Experimental Investigation of the Near-Surface Martian Water Cycle with a Salty Regolith: Implications for Brine Formation. R. A. Slank¹, E. G. Rivera-Valentin², and V. F. Chevrier³; ¹Arkansas Center for Space and Planetary Science, University of Arkansas, Fayetteville, AR (rslank@uark.edu), ²Lunar and Planetary Institute (USRA), Houston, TX.

Introduction: Recent work has shown that the present-day conditions on Mars may allow for stable brines on the surface and shallow subsurface, though only for a small fraction of the year [1]. A potential formation pathway for brines is deliquescence, the transition from a solid salt crystal into an aqueous solution when exposed to a humid atmosphere. Some experiments, though, suggest that under the Mars-relevant pairing of temperature and relative humidity, the kinetics of deliquescence may be too slow to form brines [2]. Furthermore, salts in the regolith would be competing for water vapor in a hyperarid environment against other processes, such as adsorption [1, 3], and salt hydration [4]. Such dynamics of water vapor through atmosphere-regolith interactions, particularly at short timescales (day to year), remains largely unexplored. Furthermore, experimental work thus far has focused on defining the phase space for Mars-relevant brines [5], but not much work has been done to explore the stability of brines under Mars-like conditions [2].

To explore potential brine formation under Mars-like conditions, we conducted a series of experiments focused on investigating atmosphere-regolith interactions, particularly water vapor transfer between the atmosphere and a layer of JSC Mars-1 regolith simulant with varying concentrations of Ca(ClO₄)₂ (0-10 wt.%) at a range of temperature of -23°C to 5°C. Our simulation chamber replicates well the Martian pressure, temperature, and atmospheric composition. Such experiments are vital to understanding how the water vapor diurnal and seasonal cycle may allow for the formation of liquid water on the surface of present-day Mars.

Methodology: We conducted fourteen experiments in the Ares Mars simulation chamber at the University of Arkansas under two temperature regimes. The first was a set cooled with liquid nitrogen, traveling through coiled copper tubing around the sample petri dish, along with a chiller helping to maintain the temperature in the chamber. Those experiments ranged from -23°C to -12°C. Liquid nitrogen was manually let into the chamber to maintain a specific temperature. The second set of experiments were cooled with just the chiller system. Those experiments ranged from 3°C to 5°C. A lithium chloride humidity buffer was placed in the chamber, near the sample, creating stable humidity in the chamber. The buffer has a humidity of 11.2% ± 0.5 at 0°C. While none of our samples were at 0°C, the humidity was fairly close to this average with the chiller temperature-controlled experiments. Experiments were run at a pressure of ~6 mbar.

To test for competing effects, our sample consisted of regolith mixed with 1 to 10wt% calcium perchlorate. We also had two control samples, one just regolith and another just salt. The regolith and salt were both prepared to be as water free as possible, including baking and time in a desiccator. Once they were desiccated they were moved to a freezer to cool to -25°C. The calcium perchlorate was weighed 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 CO₂ to help prevent water contamination. The entire exposure time was less than 120 seconds.

Results and Discussion: In Fig. 1, we plot the temperature and humidity conditions throughout each experiment on the phase diagram of calcium perchlorate. As can be seen, four experiments were within conditions that would permit the deliquescence of calcium perchlorate, one experiment was on the DRH boundary, and two experiments should not have achieved deliquescence. In Figure 2, we show the measured sample mass over time and the relative humidity (RH) gradient between the sample and the atmosphere.
For the three experiments that should not have deliquesced, we note that when the RH gradient was negative, sample mass would steadily increase, and while it was positive, sample mass would steadily decrease. We interpret this to be a signature of adsorption (mass gain) and desorption (mass loss) driven by the humidity gradient.

Typically, visible wetness on regolith grains can be used to identify the occurrence of deliquescence; however, we did not observe visible wetness during the four experiments that experienced the appropriate conditions for deliquescence. Nevertheless, as can be seen in Fig. 2, all four experiments experienced a sample mass increase over time. Furthermore, this occurred during a positive humidity gradient. This is in contrast to the non-deliquescence experiments where a positive humidity gradient led to sample mass loss.

This does not mean that water is not being absorbed into the salt. Mass increase is a great way to help identify water uptake by deliquescence or adsorption. Of the six experiments with increased mass, five of them were experiments conducted in the warmer conditions. (Fig. 1; Fig. 2). Three of the experiments had visible wetness shortly after the experiment, when removed from the simulation chamber and left in a terrestrial environment. This leads us to believe that water was being absorbed into the regolith and/or salt but did not fully deliquesce. This is especially true with the longer run time, where more water was able to be absorbed increasing the mass by 1.14 and 3.71g respectively.

**Conclusion:** Although there were no obvious visible signs of regolith wetness at the surface in the experiments, there were four experiments that had parameters in favor of deliquescence. Those four experiments also had a mass increase from adsorption of water into the regolith and possible deliquescence, that did not deliquesce enough to visibly wetten the regolith around the salt during the experiment. There were also three instances of deliquescence occurring shortly after the experiment had concluded. We infer this to imply be that the salt was close to saturation. That said, there was deliquescence in the controlled experiment of calcium perchlorate. This may imply that when deliquescence is in competition with adsorption, the regolith adsorption of water vapor may prevent salt deliquescence, at least under the conditions studied here. This is supported by deliquescence occurring during the control and not during the experiment, as well as why deliquescence occurred shortly after the end of some of the experiments.

The kinetics of adsorption and deliquescence are experimentally not well constrained under Mars-relevant combinations of temperature and humidity. Although our experiments may suggest that adsorption may act as a more effective water vapor sink than salt deliquescence, more experiments are needed to understand the dependence of these processes over a broader range of environmental conditions (e.g., temperature and/or humidity). Additional experiments are being conducted at cooler temperatures, to better characterize the potential of deliquescence at various humidities under ideal Martian conditions. Exposing complex subtleties in diffusion, adsorption/desorption cycles, and deliquescence processes on Mars, specifically the limits to which liquid formation is possible, has important implications for liquid stability and habitability near the surface, liquid brines, future missions to Mars, and the continuing search for liquid water.

**Acknowledgments:** This grant is funded by NASA Habitable Worlds Program award #80NSSC20K0227.