Formation of aqueous solutions on Mars via deliquescence of chloride–perchlorate binary mixtures

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A B S T R A C T

Perchlorate salts, known to exist on Mars, can readily absorb water vapor and deliquesce into aqueous solutions even at low temperatures. The multiple soluble ionic species, such as chloride salts, present in the Martian subsurface may affect this deliquescence. Here we study the deliquescence (solid to aqueous transition) and efflorescence (aqueous to solid transition) of three perchlorate/chloride mixtures: $KClO_4/KCl$ at 253 K, $NaClO_4/NaCl$ at 243 and 253 K, and $Mg(ClO_4)_2/MgCl_2$ at 243 and 253 K. A Raman microscope with an environmental cell was used to monitor the phase transitions of internally mixed ClO_4^-/Cl^- particles as a function of the perchlorate mole fraction. The eutonic relative humidity (where deliquescence begins to occur regardless of ClO_4^- mole fraction), deliquescence relative humidity (DRH, where complete deliquescence occurs), and efflorescence relative humidity (ERH) were measured for several perchlorate mole ratios for each cation system. At the temperatures studied, the eutonic relative humidity was measured to be 28% RH for $Mg(ClO_4)_2/MgCl_2$ mixtures, 38% RH for $NaClO_4/NaCl$ mixtures, and 82% RH for $KClO_4/KCl$ mixtures. The DRH depends on the perchlorate mole ratio, but is below the DRH of the least deliquescent (highest DRH) pure salt. When humidity is lowered around an aqueous salt mixture, we find that efflorescence occurs at an RH below the DRH due to the kinetic inhibition of crystallization. The ERH values of the salt solutions were as low as 5% RH for $Mg(ClO_4)_2/MgCl_2$ mixtures, as low as 13% RH for $NaClO_4/NaCl$ mixtures, and as low as 66% RH for $KClO_4/KCl$ mixtures. The low eutonic RH values for the Na^+ and Mg^{2+} perchlorate/chloride mixtures are important: wherever $Mg(ClO_4)_2$ and $MgCl_2$ or $NaClO_4$ and $NaCl$ coexist at the temperatures studied, mixtures will contain a stable aqueous phase above 28 or 38% RH, respectively, regardless of the perchlorate mole fraction. This liquid water may persist until 5 or 13% RH, respectively.

1. Introduction

1.1. Perchlorate on Mars

Perchlorate (ClO_4^-) salts, recently discovered at the Phoenix landing site (Hecht et al., 2009; Cull et al., 2010), are interesting due to their chemical and physical properties. Like many soluble salts, perchlorates are deliquescent, meaning the crystalline salt can form an aqueous solution by absorption of atmospheric water vapor. It has been suggested that deliquescence of perchlorate was observed by Phoenix (Renno et al., 2009; Smith et al., 2009) and this humidity-induced deliquescence could be an explanation for the formation of brines which may have re-

cently flowed across the Martian surface (McEwen et al., 2011; Chevrier and Rivera-Valentin, 2012).

The deliquescence phase transition occurs when the relative humidity (RH) of the local atmosphere is equal to or greater than the deliquescence relative humidity (DRH) of the salt. Previous laboratory studies by Gough et al. (2011) and Zorzano et al. (2009) have found that the DRH of sodium (Na^+) and magnesium (Mg^{2+}) perchlorate salts can be as low as 38% RH. Although the DRH varies with hydration state, temperature and cation, all Na^+ and Mg^{2+} perchlorates deliquesce at low RH values relative to many salts such as sulfates.

Efflorescence, the recrystallization of salt solution into a crystalline phase, occurs at a lower relative humidity than deliquescence for a given salt at constant temperature. The efflorescence relative humidity (ERH) is lower than the DRH for most inorganic salts (Tang, 1997; Martin, 2000) because the crystallization process is kinetically hindered. Although deliquescence occurs as

Table 1
DRH and ERH values of the six pure salts used to make the salt mixtures studied here. When known, the hydration state of the salt and the measurement temperature are given for the DRH and ERH values.

Cation	Salt	Solubility at 273 K (mass %)[a]	DRH	ERH
Na$^+$	NaClO$_4$ (anhydrous)	61.9%	38 ($\pm$3)%[b,c]	13 ($\pm$2)%[b,c]
	NaClO$_4 \cdot$H$_2$O		51 ($\pm$2)% at 273 K[c]	13 ($\pm$2)%[b,c]
			64 ($\pm$4)% at 228 K[c]	
	NaCl (anhydrous)	26.28%	75% at 293 K[d]	44% at 293 K[f]
K$^+$	KClO$_4$ (anhydrous)	0.70%	92 ($\pm$2)% at 253 K[f]	77 ($\pm$6)% at 253 K[d]
	KCl (anhydrous)	21.74%	84% at 293 K[d]	59% at 293 K[f]
Mg^{2+}	Mg(ClO$_4$)$_2 \cdot$6H$_2$O	47.8%	42 ($\pm$2)% at 273 K[c]	19 ($\pm$3)%[b,c]
			55 ($\pm$2)% at 223 K[c]	
	MgCl$_2 \cdot$6H$_2$O	33.96%	33.7 ($\pm$0.3)% at 273 K[g]	14 ($\pm$4)% at 243 K[e]

[a] CRC Handbook, 94th ed.
[b] Independent of temperature between 223 and 273 K.
[c] Gough et al. (2011).
[d] Cohen et al. (1987a).
[e] This work; not previously measured.
[f] Cohen et al. (1987b).
[g] Greenspan (1977).

soon as the free energy of the crystalline and aqueous phases are equal (i.e.: when the transition is thermodynamically favorable), salt crystallization is a phase transition to a more ordered state and requires nucleation. Supersaturated salt solutions are metastable and can exist for significant time periods at RH < DRH. NaClO$_4$ and Mg(ClO$_4$)$_2$ were found to exhibit this hysteresis; the ERH values of these salts are 13% and 19% RH, respectively (Gough et al., 2011). These low RH values are independent of temperature between 223 and 273 K and suggest that metastable perchlorate solutions may exist on Mars over a large range of RH values. Although DRH values can generally be predicted from thermodynamical calculations, ERH values must be measured by laboratory studies.

The deliquescence and efflorescence behavior of many perchlorates is now well established. However, to better understand the deliquescence and efflorescence of perchlorate salts on Mars, it is important to consider the effect of other species that may be present. In addition to perchlorate, the Wet Chemistry Laboratory (WCL) instrument onboard Phoenix found chloride (Cl$^-$), sulfate (SO$_4^{2-}$), carbonate (CO$_3^{2-}$), magnesium (Mg^{2+}), calcium (Ca^{2+}), sodium (Na$^+$), and potassium (K$^+$) in the regolith (Hecht et al., 2009). Neither the vertical nor spatial distributions of these ions are known, but all were present in each of the three 1 cm^3 soil samples tested by WCL. It is likely, therefore, that other salts coexist with perchlorate. These additional soluble components of the regolith are present at various concentrations and have different solubilities. Some salts may be more deliquescent than perchlorate, although most are likely to be less. These additional species could affect the deliquescence and efflorescence of perchlorate salts and it is important to understand this effect.

Chloride was found at the Phoenix landing site (Hecht et al., 2009) and chloride deposits are thought to be globally widespread (Osterloo et al., 2010). Quantifying the effect of chloride salts on the deliquescence of perchlorate will help determine the conditions under which water will be absorbed by ClO$_4^-$/Cl$^-$ mixtures on Mars and may also elucidate the likely behavior of other Mars-relevant salt mixtures. Based on cation measurements performed by WCL, potential Mars-relevant perchlorate salts include NaClO$_4$, Mg(ClO$_4$)$_2$ and potassium perchlorate (KClO$_4$). Potentially Mars-relevant chloride salts include sodium chloride (NaCl), magnesium chloride (MgCl$_2$) and potassium chloride (KCl). The DRH and ERH values of these six salts, as well as their solubility in water at 273 K, are shown in Table 1. In this paper, we perform laboratory experiments investigating the deliquescence and efflorescence of the following 2-salt mixtures: KClO$_4$/KCl at 253 K, NaClO$_4$/NaCl at 243 and 253 K, and Mg(ClO$_4$)$_2$/MgCl$_2$ at 243 and

253 K. We focus particularly on the effect of the perchlorate mole ratio (m$_{ClO_4^-}$/(m$_{ClO_4^-}$ + m$_{Cl^-}$)) on the DRH and ERH of these mixtures, where m$_{ClO_4^-}$ is moles of perchlorate ion and m$_{Cl^-}$ is moles of chloride ion.

1.2. Theory of mixed salt phase transitions

Although the deliquescence and efflorescence of perchlorate-containing mixtures have not been studied, other 2-salt systems have been investigated. The humidity-driven phase transitions of several binary salt mixtures have been studied experimentally (Tang and Munkelwitz, 1993; Tang, 1997; Carroll et al., 2005; Yang et al., 2006) and theoretically (Potukuchi and Wexler, 1995). A schematic of the expected deliquescence behavior of salt mixtures is shown in Fig. 1, plotted as RH (%) vs. mole fraction of salt 1 (m$_{salt\ 1}$/(m$_{salt\ 1}$ + m$_{salt\ 2}$)), where m$_{salt\ 1}$ and m$_{salt\ 2}$ are the moles of salts 1 and 2 in the mixture, respectively.

When humidity is raised around a 2-salt mixture, the following sequence of events is expected to occur: first, when RH is low (region A), any mixture of salts 1 and 2 consists entirely of a solid phase. When the humidity is raised to the eutonic relative humidity, RH$_{eut}$ (dashed line), an aqueous phase forms. The aqueous salt concentration at RH$_{eut}$ is the eutonic concentration. This initial solution is saturated with both salts 1 and 2 and a solid phase is present in most cases. If the mole ratio of salts in the original mixture is equal to the eutonic concentration, complete deliquescence (full conversion to the aqueous phase) will occur at RH$_{eut}$. For all other compositions, a solid phase will exist in equilibrium with the aqueous phase when the RH is above RH$_{eut}$ (dashed line) but below the DRH (solid line). The composition of this solid is pure salt 2 if the original mixture was enriched in salt 2 relative to the eutonic concentration (region B) and pure salt 1 if enriched in salt 1 (region C). Continuing to increase the RH around this 2-phase mixture will increase the ratio of aqueous to solid salt. Finally, when the humidity reaches the DRH (solid line), complete deliquescence occurs. Above the DRH (region D) only an aqueous phase is present. At this point, the aqueous phase contains the same mole ratio found in the original solid.

There are two ways that a mixture can boost the formation of an aqueous phase relative to a pure salt. First, RH$_{eut}$ of a 2-salt mixture is always lower than the DRH of either pure component. Therefore, the presence of even small amounts of a more deliquescent salt (salt 1 in Fig. 1) can cause partial dissolution at a RH value far below the DRH of the less deliquescent salt (salt 2). Additionally, the humidity at which a mixture fully deliquesces is
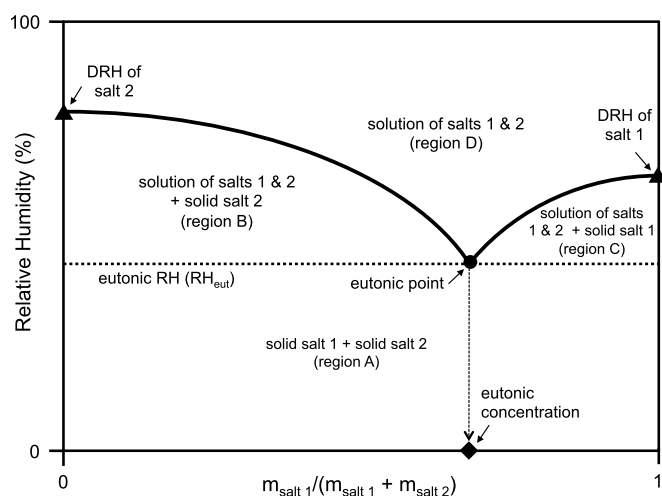
Fig. 1. Schematic diagram highlighting the important regions and points of a theoretical salt 1 + salt 2 + H_2O vapor system. The DRH values of the two pure components are represented by the solid triangles at $x = 1$ and $x = 0$. Complete deliquescence of the salt mixture occurs at the solid line. The mixtures do not deliquesce as a linear combination of the pure components; rather, the DRH values decrease to a minimum at a concentration of salts 1 and 2 known as the eutonic concentration (solid diamond symbol). Above the eutonic relative humidity (RHeut), represented by the dashed line, an aqueous phase will exist. This figure is derived from Seinfeld and Pandis (1998).

always below the DRH of the least deliquescent (highest DRH) salt. Mixtures at or near the eutonic concentration will have especially low DRH values. These attributes of salt mixtures are likely important in the Martian regolith where multiple salts coexist.

Fig. 1 is based on thermodynamic theory and is only applicable to phase transitions that occur when RH is increased around a salt mixture. When RH is lowered around an aqueous salt mixture, the events described above may not occur in reverse. There are few studies of the efflorescence of mixtures, but Tang and Munkelwitz (1993) suggest that there is a two-step crystallization process during which each salt effloresces independently, and that a hysteresis effect is observed. We have found no data regarding efflorescence of perchlorate mixtures, or low-temperature salt mixtures of any composition. Laboratory studies are likely necessary to determine the extent of the hysteresis of crystallization of salt mixtures.

In order to determine conditions of aqueous solution formation, stability and metastability in the Martian regolith, here we aim to experimentally determine the RH_{eut} (where an aqueous phase first forms), DRH (where complete deliquescence occurs) and ERH (where efflorescence of the salt solution occurs) for $NaClO_4/NaCl$, $KClO_4/KCl$ and $Mg(ClO_4)_2/MgCl_2$ mixtures. We are also able to determine the eutonic concentration of each mixture after locating the minimum DRH value for each system. None of these humidity or concentration values have been determined either experimentally or theoretically prior to this work.

2. Experimental methods

2.1. Sample selection and preparation

All salts were obtained from Sigma Aldrich and were ⩾98% pure. In the case of $NaClO_4$, $NaCl$, $KClO_4$, and KCl, the anhydrous form of the salt was used, meaning no H_2O was present in the solid at the start of the experiments. The magnesium salts were purchased as $Mg(ClO_4)_2 \cdot 6H_2O$ and $MgCl_2 \cdot 6H_2O$. For each cation system, approximately ten aqueous solutions with perchlorate mole fraction ($m_{ClO_4^-}/(m_{ClO_4^-} + m_{Cl^-})$) values between 0 and 1 were prepared. Solutions of the six pure salts were also prepared in order to measure DRH values and compare to the literature.

The aqueous solutions of sodium mixtures and magnesium mixtures contained a total ion molarity of ∼1.0 M. The potassium salts ($KClO_4$ and KCl) were less soluble and these aqueous solutions contained a total ion molarity of ∼0.1 M.
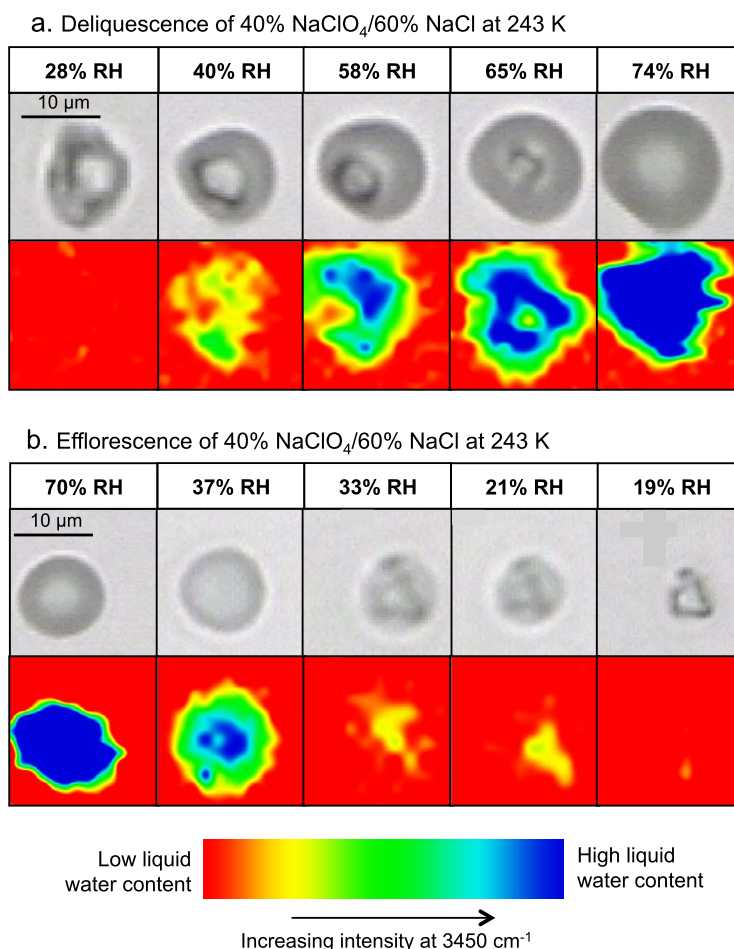
To prepare a sample for analysis, mixed salt particles were deposited onto a hydrophobic quartz substrate using a constant output atomizer at room temperature. Atomization produces a stream of small particles from an aqueous solution using pressurized nitrogen gas. After the particle samples were prepared, the quartz disc was placed into the environmental cell. The dry conditions in the environmental cell immediately effloresced all salts. No aqueous phase salts were ever observed prior to an experiment. The dry particles had diameters of 2–10 µm in the case of Na^+ mixtures, 2–20 µm in the case of Mg^{2+} mixtures, and 1–2 µm in the case of K^+ mixtures. We assume the particles have the composition of the bulk solution from which they were generated and are internally mixed. Spectra confirmed that sodium and potassium salts never contained any hydrated species, but hydrated species were present in the dry (crystalline) magnesium salt mixtures, as confirmed by Raman spectroscopy.

2.2. Environmental cell and Raman microscope

The experimental system used here to study salt phase transitions has been previously described in detail by Baustian et al. (2010). The environmental cell containing the sample can be cooled to a desired temperature with liquid nitrogen (LN_2). The sample temperature was controlled and monitored using an automated temperature controller. Salt samples were maintained at constant temperature during all experiments. The humidity in the cell can be varied from <1 to 100% RH by adjusting the relative amounts of humidified and dry N_2 flow. A chilled-mirror hygrometer measured the dew point of N_2 exiting the environmental cell. This dew point and the sample temperature can be used to calculate the relative humidity experienced by the sample. The LN_2 lines were insulated and the environmental cell walls were at room temperature ensuring that the sample was the coldest surface in the cell. Relative humidity was therefore always highest at the sample, minimizing H_2O adsorption elsewhere. In this paper, all reported RH values represent the RH with respect to liquid water at the salt sample.

Humidity-induced changes in the appearance of salt particles were imaged using an optical microscope (Olympus BX51, 50× objective). Particle composition and phase were probed using a Nicolet Almega XR Dispersive Raman spectrometer. We show in Gough et al. (2011) that Raman spectroscopy can be used to differentiate anhydrous, hydrated crystalline, and deliquesced (aqueous) perchlorate. A single mixed salt particle may contain both solid and aqueous phases at times and this spatial heterogeneity is not well characterized with a single spectrum. Therefore, changes in the visual appearance of particles as well as Raman mapping were used in this work. Continuous monitoring with optical microscopy enabled us to precisely determine important moments in an experiment such as the first appearance of an aqueous phase at the RH_{eut} or complete deliquescence at the DRH. The Raman mapping allowed confirmation of the presence or absence of an aqueous phase or crystalline H_2O.

During an experiment, H_2O vapor was increased or decreased stepwise at ∼1 to 3% RH intervals. The RH was held at each value for several minutes until the water vapor flow through the cell was constant and the Raman spectra and microscope image did not change. The system flow rate (1.0 L/min) allows a volume of air to travel from the cell to the hygrometer in ∼1 s. Because the humidity variations are occurring on much longer time scales (several minutes), we are confident that humidity is measured in real time and each reported RH value is accurate within 1% RH. Although

a. Deliquescence of 40% NaClO$_4$/60% NaCl at 243 K

b. Efflorescence of 40% NaClO$_4$/60% NaCl at 243 K

Fig. 2. Microscope images and Raman maps depicting the morphological and spectral changes of a 40% NaClO$_4$/60% NaCl particle ($T = 243$ K) as relative humidity is (a) increased until deliquescence occurs and then (b) decreased until efflorescence occurs. The Raman maps depict the abundance of liquid water contained in the mixed salt particle by plotting the intensity of the O-H stretching region (3450 cm^{-1}) on the color axis. The dry salt particle was ∼10 μm in diameter. The particles shown in (a) and (b) are different, although the composition (40% NaClO$_4$/60% NaCl) and temperature (243 K) are identical. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the hygrometer reading and temperature measurement result in an experimental uncertainty of ±1% for each individual RH measurement, the error bars obtained by averaging multiple experiments are as large as 5% in some cases but typically 3%. We attribute this to the manual introduction and control of water vapor and the difficulty in detecting the phase transitions.

3. Results of phase transition experiments
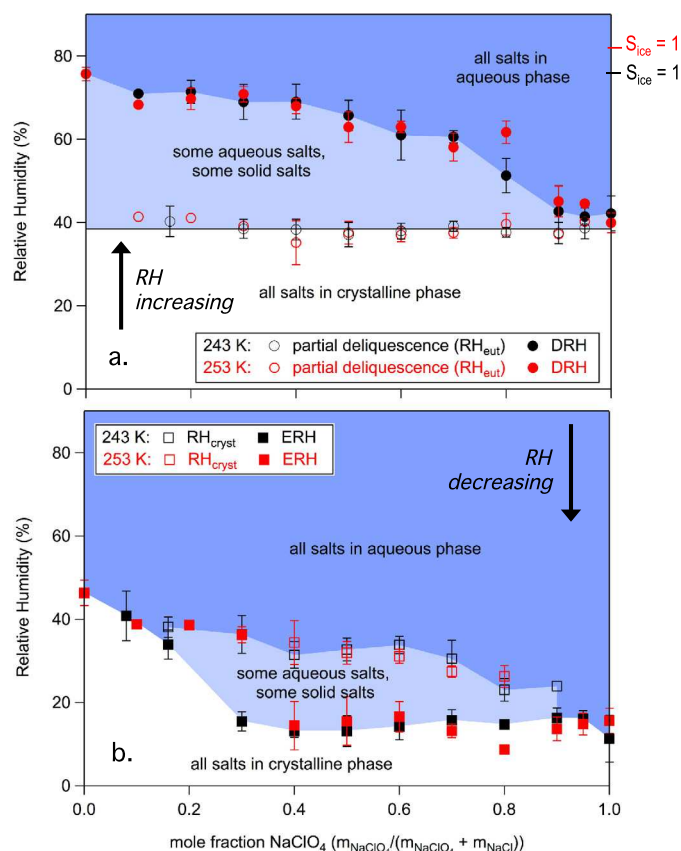
3.1. NaClO$_4$/NaCl mixtures

Fig. 2 shows the morphological and spectral changes of a 40% NaClO$_4$/60% NaCl particle as RH is (a) increased and (b) decreased while the sample temperature is held constant at 243 K. The Raman maps depict the spatial distribution and abundance of liquid water in the mixed salt particle by plotting the intensity at 3450 cm^{-1} (O-H stretching region) on the color axis. This region of the Raman spectrum (2800–3800 cm^{-1}) is composed of several broad vibrational features, the exact location of which depends on the molecular environment of the H$_2$O (phase, temperature, solute concentration, etc.) (Li et al., 2004; Auer and Skinner, 2008). A peak exists in this region regardless of the phase of the associated water (crystalline hydrate, liquid, or ice); however, the shape and location of the peak are dependent on the phase. Liquid water, which produces a very broad peak due to hydrogen bonding

interactions, is the phase seen during these experiments and is the phase mapped in Fig. 2.

It can be seen in Fig. 2a that the salt particle is entirely crystalline at 28% RH. The shape is non-spherical and the particle has visible internal heterogeneity. The Raman map confirms that there is no water of any phase associated with this particle at 28% RH. By 40% RH there is liquid water visible on the outer edges of the particle and confirmed by Raman mapping. This aqueous phase causes the particle to appear more spherical. As RH is further increased, both the images and spectral maps show an increasing ratio of aqueous to solid salt. By 65% RH there is only a small solid core inside the aqueous droplet. By 74% RH, deliquescence is complete and all salts exist in the aqueous phase.

The images in Fig. 2b show the phase transition steps that typically occur when RH is lowered around a mixed salt particle. The spherical shape and the Raman map confirm that the salt mixture is still completely aqueous at 37% RH, although the intensity of the O-H stretching region in the Raman map has decreased because there is less water in the supersaturated salt solution. Despite this salt supersaturation, no solid phase has yet formed. Lowering the humidity to 33% RH results in partial crystallization of the mixed salt particle. At 21% RH, there is still an aqueous phase present, although the volume of the aqueous phase may have decreased. By 19% RH all salts have crystallized and efflorescence is complete. There is now no water of any type associated with the particle.

Fig. 3. Phase transitions observed when RH is (a) increased and (b) decreased around NaClO$_4$/NaCl mixtures at 243 and 253 K. White regions represent conditions in which all salts are in the solid phase, light blue regions represent conditions in which there is coexistence of a solid and aqueous phase, and darker blue regions represent conditions in which all salts are in the aqueous phase. The tick marks on the right y-axis represent the RH values at which the water vapor in the system is saturated with respect to ice (i.e.: when $S_{ice} = 1$) at the two temperatures studied. The colored regions are descriptive of the phase(s) present for a given perchlorate mole ratio and relative humidity. In white regions (RH < RH$_{eut}$) all salts were observed to be in the solid phase, in light blue regions there is coexistence of solid and aqueous phases, and in dark blue regions (RH > DRH) all salts were observed to be in the aqueous phase. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 2 demonstrates that humidity can be lowered to an RH below the DRH before crystallization occurs.

All experiments performed on NaClO$_4$/NaCl mixtures progressed in a manner similar to what is pictured in Fig. 2. At most perchlorate mole fractions, we were able to report the humidity at four phase transition events: RH$_{eut}$ (first appearance of an aqueous phase), DRH (complete conversion to an aqueous phase), RH$_{cryst}$ (first appearance of a crystalline phase), and ERH (complete conversion to a crystalline phase). The summary of phase transition results for the NaClO$_4$/NaCl system are plotted in Fig. 3a (phase transitions that occur when RH is increased) and Fig. 3b (phase transitions that occur when RH is decreased). The x-axis is the perchlorate mole ratio in the sample, $m_{NaClO_4}/(m_{NaClO_4} + m_{NaCl})$, where m_{NaClO_4} and m_{NaCl} are the moles of NaClO$_4$ and NaCl, respectively. Experiments were performed at 253 K (red points) and 243 K (black points).

The RH values at which an aqueous phase was first observed, RH$_{eut}$, are represented by open symbols in Fig. 3a. This phase transition occurred at $38 \pm 2\%$ RH regardless of the perchlorate mole ratio in the starting material or temperature (243 vs. 253 K). This RH$_{eut}$ value for the NaClO$_4$/NaCl system at the temperatures studied is much lower than the DRH of pure NaCl (75%) and equal, within uncertainty, to the DRH of pure NaClO$_4$ ($41.1 \pm 3.3\%$) under

these temperature conditions. Continuing to increase the humidity past RH$_{eut}$ caused complete deliquescence to occur at the RH values denoted by the solid symbols in Fig. 3a. We can see that the DRH varies almost linearly as a function of the perchlorate mole ratio. In most cases neither the DRH nor RH$_{eut}$ of any NaClO$_4$/NaCl mixture differed significantly between 253 and 243 K. Small differences may be masked by our experimental uncertainty. Despite the lack of a distinct minimum in the DRH values at RH$_{eut}$ seen in the theoretical stability diagram (Fig. 1), we believe that the expected behavior is occurring in the NaClO$_4$/NaCl system. A distinct eutonic point is less apparent in this mixture because the eutonic concentration, based on the minimum of the DRH data points, contains $m_{NaClO_4}/(m_{NaClO_4} + m_{NaCl}) = 0.95$ (± 0.05), very close to pure NaClO$_4$. Additionally, the observed RH$_{eut}$ value is very similar to the DRH of pure perchlorate. These factors result in the mixture DRH values appearing to be a linear combination of the DRH values of the two pure components.

Also shown in Fig. 3a are the RH values at which the water vapor in the system is saturated with respect to ice ($S_{ice} = 1$). Plotted on the right y-axis are tick marks at 74.6% and 82.3% RH representing the humidity values at which $S_{ice} = 1$ at 243 K and 253 K, respectively. At the temperatures studied, these S_{ice} values are above the measured DRH values of all salts and salt mixtures, and so ice formation would not be expected to occur before deliquescence. After deliquescence, the humidity was often raised past S_{ice}; however, even when supersaturation with respect to ice was achieved, ice was never formed. Ice would be spectrally and visually differentiable from crystalline or aqueous phases. The inability of aqueous salts to freeze at or above $S_{ice} = 1$ is not surprising; significant supersaturation with respect to ice is typically necessary for ice formation to occur (Hobbs, 1974; Wise et al., 2010).

After complete deliquescence, the humidity in the environmental cell was lowered until partial and then full recrystallization of the salt mixtures occurred. These phase transition results are plotted in Fig. 3b. We observed that efflorescence of the NaClO$_4$/NaCl mixtures was a stepwise process for perchlorate mole ratios between 0.1 and 0.9. The initial crystallization, typically the formation of a small solid core in an aqueous droplet, occurred at RH values denoted by the open symbols in Fig. 3b. Pure NaCl has an efflorescence relative humidity (ERH) of 44% and pure NaClO$_4$ has an ERH of 13% at these temperatures. Generally, all mixtures appeared to first form solid cores at RH values that are linear combinations of the ERH values of the pure components. Lowering the humidity further caused complete efflorescence of the particle at RH values denoted by the solid symbols in Fig. 3b. The ERH is approximately 20% RH for $m_{NaClO_4}/(m_{NaClO_4} + m_{NaCl}) > 0.3$ increasing to $\sim$40% RH for smaller perchlorate mole ratios. In all cases, efflorescence of NaClO$_4$/NaCl mixtures resulted in formation of anhydrous salts. This result is consistent with our previous work (Gough et al., 2011), which found that NaClO$_4$ solutions effloresce into anhydrous salts. Although previous studies have observed the formation of NaCl·2H$_2$O during low temperature efflorescence of NaCl solutions (Wise et al., 2012), the NaCl present in these mixtures always formed anhydrous efflorescence products.

The differences between Figs. 3a (increasing RH) and 3b (decreasing RH) demonstrate the hysteresis effect inherent to salt phase transitions. For example, in the case of a 40% NaClO$_4$/60% NaCl particle at $T = 243$ K, the first appearance of an aqueous phase occurs at 38% RH when humidity is increased around a dry salt. When humidity is decreased around the aqueous droplet, however, some aqueous phase is present until 14% RH. Similarly, for this composition and temperature, a fully aqueous particle is not achieved until 68% RH when humidity is raised; however, when humidity is decreased, the particle is fully aqueous until 33% RH. These examples highlight the ease with which

supersaturated solutions form and illustrate the path dependence of phase transitions caused by kinetic inhibition of salt crystallization.

Introduction of a seed crystal can cause crystallization of a supersaturated solution. Therefore, it may be surprising that we observe a supersaturated solution after a portion of the salt particle has crystallized. We observe this coexistence of a solid phase and supersaturated solution in the case of $m_{NaClO_4}/(m_{NaClO_4} + m_{NaCl})$ values between 0.1 and 0.9. These two phases are visible in the 21% and 33% RH images in Fig. 2b. The most likely explanation for this is that the crystalline phase present in these particles is of a different composition than the solution. Theoretically, the solid is pure NaCl (as is the case for any 2-phase system with starting composition $m_{NaClO_4}/(m_{NaClO_4} + m_{NaCl}) < 0.95$); therefore, the solid might be a poor template for crystallization of a solution containing $NaClO_4$. However, we were not able to measure the perchlorate to chloride ratio in the crystalline phase vs. the aqueous phase in these 2-phase particles in order to confirm this nucleation template mismatch. We are able to confirm compositional differences between coexisting solid and aqueous phases in the discussion of Mg^{2+} mixtures, below (Section 3.3).

3.2. $KClO_4/KCl$ mixtures

The results of the deliquescence and efflorescence phase transition experiments on $KClO_4/KCl$ mixtures are shown in Fig. 4. All experiments were performed at 253 K. The data is presented as a function of the perchlorate mole ratio, $m_{KClO_4}/(m_{KClO_4} + m_{KCl})$, where m_{KClO_4} and m_{KCl} are the moles of $KClO_4$ and KCl in the particle, respectively. To obtain the data shown in Fig. 4a the RH was increased and to obtain the data shown in Fig. 4b the RH was decreased.

The RH values where deliquescence was observed, DRH, are represented by solid symbols in Fig. 4a. Unlike the $NaClO_4/NaCl$ mixtures discussed above, the formation of a partial aqueous solution at the eutonic RH was not observed in the case of any potassium salt mixtures. We could only definitively identify complete deliquescence. The minimum DRH value measured is 82% RH, occurring at 40% $KClO_4$/60% KCl. Based on our experimental and theoretical knowledge of the deliquescence behavior of two salt mixtures, we believe the minimum DRH value of 82% represents the RH_{eut} and the regions are shaded accordingly. The eutonic concentration, based on this minimum DRH, is 40% $KClO_4$ and 60% KCl with 10% uncertainty. The pure components, KCl (DRH = 84%) and $KClO_4$ (DRH = 92%), have high DRH values; therefore, it is not surprising that the mixtures do as well. The relative humidity at which $S_{ice} = 1$ at 253 K is 82.3% RH, denoted as a tick mark on the right axis. Although most DRH values for the $KClO_4/KCl$ mixtures were above 82.3% RH, representing conditions supersaturated with respect to ice, an ice phase was never observed to form in our experiments.

When the humidity in the environmental cell was lowered, complete efflorescence of the $KClO_4/KCl$ mixtures occurred at values represented by the filled symbols in Fig. 4b. In all cases, efflorescence of $KClO_4/KCl$ mixtures formed anhydrous salts. An intermediate state of partial crystallization was not observed, unlike in the case of the sodium mixtures. Rather, the mixed salt particles appeared to transition from fully aqueous to fully solid at a single RH value. These ERH data points are fit with a line to demonstrate that efflorescence occurs, within uncertainty, at RH values predicted by linear combination of the two pure component end points, $KClO_4$ (ERH = 77%) and KCl (ERH = 63%). There is some hysteresis between deliquescence and efflorescence in this system; an aqueous phase is observed to exist at RH values below the DRH for a given composition.
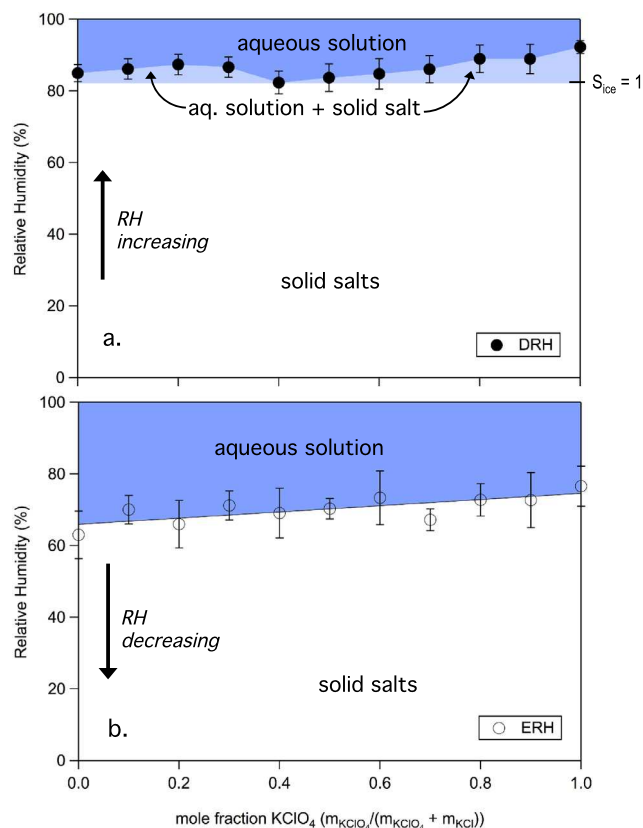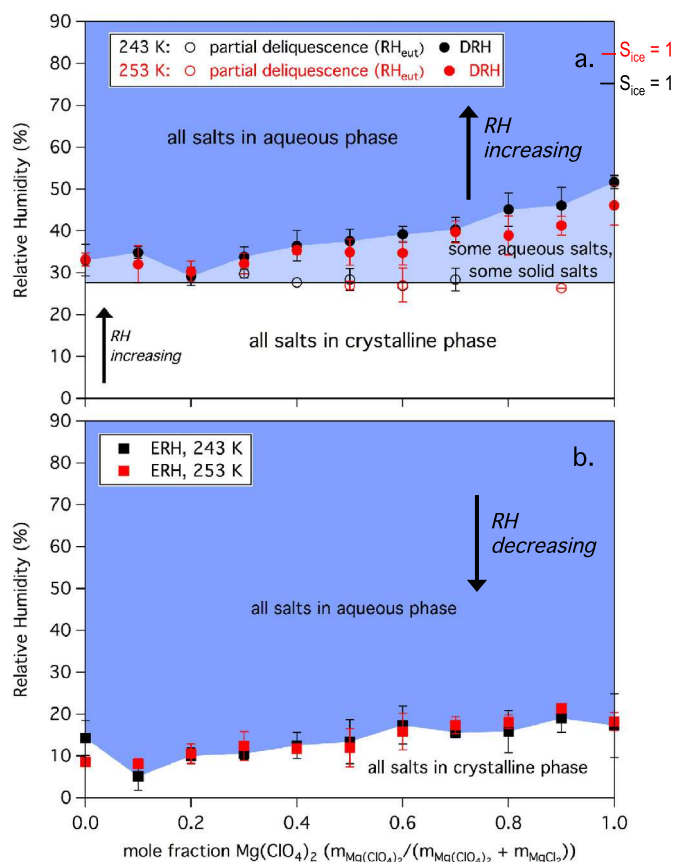

Fig. 4. Phase transitions observed when RH is (a) increased and (b) decreased around $KClO_4/KCl$ mixed particles at 253 K. The tick mark on the right y-axis represents the RH value at which the water vapor in the system is saturated with respect to ice (i.e.: when $S_{ice} = 1$) at 253 K. The white regions represent conditions in which all salts were observed to be in the solid phase, light blue regions represent conditions in which there should be coexistence of a solid and aqueous phase, and the darker blue regions represent conditions in which all salts were observed to be in the aqueous phase. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

There are several possible reasons why the transitional state containing both solid and aqueous phases was not seen during deliquescence or efflorescence of $KClO_4/KCl$ mixtures. First, the low solubility of both potassium salts caused the atomized particles to be small (diameters of 1–2 μm). The atomizer outputs similar particle size distribution regardless of composition or concentration; thus droplets of dilute solution will recrystallize into smaller particles than will droplets of concentrated solution. Small particle sizes made visual and spectral detection of the first aqueous or solid phases difficult. These initial phases, if formed, would likely be a small portion of the already small particle volume. Also complicating the detection of these intermediate phase transitions was the small RH range over which both events (first appearance of an aqueous phase and complete deliquescence) occurred. For example, if a partial aqueous phase first appeared at 82% RH and complete deliquescence occurred at 84% RH, the uncertainty in water vapor addition and other experimental factors may cause the progression from solid to aqueous to appear to occur in a single step. Finally, perhaps a single efflorescence event, as opposed to a 2-step transition, simply occurs in some cases. This may happen because the formation of a solid phase immediately initiates heterogeneous nucleation of any remaining aqueous salts.

3.3. $Mg(ClO_4)_2/MgCl_2$ mixtures

The deliquescence and efflorescence phase transition results for $Mg(ClO_4)_2/MgCl_2$ mixtures are shown in Fig. 5 as a function of

Fig. 5. Phase transitions observed when RH is (a) increased and (b) decreased around $Mg(ClO_4)_2/MgCl_2$ mixed particles at 243 and 253 K. The colored regions represent the same phases as in Fig. 3. The tick marks on the right y-axis represent the RH values at which the water vapor in the system is saturated with respect to ice (i.e.: when $S_{ice} = 1$) at the two temperatures studied. As in the previous stability diagrams, white regions represent conditions in which all salts are in the solid phase, light blue regions represent conditions in which a solid and aqueous phase coexist, and darker blue regions represent conditions in which all salts are in the aqueous phase. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the perchlorate mole ratio, $m_{Mg(ClO_4)_2}/(m_{Mg(ClO_4)_2} + m_{MgCl_2})$, where $m_{Mg(ClO_4)_2}$ and m_{MgCl_2} are the moles of $Mg(ClO_4)_2$ and $MgCl_2$, respectively, in the particle. Humidity was increased to obtain data shown in (a) and decreased to obtain data shown in (b). Experiments were performed at 253 K (red points) and 243 K (black points).

The open symbols in Fig. 5a represent the RH values at which an aqueous phase was first observed when humidity was raised. As expected, this initial eutonic solution was formed at constant humidity for all perchlorate mole ratios. This value, the RH_{eut} of the $Mg(ClO_4)_2/MgCl_2$ system, was measured to be 28% RH at both temperatures studied. When RH was greater than or equal to RH_{eut}, an aqueous phase was present and stable. The relative concentrations of the two salts at the eutonic point was seen to be 20% $Mg(ClO_4)_2$ and 80% $MgCl_2$ with 10% uncertainty. The solid symbols in Fig. 5a represent the observed DRH values where complete deliquescence occurred. Above these RH values, only an aqueous phase was present. The magnesium salts, $MgCl_2$ (DRH = 33% at 243 and 253 K) and $Mg(ClO_4)_2$ (DRH = 46% at 253 K and 52% at 243 K), are very deliquescent, thus it is not surprising that the mixtures have low DRH values as well. The RH values above which ice supersaturation occurs at both 243 and 253 K are plotted on the right axis. Because all magnesium mixtures deliquesced below 50% RH, the humidity was never raised above values corresponding to $S_{ice} \geq 1$.

When humidity was lowered, complete efflorescence of the $Mg(ClO_4)_2/MgCl_2$ mixtures occurred at values represented by the solid symbols in Fig. 5b. In all cases, efflorescence of $Mg(ClO_4)_2/MgCl_2$ mixtures formed hydrated salts. Like in the case of the potassium mixtures, mixed salt particles appeared to transition from fully aqueous to fully solid at a single RH value, never forming an intermediate 2-phase state. At the temperatures studied, the ERH values of $Mg(ClO_4)_2/MgCl_2$ are quite low, ranging from 5 to 21% depending on $m_{Mg(ClO_4)_2}/(m_{Mg(ClO_4)_2} + m_{MgCl_2})$. The expected hysteresis effect is observed; all ERH values are below the DRH for a given composition.

Both $Mg(ClO_4)_2$ and $MgCl_2$ form hydrated salts with distinct spectral features in the O-H stretching region. Therefore, we can determine whether perchlorate and/or chloride are in the solid and/or aqueous phases, allowing us to see if phase transitions are occurring in the mixtures in the manner that theory would predict. Figures S1 and S2 in the supplementary material show the Raman spectra of pure $Mg(ClO_4)_2$ and $MgCl_2$ hydrates at different humidities. To summarize, $Mg(ClO_4)_2$ is hexahydrated ($Mg(ClO_4)_2 \cdot 6H_2O$) under both ambient and experimental conditions prior to deliquescence, consistent with previous stability results (Robertson and Bish, 2011). The spectrum of $Mg(ClO_4)_2 \cdot 6H_2O$ contains a single sharp peak at 3516 cm^{-1}. Two $MgCl_2$ hydrates were observed: a tetrahydrate ($MgCl_2 \cdot 4H_2O$) and a hexahydrate ($MgCl_2 \cdot 6H_2O$). The tetrahydrate, present under room temperature and dry (<1% RH) conditions, contains a single sharp feature at 3440 cm^{-1} (Gurevich et al., 1977). Cooling the sample to 253 or 243 K and raising the RH to 3–6% formed $MgCl_2 \cdot 6H_2O$, the spectrum of which contains three peaks (3512, 3394 and 3352 cm^{-1}) (Dubessy et al., 1982). The characteristic spectra of the three salts likely to exist in our mixtures ($Mg(ClO_4)_2 \cdot 6H_2O$, $MgCl_2 \cdot 4H_2O$ and $MgCl_2 \cdot 6H_2O$) will allow us to identify the phase of the perchlorate and chloride.

Fig. 6a shows the O-H stretching region of the Raman spectra for a 50% $Mg(ClO_4)_2$/50% $MgCl_2$ particle at 243 K as humidity is raised and lowered. At each RH value, the black spectrum is of the perchlorate/chloride mixture and the red and blue traces are spectra of pure $Mg(ClO_4)_2$ or $MgCl_2$, respectively, in the relevant state (hydrated or aqueous). Fig. 6b shows microscope images of mixed salt particles under the same conditions as (a). In each case, the spectrum of the mixture can be approximately achieved by summing the two appropriate pure component spectra.

At 1.5% RH and 243 K, both salts are crystalline. We can confirm spectrally that $Mg(ClO_4)_2 \cdot 6H_2O$ and $MgCl_2 \cdot 4H_2O$ are present, as expected from the pure component behavior. Microscope images taken under these conditions show crystalline particles. By 27.6% RH, the particles appear visually similar; however, the black spectrum indicates that magnesium chloride is now $MgCl_2 \cdot 6H_2O$, as expected, while $Mg(ClO_4)_2 \cdot 6H_2O$ remains, as indicated by the 3516 cm^{-1} feature. At 30.6% RH, the humidity is just above the RH_{eut} of 28% for the this mixed salt system at 243 K, and so both aqueous and solid phases are present. The particles appear more spherical due to the presence of an aqueous outer layer. The peak at 3516 cm^{-1} is still present, confirming that solid $Mg(ClO_4)_2 \cdot 6H_2O$ remains. A crystalline perchlorate phase is expected here (between RH_{eut} and the DRH) because the original salt composition (50% $Mg(ClO_4)_2$/50% $MgCl_2$) is enriched in perchlorate relative to the eutonic concentration (20% $Mg(ClO_4)_2$/80% $MgCl_2$). The aqueous phase present at 30.6% RH likely contains a near-eutonic composition because the humidity is just above the RH_{eut} (28% RH). We have represented the aqueous phase at 30.6% RH as pure aqueous $MgCl_2$ because it is the most abundant salt in solution. Raising the RH to 37.6% visibly increases the aqueous phase and decreases the amount of solid $Mg(ClO_4)_2 \cdot 6H_2O$. The aqueous phase is approaching the original bulk composition of 50% $Mg(ClO_4)_2$ and 50% $MgCl_2$, but still contains more chloride than perchlorate salt. (We again represent the aqueous phase as $MgCl_2$
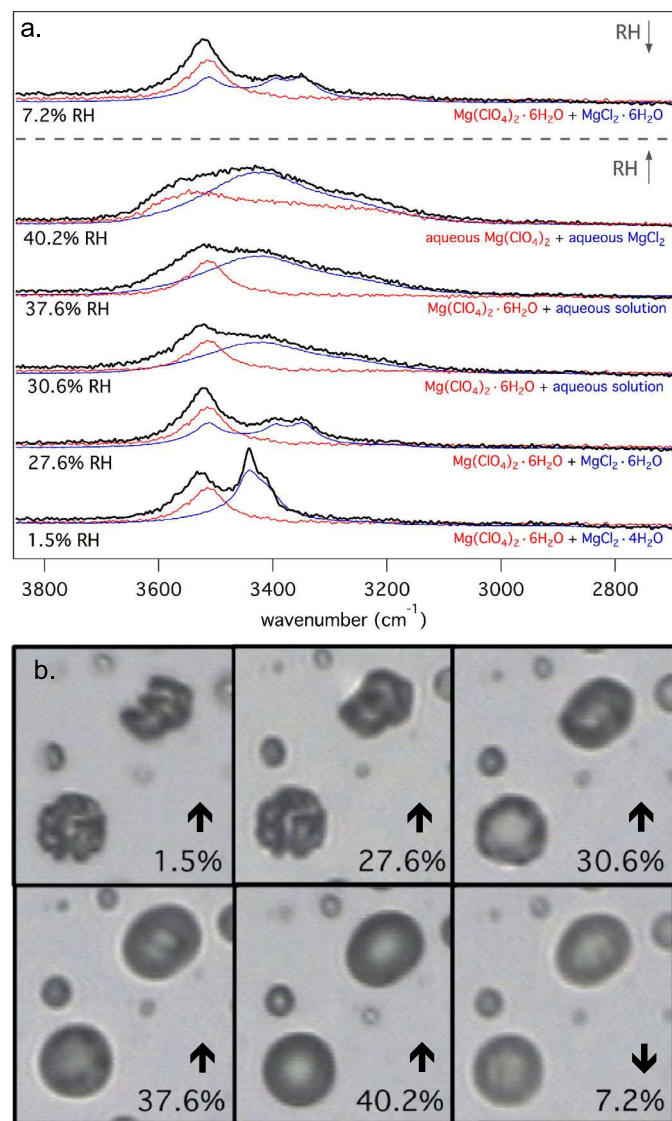
Fig. 6. Raman spectra (a) and microscope images (b) of 50% $Mg(ClO_4)_2$/50% $MgCl_2$ particles as RH is raised until full deliquescence occurs, and then lowered until efflorescence occurs. In (a), the black spectra are of perchlorate/chloride mixtures and the red and blue spectra are of pure $Mg(ClO_4)_2$ or $MgCl_2$ (either the relevant hydrate or aqueous solution). In each case, the spectrum of the mixture can be approximately achieved by summing the two pure component spectra. The lower five spectra in (a) were collected while the relative humidity was increasing, and the upper spectrum in (a) was collected while the relative humidity was decreasing. The black arrows in each image panel in (b) signify if the relative humidity was being increased or decreased when the image was collected. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 2
Summary of experimentally determined eutonic relative humidity (RH_{eut}) values and eutonic concentrations for each of the three mixed salt systems studied here. The uncertainties are also given for each value.

	RH_{eut}	Eutonic concentration
$NaClO_4$/NaCl	38 (± 2)%	95% $NaClO_4$/5% NaCl (± 5%)
$KClO_4$/KCl	82 (± 3)%	40% $KClO_4$/60% KCl (± 10%)
$Mg(ClO_4)_2$/$MgCl_2$	28 (± 3)%	20% $Mg(ClO_4)_2$/80% $MgCl_2$ (± 10%)

relationship of the original bulk composition to the eutonic concentration.

4. Discussion

There were significant differences observed in the values of RH_{eut} and DRH among mixtures containing different cations (Na^+ vs. K^+ vs. Mg^{2+}). Such differences are expected based on the large variation in DRH values among the six pure salts used to create the mixtures. In general terms, the sodium mixtures contained a low DRH salt ($NaClO_4$) and a high DRH salt (NaCl), potassium mixtures contained two high DRH salts ($KClO_4$ and KCl), and magnesium mixtures contained two low DRH salts ($Mg(ClO_4)_2$ and $MgCl_2$) (see Table 1). The relative deliquescent abilities of the pure salts can broadly predict the relative RH_{eut} of the mixture: as expected, the Mg^{2+} mixtures have the lowest RH_{eut} (28% RH), the Na^+ mixtures have a moderate RH_{eut} (38% RH), and the K^+ mixtures have the highest RH_{eut} (82% RH). In all cases, the RH_{eut} value was slightly (2–5% RH) below the DRH of the most deliquescent pure component. Table 2 lists the RH_{eut} values and also the eutonic concentration (relative amounts of salts at the eutonic point) for each of the three mixed salt systems studied here.

The observed RH_{eut} value of a cation system is constant for any combination of the two salts, therefore it is not necessary to know the exact composition of a ClO_4^-/Cl^- mixture in order to predict where an aqueous phase will form. The RH at which complete deliquescence occurs, however, cannot be predicted without mole fraction information.

A hysteresis effect was observed in all experiments performed (all cations and all mole ratios). The RH at which an aqueous phase fully recrystallized (ERH) was typically 10 to 25% RH lower than the humidity at which liquid water first appeared in the salt (RH_{eut}). The efflorescence of the mixtures did vary in behavior (one-step recrystallization in the case of Mg^{2+} and K^+ mixtures vs. two steps for Na^+ mixtures) and in magnitude (ERH values as low as 5% in the case of Mg^{2+} mixtures vs. ERH values >70% RH in the case of K^+ mixtures). These results confirm our previous finding (Gough et al., 2011) that supersaturated and metastable perchlorate solutions form readily and must be considered.

At most, we studied two temperatures for each salt mixture and therefore only limited conclusions can be drawn about the temperature dependence of these phase transitions. There is no detectable difference in the RH_{eut}, DRH, or ERH values for the $NaClO_4$/NaCl mixtures measured at the two temperatures studied; however, smaller temperature dependences may be masked by experimental uncertainty. Only a small temperature dependence would be expected at these temperatures because neither NaCl nor $NaClO_4$ exhibit significant temperature dependence during deliquescence or efflorescence between 223 and 273 K (Koop et al., 2000; Gough et al., 2011). In the case of $Mg(ClO_4)_2$/$MgCl_2$ mixtures, RH_{eut} and ERH values did not vary with temperature within experimental uncertainty; however, temperature dependence was potentially observed in the DRH of $Mg(ClO_4)_2$-rich mixtures. This behavior (higher DRH at lower temperatures) is expected because the DRH of pure $Mg(ClO_4)_2$ increases with decreasing temperature (Gough et al., 2011).

solution for simplicity.) By 40.2% RH, the particles are fully aqueous and no spectral features of solid hydrates remain.

When the humidity is lowered around the aqueous mixtures, the sample effloresces completely at a single RH value (ERH = 13.4 (± 2.8%) RH). We can confirm spectrally that efflorescence products at 243 K are $MgCl_2 \cdot 6H_2O$ and $Mg(ClO_4)_2 \cdot 6H_2O$. At 7.2% RH, the particles appear visually different than the original dry sample (1.5% RH), but internal heterogeneity is visible indicating crystallinity.

All spectra of the 2-salt mixtures collected during deliquescence are consistent with the theory depicted in Fig. 1. In addition, we were able to qualitatively visualize the distribution of perchlorate and chloride when two phases, solid and aqueous, exist. As expected, the composition of the solid portion is predicted by the

5. Martian implications

Limitations of our data and of Martian observations prevent us from predicting the phase of a salt mixture over a complete diurnal temperature and humidity cycle. Here we have measured the DRH and ERH of each mixture at only one or two temperatures and so the broader temperature dependence of these phase transitions is not known. Many salts, including perchlorates, have temperature-dependent DRH values (Tang and Munkelwitz, 1993; Onasch et al., 1999; Gough et al., 2011). Additionally, we have not yet determined the minimum temperature at which each aqueous perchlorate/chloride mixture can exist (i.e.: the freezing point depressing ability of each mixture and the absolute eutectic/eutonic).

We can, however, relate our data to the Martian environment by specifying the humidity values above which a Mars-relevant salt mixture would contain an aqueous phase, assuming the temperatures used in our experiments. The relative mole fractions of perchlorate and chloride and relevant cations were measured at the Phoenix landing site. The WCL instrument onboard Phoenix measured an average Cl^- concentration of 0.54 (± 0.09) mM and an average ClO_4^- concentration of 2.4 (± 0.28) mM. Cation concentrations were also measured: $[K^+] = 0.38$ mM, $[Na^+] = 1.4$ mM, and $[Mg^{2+}] = 3.3$ mM (Hecht et al., 2009). These anion and cation concentrations may not be representative of salt mixtures occurring elsewhere on Mars, but these are the only soluble ion measurements that exist at this time. According to the WCL measurements, the most relevant cation is Mg^{2+} followed by Na^+, and the mole fraction perchlorate, $m_{ClO_4^-}/(m_{ClO_4^-} + m_{Cl^-})$, is approximately 0.8. Potassium salts, which we found to have high RH_{eut} and DRH values, are probably not abundant on Mars.

Our experimental results, specifically the data in the $NaClO_4/NaCl$ (Fig. 3) and $Mg(ClO_4)_2/MgCl_2$ (Fig. 5) diagrams, allow us to predict the phase transition behavior of a Mars-relevant salt as humidity increases and decreases at a temperature of 243 or 253 K. As seen in Fig. 5, a magnesium mixture with $m_{Mg(ClO_4)_2}/(m_{Mg(ClO_4)_2} + m_{MgCl_2}) = 0.8$ will have a partial aqueous phase above 28% RH and will be completely aqueous above 43% RH. If the salt mixture exists in the aqueous phase and the humidity is lowered, liquid will persist until efflorescence occurs at 17% RH. If the perchlorate/chloride mixture on Mars is dominated by sodium, the results in Fig. 3 show that a salt with $m_{NaClO_4}/(m_{NaClO_4} + m_{NaCl}) = 0.8$ and a temperature of 243 K will contain some aqueous phase above 38% RH and will be completely aqueous above 51% RH. If the RH is lowered around this Mars-relevant $NaClO_4/NaCl$ mixture, some aqueous phase will persist until approximately 15% RH. Because of this hysteresis, it is essential to know the past relative humidity history in order to predict the phase of a perchlorate/chloride mixture under a given set of environmental conditions.

It is not known if these RH values coexist with the studied temperatures at locations on Mars where these salts are found. Initial results from the Thermal and Electrical Conductivity Probe onboard Phoenix found that the RH was low ($<5\%$) during the day and approached 100% at night and that measured soil temperatures ranged from 181 to 253 K (Zent et al., 2009); however, a detailed data set of correlated RH and temperature data is not currently available. It is likely that the low measured eutonic RH, DRH, and ERH values of the $Mg(ClO_4)_2/MgCl_2$ and $NaClO_4/NaCl$ systems extend to the lower temperatures found on Mars. These studies point to a possible mechanism for the formation of stable or metastable aqueous solutions on the surface of Mars today.

Appendix A. Supplementary material

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.epsl.2014.02.002.

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