

**REGOLITH INHIBITS SALT CRYSTALLIZATION IN MAGNESIUM PERCHLORATE BRINE, SUGGESTING MORE PERSISTENT AND HABITABLE BRINES ON MARS.** A. O. Shumway<sup>1</sup>, D. C. Catling<sup>1</sup>, and J. D. Toner<sup>1</sup>, <sup>1</sup>Department of Earth and Space Sciences, University of Washington, Seattle WA. USA ([shumway@uw.edu](mailto:shumway@uw.edu))

**Introduction:** Brines affect the geochemistry and habitability of Mars' surface and are central to astrobiological investigations of the planet. Despite extensive research of pure brines, mixtures of brines in Martian regolith are poorly studied. Brines on Mars will exist in contact with regolith, which alters brine properties through interactions with water molecules and ions in solution. Specifically, we show that regolith increases water content of brine through adsorption, and suppresses salt crystallization over a wide range of Mars-relevant temperatures, relative humidities (RH), and salt concentrations.

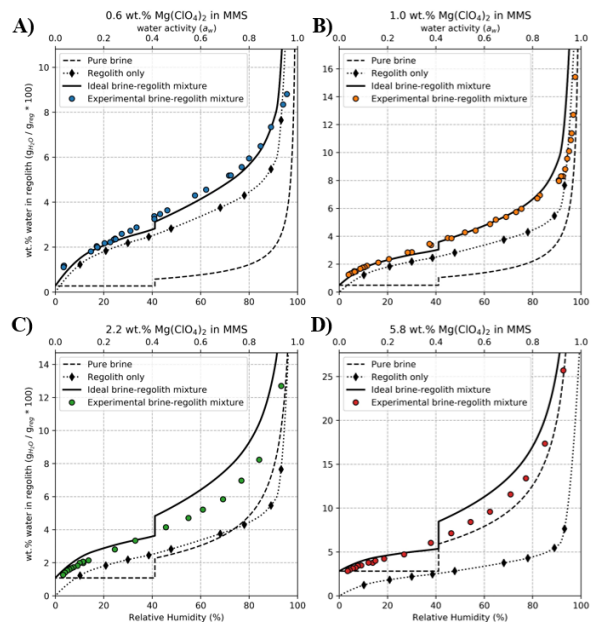
**Methods:** We used  $\text{Mg}(\text{ClO}_4)_2$  as the salt in our experiments because data suggest it was present in regolith at the Phoenix landing site [1, 2]. We used Mojave Mars Simulant (MMS) regolith because of good physical and chemical resemblance to Martian soils [3].

We measured water content as a function of RH for brine-regolith mixtures at 0-5.8 wt. % salt. Following the isopiestic method [4], brine-regolith samples were equilibrated with a reference solution ( $\text{H}_2\text{SO}_4$ ) in an evacuated chamber at 25°C. The brine-regolith mixtures exchanged water with the reference solution until equilibrium was reached. By taking the masses of sample and reference both before and after equilibration, we measured the water content and salt concentration from 3 to 98% RH.

We also investigated phase transitions in briny regolith at lower temperatures (20°C to -150°C) using a Differential Scanning Calorimeter (DSC). A DSC measures heat flow through a sample as temperature changes, which we used to identify phase changes (i.e., precipitation) via their characteristic heat flux patterns.

**Results:** Experiments show that brine-regolith mixtures exhibit unique properties not expected for an ideal mixture of the two endmembers. In Fig. 1, we compare the measured or modeled water content of brine, regolith, and brine-regolith mixtures as a function of RH at various wt. % salt. We modeled the pure brine component (dashed lines in Fig. 1) using a revised Pitzer model [5], and assumed a fixed amount of salt exists within—but behaves independently from—the regolith. This is the default assumption of any brine study that neglects regolith. For salt-free regolith systems, we measured adsorbed water content using the isopiestic method, then fit a spline between the data points (diamonds and dotted lines in Fig. 1, respectively). We predicted the behavior of an ideal brine-regolith mixture

by summing the water contents of each component (pure brine + regolith) at every RH (solid lines in Fig. 1). Measured water content in brine-regolith mixtures (circles in Fig. 1) greatly differs from the predicted behavior of an ideal mixture.

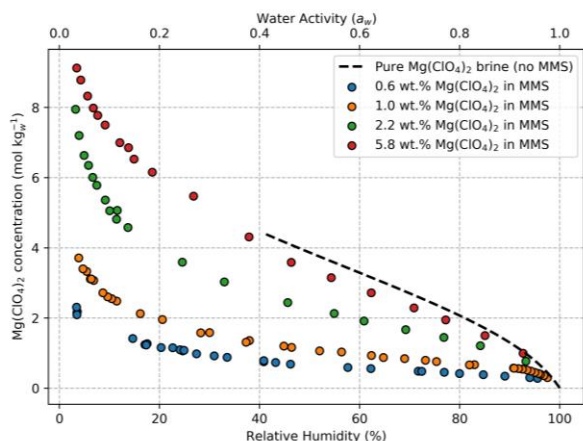


**Fig. 1** Experimental brine-regolith mixtures (circles) deviate significantly from ideal mixtures of brine and regolith (solid line). Salt crystallization causes the step changes at 41% RH in the brine and ideal brine-regolith systems (dashed and solid lines, respectively). Notably, there is no evidence of salt precipitation in the brine-regolith experiments, even at conditions where salt would precipitate in pure brine,  $\text{RH} < 41\%$ .

For samples with 0.6 wt. % salt in regolith (Fig. 1A), the experimental mixture tended to be wetter than the ideal case at all but the highest RH. Meanwhile, samples with 1 wt. % salt (Fig. 1B) were close to ideal for 0-80% RH, but contained less water than predicted for  $\text{RH} > 80\%$ . Samples with 2.2 and 5.8 wt. % salt tended to be drier than the ideal case at all RH (Fig. 1C and 1D).

One major deviation from ideal behavior is that experimental brine-regolith mixtures showed no evidence of salt crystallization, even at conditions that could cause salt to precipitate from a pure brine or ideal mixture. In Fig. 1, salt crystallization appears as the step change at  $\text{RH} = 41.1\%$  (dashed and solid lines in Fig. 1). However, such a phase change is absent from the

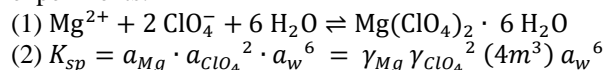
experimental brine-regolith data, even at very dry conditions (circles in Fig. 1). The lack of the expected step change suggests that salt never crystallized in these experiments. At lower temperatures, salt precipitation was similarly inhibited, and we did not observe any salt crystallization phase changes with the DSC between 20°C to -150°C.



**Fig. 2** Brines in regolith (circles) are less concentrated than pure brine (dashed line) at any given RH. The model for the pure brine terminates at the saturation point (~4.4 molal and 41% RH at 25°C), where no additional salt can dissolve in solution.

**Discussion:** Salt formation may be inhibited because brines in regolith tend to be more dilute than pure brine at a given RH (Fig. 2). Salt precipitates from pure  $\text{Mg}(\text{ClO}_4)_2$  brine at the saturation point of 4.4 molal at 25°C; in more dilute solutions, all ions remain dissolved. Brines in regolith are more dilute and can remain below saturation even at  $\text{RH} < 41\%$ . Notably, the samples with the most Mars-like salt contents (blue and orange circles in Fig. 2) maintained a concentration below 4.4 molal at 3–98% RH, which could explain why salt precipitation was never observed in those samples. Meanwhile, higher wt.% samples (green and red circles in Fig. 2) sometimes exceeded the saturation concentration at low RH—which is not possible for a pure brine—yet still salt precipitation was not observed.

The equations that describe the precipitation of  $\text{Mg}(\text{ClO}_4)_2$  hexahydrate provide one plausible explanation for why salt never crystallized in the experiments:



Here,  $K_{sp}$  is the solubility constant that describes salt precipitation,  $a_i$  is the activity of each ion or water,  $\gamma_i$  is the ion activity coefficient, and  $m$  is the saturation concentration of brine. In our experiments,  $a_w$  tends to be lower in regolith-brine mixtures than in a pure brine

at the same concentration (see Fig. 2). Because  $K_{sp}$  remains constant regardless of whether or not the reaction occurs in regolith, if regolith reduces  $a_w$  of brine, then it must also increase the saturation concentration ( $m$ ) and/or activity coefficient ( $\gamma$ ) proportionally. Considering the respective powers of each term in eq. (2), even a small decrease in  $a_w$  could exponentially increase the concentration required to precipitate salt, which may explain the observed increase in solubility.

Another explanation for the lack of salt formation is that brines in regolith become supersaturated. Supersaturated brines are metastable and have a dissolved ion concentration that exceeds the maximum concentration that is possible at equilibrium. Perchlorates are particularly prone to similar supercooling metastability [6]. Other mechanisms could allow metastable states where both salt and ice crystallization are inhibited in perchlorate brines in regolith. Further experiments probing the phase transitions during supercooling and potential supersaturation are needed to understand the mechanisms responsible for both processes.

**Implications for Habitability:** Our results demonstrate that salt precipitation is inhibited in brine-regolith mixtures, which indicates that water persists in briny regolith at drier conditions than in pure brine. We do not see any evidence of salt crystallization at any RH or temperature in the experiments, indicating that regolith completely suppresses salt formation in  $\text{Mg}(\text{ClO}_4)_2$  brine between 25°C and -150°C and at RHs as low as 3%. Crystallization can damage cells and lock away  $\text{H}_2\text{O}$  molecules in a form inaccessible to life (i.e., hydrated salt), so by suppressing salt precipitation, regolith stabilizes brines over a wide range of Mars-relevant conditions. With the crystallization-suppressing effects of regolith, brines on Mars may retain more water and pose fewer hazards for life than previously thought possible based on studies of pure brine. These effects are astrobiologically significant because they increase the range of conditions where life might be found. They are similarly relevant for planetary protection because they expand the regions where terrestrial microbes could survive on Mars.

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**References:** [1] Toner J. D. et al. (2014) *Geochim Cosmochim Acta*, 136, 142-168. [2] Hecht M. H. et al. (2009) *Science*, 325, 64-67. [3] Peters G. H. et al. (2008) *Icarus*, 197, 470-479. [4] Rard J. A. and Platford R. F. (1991) Experimental Methods: Isopiestic. In *Activity Coefficients in Electrolyte Solutions*, 209-277. [5] Toner J. D. et al. (2015) *Geochim Cosmochim Acta*, 166, 327-343. [6] Toner J. D. et al. (2014) *Icarus*, 233, 36-47.