} \text{ K}^{-1} \text{ s}^{-1/2}$ such as Rocknest and Dingo Gap [6].

Conclusions: We address the DAN inferred subsurface “wet” layer at Gale crater, Mars [3] by simulating the behavior of calcium perchlorate, a likely component of the regolith [1], using a coupled heat and mass transfer model [5] along with experimental constraints [2]. Our results suggest that deliquescence of $\text{Ca}(\text{ClO}_4)_2$ may be possible to depths of 40 cm, assuming the salt is present. At depth, the formed brine remains stable for much longer periods and experiences water activities ranging from $0.3 \lesssim a_w \lesssim 0.6$, while at shallow depths (< 5 cm) more constrained activities are only possible, typically $0.4 \lesssim a_w \lesssim 0.6$.

The environmental conditions while the brine is present may permit for the transition into hydrated phases at depths below 5 cm; however, RH for depths above ~ 15 cm permits the re-formation of the anhydrous phase. Therefore at depths near the DAN

inferred hydration region (~ 17 cm), our results suggest RH does not reach 0%, inhibiting dehydration of the hydrated salt phases.

Our results combined with DAN and REMS observations imply that a subsurface “wet” layer at Gale crater may be formed ~ 15 cm deep by hydrated salts, which are produced during deliquescence. Additionally, we propose that deliquescence-induced hydration of subsurface minerals on Mars may act as an active sink for atmospheric water vapor.

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