PRELIMINARY IN-SITU AND MODELING RESULTS OF DELIQUESCENCE AND EFFLORESCENCE OF MAGNESIUM PERCHLORATE MIXED WITH REGOLITH. D. E. Stillman¹, K. M. Primm¹, and T. I. Michaels², ¹Dept. of Space Studies, Southwest Research Institute, 1050 Walnut St. #300, Boulder, CO 80302. ²SETI Institute, 189 Bernardo Ave Suite 200, Mountain View, CA 94043. (<u>dstillman@boulder.swri.edu</u>)

Introduction: Perchlorates (ClO₄⁻) are highly hygroscopic salts and are ubiquitous within the martian regolith, raising the possibility of brine on much of Mars. Several findings suggest that liquid brines might be possible on the surface of Mars today due to either deliquescence (salts absorbing water vapor, transitioning to a saturated liquid solution) or the freezing point depression of the salt (melting occurring when the salt is in contact with water ice) [2-5]. Possible detections of liquid water on Mars have been hypothesized to occur below the Southern Polar Layer Deposits (SPLD) in the form of a subglacial lake [6-7] and within Recurring Slope Lineae (RSL) [8].

However, there is a large gap in the understanding of the complex interaction between salt, water-vapor, and regolith under Martian conditions. Experiments done by Tolbert's research group [e.g., 2,4,5,9] and *Nikolakakos and Whiteway* [10] confirm that deliquescence occurs within minutes when the liquid phase is thermodynamically favored. However, experiments by *Fischer et al.* [11] demonstrate that deliquescence via water vapor takes over 3.5 hours to start, implying that deliquescence could not currently take place near Mars' surface.

To determine if deliquescence can occur within martian regolith, we constructed a Mars chamber in which we controlled temperature and relative humidity of a sample comprised of simulated martian regolith mixed with geologically-relevant amounts of perchlorate. We monitored the amount of brine using electrical property measurements during experiments that lasted for days.

Electrical properties of materials are represented by the real part of the relative dielectric permittivity ε' that represents charge storage in bound charges, and whose imaginary part ε'' represents energy loss. Briefly, the dielectric permittivity drastically changes when liquid water is present (e.g., ice $\varepsilon'=3.1$, salt hydrate $\varepsilon'=4.5$, while liquid water $\varepsilon' \sim 80$). Through this measurement, we are able to unambiguously determine if liquid water is within our sample.

In addition to our chamber experiments, we are developing a salt kinetics model to better model the migration of subsurface H₂O, including salt effects.

Mars Chamber: We commissioned a custom-built Mars chamber (**Fig. 1**) that is able to: control temperature via a LN_2 cold plate with temperature-controlled heaters within the cold plate, humidify CO_2 flow controlled by Alicat mass flow controllers, monitor the relative humidity with a Vaisala DMT 152 dew point transmitter, and hold the chamber pressure at Mars values with a Welch vacuum pump. This Mars chamber allows us to place our three-electrode sample holder [e.g., 12,13] onto the cold plate to simultaneously measure the electrical properties, temperature, pressure, and relative humidity within the chamber.

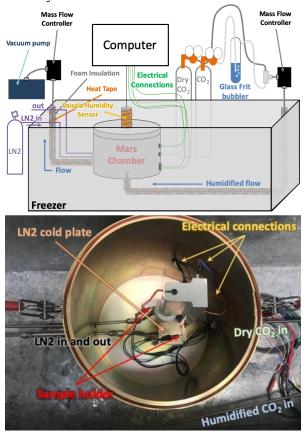


Figure 1. (top) Diagram of our Mars chamber. (**bot-tom**) The electrical leads are connected to the Solartron 1260A\1296A Impedance Analyzer and Dielectric Interface.

Model Methods: To realistically model the Martian subsurface environment to determine under what conditions Mg(ClO₄)₂ would deliquesce, freeze, or effloresce, we modified MarsFlo [e.g., 14] and integrated it with the Mars Atmospheric Regional Modeling System (MRAMS [15]). The role of the MarsFlo component was to simulate three-phase (liquid, ice, vapor) H₂O migration and thermal evolution in porous media, while the MRAMS component would provide realistic surface boundary conditions (surface energy balance, atmospheric pressure, and water vapor content) as functions of time-of-day, season, and latitude. Since MarsFlo could not explicitly include the effects of salt, we have named our version MarsFloSalt.

Results: Several different experiments were performed to test the apparatus out (Fig. 2). The black dotted line shows that pure fine sand does not increase in permittivity when the humidity is high, confirming that when the permittivity of the perchlorate and sand mixture increases, it is due to the perchlorate absorbing the water. The gray line (2.5 wt% magnesium perchlorate) shows that after the first day when the humidity is near the deliquescence relative humidity, the permittivity immediately increases. Although deliquescence starts immediately, it takes almost a full day for deliquescence to completely saturate the pores. The second row in Fig. 2 shows how using a power law mixing of the high-frequency real part of dielectric constant can be used to model the volume percent of the brine. Note that the brine fills the pore space as more water vapor is deliquesced into the sample.

An example of MarsFloSalt results for near-equatorial Mars conditions is provided below (**Fig. 3**). **Conclusion:** The results show that deliquescence does occur quickly at warmer temperatures, and continues to occur over a time period of about a day until the entire regolith is saturated with brine. Future measurements will investigate if similar behavior occurs at colder temperatures and how kinetics might also change this behavior.

Our results also showed that even at very low concentrations (0.5 wt%) the effect of deliquescence was easily observable. However, our JSC Mars-1 measurements did not convince us that any deliquescence in that medium was ever measured. Future measurements will investigate this behavior. **References:** [1] Hecht et al. (2009) *Icarus*, 233, 36-47. [2] Gough et al. (2011) *EPSL*, 312, 371-377. [3] Toner et al. (2014) *Icarus*, 233, 36-47. [4] Nuding et al. (2014) *Icarus*, 243, 420-428. [5] Primm et al. (2017) *GCA*, 212, 211-220. [6] Orosei et al. (2018) *Science*, 361, 490-493. [7] Sori and Bramson (2019) *GRL*, doi: 10.1029/2018GL080985, 1-10. [8] Ojha et al. (2015) *Nat. Geosci.*, doi: 10.1038/NGEO2546, 1-4. [9] Primm et al. (2018) *JGR: Planets*, 123, 2076-2088. [10] Nikolakakos and Whiteway (2015) *GCA*, 42, 7899-7906. [11] Fischer et al. (2016) *Astrobio.*, 16, 937-948. [12] Stillman et al. (2010) *JPC B*, 114,6065-6073 [13] Stillman et al. (2013) *JGR: Earth Surface*, 1, 1-16. [14] Painter (2011) *Comput. Geosci.*, 15, 69-85. [15] Michaels and Rafkin (2008) *JGR*, 113, doi:10.1029/2007JE003013.

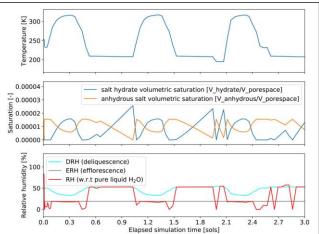


Fig. 3. Time-series (3 Mars-days, or sols, in duration) from a low-salinity $Mg(ClO_4)_2$ MarsFloSalt model run. Note that nearly all the H₂O in the system evaporates/sublimates quickly, and afterwards, the moisture and phase variations seen are due to salt deliquescence and efflorescence. (**top**) Ground surface temperature. (**middle**) Volumetric saturation of salt hydrate and anhydrous salt and (**bottom**) RH in the shallow surface.

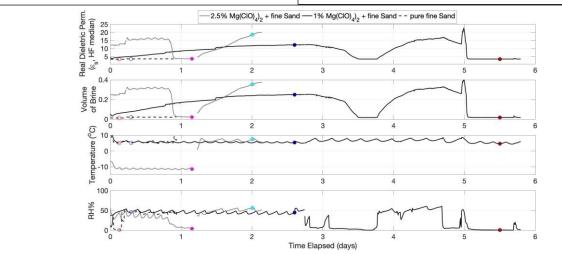


Fig. 2. Mars chamber results of dielectric permittivity and volume of brine throughout temperature and relative humidity changes. Three cases: 2.5 wt% and 1 wt% magnesium perchlorate with fine sand, and pure fine sand alone. Colored circles mark traces of interest that will be presented.