

**EXPERIMENTAL SIMULATION OF CALCIUM PERCHLORATE LIQUID BRINE FORMATION THROUGH DELIQUESCENT ON MARS.** R. A. Slank<sup>1</sup>, V. F. Chevrier<sup>1</sup>, E. G. Rivera-Valentin<sup>2</sup>, <sup>1</sup>Arkansas Center for Space and Planetary Science, University of Arkansas, 346 Arkansas Ave., Fayetteville, AR 72701, <sup>2</sup>Lunar and Planetary Institute, USRA, Houston, TX, rslank@uark.edu.

**Introduction:** Variability in the parameters of Mars' orbit allows for mass transport of seasonal water vapor from the equatorial regions to the poles. The stability of this water ice on Mars is largely due to the diffusive and thermal properties of the regolith. While diffusion can explain this process over large timescales, the dynamics of water vapor at shorter timescales (day to year) remain largely unknown. Local effects, mostly related to phase changes of water, including adsorption [1], melting of ice [2], interaction with hygroscopic salts, like perchlorates [3, 4, 5] through hydration, deliquescence, and dissolution [2, 5, 6], the presence of an ice layer [1], can all be attributed to this uncertainty. Experimental work thus far has focused on defining the phase space for Mars-relevant brines, but not much work has been done to define the stability of these brines under Mars-like conditions. Therefore, deliquescence experiments were conducted in a simulation chamber that can mimic Martian pressure, temperature, and atmospheric composition. These experiments are vital in understanding how the water vapor diurnal or seasonal cycle can allow for the creation of liquid water on the surface of Mars.

A series of experiments were conducted, which focused on determining water vapor transfer and deliquescence by weight, temperature, and relative humidity between the atmosphere and a layer of JSC Mars-1 regolith simulant with varying concentrations of  $\text{Ca}(\text{ClO}_4)_2$  (0-5 wt.%). The experiments were conducted to understand the range over which deliquescence may account for brine formation. All the experiments were conducted in the Ares Mars simulation chamber at the University of Arkansas.

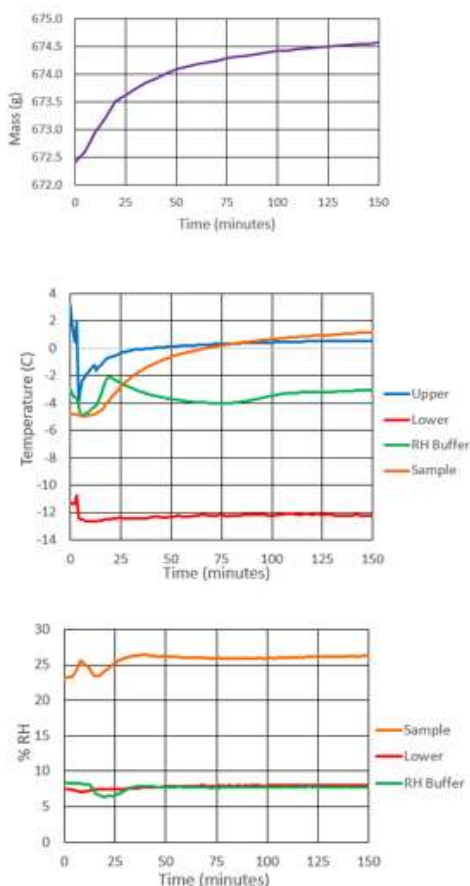
**Methodology:** The temperature varied from  $-15^\circ$  to  $8^\circ\text{C}$ . A lithium chloride humidity buffer was placed in the chamber, near the sample, creating a stable humidity in the chamber. JSC Mars-1 was baked for 24 hours above  $100^\circ\text{C}$ , placed in a desiccator, pulled to vacuum, and then placed in a freezer to cool to  $-50^\circ\text{C}$ . The JSC Mars-1 regolith varied from 0.5-1.5 cm in depth. The calcium perchlorate salt was placed in a desiccator, pulled to vacuum, and then placed in a freezer. The calcium perchlorate was weighed at 0, 1, 3, or 5wt% and then evenly mixed within the regolith. Although there was a short exposure to the atmosphere while the sample was removed from the desiccator and placed in the chamber, the chamber was filled with  $\text{CO}_2$  to help prevent water contamination. The entire exposure time was less than 120 seconds.

**Results and Discussion:** Using a lithium chloride humidity buffer (maintaining an average humidity of  $11.2\% \pm 0.5$  at  $0^\circ\text{C}$  in the atmosphere) at the minimum weight percent and sample depth we found potential deliquescence at the surface, through visual observations, temperature and humidity changes, and increase in mass. The lithium chloride humidity buffer (Fig. 1 and Fig. 2), sampled over the humidity buffer and in the lower chamber, oscillated between 6% and 9% RH throughout the experiment. These humidity values are to be expected for temperatures below  $0^\circ\text{C}$ . However, the humidity varied between 19% and 29% above the sample, stabilizing out around 26%, after approximately one hour.

Temperatures profiles exhibited two major variations. The first one happened within the first few minutes of the experiment and is caused by the vacuum removing the air from the chamber. The most noticeable change in the first few minutes was the temperature from the upper chamber. When the chamber lid is open this thermocouple is exposed to the lab's environment. As the lid closes the thermocouple is lowered back into the cold atmosphere, hence the temperature drop. The second variation is most noticeable with the sample temperature and RH buffer. At approximately the 15 minute mark the sample and buffer temperatures increase. The RH buffer rapidly increases by  $3^\circ\text{C}$  and then decreases, before stabilizing out, to  $-3^\circ\text{C}$  for the 3.5 cm sample and  $-4.2^\circ\text{C}$  for the 2 cm sample. The sample continued to increase in temperature until it stabilized at  $2.2^\circ\text{C}$ . For the 3.5 cm sample this stabilization took 150 minutes, but only took 15 minutes for the 2 cm sample.

As the calcium perchlorate absorbs water and deliquesces, heat is released (deliquescence is exothermic for most salts), causing the temperature to increase until the salt deliquesces completely. During this temperature variation, the humidity above the sample and humidity buffer decreases and then increases, creating a dip, before stabilizing out. During this humidity and temperature change, the JSC Mars-1 became visibly wet around the calcium perchlorate fragments (Fig. 3). The humidity above the sample was higher than the rest of the chamber, probably because the calcium perchlorate was acting like a "pump" for water vapor during deliquescence. This caused the humidity to be higher above the sample than in the rest of the chamber.

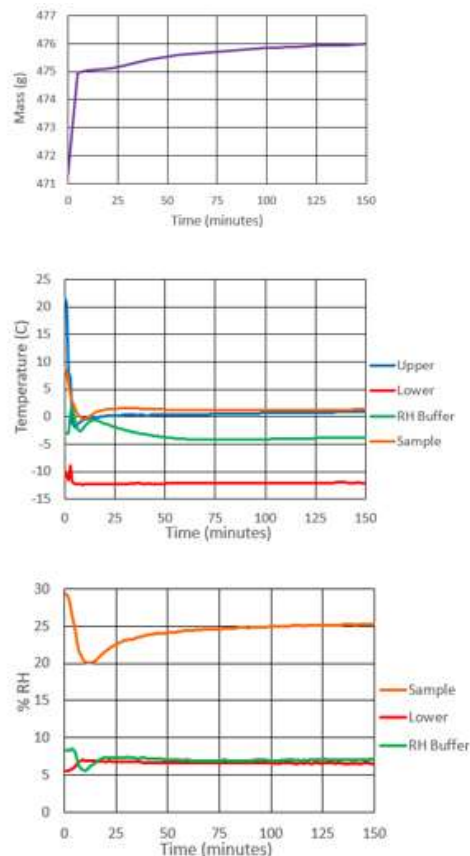
The mass of the sample increased over the entire experiment, although more rapidly at the beginning of the experiment, as the salt absorbed water. After soil wetting had occurred the mass increased much more slowly. JSC Mars-1 also absorbed water, which accounts for the most increasing even after deliquescence had occurred.



**Figure 1:** 3.5cm JSC Mars-1, 5 wt%  $\text{Ca}(\text{ClO}_4)_2$ . Top: mass, middle: temperature and bottom: relative humidity.

**Conclusion:** These experiments are heavily dependent on relative humidity and temperature of the environment. The dark discoloration around the perchlorate suggest wetness and therefore that deliquescence has occurred. The deliquescence occurred during the decrease in humidity and temperature spike of the humidity buffer and sample. The mass may also have indicated deliquescence, with the increase in mass slowing after wetting had occurred. More experiments are being conducted to better observe deliquescence occurring at different humidities under Martian conditions. Deliquescence at the surface of Mars could account for small amounts of transient, metastable liquid brines. Exposing complex subtleties in diffusion, adsorption/desorption cycles, and

deliquescence processes on Mars, specifically the limits to which this liquid formation is possible, has important implications for liquid stability and habitability near the surface, for future missions to Mars, and the continuing search for liquid water.



**Figure 2:** 2cm JSC Mars-1, 5 wt%  $\text{Ca}(\text{ClO}_4)_2$ . Top: mass, middle: temperature and bottom: relative humidity.



**Figure 3:** Left: Image of  $\text{Ca}(\text{ClO}_4)_2$  JSC Mars-1 sample after 48 hours in the Ares chamber. The thermocouple is seen in the far right of the image. The darkened areas around the salt is where deliquescence has occurred. Right: Zoomed in image of the deliquescence at the bottom of the sample.

**References:** [1] Chevrier V. F. et. al (2008) *Icarus*, 196, 459-476. [2] Sears D. W. G. et al. (2005) *GRL*, 32. [3] Hecht, S. P. et al. (2009) *Science*, 5936, 64-67. [4] Nuding, D. L. et al. (2014) *Icarus*, 243, 420-428. [5] Chevrier V. F. et. al (2009) *GRL*, 36. [6] Chevrier V. F. et. al (2008) *GRL*, 35.