

FORMATION OF (META)STABLE BRINES ON PRESENT-DAY MARS: IMPLICATIONS FOR HABITABILITY. E. G. Rivera-Valentín¹, V. F. Chevrier², A. Soto³, G. Martínez¹; ¹Lunar and Planetary Institute (USRA), Houston, TX 77058. ²Arkansas Center for Space and Planetary Sciences, University of Arkansas, Fayetteville, AR 72701, ³Southwest Research Institute, Boulder, CO 80302.

Introduction: Whether present-day Mars can support terrestrial-like life depends on multiple factors, such as temperature, radiation, and availability of nutrients, and, importantly, liquid water. Pure liquid water, though, is unstable on the Martian surface due to rapid phase changes. With an average surface pressure of 600 Pa, the boiling point on Mars is ~ 273 K, and with an average surface temperature of ~ 220 K pure liquid water rapidly freezes. Additionally, in-situ meteorological measurements have indicated that, at most, the near-surface water vapor pressure reaches some $e \approx 2$ Pa [1]. Thus to avoid rapid evaporation, pure liquid water would need to be stable at ~ 215 K, well below its freezing point. Even in the shallow subsurface where evaporation is slowed due to diffusion through a porous overburden [2] the large concentration gradient can quickly drive mass loss.

Brines, though, are proposed to form and persist as they have increased stability against the cold and hyper-arid surface conditions. Salty aqueous solutions have reduced water vapor pressures above the liquid because their water activity $a_w < 1$, where $a_w = e_b/p_{sat,l}$, e_b is the water vapor pressure above the brine, and $p_{sat,l}$ is the temperature (T) dependent saturation vapor pressure above pure liquid water. This results in a brine boiling at a higher temperature and evaporating slower. Dissolved salts also lead to reduced freezing temperatures. As such, brines are stable under a broader range of Mars-relevant environmental conditions. Brines may be forming on Mars through melting via salt-ice interactions, such as at the regolith-ice table interface [3], or via salt deliquescence [4-6]. Furthermore, experimental work under Mars-relevant conditions have shown that brines may persist beyond their predicted stable region, leading to metastable liquids [5,7].

To date, though, the only potential direct observation of liquid on Mars were droplets on the struts of the Phoenix lander [8]. Phoenix (PHX) also provided indirect evidence of brine formation in the subsurface by way of variations in the measured dielectric properties of the regolith [9] and the heterogeneous distribution of salts [10]. In-situ meteorological measurements by PHX further support brine formation through both melting [3] and deliquescence [11], while measurements by the Mars Science Laboratory (MSL) support the potential formation of brines by deliquescence at the near-surface of low thermal inertia terrains [6].

Here we explore the stability of brines on Mars, by reviewing recent work [12,13] that has used in-situ measurements and general circulation models to predict where, when, and for how long brines may be stable on the near-surface. We particularly focus on calcium perchlorate due to its low freezing-point ($T = 198$ K) at $a_w = 0.52$. The Mars Special Regions criteria (water activity $a_w \geq 0.6$ and temperature $T \geq 255$ K) [14] is adopted to assess the habitability of such brines.

Methods: For this study, we used the Mars Weather Research and Forecasting (MarsWRF) general circulation model (GCM). For surface temperature calculations, a multilayer subsurface thermal diffusion and surface energy balance model uses surface albedo and thermal inertia maps derived from orbital observations. For the water cycle, MarsWRF employs the microphysics scheme implemented by [15]. For this work, simulations were run at 5° by 5° horizontal resolution with 52 vertical levels. Simulated hourly surface temperature, pressure, and water mixing ratio, which we then translated to relative humidity w.r.t. liquid (RH_l), were then used to test for brine formation and stability. Additionally, we used temperature and humidity measurements by PHX and MSL.

Results: In Fig. 1, we plot the simulated combinations of temperature and relative humidity w.r.t. liquid experienced on the martian surface, against in-situ measurements, the deliquescence relative humidity (DRH) of calcium, magnesium, and sodium perchlorate, and the ice line (i.e., where saturation w.r.t. ice is reached, $RH_{ice} = 100\%$).

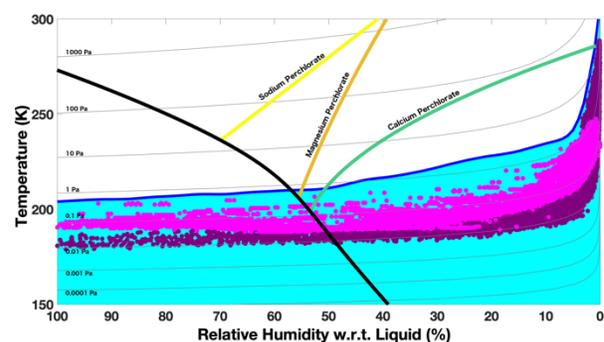


Figure 1: Phase diagram for Mars-relevant deliquescent salts along with the possible combination of conditions as simulated by the MarsWRF GCM (cyan space) and PHX (magenta) and MSL (purple) in-situ measurements. Light gray lines are isobars of constant water vapor pressure.

In order for a brine to be stable on the surface of Mars against freezing and evaporation, its freezing point, which follows the ice line, must be within the possible combination of temperature and relative humidity that can occur on Mars. Should a brine form outside of this phase space, it would quickly evaporate away due to the high vapor pressure associated with its liquid phase. As such, from Fig. 1 we see that Mars-relevant brines are those with freezing temperatures < 210 K.

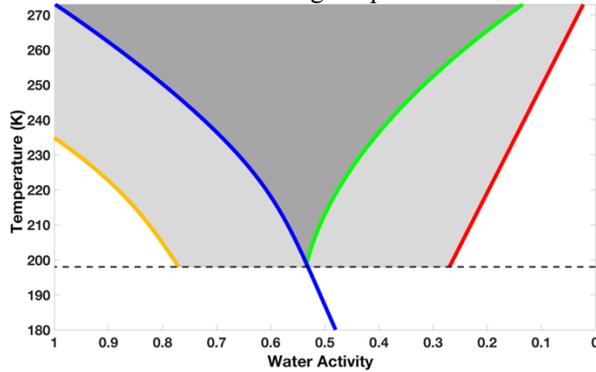


Figure 2: Phase diagram for $\text{Ca}(\text{ClO}_4)_2$ including stable (dark gray) and metastable (light gray) liquid phases. Blue is the ice line, green is DRH, red is ERH, and orange is $RH_{ice} = 145\%$.

In Fig. 1, we also see that calcium perchlorate should more readily lead to brine formation through deliquescence. As such, we further explored its stability on Mars. In order for a salt to deliquesce, the temperature must be above the eutectic and $RH_l > \text{DRH}$. Though thermodynamically solutions should recrystallize once $RH_l < \text{DRH}$, due to a hysteresis effect, efflorescence occurs at a lower relative humidity [4,5], allowing for metastable liquids. Furthermore, experiments under Mars-like conditions have shown that solutions persist even after saturation with respect to water ice is reached [7], up to $RH_{ice} = 145\%$. In Fig. 2, we show the stable and metastability conditions for $\text{Ca}(\text{ClO}_4)_2$.

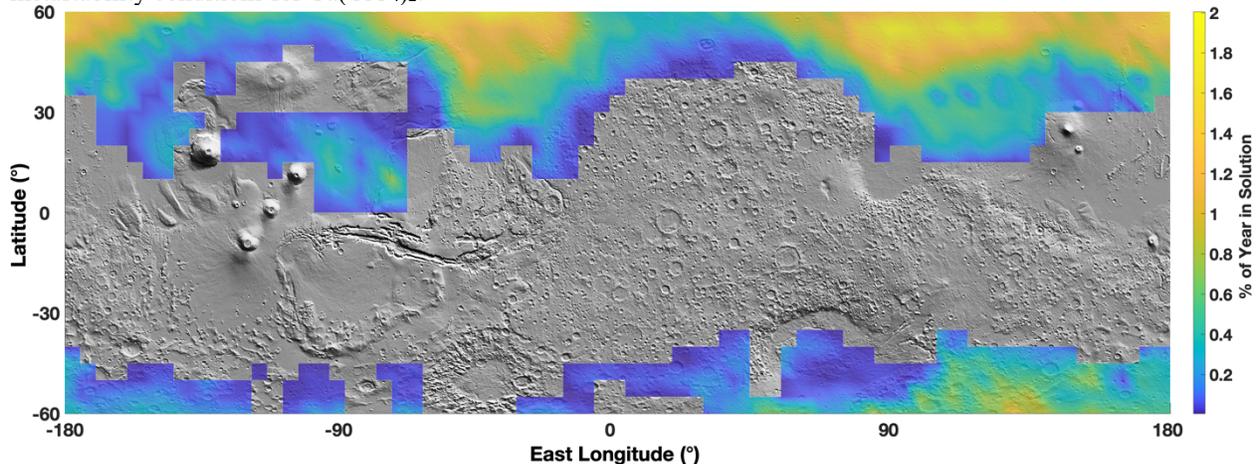


Figure 3: Modeled stable calcium perchlorate brines formed via deliquescence on the surface of Mars. The percent of the year a solution is present is shown in color overlay onto a shaded relief map of Mars.

Given the experimentally-constrained (meta)stable phase space for $\text{Ca}(\text{ClO}_4)_2$, we used the model outputs from MarsWRF to investigate where, when, and for how long such solutions could form via deliquescence (Fig. 3). $\text{Ca}(\text{ClO}_4)_2$ brines can form over some 40% of the Martian surface. These brines are most likely at high northern latitudes, where they are (meta)stable for up to 2% of the year. Although $\text{Ca}(\text{ClO}_4)_2$ brines may persist for at most half a sol per sol, they may be liquid for at most six consecutive hours. In the northern hemisphere, $\text{Ca}(\text{ClO}_4)_2$ brines occur around $L_s 140^\circ$ while in the southern hemisphere around $L_s 225^\circ$.

We find that the maximum water activity of such brines is 0.8 with a corresponding temperature of 205 K. These conditions are met just before complete freezing. On the other hand, the maximum possible brine temperature is 225 K with an associated $a_w = 0.24$. These conditions are met just prior to efflorescence. As such, although metastability extends the locations where brines may form, they do not simultaneously meet the required conditions for habitability.

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