

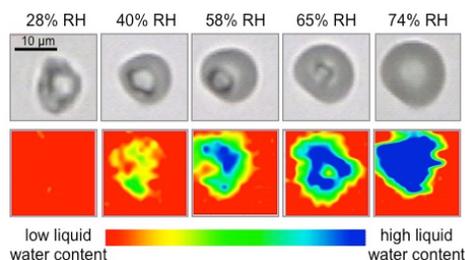
**DELIQUESCENT OF PERCHLORATE/CHLORIDE MIXTURES: IMPLICATIONS FOR STABLE AND METASTABLE AQUEOUS SOLUTIONS ON MARS.** R.V. Gough<sup>1</sup>, V. Chevrier<sup>2</sup> and M.A. Tolbert<sup>1</sup>, <sup>1</sup>Cooperative Institute for Research In Environmental Sciences, University of Colorado, Boulder, CO 80305 (raina.gough@colorado.edu), <sup>2</sup>WM Keck Laboratory for Space Simulations, Arkansas Center for Space and Planetary Sciences, University of Arkansas, Fayetteville, AR 72701.

**Introduction:** Perchlorate ( $\text{ClO}_4^-$ ) salts may be responsible for formation of aqueous solutions on Mars due to their low eutectic temperatures [1] and their ability to readily absorb water vapor and deliquesce into an aqueous phase [2]. We have previously shown that spontaneous formation of saturated  $\text{NaClO}_4$  solution occurs at low relative humidity (RH) values (~40%), and supersaturated  $\text{NaClO}_4$  solutions can exist under even drier conditions (down to 13% RH) [2]. Perchlorate deliquescence may have been observed by Phoenix [3] and this humidity-induced phase transition could be an explanation for the formation of brines that may have recently flowed on Mars [4].

Although  $\text{ClO}_4^-$  is a major anion in the regolith, there are other salts and minerals present as well. To understand the environmental conditions that may allow aqueous solutions to form and persist on Mars, the effects of these other components on the deliquescence RH (DRH) must be considered. For example, the addition of  $\text{NaCl}$  (DRH = 75%), also found near the Phoenix lander, [5] could affect the deliquescence of highly hygroscopic  $\text{NaClO}_4$  (DRH = 40%). Here we use Raman microscopy to study the deliquescence (solid to aqueous transition) and efflorescence (aqueous to solid transition) of three perchlorate/chloride mixed salt systems:  $\text{KClO}_4/\text{KCl}$  at 253 K,  $\text{NaClO}_4/\text{NaCl}$  at 243 K and  $\text{Mg}(\text{ClO}_4)_2/\text{MgCl}_2$  at 243 K.

**Experiments and results:** Phase transition experiments were performed using a Raman microscope with an environmental cell [6]. Humidity and temperature inside the cell were controlled and phase transitions of the salts were monitored with optical microscopy or Raman spectroscopy. Salt samples containing both  $\text{Cl}^-$  and  $\text{ClO}_4^-$  were produced by atomizing salt solutions. Internally-mixed, micron-sized crystalline particles were deposited onto a quartz substrate. For each system ( $\text{NaClO}_4/\text{NaCl}$ ,  $\text{MgCl}_2/\text{Mg}(\text{ClO}_4)_2$  and  $\text{KClO}_4/\text{KCl}$ ), several mole ratios (moles  $\text{ClO}_4^-/(\text{mol } \text{ClO}_4^- + \text{mol } \text{Cl}^-)$ ) between 0 and 1 were studied.

Figure 1 depicts typical deliquescence of a salt mixture. A 10  $\mu\text{m}$  40%  $\text{NaClO}_4/60\%$   $\text{NaCl}$  particle is deliquesced at 243 K by gradually adding water vapor to the environmental cell. Microscope images (top row) and corresponding Raman spectral maps (bottom row) show the morphological and compositional changes during deliquescence. The color of the spectral maps corresponds to the intensity of the liquid water peak at  $3450 \text{ cm}^{-1}$  (an O-H stretch). We observe

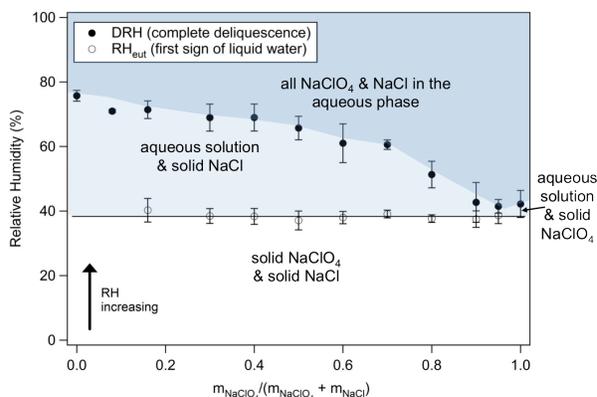


**Fig. 1.** Microscope images and Raman spectral maps illustrating deliquescence of a 40%  $\text{NaClO}_4/60\%$   $\text{NaCl}$  particle as RH is increased at 243 K. An aqueous phase is present by 40% RH and deliquescence is complete by 74% RH.

that deliquescence of salt mixtures occurs gradually; while there is an aqueous phase present by 40% RH, solid persists until 74% RH. We define DRH as the humidity at which the entire particle is aqueous.

Figure 2 summarizes the results of our  $\text{NaClO}_4/\text{NaCl}$  mixed salt deliquescence experiments. The RH values at which a mixture first contains a detectable aqueous phase (open circles) and then completely deliquesces (solid circles) are plotted as a function of  $\text{NaClO}_4$  mole fraction. The DRH of these mixtures appears to be approximately a linear combination of the DRH of pure  $\text{NaClO}_4$  (40% RH) and pure  $\text{NaCl}$  (75% RH). Despite the significant variation of DRH with salt composition, we find that all mixtures contain an aqueous phase by 38% RH.

The shading in Fig. 2 (also in Fig. 3) provides a visual understanding of the phases present: in the white region, all salts are in a solid phase. In the light blue regions, both aqueous and solid phases are present. In

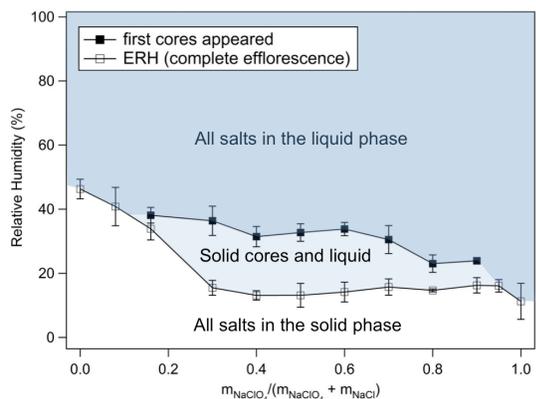


**Fig. 2.** Phase transitions observed when RH is increased around  $\text{NaClO}_4/\text{NaCl}$  particles held at 243 K. Although the DRH of a salt mixture is highly dependent on composition, there is always an aqueous phase present above 38% RH.

the dark blue region, all salts are fully deliquesced.

This observed behavior is predicted by theory and is well understood for a two salt system [7]. The humidity at which an aqueous phase first forms is the eutonic relative humidity ( $RH_{\text{eut}}$ ). At this point, the aqueous phase is saturated with both salts regardless of the initial composition of the solid. The concentration at which the DRH is at a minimum (and equals the  $RH_{\text{eut}}$ ) is the eutonic concentration. For the  $\text{NaClO}_4/\text{NaCl}$  system, we find that  $RH_{\text{eut}}$  is 38% and the eutonic concentration is 95%  $\text{NaClO}_4/5\%$   $\text{NaCl}$ .

When humidity is decreased around a fully deliquesced salt mixture, crystallization proceeds in a manner that mirrors deliquescence. First, a solid core forms in the aqueous droplet. Lowering RH further causes complete efflorescence, during which all liquid water is expelled. We have previously reported that the RH at efflorescence (ERH) is lower than the DRH for pure perchlorate due to the kinetic inhibition of crystallization [2]. Here we find this hysteresis effect is also observed for perchlorate/chloride mixtures. Any aqueous phases observed at humidities below  $RH_{\text{eut}} = 38\%$  are supersaturated with respect to both  $\text{NaClO}_4$  and  $\text{NaCl}$ . These metastable solutions were observed during the efflorescence of all  $\text{NaClO}_4/\text{NaCl}$  mixtures.



**Figure 3.** Phase transitions observed when RH is lowered around aqueous  $\text{NaClO}_4/\text{NaCl}$  salt particles at 243 K. Partial crystallization occurs between 23 and 40% RH (solid squares). An aqueous phase persists until lower humidity values are reached and efflorescence occurs (open squares).

**Martian implications:** It is likely that perchlorates and chlorides coexist in the Martian regolith. The Wet Chemistry Laboratory onboard Phoenix detected both anions in all soil samples studied [5]. Additionally, it has been suggested that both perchlorate [8,9] and chloride [10] salts may be widespread across Mars and are therefore likely to coexist elsewhere on the planet.

Our experimental results allow us to predict the likely phase transition behavior of any specific low-temperature mixture of  $\text{NaClO}_4$  and  $\text{NaCl}$ . If only these two species are considered, the  $\text{NaClO}_4$  mole fraction

at the Phoenix landing site is  $\sim 0.85$  [5]. As seen in Fig. 2, a salt mixture of this composition would first form an aqueous phase at 38% RH (as would any  $\text{NaClO}_4/\text{NaCl}$  mixture) and would then fully deliquesce by 46% RH. Therefore, although the presence of  $\text{NaCl}$  may raise the DRH of this Mars-relevant salt mixture slightly relative to pure  $\text{NaClO}_4$ , an aqueous phase will be formed at a similar RH as if only  $\text{NaClO}_4$  was present.

As seen in Fig. 3, an 85%  $\text{NaClO}_4/15\%$   $\text{NaCl}$  salt partially crystallizes at 24% RH but maintains an aqueous phase down to 15% RH. For comparison, pure  $\text{NaClO}_4$  solution would completely transition from aqueous to solid at 13% RH. Therefore the presence of  $\text{Cl}^-$  ions does not significantly change the lower limit of aqueous perchlorate solution metastability.

Humidity at the Phoenix lander site varies from near 0% to 100% RH diurnally, mainly driven by temperature fluctuations [11]. It seems probable then that any  $\text{NaClO}_4$  and  $\text{NaCl}$  mixtures present at this location will enter the aqueous phase during a diurnal cycle. Studies of the temperature dependence of these phase transitions, as well as a better understanding of the RH conditions in the Martian subsurface, are needed to accurately predict periods during which aqueous solutions can form from salt mixtures.

Although not discussed in this abstract, we will also present the results of the two other  $\text{ClO}_4^-/\text{Cl}^-$  systems studied (potassium, magnesium).

**Conclusions:** We have experimentally studied the deliquescence and efflorescence of perchlorate/chloride mixtures. We find that adding increasing amounts of a less deliquescent salt ( $\text{NaCl}$ ) to highly deliquescent  $\text{NaClO}_4$  will raise the complete DRH of the mixture. However, an aqueous phase first forms at the eutonic RH, a value always below the DRH of either of the two pure components. Therefore consideration of the effect of salt mixtures is important, as the presence of a highly deliquescent salt can extend the range of RH values for which aqueous solutions exist on Mars, even if present in small amounts in a mixture.

**References:** [1] Chevrier et al. (2009) *GRL*, 36, L10202. [2] Gough et al. (2011) *EPSL*, 312, 371-377. [3] Renno et al. (2009) *JGR-Planets*, 114, E00E03. [4] McEwen et al. (2011) *Science*, 333, 740-743. [5] Hecht et al. (2009) *Science*, 325, 64-67. [6] Baustian et al. (2009) *ACP*, 10, 2307-2317. [7] Seinfeld & Pandis (2006) *Atmospheric Chemistry and Physics – From Air Pollution to Climate Change*, John Wiley & Sons [8] Catling et al. (2010) *JGR-Planets*, 15, E00E11. [9] Navarro-Gonzalez et al. (2011) *JGR-Planets*, 116, E08011. [10] Osterloo et al. (2010) *JGR-Planets*, 115, E10012. [11] Zent et al. (2010), *JGR-Planets*, 115, E00E14.