

WATER UPTAKE BY MARS SALT ANALOGS: AN INVESTIGATION OF STABLE AQUEOUS SOLUTIONS USING RAMAN MICROSCOPY. D. L. Nuding^{1,2}, R.D. Davis^{1,3}, R. V. Gough^{1,3}, M. A. Tolbert^{1,3}.

¹Cooperative Institute for Research in Environmental Sciences, ²Department of Atmospheric and Oceanic Sciences, ³Department of Chemistry and Biochemistry; University of Colorado, Boulder, CO 80309.

Introduction: Briny aqueous solutions are the favored explanation for liquid water features observed on present-day Mars due to their stability in low temperature conditions. Examples of such features are subsurface thin film liquids [1], spheroids on the Phoenix lander leg [2] and recurring slope linea (RSL) [3,4]. Perchlorate and chloride salts are known to be present in the Martian soil, readily absorb water vapor from the atmosphere and deliquesce into aqueous solutions [5,6]. In an attempt to understand the stability of briny aqueous solutions on Mars, several single salt and simple salt mixtures have been characterized in martian environmental conditions.

NaClO_4 and $\text{Mg}(\text{ClO}_4)_2$ are highly deliquescent, forming aqueous solutions at humidity values as low as 40% RH and at temperatures as low as 223 K. A significant hysteresis effect is observed that occurs during efflorescence of these salt solutions, expected due to the kinetic inhibition of crystal nucleation. The efflorescence relative humidity values of sodium and magnesium perchlorate solutions are 13% RH and 19% RH, respectively, indicating that perchlorate salts could exist as stable or metastable aqueous solutions over a wide range of Martian RH and temperature conditions [6].

Laboratory studies of $\text{NaClO}_4/\text{NaCl}$ and $\text{Mg}(\text{ClO}_4)_2/\text{MgCl}_2$ mixtures found that the stable aqueous solutions can form and persist in RH conditions above 38% and 28%, respectively at temperatures as low as 243 K. The hysteresis effect is also observed in these mixtures, allowing for metastable solutions to persist down to 5% RH for $\text{Mg}(\text{ClO}_4)_2/\text{MgCl}_2$ and 13% for $\text{NaClO}_4/\text{NaCl}$. This work quantified the effect of multiple soluble ionic species in a mixture, further supporting the stability of briny aqueous solutions on Mars [7].

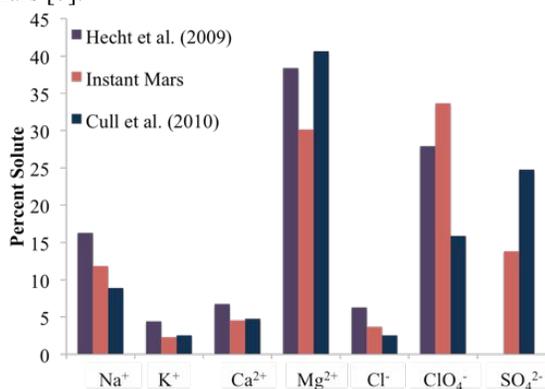


Figure 1 Instant Mars solution developed to closely match Phoenix landing site Wet Chemistry Laboratory results.

In the present study, a salt analog was developed to closely match the individual cation and anion concentrations as reported by the Wet Chemistry Laboratory aboard the Phoenix Lander. ‘Instant Mars’ is a salt analog developed to fully encompass the correct concentrations of magnesium, calcium, potassium, sodium, perchlorate, chloride, and sulfate ions [1,8]. Instant Mars and results from the Phoenix landing site are compared in Figure 1.

Experiments and Results: To understand the water uptake properties of ‘Instant Mars’ on the Martian surface, we have used a Raman microscope equipped with an environmental cell. A MicroJet droplet generator was used to produce 40 μm diameter particles that were deposited onto a quartz disc. The particles undergo visual transformations as the relative humidity (RH) is increased and water uptake is confirmed by Raman spectroscopy.

An example of an Instant Mars water uptake experiment is shown in Figure 2. At 243 K, water uptake begins at 44% RH (green) as humidity is increased. Water uptake is indicated by the shift of the Cl-O peak from 1025 cm^{-1} to 990 cm^{-1} , as the perchlorate anion becomes solvated. In addition, the Instant Mars particles undergo a solid-solid phase transition at 44%, indicated by the particle growth and change in brightness. Visual changes in the core structure are also observed. As the RH continues to increase, additional water uptake is apparent as the peak in the O-H region ($\sim 3500 \text{cm}^{-1}$) broadens as more liquid water accumulates in the particles at 69% (blue). The O-H stretch shifts from 3525 cm^{-1} to 3390 cm^{-1} as liquid water content increases. The Instant Mars particles have fully transitioned to the aqueous phase at 99% (purple), indicated both visually and with Raman spectroscopy.

The gradual water uptake observed suggests that deliquescence of the Instant Mars particles is not an immediate process, but that it occurs in steps marked by the deliquescence of the individual salts. Once Instant Mars particles are fully deliquesced, a hysteresis effect is still observed, but it is not as significant as the single salt or two salt systems. Figure 3 shows as RH is decreased, the shoulder of the O-H stretch narrows and the particle maintains a uniform surface with a dark rim at 82%. By 40%, solids begin to precipitate in the surrounding liquid solution. By 37%, the particle is completely crystallized indicated by the split peak in the O-H stretch region. No further visual or spectral changes are observed as the RH is decreased to 5% RH.

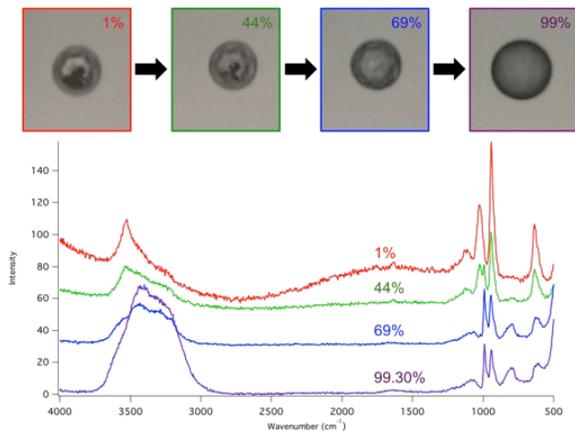


Figure 2 Visual images (top) and Raman spectra of a water uptake experiment of an Instant Mars particle at 243 K. Initial particle size is $\sim 40 \mu\text{m}$.

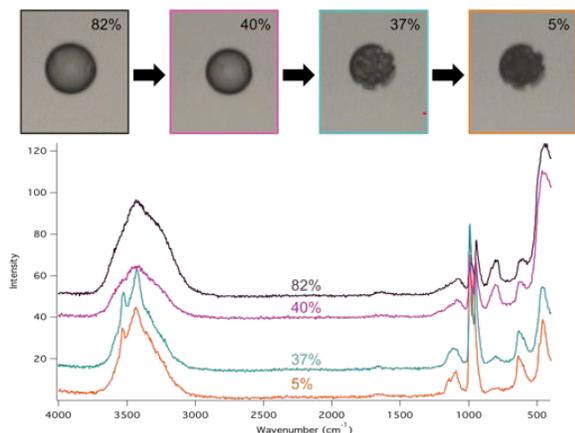


Figure 3 Visual images (top) and Raman spectra of an Instant Mars particle as RH is decreased at 243 K. Initial particle size is $\sim 45 \mu\text{m}$.

To probe the phase state and morphology of individual ‘Instant Mars’ droplets free from any substrate, droplets were levitated in an optical trap recently developed in our laboratory. The particle is levitated in a controlled RH environment and equipped with a CCD camera to observe water uptake properties. In the far-field images, the elastically scattered laser light from a levitated particle will take the form of a series of linear horizontal interference fringes if the particle is spherical, but will be chaotic and irregular if the particle is non-spherical (i.e. crystalline).

Figure 4 shows the Instant Mars droplet that was initially levitated at 81% RH at 298 K. Solid particulate is evident by the distorted interference fringes in the far-field although the droplet remains spherical and predominately liquid. At 58% the droplet has decreased in size, but liquid water is still present. By 26% the particle rapidly loses water and crystallizes.

Further decreasing RH results in a gradual loss of residual water.

When RH is increased, water uptake is not observed until 33% RH. After initial water uptake, a portion of the particle remains solid. As RH continues to increase, the particle continues to gradually uptake water with solid particulate remaining up to 85%.

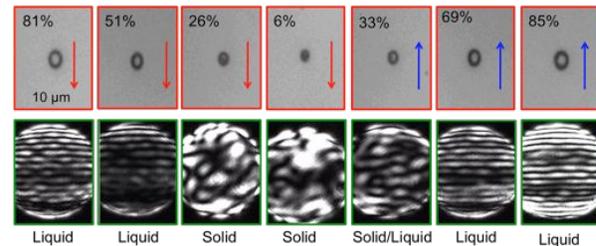


Figure 4 Bright-field (red boxes, top) and far-field (green boxes, bottom) images of an Instant Mars water uptake experiment at 298 K.

Conclusion: We have experimentally examined the water uptake properties of Instant Mars under relevant Martian temperatures and RH conditions. In the representative experiment at 243 K, Instant Mars particles undergo liquid water absorption beginning at 44% RH. When compared to the levitation experiment at 298 K, the results are consistent as water uptake is initially observed at 33%. The difference can be explained by the lack of contact with a substrate. As RH is decreased, a metastable solution is present until 37% RH at 243 K, indicating that the hysteresis effect still occurs in complex salt mixtures. The levitation experiment indicates the phase transition occurs at 26% RH at 298 K. The extreme hysteresis effect is not present, as observed in perchlorate and perchlorate/chloride salt systems. The earlier phase transition is likely impacted by the presence of particulates forming in the liquid solutions at higher RH. The particulates may act as heterogeneous nuclei, preventing the salt supersaturation that occurs in other characterized salt systems. However, even without an extreme hysteresis effect, Instant Mars particles initiate stable and metastable aqueous solutions under Mars relevant temperature and RH conditions.

References: [1] Cull S. C. et al. (2010). *GRL*, 37. [2] Renno N. O., et al. (2009) *JGR*, 114, E00E03. [3] McEwen, A.S., et al. (2014) *Nature Geoscience* 7, 53. [4] McEwen et al. (2011) *Science*, 333, 740-743. [5] Chevrier, V., et al. (2009) *GRL*, 36, L10202. [6] Gough R. V. et al. (2011) *EPSL*, 312, 371-377. [7] Gough R. V. et al. (2014) *EPSL* (submitted). [8] Hecht M. H. et al. (2009) *Science*, 325, 64–67.