EXPERIMENTAL CONSTRAINTS ON WATER VAPOR EXCHANGE WITH A SALTY MARS REGOLITH ANALOG: IMPLICATIONS FOR BRINE FORMATION.
R. A. Slank[1], E. G. Rivera-Valentín[2], and V. F. Chevrier[1]; [1]Arkansas Center for Space and Planetary Science, University of Arkansas, 346 Arkansas Ave., Fayetteville, AR 72701, [2]Lunar and Planetary Institute, USRA, Houston, TX. rslank@uark.edu.

Introduction: Understanding near-surface atmosphere-regolith interactions can help improve our understanding of the modern Martian water cycle at short time and spatial scales. Given that the near-surface conditions on Mars may lead to brine formation [1, 2], and its implications for present-day habitability [1], resolving local scale processes and their interactions is important to also understand the biologic potential of Mars. Local effects mostly related to phase changes of water include adsorption [3], melting of ice [3, 4], and interaction with hygroscopic salts, like perchlorates [5-6] through hydration, deliquescence, and dissolution [4, 6, 7]. Experimental work thus far has focused on defining the thermodynamic phase space for Mars-relevant brines [8], but not much work has been done to define the stability of these brines under conditions where water vapor exchange processes may interact with each other [9]. Here we conducted deliquescence experiments in a simulation chamber that can mimic Martian pressure, temperature, and atmospheric composition. Our work focused on deliquescence in a regolith and salt mixture where solid state salt hydration, adsorption/desorption, and deliquescence may interact.

Methodology: A series of eleven experiments (Table 1) were conducted, which focused on determining water vapor transfer between the atmosphere and a layer of JSC Mars-1 regolith simulant with varying concentrations of $Ca(ClO_4)_2$ (0-5.5 wt.%) and possible deliquescence therein, using weight, temperature and relative humidity measurements. We used the Ares Mars simulation chamber in the W.M. Keck Laboratory for Space and Planetary Simulations at the University of Arkansas. Six of the experiments were controls: two with an empty petri dish, two filled with 2 mm of JSC Mars-1, and two with 64.5 g of pure calcium perchlorate. One control set was run without a humidity buffer, with a low relative humidity (Rh<7%) and one set with a LiCl humidity buffer, at a higher Rh~20%. The controls were conducted at temperatures of 1.5°C and 4°C, respectively. Each of the controls were run in duplicates. We conducted three deliquescence experiments at temperatures of approximately 4°C over 5 hours. An additional two experiments were run for longer timeframes than the previous experiments, one at 24 hours and the other at 48 hours. All deliquescence experiments were conducted with 2 cm of JSC Mars-1 and varying abundances of $Ca(ClO_4)_2$ (0-5.5 wt%).

JSC Mars-1 was baked for 24 hours above 100°C, placed in a desiccator, pulled to vacuum, and then placed in a freezer to cool to -25°C. The calcium perchlorate salt was placed in a desiccator, pulled to vacuum for 24 hours, and then placed in a freezer. The calcium perchlorate was weighed at the proper weight percent amount and then lightly mixed within the top layer of the regolith. Although there was some exposure to the atmosphere while the sample was removed from the desiccator and placed in the chamber, the chamber was filled with CO_2 to help prevent water contamination. The entire exposure time was less than 120 seconds. The experiments were cooled with a chiller cooling system, that allowed the sample to range in temperature of 1.5°C to 5°C. A lithium chloride humidity buffer was placed in the chamber, near the sample, to maintain a theoretical average humidity in the atmosphere of 11.2±0.5% at 0°C, although the Rh varied with temperature and the presence of a sample also affected the Rh value in the atmosphere (see results section). Experiments were run at a pressure of ~6 mbar.

Experiment #	Wt% of Calcium Perchlorate	Temperature (°C)	Time (minutes)	Relative Humidity at Sample (%)	Sample Thickness
1	0	1.5	420	7.4	0 cm
2	0	3.5	640	18.5	0 cm
3	0	1.5	407	7.1	2 cm
4	0	3.5	418	19.7	2 mm
5	all salt	1.5	428	7.4	2 mm
6	all salt	3.5	332	19.2	2 mm
7	1.0	4.0	306	10.0	2 cm
8	0.97	4.0	274	20.4	2 cm
9	5.5	4.0	384	21.5	2 cm
10	5.2	4.5	1404	21.8	2 cm
11	5.3	5.0	2926	20.5	2 cm

Table 1: List of experiments and their parameters.

Results and Discussion: Six control experiments were conducted: 3 at low humidity and 3 at humidity. For the control with pure calcium perchlorate at low Rh (7%), there was no observed changes to the salt properties at the end of the experiment, as was expected. However, for the control with the LiCl buffer (~20%), the salt crystals presented noticeable changes. The salt crystals became transparent and appeared partially dissolved. We infer this as evidence in support of deliquescence occurring in the experiment. This implies that pure calcium perchlorate is capable of deliquescing in the chamber under the temperature (4°C) and humidity (19%) conditions of our experiments.

Five experiments with $Ca(ClO_4)_2$ mixed with regolith were used to test for deliquescence by mass change and visual inspection, specifically by grain darkening due to wetting. These experiments were

conducted at a temperature range of 3.5-5°C and Rh range of 10-22%. In Figure 1, we summarize the temperature and relative humidity with respect to liquid throughout each experiment on the phase diagram of calcium perchlorate [1]. Deliquescence is expected if the experiment crosses over the deliquescence relative humidity line (DRH) into the dark gray area. As can be seen, four out of the five experiments reached and maintained conditions that would have permitted deliquescence, and one experiment was close to the required conditions.

Although the experiments that should have deliquesced did not show evidence of grain wetting and darkening at the surface, they showed other lines of evidence that together suggested deliquescence occurred. Although all five of the salty regolith experiments, including the experiment where no brine formation was expected, had a mass increase over the span of the experiments, the rate of water uptake was different. The regolith-only experiment on average increased in mass at a rate of 22 ± 5 mg/hour. On the other hand, experiments with regolith and salt experienced on average a mass gain of 45 ± 18 mg/hour, 2 times higher than the regolith-only experiment. Furthermore, experiments with favorable conditions and with more than 5wt% salt experienced on average a mass gain of 52 ± 16 mg/hour. As such the inclusion of salt in the regolith resulted in a measurable increase in the rate of water uptake. Furthermore, similar to our salt-only experiment at high Rh, changes in salt morphology were observed for only experiments where the conditions would have permitted deliquescence. Finally, in only the cases where deliquescence was favored within the chamber, the water vapor pressure gradient between the sample and the atmosphere was positive, i.e., larger at the sample than in the chamber's atmosphere. In Figure 2, we compare examples of an experiment where (a) deliquescence was favored and (b) where it was not. A positive gradient should lead to mass loss as the concentration gradient would drive water vapor out of the sample, and yet there was appreciable mass gain for those experiments. Additionally, the water vapor pressure gradient increased and then stabilized at the end of the experiment with a difference between the sample and atmosphere of 30-50 Pa. For example, the longer experiments reached a gradient of 50 Pa within 10 hours and kept this gradient until the end of the experiment (>30 hours). Therefore, an active process at the sample that forces and maintains the chamber out of equilibrium is required.

Conclusion: We find that the rate of water uptake of a salty Mars regolith analog is nearly twice as high as that of our regolith-only experiments. This is likely due to additional active water vapor sinks in the salty regolith samples, such as solid-state salt hydration and deliquescence. Furthermore, our results imply that an adsorbing regolith does not out compete salt-related water vapor sinks in a hyper arid environment. Indeed, we found evidence to suggest that deliquescence occurred at the studied low relative humidity conditions. As such, adsorption did not constrain deliquescence.

It is important to note that the chamber environment contained an order of magnitude more water vapor than what has been typically measured at the surface of Mars (~100 Pa in the chamber compared to <10 Pa on Mars) [1]. Furthermore, more experiments are needed to understand the interaction of water vapor sinks and sources within the martian regolith over a broader range of environmental conditions (e.g., temperature and/or humidity). Additional experiments at cooler temperatures and lower water vapor are particularly needed to better characterize the potential of deliquescence 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, future missions to Mars, and the continuing search for liquid water.
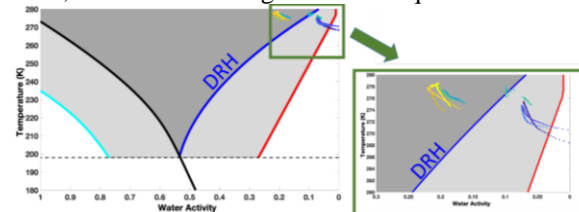

Figure 1: Temperature versus water activity phase diagram of calcium perchlorate –water binary mixture, with experimental conditions plotted.
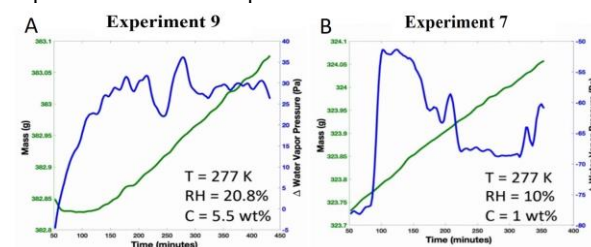

Figure 2: Mass (green) and water vapor pressure (blue) as a function of time for experiments in the deliquescence zone. A: An experiment where deliquescence is expected. B: An experiment where deliquescence was not expected.

References: [1] Rivera-Valentín, E.G., et al. (2020), *Nat Astron*, 4 (756-761). [2] Chevrier, V.F. et al. (2020) *PSJ* 1:64 (12pp). [3] Chevrier V. F. et al. (2008) *Icarus,* 196, 459-476. [4] Sears D. W. G. et al. (2005) *GRL,* 32. [5] Hecht, S. P. et al. (2009) *Science*, 5936, 64-67. [6] Chevrier V. F. et al. (2009) *GRL,* 36. [7] Chevrier V. F. et al. (2008) *GRL*, 35. [8] Fisher, E., et al. (2014) *Geophys. Res. Let.*, 41(13), pp.4456-4462. [9] Fisher, E. et al. (2016) *Astrobiology*, 6(12), pp.937-948.