

**WATER UPTAKE AND RELEASE BY MAGNESIUM PERCHLORATE MIXED WITH MARS RELEVANT MINERALS.** K.M. Primm<sup>1,2</sup>, R.V. Gough<sup>1,2</sup>, and M.A. Tolbert<sup>1,2</sup>. <sup>1</sup>Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO, 80309, USA, Katherine.primm@colorado.edu; <sup>2</sup>Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO, 80309, USA, raina.gough@colorado.edu.

**Introduction:** Hecht et al. found that 0.5% of the regolith of Mars is comprised of perchlorate salts [1]. These highly hygroscopic salts were found to exist at Gale Crater and possibly at the Viking landing sites [2,3]. Salts such as perchlorate have been linked to the formation of recurring slope lineae [4]. Thus, there is liquid water in certain locations on the surface or in the shallow subsurface of current Mars the liquid water may be in the form of a salty brine.

Perchlorates provide multiple mechanisms for forming liquid water on current day Mars. These highly soluble salts could depress the freezing point of brine down to the very low eutectic temperature of some perchlorate salts (~200 K). Further the perchlorate salts could absorb atmospheric water vapor and deliquesce into a liquid solution [4-11].

Deliquescence is the transition of a solid to an aqueous brine phase by absorption of water vapor. It occurs when the relative humidity surpasses the deliquescence relative humidity of the salt and leads to the formation of a saturated salt solution. If a salt has a low eutectic temperature, as do most perchlorate salts, there is a very large temperature range over which perchlorate salts can deliquesce and thus provide a pathway to form liquid water on Mars. Perchlorate salts also have low efflorescence (recrystallization) relative humidity values, often far below the DRH.

To fully understand the extent to which liquid water can exist on Mars, the freezing of these potential Martian salt brines must be considered as well. It is thermodynamically predicted that ice should begin to form when the partial pressure of water equals the vapor pressure of ice ( $S_{ice}=1$ ); however, this is often not the case. Critical clusters of ice must form for ice to grow, i.e.  $S_{ice}$  must be greater than one before freezing begins. Although currently most models predict that ice will form at the thermodynamically predicted value of  $S_{ice} = 1$ , we have recently shown that values of  $S_{ice}$  larger than 1 need to be reached for a brine droplet to freeze [12].

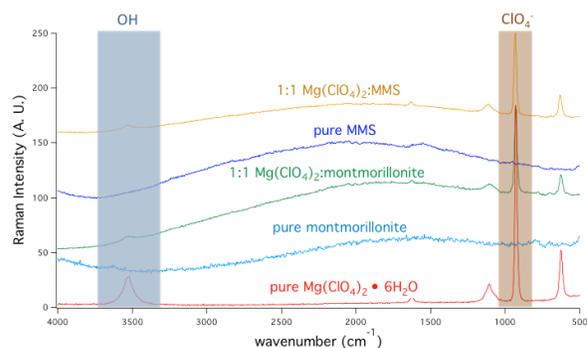
Many recent studies have examined the deliquescence, efflorescence or freezing of pure perchlorate salts or perchlorate brines [10-14]. The low temperature phase transition behavior of many perchlorates is therefore fairly well understood. No studies, however, have examined the effect that the Martian regolith has on the phase transitions. The surface of Mars is primarily (~99%) insoluble minerals and dust [15]. It is con-

ceivable that the presence of insoluble minerals in contact with, or in the interior of, a salt grain would affect the uptake of atmospheric water vapor by the salt (due to competition for water molecules) and also the efflorescence and freezing of small brine droplets (because the presence of insoluble nuclei could prevent supersaturated or supercooled brines). To accurately understand the interaction between water vapor and hygroscopic salts on Mars and the potential for small scale liquid brines, the effect of minerals and dust on salt phase transitions must be experimentally studied.

Here we examine the effect of two different minerals, montmorillonite clay and a Martian regolith analog called Mojave Mars Simulant (MMS), on the conditions under which pure magnesium perchlorate deliquesces, effloresces, and forms ice.

### Experimental Methods:

**Sample preparation.** Equal masses of magnesium perchlorate hexahydrate and either montmorillonite or MMS were mixed in HPLC grade water. These solutions were then nebulized using nitrogen gas onto a hydrophobically coated silica quartz disc.



**Figure 1.** Raman Spectra of pure  $Mg(ClO_4)_2 \cdot 6H_2O$ , pure montmorillonite, pure MMS, and mixtures of perchlorate with montmorillonite and MMS. The blue shaded region highlights where the O-H stretch of liquid water appears and the brown shaded region highlights where the  $ClO_4^-$  stretch is found. Pure  $Mg(ClO_4)_2 \cdot 6H_2O$  exhibits an intense  $ClO_4^-$  peak and also an O-H stretch due to the crystalline phase water, while the montmorillonite and MMS spectra show intense fluorescence. The mixture spectra show that when  $Mg(ClO_4)_2 \cdot 6H_2O$  is mixed with either montmorillonite or MMS, the OH from the hexahydrate and the  $ClO_4^-$  are both visible on top of the fluorescent baseline, evidence that the particles are in fact mixtures of perchlorate and mineral.

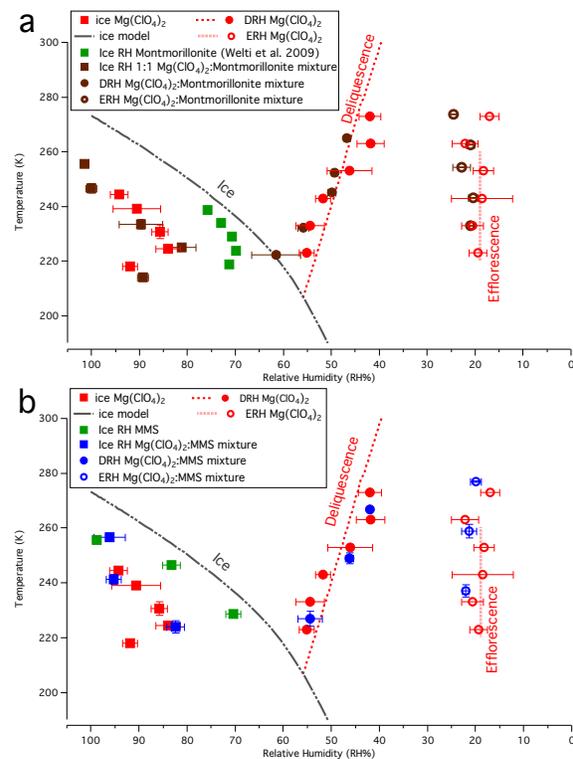
**Instrumentation.** The sample was placed into an environmental cell within a Raman microscope [10, 16,17]. The environmental cell allows for relative humidity (RH) and temperature control; while pure CO<sub>2</sub> flows through the system. The disc with the particles was allowed to dry in a ~0% RH environment prior to beginning an experiment.

**Spectral analysis.** The particles on the disc were analyzed by Raman spectroscopy to ensure that they were internally mixtures of Mg(ClO<sub>4</sub>)<sub>2</sub>•6H<sub>2</sub>O and montmorillonite (or MMS). Figure 1 shows Raman spectra of pure Mg(ClO<sub>4</sub>)<sub>2</sub>•6H<sub>2</sub>O, pure montmorillonite, and pure MMS as well as the mixtures of 1:1 Mg(ClO<sub>4</sub>)<sub>2</sub>•6H<sub>2</sub>O:montmorillonite and 1:1 Mg(ClO<sub>4</sub>)<sub>2</sub>•6H<sub>2</sub>O:MMS. The spectra show that the mixture particles that were probed (green and gold spectra) are each internal mixtures because the mixture sample contains the ClO<sub>4</sub><sup>-</sup> stretch as well as the fluorescence characteristic of an insoluble mineral. After the composition of the particle was analyzed at room temperature, the RH was increased and the temperature was decreased until the particles visually deliquesced. Deliquescence was also confirmed with Raman spectroscopy. The RH was then increased (and the temperature decreased) further until ice nucleation occurred and at least one of the brine droplets froze into a solid ice particle. This freezing could be seen visually and spectrally. After ice nucleation occurred, the RH was decreased until melting occurred and then further lowered until efflorescence was observed. This procedure was repeated for at least 5 different temperatures.

**Results:** Figure 2 shows preliminary data of the deliquescence, efflorescence, and freezing phase transitions of mixtures of 1:1 Mg(ClO<sub>4</sub>)<sub>2</sub>•6H<sub>2</sub>O:montmorillonite (part a) and 1:1 Mg(ClO<sub>4</sub>)<sub>2</sub>•6H<sub>2</sub>O:MMS (part b) plotted on the magnesium perchlorate stability diagram. The red points in both figures represent pure perchlorate salt. Then, the brown points in part a and the purple points in part b represent the salt/mineral mixtures. It can be seen that the montmorillonite and the MMS have little to no effect on the water uptake of pure Mg(ClO<sub>4</sub>)<sub>2</sub>•6H<sub>2</sub>O. Regarding the freezing of brine droplets (square symbols), we find that the presence of the insoluble mineral does not affect the extent of supersaturation with respect to ice that can occur. S<sub>ice</sub> values as high as 1.45 were reached even though the S<sub>ice</sub> value of the mineral was typically close to 1.0. Similarly, the presence of the insoluble mineral does not hinder the supersaturation of the salt brine that occurs when the RH is below the DRH (open circles). We can conclude that the minerals are likely a poor lattice match for perchlorate crystals and therefore are not effective nuclei for recrystallization.

## Conclusions:

These results show that small-scale liquid solutions can occur via deliquescence of perchlorate salts on the surface of Mars, even with the incorporation of insoluble minerals representative of the Martian regolith within the salt particles. The liquid brine droplets containing both perchlorate and Martian regolith can remain liquid as droplets rather than freeze or recrystallize.



**Figure 2.** Plots showing the DRH, ice RH ( $S_{ice}$ ), and ERH of pure Mg(ClO<sub>4</sub>)<sub>2</sub>•6H<sub>2</sub>O and compared to mixtures of perchlorate and mineral. Part (a) shows mixtures of perchlorate with montmorillonite and part (b) shows mixtures of perchlorate with MMS. Neither mineral has a significant effect on the deliquescence, efflorescence or freezing phase transitions of perchlorate salt.

**References:** [1] Hecht et al. (2009) *Science* 325. [2] Glavin et al. (2013) *JGR* 118. [3] Navarro-González et al. (2010) *JGR* 115. [4] Ojha et al. (2015) *Nature Geosci.* 8. [5] Chevrier and Rivera-Valentin (2012) *GRL* 39. [6] McEwen et al. (2013) *Nat. Geosci.* 7. [7] Chojnacki et al. (2016) *JGR E Planets* 121. [8] Martín-Torres et al. (2015) *Nat Geosci.* [9] Rennó et al. (2009) *JGR* 114. [10] Gough et al. (2011) *EPSL* 312. [11] Nuding et al. (2014) *Icarus* 243. [12] Primm et al. (2017) *submitted GCA under review*. [13] Nikolakakos and Whiteway (2015) *JGR* 42. [14] Fischer et al. (2014) *GRL* 41. [15] Ehlmann and Edwards (2014) *AREPS* 42. [16] Baustian et al. (2010) *ACP* 10. [17] Schill and Tolbert (2013) *ACP* 9.