Exploring the water uptake and release of Mars-relevant salt and surface analogs through Raman microscopy

by

Katherine M. Primm

B.S. University of Central Arkansas, 2012
M.S. University of Colorado Boulder, 2014

A thesis submitted to the
Faculty of the Graduate School of the
University of Colorado in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
Department of Chemistry
2018
This dissertation entitled:
Exploring the water uptake and release of Mars-relevant salt and surface analogs through Raman microscopy
written by Katherine M. Primm
has been approved for the Department of Chemistry

Professor Margaret A. Tolbert (Principal Advisor)

Raina V. Gough, Ph. D.

The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above-mentioned discipline.
Abstract

Primm, Katherine M. (Ph.D., Chemistry)

Exploring the water uptake and release of Mars-relevant salt and surface analogs through Raman microscopy

Dissertation directed by Distinguished Professor Margaret A. Tolbert

Pure liquid water is not stable on the surface of Mars because of low pressures and temperatures. The possibility of liquid water seemed more achievable since 2008 when the Phoenix lander detected ~0.5-1% perchlorate (ClO$_4^-$) in the Martian soil. Perchlorate and chloride (Cl$^-$) salts are of interest because they readily absorb water vapor and transition into aqueous solutions, a process called deliquescence. This thesis explores the interaction of several Martian surface analogs with water. To study the phase transitions of the Mars-relevant surface analogs, we use a Raman microscope and an environmental cell. Different combinations of salts and soil analogs were studied: pure Mg(ClO$_4$)$_2$, MgCl$_2$, CaCl$_2$, Ca(ClO$_4$)$_2$, and also Mg(ClO$_4$)$_2$ mixed with Mojave Mars Simulant (MMS) and montmorillonite clay.

We found that Mg(ClO$_4$)$_2$ and MgCl$_2$ solutions can supercool, forming ice only at higher relative humidity than the theoretical ice saturation conditions. It was also found that MgCl$_2$ has a large hysteresis between deliquescence and recrystallization and can also form liquids below the eutectic temperature. These results suggest that brines can persist longer than predicted by thermodynamics alone, and longer than previously predicted in the literature. It was also found that the phase transitions of magnesium perchlorate were not affected by the presence of insoluble, Mars-relevant soil analogs. Using data from past and current spacecraft, it was found that aqueous solutions are predicted in the shallow subsurface of the Phoenix landing site, but not where the Curiosity rover has traversed. We also showed that MgCl$_2$, CaCl$_2$, Ca(ClO$_4$)$_2$ can hydrate (incorporate H$_2$O into the crystal structure) without passing through a liquid phase. This
helps shed light on the potential formation of chemical signatures found in recurring slope lineae, a current Martian mystery.

Our previous studies have measured RH with respect to liquid (RH_L), but data from Martian landers is collected as RH with respect to ice (RH_i). This difference can drastically alter the interpretation of potential brine formation and some previously stated brine stability in the literature may be incorrect. However, the results in this thesis support liquid solutions existing in the subsurface at the northern regions of Mars (Phoenix landing site).
To: Mrs. Monica Smith

*The best high school chemistry teacher a girl could ask for.*
Acknowledgments

First off, I would like to thank my advisor, Maggie Tolbert. She was there when I was a lost first year graduate student not sure what she wanted to do, but I couldn’t have picked a better advisor for my 6 years here. She has been a great influence on my presentation style and gave me confidence and excitement for speaking in front of people. I’m always proud of my presentations and I cannot thank her enough for the guidance. Maggie has always been there throughout the hard times (orals re-do) and never gave up on me. Her hands-off style of teaching gave me the confidence and independence in the lab that I will carry-on throughout my career. Maggie has been a strong female role model in the science field and I’ll never forget my experience being a part of her lab here at CU Boulder.

Raina Gough was like a second advisor to me. She has been the resident Mars expert for any questions I had when I quickly transitioned from the Earth cloud experiments to Mars surface chemistry. She has guided me through the Mars science community knowledge, introduced me to several collaborators like Edgard Rivera-Valentin and German Martinez (among others), and helped me network to eventually get a job after graduation. Not only has she been a work-related advisor, she has also been a friend in need about graduate school life and after. Her excitement and personality about teaching and science is what I strive to be in the future. I cannot thank her enough for being there editing my papers, suggesting conferences, helping me land a trip to Spain, and helping me find a job.

Melissa Ugelow is my partner in crime. She started graduate school with me and we will be ending it together. She has been there when we were both clueless in our atmospheric classes, joining laboratory groups, taking orals, and many more. Melissa has been the best office mate to
discuss life and science. She helped me on a personal level to figure out the trials and tribulations of graduate school and future careers. Best lab-mate, best office-mate, Best friend. I wish her good luck in Maryland at her NASA Postdoctoral Program. This small amount of words cannot describe my sentiment towards, Melissa Ugelow.

Paul Schroeder, dearest boyfriend, has been there for the majority of my graduate career and has been my rock through the hard and exciting times. He has loved me no matter the situation, helped with the stressful home-life, and served as an example of how to successfully wrap up graduate school. He motivates me to be a better scientist, better person, and better career woman for the future. Paul has been my cheerleader for my career and life, along with being the love of my life. Paul. I cannot wait to do exciting things with you in our future. You rock, don’t change.

My family. They have literally been there this entire time when I decided to major in chemistry even though I had no idea what I wanted to do, being at 18-year-old. They were supportive when I then decided to go to graduate school, still, with no direction. Mom and Dad, not only have you been financially supportive in emergencies, but you raised me to be hard-working just like the both of you and I cannot thank you enough for that in my formative years as a child. They have been the best role models for successful, hard-working, parents. Kara, whom I’ve called almost every day for the last 6 years after work to talk about the exciting and rough times for that day, is second half. She has been the creative eye for all of my posters, presentations, and even reading some of my papers. She is the best sister a girl could ask for and all the phone calls, texts, and skype calls will never be enough to not miss you. I’m so proud of you and I hope you approve of the figures in this thesis.
# Table of Contents

1 Introduction
   1.1 Comparing Earth and Mars
   1.2 The surface of Mars
   1.3 Evidence for H₂O on Mars
   1.4 Evidence for Liquid Water Today
   1.5 Perchlorates and Chlorides
   1.6 Regolith Analogs
   1.7 Deliquescence, Efflorescence, and Ice formation
      1.7.1 Deliquescence
      1.7.2 Efflorescence
      1.7.3 Ice formation

2 Experimental Methods
   2.1 Sample Preparation
   2.2 Raman Microscopy and Environmental Cell
   2.3 Experimental Procedure
   2.4 RH<sub>L</sub> and S<sub>ice</sub> Determination
   2.5 Spectral and Visual Determination of Phase Procedure
   2.6 N₂ vs CO₂ atmosphere

3 Freezing of Perchlorate and Chloride Brines under Mars-relevant Conditions
   3.1 Introduction
   3.2 Experimental Methods
      3.2.1 Sample Preparation
   3.3 Results
      3.3.1 Spectral and visual analyses
      3.3.2 Mg(ClO₄)₂
      3.3.3 MgCl₂
   3.4 Martian Implications
   3.5 Conclusion

4 Relative Humidity with respect to Liquid and Ice
   4.1 Introduction
   4.2 Results
   4.3 Conclusions
Tables

Table 1-1. Comparison of key physical, orbital, and atmospheric parameters for Earth and Mars. ................................................................................................................................................ 2

Table 1-2. Chemical composition of Martian soil measured by the APXS (Alpha Particle X-Ray Spectrometer) instrument aboard Mars Pathfinder, Sojourner. .................................................. 6

Table 1-3. Average ion concentration at the Phoenix landing site from Rosy Red and Sorceress 1 and 2 samples. ........................................................................................................................ 7

Table 1-4. Concentration of species in JSC Mars-1 compared to MMS. *LOI usually includes \( \text{H}_2\text{O} \), \( \text{SO}_3 \), and \( \text{Cl} \). .......................................................................................................................... 18
Figures

Figure 1-1. Image of "Twin Peaks" on Mars from Mars Pathfinder................................................................. 4

Figure 1-2. Viking 2 Lander images of surface during the day (a) and in the morning when frost formed (b).................................................................................................................................................................. 9

Figure 1-3. Hubble Space Telescope images of Mars' North Polar Cap. The three images are from October 1996 to March 1997 showing the water ice cap disappearing. ................................................................. 10

Figure 1-4. Locations of RSL on Mars. Chryse and Acidalia Planitia (CAP); equatorial (EQ); Valles Marineris (VM); SML: southern mid-latitude (SML). Taken from Stillman et al. 2017. ......................... 12

Figure 1-5. a) Globules on the arm of the Phoenix Lander. The globules that seem to coalesce into one droplet are artificially colored green to easily follow. This image was adapted from Renno et al., 2009. b) Mars Reconnaissance Orbiter image of Recurring Slope Lineae in Newton Crater on Mars. c) A false color image of RSL on Hale crater taken by MRO High Resolution Imaging Science Experiment where Ojha et al., 2015 detected hydrate perchlorate salts where the RSL appear. .............................................. 13

Figure 1-6. a) Rosy Red and Sorceress 1 and 2 scoops from the Phoenix Mars Lander and analyzed by the Wet Chemistry Lab (WCL) Ion-selective electrode (ISE) and detected perchlorate ions (Hecht et al., 2009). b) Thermal Emission Imaging System (THEMIS) onboard Mars Odyssey data showing chloride-bearing materials in blue (Osterloo et al., 2008). ........................................................................................ 15

Figure 1-7. Plot of general water content and relative humidity (RH) increases and decreases as a particle undergoes deliquescence and efflorescence. A particle experiences hysteresis because the efflorescence relative humidity is lower than the predicted deliquescence relative humidity. .............................................. 21

Figure 1-8. Plot of different ice nucleation regimes depending on temperature and saturation ice conditions. S_i represents the same value as relative humidity with respect to ice divided by 100. Taken from Hoose and Mohler 2012 ............................................................... 23

Figure 2-1. Schematic of a Raman microscope outfitted with an environmental cell. The environmental cell allows for relative humidity and temperature control. This is done by flowing humidified N_2 or CO_2 into the cell and hygrometer where it measures the dew/frost point and the temperature controller can set a starting temperature, temperature rate, and final temperature................................................................. 25

Figure 2-2. Example different experimental trajectories where the frost point is kept constant while the temperature is decreased to increase the relative humidity. The blue lines are the ice formation line (left) and the modeled DRH of Mg(ClO_4)_2·6H_2O (right). ............................................................... 28

Figure 2-3. Plot of deliquescence, efflorescence, and ice formation in different carrier gas atmospheres. There are no detectable differences between the DRH, ice RH, and ERH of Mg(ClO_4)_2·6H_2O when a N_2 (blue markers) vs. CO_2 atmosphere (red markers) is present ............................................................... 31

Figure 3-1. Experimental trajectory through each phase of magnesium perchlorate. Because the RH was increased by keeping water vapor pressure constant and decreasing temperature the temperature range
was between 298K (for lowest RH) and 230K (highest RH). The figure starts with the hexahydrate and then increasing RH to form ice, followed by decreasing RH. Each colored spectrum correlates with the same color framed image to the right of the series of spectra. The two images labeled (1) are the same particle and the three images labeled (2) are the same particle, but different from (1). The series of Raman spectra are divided into two sections focusing in on the O-H stretch (3700-2700 cm\(^{-1}\)) and Cl\(_{4}\) stretch (932 cm\(^{-1}\)) regions. 

Figure 3-2. Experimental trajectory through each phase of MgCl\(_2\). Because the RH was increased by keeping water vapor pressure constant and decreasing temperature the temperature range was between 298K (for lowest RH) and 233K (highest RH). Each colored spectrum correlates with the same color framed image to the right of the series of spectra. The three images labeled (1) are the same particle and the three images labeled (2) are the same particle, but different from (1). The series of Raman spectra is isolated on the O-H stretch (3900-2900 cm\(^{-1}\)) because MgCl\(_2\) has no other functional groups that exhibit a Raman feature.

Figure 3-3. Stability diagram of Mg(ClO\(_4\))\(_2\) with overlaid stable and metastable liquid solution regions. The RH and T line for deliquescence is model taken from Chevrier et al. 2009, the line between liquid and ice represents S\(_{ice}=1\), the limits for the metastable regions for liquid are a best general fit of the data points (not the result of a calculation). A Mars diurnal cycle is also plotted (solid black line) on top to show the RH and temperature fluctuations that correlate with the liquid solution regions (Nuding et al. 2014).

Figure 3-4. Stability diagram and experimental data for DRH, ice RH, and ERH for MgCl\(_2\) with overlaid stable and metastable liquid solution regions. Two hydrates are observed, tetra- and hexahydrate, with different DRH. Modeled RH and T boundary for the deliquescence of the hexa-, octa, and dodecahydrates (red, purple, and pink, respectively) are plotted using the model from Chevrier et al. 2009. The dotted continuation of these modeled lines are the metastable deliquescence lines of the hydrates. The line between liquid and ice represents S\(_{ice}=1\) (Murphy and Koop 2005). A Mars diurnal cycle (solid black line) shows the RH and temperature fluctuations that could occur in the subsurface (Nuding et al. 2014). The DRH of MgCl\(_2\)•6H\(_2\)O from Gupta et al. 2015 is reported as a range and thus plotted as a range.

Figure 3-5. a) Liquid stability regions of Mg(ClO\(_4\))\(_2\)•6H\(_2\)O for a Martian subsurface diurnal cycle of RH and temperature (Nuding et al. 2014). b) Liquid metastability regions of MgCl\(_2\)•6H\(_2\)O over the same Martian diurnal cycle plotted in a). For this salt, any liquid formed is metastable, and so each region is labeled to note the particular type of metastable liquid solution that can form.

Figure 4-1. Comparison of RH\(_l\) (blue trace) and RH\(_i\) (grey trace). These values are plotted on a RH\(_l\) plot and used the same temperatures showing that at 180K the difference is 50%.

Figure 4-2. a) Mg(ClO\(_4\))\(_2\) and b) MgCl\(_2\) phase diagram adapted from Primm et al. (2017) with corrected Mars diurnal cycle in black with the previous diurnal cycle in grey to show the difference.

Figure 5-1. Raman spectra of pure Mg(ClO\(_4\))\(_2\)•6H\(_2\)O, pure montmorillonite, pure MMS, and 1:1 mixtures of perchlorate with montmorillonite or with MMS. The blue shaded region highlights the O-H stretch of water and the brown shaded region highlights the Cl\(_{4}\) stretch.
Figure 5-2. Spectra and images showing the phase transitions of pure Mg(ClO$_4$)$_2$•6H$_2$O (left panel) compared to 1:1 Mg(ClO$_4$)$_2$•6H$_2$O: montmorillonite (right panel). The following colors correspond to the phase either of Mg(ClO$_4$)$_2$•6H$_2$O (left panel) and 1:1 Mg(ClO$_4$)$_2$•6H$_2$O: montmorillonite: dry crystalline phase (red curve), deliquescence (blue curve), ice formation (green curve), and efflorescence (black curve) The images above the spectra correspond to the Raman spectra. The values above each spectrum are temperature and RH. It can be seen that all perchlorate phase transitions - deliquescence, efflorescence and ice formation - happen at under similar conditions in the presence and absence of montmorillonite........................................................................................................................................... 62

Figure 5-3. Plots showing the DRH, ice RH ($S_{\text{ice}}$), and ERH of pure Mg(ClO$_4$)$_2$•6H$_2$O and of 1:1 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. ................................................................. 65

Figure 5-4. a) MSL REMS data (black circles) and Gale Crater subsurface model results from different depths (colored lines, all Ls = 90°) overlaid on a magnesium perchlorate stability containing all experimental data from this paper (grey markers). b) Phoenix TECP data (black circles) and Phoenix subsurface model results (Ls=90°) overlaid on same stability diagram and data as a). The red line represents the modeled subsurface conditions at 1cm depth. ................................................................................. 73

Figure 6-1. Hydration of a MgCl$_2$•4H$_2$O particle to MgCl$_2$•6H$_2$O is shown spectrally (upper panel) and optically (lower images). In all cases, the spectra color and the image frame color correspond to the same RH and T conditions. .................................................................................................................................. 79

Figure 6-2. RH and temperature conditions under which (a) CaCl$_2$, (b) Ca(ClO$_4$)$_2$, and (c) MgCl$_2$ hydrate (solid circles) and dehydrate (open circles). MSL REMS RH$_g$ and T$_g$ through sol 1527 (grey circles) and modeled subsurface conditions (10 cm depth) at L$_s$ = 62, 151, 241, and 330. MgCl$_2$ experiments were performed at Earth atmospheric pressures and Mars atmospheric pressures; no difference was observed.82
Appendices

Figure A- 1. a) Mars subsurface diurnal cycle (3cm) (Nuding et al. 2014) plotted over modeled deliquescence (Chevrier et al. 2009) and water ice lines of Mg(ClO$_4$)$_2$. Each point on the line represents the conditions for every hour on Mars. This experiment was performed under a compressed Martian Sol where every hour was compressed to 10 minutes. Each hour is labeled on the diurnal cycle and corresponds to the same numbered spectra. Experimental hour 1 corresponds to 5PM on Mars, while hour 12 corresponds to 6AM on Mars. (b) Shows when the RH is increased and the images show where the deliquescence phase change occurs, and (c) shows when the RH is decreased and the images show where the particle effloresced. The spectrum that is bolded is where the phase change occurred. 

Table B- 1. Calculated values of RH, from RH$_L$ and Temperature to show the difference in value at lower temperatures. These values are plotted in Figure 4-1.

Figure C- 1. Raman spectra of the perchlorate region (934 cm$^{-1}$) of magnesium perchlorate and montmorillonite mixtures. The range is from 1:1 to 1:50 magnesium perchlorate: montmorillonite. The spectra show that the perchlorate peak is the strongest in the 1:1 mixture and completely disappears at 1:10, thus the reason for choosing a 1:1 mixture of salt to mineral.

Figure C- 2. Optical images of pure Mg(ClO$_4$)$_2$·6H$_2$O undergoing phase transitions (left) compared to images of the same phase transitions for the mixture of 1:1 Mg(ClO$_4$)$_2$·6H$_2$O: MMS (right). Although Raman spectra was unable to be obtained due to laser absorption of MMS, the following images show the visual changes while the mixture particle took up and released water. These images were taken where 25°C ≥ T ≥ -53°C.

Table C- 1. Complete data set of DRH, ERH, and ice formation RH of pure Mg(ClO$_4$)$_2$·6H$_2$O, 1:1 Mg(ClO$_4$)$_2$·6H$_2$O: montmorillonite, and 1:1 Mg(ClO$_4$)$_2$·6H$_2$O:MMS.

Table C- 2. Unit cell constants for crystalline compounds.
1 Introduction

1.1 Comparing Earth and Mars

In this thesis, I perform laboratory experiments to constrain the possibility and duration of liquid solutions potentially present on Mars today. In considering water on Mars, it’s useful to compare Mars to Earth. Table 1-1 shows the different physical properties of both Earth and Mars.

From an outside perspective, Earth and Mars seem to be very different, and there are key differences relevant to the existence liquid water on current Mars. Earth is within the region known as the “habitable zone” where liquid water is stable on the surface and is able to support life. However, Mars is 78 million miles further from the sun than Earth with a thin atmosphere, making it just outside of this habitable zone. Another issue with supporting liquid water stability on Mars is the surface temperature. Table 1-1 shows that the temperature of Mars is on average 210 K vs. 286 K on Earth. For most days (or sols) on Mars, if liquid water existed, it would rapidly freeze to ice. This is the case on the north and south poles of Mars. Each pole has a water and CO₂ ice cap and depending on the time of year, the northern pole has a permanent water ice cap after CO₂ ice has sublimed away. It is widely known that water exists as ice and vapor, but the presence of the liquid phase is still in question.
Table 1-1. Comparison of key physical, orbital, and atmospheric parameters for Earth and Mars.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Earth</th>
<th>Mars</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter</td>
<td>12,756 km</td>
<td>6,794 km</td>
</tr>
<tr>
<td>Mass</td>
<td>$5.97 \times 10^{24}$ kg</td>
<td>$0.642 \times 10^{24}$ kg</td>
</tr>
<tr>
<td>Average distance from the Sun</td>
<td>1 AU</td>
<td>1.524 AU</td>
</tr>
<tr>
<td>Solar irradiance</td>
<td>1380 W/m$^2$</td>
<td>595 W/m$^2$</td>
</tr>
<tr>
<td>Rotation period (length of day)</td>
<td>23.93 hr</td>
<td>24.62 hr</td>
</tr>
<tr>
<td>Revolution period (length of year)</td>
<td>1 year</td>
<td>1.88 year</td>
</tr>
<tr>
<td>Obliquity (axial tilt)</td>
<td>23.44°</td>
<td>25.19°</td>
</tr>
<tr>
<td>Average temperature</td>
<td>286 K</td>
<td>210 K</td>
</tr>
<tr>
<td>Minimum/maximum temperature</td>
<td>208 K / 328 K</td>
<td>148 K / 293 K</td>
</tr>
<tr>
<td>Surface pressure</td>
<td>1 bar</td>
<td>6-9 mbar</td>
</tr>
<tr>
<td>Atmospheric scale height</td>
<td>7.6 km</td>
<td>11 km</td>
</tr>
<tr>
<td>Topographic range</td>
<td>20 km</td>
<td>30 km</td>
</tr>
<tr>
<td>Gravity</td>
<td>9.8 m/s$^2$</td>
<td>3.7 m/s$^2$</td>
</tr>
<tr>
<td>Major atmospheric components</td>
<td>78.1% N$_2$</td>
<td>95.3% CO$_2$</td>
</tr>
<tr>
<td></td>
<td>20.9% O$_2$</td>
<td>2.7% N$_2$</td>
</tr>
<tr>
<td></td>
<td>0.93% Ar</td>
<td>1.6% Ar</td>
</tr>
<tr>
<td>Mean molecular weight</td>
<td>28.97 g/mol</td>
<td>43.34 g/mol</td>
</tr>
</tbody>
</table>
While Earth and Mars are very different in several ways, they are also very similar. The surface of Mars is very mountainous, contains volcanoes, has similar icy poles, and it undergoes a similar diurnal cycle of temperature and humidity at the surface. Earth has different seasons throughout the year and Table 1-1 shows that Mars has a similar obliquity and it experiences seasons in a similar way. Because of these similarities, the search for liquid water, and possibly life, has continued.

1.2 The surface of Mars

The age of the surface of Mars is still debated because of different dating methods such as crater counting and aging meteorites, but the last volcanic eruption was approximately 100-200 Ma (million years ago) (Mitchell, K.L., Wilson, 2003). These dating methods along with images of the surface show that the surface of Mars has not been geologically active for a while. Despite Mars being geologically inactive, there are many similarities between surface of Mars and the surface of Earth.

Although the radius of Mars (3390 km) is almost half that of Earth (6371 km), the surface area of Mars (1.448×10^8 km) is almost equivalent to the surface area of dry land on Earth (1.489×10^8 km). And, many of the places on Mars look very similar to those on Earth. Figure 1-1 shows an image of the surface taken by Mars Pathfinder. Figure 1-1 is the famous “twin peaks” taken by Mars Pathfinder, which shows mountains in the background, rocks, and quite a bit of dust. Mars Pathfinder mission included the lander, (later named the Carl Sagan Memorial Station) and the rover, Sojourner. Mars Pathfinder landed in 1997 in Ares Vallis (in the region called Chryse Planitia in the equatorial region of Mars). This mission goal was to study the atmosphere, climate, and the composition of rocks and soil.
Figure 1-1. Image of "Twin Peaks" on Mars from Mars Pathfinder.
In addition, the mission was the first to have a rover on another planet (not including the moon or Earth) and was a proof-of-concept for rovers outside the Earth-moon system. Table 1-2 shows composition of the surface of Mars found by Mars Pathfinder rover (Bell et al., 2000).

Table 1-2 shows that the surface of Mars is mainly composed of SiO₂. The surface is characterized to be mainly Basalt which is typically approximately 50% silica (SiO₂), 10% feldspathoid (type of silicate), and around 65% plagioclase (form of feldspar). Mars Pathfinder lead to several other successful missions on the surface of Mars that would continue to study the composition of the surface at several locations.

One well-known mission that analyzed the surface of Mars is the Phoenix Lander. The Phoenix Lander landed on Mars in 2008 in the region of Vastitas Borealis (north, close to the north pole) with the intent to search for microbial life along with the history of water on Mars. To study the composition of the soil, the Phoenix Lander had the Wet Chemistry Laboratories (WCLs) part of the Microscopy, Electrochemistry, and Conductivity Analyzer (MECA). The WCL performed wet chemistry analysis on the samples that the Phoenix arm would scoop from the surface of Mars and deliver MECA. From these experiments, a composition of the ions and salts in the soil were quantified. These scoops were analyzed by the ion-selective electrodes (ISEs) part of the WCL (Hecht et al., 2009). Table 1-3 shows the composition of the soil near the Phoenix Lander (Hecht et al., 2009).
Table 1-2. Chemical composition of Martian soil measured by the APXS (Alpha Particle X-Ray Spectrometer) instrument aboard Mars Pathfinder, *Sojourner*.

<table>
<thead>
<tr>
<th>Species</th>
<th>% of Soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$O</td>
<td>2.2±0.9</td>
</tr>
<tr>
<td>MgO</td>
<td>7.5±1.2</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>8.3±0.8</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>48.6±2.5</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>5.4±1.1</td>
</tr>
<tr>
<td>Cl</td>
<td>0.6±0.2</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.3±0.1</td>
</tr>
<tr>
<td>CaO</td>
<td>6.3±1.0</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>1.1±0.2</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>17.5±1.8</td>
</tr>
</tbody>
</table>
Table 1-3. Average ion concentration at the Phoenix landing site from Rosy Red and Sorceress 1 and 2 samples.

<table>
<thead>
<tr>
<th>Species</th>
<th>Average Equilibrium Concentration in Solution (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(^+)</td>
<td>1.4</td>
</tr>
<tr>
<td>K(^+)</td>
<td>0.38</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>0.58</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>3.3</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>0.54</td>
</tr>
<tr>
<td>ClO(_4)^-</td>
<td>2.4</td>
</tr>
<tr>
<td>pH</td>
<td>7.7</td>
</tr>
<tr>
<td>ClO(_4)^- (mass, mg)</td>
<td>6.00</td>
</tr>
</tbody>
</table>
No such life had been detected, but the short 6-month mission led to the discovery and quantification of water loving salts, like perchlorate, on the surface. This is discussed more in section 1.5.

1.3 Evidence for H$_2$O on Mars

One of the first pieces of evidence for H$_2$O on Mars were images taken by the Viking 2 Lander in 1976. The Viking mission included 2 orbiters and 2 landers in Chryse Planitia (equatorial region) and Utopia Planitia (northern region) and landed in 1976. The goal of this mission was to look for signs of life, but no clear evidence was found. But instead, water ice was found on the surface. Figure 1-2 shows two images from the Viking 2 Lander, top image (Fig. 1-2a) is of the surface during the day with no frost and the bottom (Fig. 1-2b) image shows the same area but in the morning and frost has formed on top of the rocks. These two images show evidence for H$_2$O in the form of gas and solid; H$_2$O vapor from the air condensing on the surface in the form of ice.

Other pieces of evidence for H$_2$O on Mars include images taken by the Hubble Space Telescope. Figure 1-3 shows 3 images of the North Pole of Mars from October 1996 to March 1997 showing a white cap disappearing (discussed in previous section). The Gamma Ray Spectrometer aboard Mars Odyssey (Mars Orbiter) detected water equivalent hydrogen (WEH) in the subsurface in 2002 and images from the High Resolution Imaging Science Experiment (HiRISE) aboard the Mars Reconnaissance Orbiter (Launched in 2005) showed white material with high albedo inside of a crater and later the albedo decreased and no white material is seen (Byrne et al., 2009).
Figure 1-2. Viking 2 Lander images of surface during the day (a) and in the morning when frost formed (b).
Figure 1-3. Hubble Space Telescope images of Mars' North Polar Cap. The three images are from October 1996 to March 1997 showing the CO$_2$ and water ice cap disappearing.
More recently, the Phoenix Lander (2008) scooped regolith, exposed white material underneath and the white material disappeared after a couple of days. This is thought the be ice from the subsurface sublimating after being exposed to the warmer air (Mellon et al., 2009).

1.4 Evidence for Liquid Water Today

There are several pieces of evidence for liquid water on Mars today, but many are controversial. The first piece of evidence is the globules found on the arm strut of the Phoenix lander shown in Figure 1-4a (Rennó et al., 2009). After the Phoenix lander landed in the northern region of Mars, it took a series of images of its leg strut and saw two globules move and merge into one globule. This movement is an indication of two liquid droplets coalescing into one liquid droplet, and is unlike the behavior of two solids that come in contact and stick together. This potential liquid has been a widely debated topic because, it is not clear if the potential liquid droplet material originated on Earth. The second line of evidence for potential liquid water on current Mars are dark streaks on the surface that are observed to lengthen and recede every warm season, these are known as Recurring Slope Lineae (RSL). RSL are thought to be liquid flowing because the RSL form on slopes and incrementally lengthen downward. Figure 1-4 shows a map of the locations of all RSL on the surface of Mars (Stillman et al., 2017). From Figure 1-4 you can see that RSL occur everywhere on Mars and mainly in the equatorial regions on Mars. However, many of them are not confirmed (i.e. do not meet the three criteria: recur, lengthen, and fade), they either recur, but may not fade or lengthen, while others are RSL-like or just recur.
**Figure 1-4.** Locations of RSL on Mars. Chryse and Acidalia Planitia (CAP); equatorial (EQ); Valles Marineris (VM); Southern mid-latitude (SML). Taken from Stillman et al. 2017.
Figure 1-5. a) Globules on the arm of the Phoenix Lander. The globules that seem to coalesce into one droplet are artificially colored green to easily follow. This image was adapted from Renno et al., 2009. b) Mars Reconnaissance Orbiter image of Recurring Slope Lineae in Newton Crater on Mars. c) A false color image of RSL on Hale crater taken by MRO High Resolution Imaging Science Experiment where Ojha et al., 2015 detected hydrate perchlorate salts where the RSL appear.
Figure 1-5b shows an image of RSL on the surface of Mars in Newton Crater. Many of these RSL are observed on the surface of Mars, but have yet to be confirmed or dismissed as a liquid flow.

Figure 1-5c, shows an image of an RSL that was studied via the Compact Reconnaissance Imaging Spectrometer for Mars or CRISM aboard the Mars Reconnaissance Orbiter (MRO) (Ojha et al., 2015). In 2015, Ojha et al. found the detection of hydrated perchlorate salts in these slope streaks. This discovery caused NASA to claim that it had found liquid flows on the surface of Mars, which then generated a large amount of press. But these observed hydrated salts are not in the liquid phase, rather, hydrated salts are crystalline salts with H$_2$O incorporated into the crystal structure. The explanation for how these salts became hydrated is still up for debate, but these hydrated salts do not definitively confirm a liquid phase of water.

A recent study argues that RSL are actually dry, granular flows rather than liquid flows (Dundas et al., 2017). Dundas et al. (2017) explains that the slope that RSL are forming are at the angle of repose (the steepest angle at which a sloping surface of loose material is stable); however, the flow might be initiated by small amounts of liquid formed via a phase transition involving salts.

1.5 Perchlorates and Chlorides

Perchlorate salts (i.e. Mg(ClO$_4$)$_2$, Ca(ClO$_4$)$_2$, KClO$_4$, and NaClO$_4$) have been detected in the shallow subsurface of Mars by instruments onboard the Viking Lander (Navarro-González et al., 2010), Phoenix lander, (Hecht et al., 2009) and
Figure 1-6. a) Rosy Red and Sorceress 1 and 2 trenches from the Phoenix Mars Lander and analyzed by the Wet Chemistry Lab (WCL) Ion-selective electrode (ISE) detected perchlorate ions (Hecht et al., 2009). b) Thermal Emission Imaging System (THEMIS) onboard Mars Odyssey data showing chloride-bearing materials in blue (Osterloo et al., 2008).
the *Curiosity* rover (Glavin et al., 2013) and may exist globally due to a potential atmospheric formation mechanism (Catling et al., 2010). Figure 1-6a is an image of the first detection and quantification of perchlorate at the Phoenix landing site; the three trenches from sampled soil that was delivered to the WCL instrument; Rosy Red and Sorceress 1 and 2.

Although the Phoenix Lander was the first to discover and quantify the amount of perchlorate in the soil (section 1.2), later re-analyses of the Viking surface sample tests found perchlorate (Navarro-González et al., 2010). The analysis of the surface from Viking 1 and 2 Landers included Thermal Volatilization Gas Chromatography Mass Spectrometry where the evolved gases from heating enter the Gas Chromatogram (TV–GC–MS), separated, then flown through the Mass Spectrometer to be chemically analyzed. The resulting gases were water, chloromethane, dichloromethane and carbon dioxide (Biemann et al., 1976). The resulting carbon dioxide and water was thought to not be biological because the small amounts and the chlorohydrocarbons were terrestrial contaminants. After perchlorate was detected at the Phoenix landing site, Navarro-González et al. (2010) re-analyzed the Viking data. This re-analysis was done by performing similar TV–GC–MS experiments on Mars-like soil found in the Atacama Desert where perchlorate is found (1 wt%). By heating up the Atacama Desert samples, carbon dioxide, water, and chlorohydrocarbons were evolved indicating that the Viking samples also contained perchlorate (Navarro-González et al., 2010).

More recently, the *Curiosity* rover currently still traversing Mars has discovered perchlorate at several locations along its trek. Calcium Perchlorate (Ca(ClO₄)₂) was detected at Gale Crater using the Sample Analysis at Mars (SAM) onboard *Curiosity*
(Glavin et al., 2013). SAM contains a suite of instruments for sample analysis, but for perchlorate detection the instruments used were the evolved gas analysis (EGA) where the sample was heated for thermal decomposition and the gas was then analyzed with QMS (quadrupole mass spectrometer) and GCMS (Mahaffy et al., 2012).

In addition to perchlorate salts, chloride salts have been observed on Mars are also hygroscopic. Chloride salts were also found by the Phoenix WCL (Hecht et al., 2009) on the Phoenix Lander and were also found to be globally distributed on Mars using the Thermal Emission Imaging System (THEMIS) onboard Mars Odyssey (Osterloo et al., 2010). Figure 1-6b shows the surface of Mars in false color using the THEMIS data (Osterloo et al., 2008). The blue colors are assigned as chloride bearing materials. Perchlorate and chloride salts are of interest to the Mars community because of their hygroscopic behavior (high water vapor absorption). This behavior is explained in Section 1.7.

1.6 Regolith Analogs

There are several Martian regolith analogs that have either been obtained in different areas on Earth that are similar to the Mars in terms of climate or are mineralogically or chemically similar to the Martian regolith. A few of these regolith analogs include JSC Mars-1 and Mojave Mars Simulant (MMS) (Peters et al., 2008). JSC Mars-1 is a glassy, altered volcanic ash from Mauna Kea, Hawaii and characterized to be basaltic and a good spectral analog for high albedo areas on Mars. MMS is mainly plagioclase feldspar, Ca-rich pyroxene and minor amounts of magnetite (Fe₃O₄) and is classified as olivine basalt. Table 1-4 shows a comparison of the composition of JSC Mars-1 and MMS (Peters et al., 2008).
Table 1-4. Concentration of species in JSC Mars-1 compared to MMS. *LOI usually includes H₂O, SO₃, and Cl.

<table>
<thead>
<tr>
<th>Concentration (wt%)</th>
<th>JSC Mars-1</th>
<th>MMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>43.48</td>
<td>49.4</td>
</tr>
<tr>
<td>TiO₂</td>
<td>3.62</td>
<td>1.09</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>22.09</td>
<td>17.1</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.03</td>
<td>0.05</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>16.08</td>
<td>10.87</td>
</tr>
<tr>
<td>MnO</td>
<td>0.26</td>
<td>0.17</td>
</tr>
<tr>
<td>MgO</td>
<td>4.22</td>
<td>6.08</td>
</tr>
<tr>
<td>CaO</td>
<td>6.05</td>
<td>10.45</td>
</tr>
<tr>
<td>Na₂O</td>
<td>2.34</td>
<td>3.28</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.70</td>
<td>0.48</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.78</td>
<td>0.17</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.31</td>
<td>0.10</td>
</tr>
<tr>
<td>LOI (Loss on ignition)*</td>
<td>17.36</td>
<td>3.39</td>
</tr>
</tbody>
</table>
Table 1-4 shows that there are similar concentrations of each species in the regolith simulants, but there are several key differences in JSC Mars-1 and MMS. JSC Mars-1 resembles global dust and is glassy, while MMS represents a mineralogical analog for igneous rocks on Mars and is crystalline. The density of MMS and the process by which the MMS sample was crushed to get a uniform size is closer to that observed on Mars than JSC Mars-1 (Peters et al., 2008).

Other minerals used as regolith analogs are mineral clays such as montmorillonite and kaolinite. For my thesis, the regolith analogs chosen were MMS and montmorillonite because of their compatibility with Raman spectra and water uptake properties, respectively.

1.7 Deliquescence, Efflorescence, and Ice formation

To understand the possibility of the duration of liquid solutions on the surface of Mars, the three phases that a salt can undergo must be discussed.

1.7.1 Deliquescence

Deliquescence is the process of absorption of water vapor by salts, leading to the formation of a saturated aqueous solution. Deliquescence occurs when the relative humidity around a dry crystalline salt increases to a point when the particle favors the liquid phase and picks up water to turn into a saturated aqueous solution. This deliquescence occurs at a specified deliquescence relative humidity (DRH) and is unique for all different salts, even different hydrated forms of salts. This process is of interest to
Mars scientists because it can happen at temperatures below the freezing point of pure liquid water, allowing for liquid at Mars-relevant conditions.

1.7.2 Efflorescence

Efflorescence is the opposite process of deliquescence, where the aqueous salt droplet loses water leading to recrystallization of the salt. Efflorescence occurs when the relative humidity around an aqueous solution decreases and the particle supersaturates (with respect to salt) and recrystallizes at the efflorescence relative humidity (ERH). The DRH and ERH experience a hysteresis effect, where the ERH occurs at a lower relative humidity (RH) than the DRH and is typically not predicted through thermodynamics. Figure 1-7 shows a plot of the hysteresis between DRH and ERH and the region in between where the history of the particle must be known in order to determine the phase.

1.7.3 Ice formation

Deliquescence can be easily predicted through solubility and thermodynamics, while efflorescence and ice formation cannot accurately be predicted because of kinetic effects. The predicted ice formation conditions are typically described by the ice saturation ratio,

\[ S_{\text{ice}} = \frac{P_{H_2O}}{P_{s,\text{ice}(T)}} \]

where \( P_{H_2O} \) is the partial pressure of water and \( P_{s,\text{ice}(T)} \) is the equilibrium saturation vapor pressure of ice at the temperature of interest. Ice formation involving Martian salts is often assumed to occur at the point where ice is thermodynamically stable, i.e. \( S_{\text{ice}} = 1 \). However, ice nucleation is often hindered by the kinetics of critical cluster formation and
Figure 1-7. Plot of general water content and relative humidity (RH) increases and decreases as a particle undergoes deliquescence and efflorescence. A particle experiences hysteresis because the efflorescence relative humidity is lower than the predicted deliquescence relative humidity.
thus $S_{\text{ice}} > 1$ is observed (Hoose and Mohler, 2012). Because $S_{\text{ice}} > 1$ is required for freezing to occur, aqueous perchlorate and chloride salt solutions would persist as supersaturated (with respect to ice) liquid brines prior to ice nucleation.  

Ice formation can happen either homogeneously (pure liquid water freezing) or, in this case, heterogeneously (seeded by a non-H$_2$O particle). Heterogeneous ice nucleation has several different subcategories, but for this thesis I will focus on homogeneous ice nucleation and depositional ice nucleation. Homogeneous ice nucleation occurs when a homogeneous liquid droplet freezes. Koop et al., (2000) defined and determined the conditions in which homogeneous freezing occurs. In this thesis, the homogeneous liquid droplet is a salty brine. Depositional ice nucleation occurs when ice deposits directly onto a dry particle without going through a liquid phase. Figure 1-8 shows the different ice nucleation regimes depending on the RH and temperature conditions.
Figure 1-8. Plot of different ice nucleation regimes depending on temperature and saturation ice conditions. $S_i$ represents the same value as relative humidity with respect to ice divided by 100. Taken from Hoose and Mohler 2012.
2 Experimental Methods

2.1 Sample Preparation

To generate the particles for this thesis, the solution of interest is aspirated into a Meinhard TR 50 glass concentric nebulizer. The nebulizer works by way of Bernoulli’s principle; air flow through the nebulizer creates a pressure difference which then pulls the sample solution up into the apparatus and is finally aspirated out the tip onto the area of interest. The droplets are directed toward a hydrophobically coated fused silica disc and placed into a low-humidity-controlled environmental cell to allow the water to evaporate, leaving dry aggregated salt or salt/dust mixture particles on the disc. Particles ranging from 1 to 50 μm in diameter are viewed on the disc through the Raman microscope.

2.2 Raman Microscopy and Environmental Cell

Figure 2-1 shows a schematic of the instrument setup used to study each phase transition of the particle of interest. The experiment uses a Nicolet Almega XR Dispersive Raman spectrometer with two lasers, 532nm and 780nm (532nm laser is used for these analyses), outfitted with a Linkham THMS600 environmental cell, a Buck Research CR-1A chilled-mirror hygrometer, and an Olympus BX51 research-grade optical microscope with 10x, 20x, 50x, and 100x magnification abilities (Baustian et al., 2010; Gough et al., 2011; Schill and Tolbert, 2013). This configuration allows visual and spectral information to be obtained on single particles throughout this study.

The Linkam environmental cell is mounted on an Almega Prior high precision motorized microscope stage. The cell has a temperature range of –196°C to 600°C, which is controlled by a platinum resistance sensor (±0.1°C) and a continuous flow of liquid N₂.
Figure 2-1. Schematic of a Raman microscope outfitted with an environmental cell. The environmental cell allows for relative humidity and temperature control. This is done by flowing humidified N₂ or CO₂ into the cell and hygrometer where it measures the dew/frost point and the temperature controller can set a starting temperature, temperature rate, and final temperature.
The flow rate of liquid N\textsubscript{2} and temperature of the cold stage can hold temperature and set temperature ramping rates using the Linkam TMS94 temperature controller. In addition, the cell has inlets for gas flow in and out to control the environment within the cell.

The dew or frost points as low as \(-120^\circ\text{C} (\pm 0.15^\circ\text{C})\) within the cell (which is used to calculate relative humidity) is measured by the Buck Research CR-1A chilled-mirror hygrometer. The humidified air is pumped through the system using a Gast Manufacturing diaphragm pump pulling at a rate of 1L/min, which is attached to the outlet of the hygrometer. This humidified air passes over the chilled mirror within the CR-1A hygrometer that constantly changes the temperature until the water vapor in the air condenses onto the mirror and reaches equilibrium and shows a digital output of the temperature of the mirror in real-time.

To ensure that the cold stage is the coldest part inside the environmental cell, it is important to note that the N\textsubscript{2} supply lines are located within the sample compartment and aren’t introduced into the sample compartment (the exposed lines that feed the liquid N\textsubscript{2} are wrapped in several layers of polystyrene). Within the cell, the walls are covered in low vapor pressure putty, apeizon, to further prevent cold spots for potential condensation.

### 2.3 Experimental Procedure

To perform the deliquescence, ice formation, and efflorescence experiments, the following procedure was followed. To increase the relative humidity (w.r.t. liquid) throughout the experiment, pre-purified N\textsubscript{2} or “bone dry” CO\textsubscript{2} was flowed through a glass frit bubbler to humidify the gas. This humidified gas is then mixed with varying ratios of dry gas for a humidified flow. Increasing the flow through the glass frit will decrease the
temperature of the frost point and vice versa. For these experiments, the equilibrium water vapor concentration (or frost point) was kept constant while the temperature was decreased at 0.1 K min\(^{-1}\) which produced an RH\(_L\) rate of change between 0.05% and 0.8% min\(^{-1}\). The humidity throughout the experiment was monitored using the CR-1A hygrometer.

To obtain data at different temperatures, the equilibrium water vapor concentration was changed at the beginning of each experiment via a constant flow rate of either N\(_2\) or CO\(_2\) through a glass frit bubbler. Figure 2-2 shows the experimental trajectory in temperature and RH\(_L\) space and the modeled DRH line of Mg(ClO\(_4\))\(_2\)·6H\(_2\)O (Chevrier et al., 2009) and ice formation line (Murphy and Koop, 2005) for reference. Each dotted line represents an experimental trajectory at a constant frost point where the experiment starts at ~0% RH\(_L\), 298K and ends at a lower temperature and ~100% RH\(_L\), following the arrows.

2.4 \(RH_L\) and \(S_{\text{ice}}\) Determination

The RH\(_L\) and \(S_{\text{ice}}\) experienced by the particles were calculated from the calibrated environmental cell temperature and the dew point measured by the hygrometer. As stated before, \(S_{\text{ice}}\) is defined as:

\[
S_{\text{ice}}(T) = \frac{P_{\text{H}_2\text{O}}}{P_{s,\text{ice}}(T)}
\]

where \(P_{\text{H}_2\text{O}}\) is the vapor pressure of water at the temperature at which ice forms and \(P_{s,\text{ice}}(T)\) is the equilibrium saturation vapor pressure of water over ice at that same temperature.

The hygrometer gives us a dew or frost point temperature and the \(P_{\text{H}_2\text{O}}\) is calculated from that temperature and the \(P_{s,\text{ice}}(T)\) is calculated using Clausius-Clapeyron derived equations.
Figure 2-2. Example different experimental trajectories where the frost point is kept constant while the temperature is decreased to increase the relative humidity. Each black dotted line represents a different experimental trajectory. The blue lines are the ice formation line (left) and the modeled DRH of Mg(ClO$_4$)$_2$ 6H$_2$O (right).
from temperature \((Murphy \text{ and Koop 2005})\). The relative humidity (\(R_{HL}\)) with respect to liquid water is defined as:

\[
R_{HL}\% = \frac{P_{H_2O}}{P_{S,H_2O,l}(T)} \times 100
\]

where \(P_{H_2O}\) is the vapor pressure of water and \(P_{S,H_2O,l}\) is the equilibrium saturation vapor pressure of liquid water. These values are calculated in a similar way to \(S_{ice}\), but calculate the saturated vapor pressure over ice in the denominator (Murphy and Koop, 2005).

### 2.5 Spectral and Visual Determination of Phase Procedure

To determine the DRH, ERH, and \(R_{HL}\) of ice formation, particles were monitored both visually and spectrally as the \(R_{HL}\) was increased or decreased. As stated in section 2.3, the equilibrium water vapor concentration was held constant while the temperature was decreased. For deliquescence experiments, particles <10 \(\mu\text{m}\) in diameter were monitored to avoid any kinetic effects due to size. Once the particle in the field of view was visually identified as being fully deliquesced a Raman spectrum was taken to validate the visual determination. A similar procedure to determine the ERH was performed, but decreasing the temperature until the particle lost the water visually and spectrally.

To determine the \(R_{HL}\) of ice formation, the sample disc containing the particles was raster scanned manually to find the first particle that formed ice and a Raman spectrum was obtained, again to confirm the identity of the phase. Because of local decrease in \(R_{HL}\) near particle that formed ice, only the first ice formation event is recorded for the most accurate temperature and relative humidity values.
2.6 $N_2$ vs $CO_2$ atmosphere

*A majority of this text in this sub-chapter is in the submitted manuscript Primm et al., 2018*

Previously in our lab, experiments in the Raman microscope flow system were performed using nitrogen as the flow gas. For the present work, we use $CO_2$ as the flow gas (Airgas Bone Dry 3.0 Grade) to make these studies more Mars-relevant. Prior to beginning the studies of mineral/salt mixtures, we performed experiments to determine the DRH, freezing, and ERH of pure $Mg(ClO_4)_2\cdot 6H_2O$ under a $CO_2$ atmosphere and compared these values to the ones measured in a $N_2$ atmosphere.

Figure 2-3 shows the DRH, ERH, and $S_{ice}$ values of pure $Mg(ClO_4)_2\cdot 6H_2O$ measured in a $CO_2$ atmosphere compared to earlier work performed in a $N_2$ atmosphere. These data points are overlaid on the $Mg(ClO_4)_2 +$ water stability diagram (Chevrier et al., 2009). The blue symbols represent phase transitions experimentally measured with $N_2$ as the carrier gas and the red symbols represent phase transitions experimentally measured with $CO_2$ as the carrier gas. Atmospheric composition does not affect, within estimated uncertainties, the temperature or $RH_L$ conditions needed for the observed phase transitions of $Mg(ClO_4)_2\cdot 6H_2O$ to occur. Because there is no significant difference within experimental uncertainty when $N_2$ or $CO_2$ are used, the phase transitions of pure $Mg(ClO_4)_2\cdot 6H_2O$, which were performed under $N_2$ atmospheric conditions here and previously (Gough et al., 2011), can be confidently compared to studies performed in this paper under $CO_2$ atmospheric conditions.
Figure 2-3. Plot of deliquescence, efflorescence, and ice formation in different carrier gas atmospheres. There are no detectable differences between the DRH, ice RH, and ERH of Mg(ClO$_4$)$_2$•6H$_2$O when a N$_2$ (blue markers) vs. CO$_2$ atmosphere (red markers) is present.
3 Freezing of Perchlorate and Chloride Brines under Mars-relevant Conditions

*A majority of text in this chapter is identical to the published version of the cited paper.*

3.1 Introduction

To accurately understand the duration of potential salty solutions on Mars, the freezing of brines into ice, as well as their recrystallization into solid salt, must be studied. There is strong evidence for water ice on Mars (Bell et al., 2008; Kieffer, 1979), but understanding the conditions needed for the transition from brine to ice, and how these conditions differ from equilibrium predictions, will provide insight to the stability and metastability of aqueous solutions on Mars.

As stated in section 1.4, perchlorate and chloride salts have been detected in the shallow subsurface of Mars by many instruments and these salts may exist globally by way of an atmospheric formation mechanism. Perchlorate salts have been shown to exhibit a strong hysteresis effect; the observed ERH is significantly lower than the observed DRH (Gough et al., 2011), although under thermodynamic equilibrium conditions, efflorescence should occur at the same RH as deliquescence. Some supersaturated perchlorate solutions could persist down to RH_L < 20%.

The DRH and ERH of the chloride salts, KCl and NaCl, have been studied for Earth-like conditions (Martin, 2000; Wise et al., 2012) and a few studies of MgCl_2 and CaCl_2 have been studied under a small range of Mars-like temperatures (Gough et al., 2014, 2016; Greenspan, 1977). However, the DRH and ERH values of MgCl_2 have only been reported at room temperature and two lower temperatures (Gough et al., 2014; Greenspan, 1977; Gupta et al., 2015; Schindelholz et al., 2014) and the reported eutectic
temperature is quite high, 237K (Marion and Farren, 1999). Several other studies have reported similar eutectic points for the MgCl₂•12H₂O which have been between 240K and 237K (Bakker, 2004; Brass, 1980; Marion & Farren, 1999), but the dodecahydrate was not observed in our work. From these differing eutectic points, it is not clear if aqueous solutions of MgCl₂ will form and persist under temperatures as low as those found on Mars. The present work explores perchlorate and chloride brine metastability at low RH in the crystalline hydrate stability regime and at high RH in the ice stability regime (Gough et al., 2014).

Because S_{ice} > 1 is required for freezing to occur, aqueous perchlorate and chloride salt solutions would persist as supersaturated (with respect to ice) liquid brines prior to ice nucleation. This supersaturation of ice could extend the presence of liquid solutions on Mars’ surface further into the morning, then previously assumed. This is because the morning on Mars is when the temperature is low and RH is high, which are the conditions when supersaturation of ice occurs (Gough et al., 2011; Nuding et al., 2014).

Perchlorate models have shown that, in theory, ice can exist whenever S_{ice} ≥ 1 (Chevrier et al., 2009; Marion et al., 2010). However, other studies have found that perchlorate and chloride brines can exist at temperatures below their eutectic point (Stillman and Grimm, 2011; Toner et al., 2014). This ice formation requires supersaturation with respect to ice (also called supercooling) within the metastable brine. These previous studies did not quantify the supersaturation with respect to ice that was achieved. Knowledge of the extent of supersaturation with respect of ice of a potential brine will enable the prediction of the conditions and thus time periods that permit the brine to exist. Additionally, the surface of Mars is likely to contain small perchlorate grains and small
droplets of perchlorate solution rather than bulk solutions. Therefore, studying ice nucleation on small particles, as is done here, is relevant to the brine/ice formation mechanisms present on current Mars.

3.2 Experimental Methods

A Raman microscope outfitted with an environmental cell was used for this analysis. This instrument along with spectral analysis is discussed in section 2.2 and 2.3.

3.2.1 Sample Preparation

Approximately 0.1 wt% solutions of either Mg(ClO₄)₂ or MgCl₂ in water (HPLC grade, submicron filtered, purchased from Fischer Scientific) were prepared and then nebulized onto a fused silica disc. The particles that were formed by nebulization typically ranged from 1 to 30μm in diameter. The sample was then placed into the environmental cell at 0% RH and room temperature to allow the particles to dry and lose all liquid phase water. Raman spectroscopy confirmed the lack of liquid water present after drying.

3.3 Results

3.3.1 Spectral and visual analyses

Raman and visual analysis were used to determine the composition and phase of particles examined in this study. Figures 3-1 and 3-2 show representative optical images and Raman spectra of magnesium perchlorate and magnesium chloride as the RH was increased and then decreased. This is shown to express how the experiments and analyses in this paper are performed.
In Figure 3-1, the first two Raman spectra and images are of the same particle, labeled (1), as it undergoes deliquescence. The last three spectra and associated images are of the same particle labeled (2), but different from (1). Because ice nucleation is a stochastic process, it is not possible to predict, a priori, which salt particle will nucleate ice. As the RH was increased and then decreased around magnesium perchlorate, there was no visible change in the location of the ClO$_4^-$ Raman stretch (932 cm$^{-1}$). However, the features in the O-H stretching region (3700 - 2700 cm$^{-1}$) change dramatically as the particle deliquesced, formed ice, melted, and finally effloresced.

In Figure 3-1, the black trace shows a dry Mg(ClO$_4$)$_2$$\cdot$6H$_2$O particle and its optical image outlined in the same color. This irregularly shaped crystal is assigned to be the hexahydrate based on the location and shape of the OH stretch (Chevrier et al., 2009; Gough et al., 2011). The red trace shows the Raman spectrum and image of the same particle at 50% RH after the Mg(ClO$_4$)$_2$ particle has deliquesced into a liquid brine. The Raman spectrum shows a broad peak in the O-H stretching region, indicating the presence of liquid water, and the microscope image shows a dark, spherical particle indicative of a liquid. As the RH is increased further to 95% RH, ice is formed. The green trace in Figure 1 shows the O-H stretch for solid ice, and the microscope image shows a more irregular shape indicative of ice. After ice is formed, the RH is decreased. By 59% (blue trace), melting has occurred and a liquid phase droplet is seen visually and spectrally, similar in appearance to the liquid particle formed via deliquescence. The RH is decreased further to 0% (purple trace), by which time efflorescence has occurred. The brine recrystallized into the dry hexahydrate with an irregular crystalline shape and a sharp hydrate peak in the Raman O-H stretch region.
Figure 3-1. Experimental trajectory through each phase of magnesium perchlorate. Because the RH was increased by keeping water vapor pressure constant and decreasing temperature the temperature range was between 298K (for lowest RH) and 230K (highest RH). The figure starts with the hexahydrate and then increasing RH to form ice, followed by decreasing RH. Each colored spectrum correlates with the same color framed image to the right of the series of spectra. The two images labeled (1) are the same particle and the three images labeled (2) are the same particle, but different from (1). The series of Raman spectra are divided into two sections focusing in on the O-H stretch (3700-2700 cm$^{-1}$) and ClO$_4^-$ stretch (932 cm$^{-1}$) regions.
The DRH, ERH, and RH of ice formation were determined for MgCl$_2$ using the same visual and spectral criteria discussed above for Mg(ClO$_4$)$_2$. In Figure 3-2, the solid yellow trace at 0% RH shows the 3430 cm$^{-1}$ O-H stretch for MgCl$_2$ tetrahydrate (Gurevich et al., 1978), and the corresponding optical image on the right outlined in yellow shows a round, but not completely homogenous crystalline particle. As the RH is increased to 12% the same particle (1) is observed to convert to the hexahydrate, indicated by the change in the O-H stretch region of the Raman spectrum (Gurevich et al., 1978). The optical image shows a similarly non-homogeneous, crystalline particle. The RH is increased further to deliquesce the same particle at 33% and the purple trace shows a broad O-H stretch and the optical image shows a rounder, homogeneous liquid droplet. As the RH is increased further to 82%, a second particle (2) is observed to nucleate ice. The Raman O-H stretching region of the blue trace shows ice and the optical image shows a large water ice crystal that has formed to the left of the particle. The RH is then decreased to 23%, at which point the green trace indicates that the same particle has now melted into a liquid droplet. At 1% RH, the red trace shows the same particle has effloresced into crystalline MgCl$_2$ tetrahydrate. It can be seen in this figure that the features in the O-H stretch region change significantly as magnesium chloride deliquesces, forms ice, melts, and finally effloresces. The optical images also change in a consistent manner when going from a solid crystal to aqueous brine to ice and back. According to Ohja et al. 2015, MgCl$_2$•6H$_2$O is inferred through CRISM data to possibly be present in RSL. In the next section, we examine the DRH of two hydrates.
Figure 3-2. Experimental trajectory through each phase of MgCl$_2$. Because the RH was increased by keeping water vapor pressure constant and decreasing temperature the temperature range was between 298K (for lowest RH) and 233K (highest RH). Each colored spectrum correlates with the same color framed image to the right of the series of spectra. The three images labeled (1) are the same particle and the three images labeled (2) are the same particle, but different from (1). The series of Raman spectra is isolated on the O-H stretch (3900-2900 cm$^{-1}$) because MgCl$_2$ has no other functional groups that exhibit a Raman feature.
3.3.2 Mg(ClO₄)₂

Figure 3-3 shows a summary of the deliquescence, ice nucleation, and efflorescence data for several different temperature cycles of magnesium perchlorate. Each data point shown is the average of 3 to 5 trials at each temperature. The experimental data points are plotted on the stability diagram for the Mg(ClO₄)₂ - H₂O system (Chevrier et al., 2009; Gough et al., 2011). The S_{\text{ice}} = 1 is plotted for reference. The subsurface diurnal cycle (taken from Nuding et al. 2014) is a plot of RH and temperature values modeled for the subsurface conditions during a sol.

The stability diagram was initially published in Chevrier et al. (2009) as temperature vs. salt concentration and was converted in Gough et al. (2011) to temperature vs. RH%, which is the form of the diagram being used here. The Mg(ClO₄)₂ model (deliquescence line) was determined by converting salt concentration into water activity using the Pitzer model on empirical fits of the solubility data of each hydrate, see Chevrier et al. (2009) auxiliary material for equations. The authors chose the model within Chevrier et al. (2009) because the model is a simple system that is consistent with more recent models such as Toner and Catling (2016). The model from Chevrier et al., 2009 (black dashed line) and Toner and Catling (2016) (diamond red point) for Mg(ClO₄)₂ is plotted in Figure 3-3.

The values determined in this work are shown in red symbols, with previous experiments shown in black. The deliquescence relative humidity values we measured are consistent with Gough et al. 2011 and also the theoretical phase transition line, modeled by
Figure 3-3. Stability diagram of Mg(ClO$_4$)$_2$ with overlaid stable and metastable liquid solution regions. The RH and T line for deliquescence is model taken from Chevrier et al. 2009, the line between liquid and ice represents $S_{\text{ice}}$=1, the limits for the metastable regions for liquid are a best general fit of the data points (not the result of a calculation). A Mars diurnal cycle at the Phoenix landing site at 3cm depth is also plotted (solid black line) on top to show the RH and temperature fluctuations that correlate with the liquid solution regions (Nuding et al. 2014).
Chevrier et al. 2009. For each ice formation experiment, the Mg(ClO$_4$)$_2$ particles were allowed to completely deliquesce into aqueous brine droplets and then the RH was increased continuously until ice formation was observed (red squares). In the temperature range studied, (218-245 K) ice was observed to nucleate in the range 83-95% RH. These values correspond to $S_{\text{ice}} = 1.3 - 1.54$. Because ice nucleation occurred at $S_{\text{ice}}$ values larger than 1, supersaturation with respect to ice occurred. According to Hoose and Möhler (2012), heterogeneous ice nucleation occurs below the homogeneous freezing line; i.e. $S_{\text{ice}}$ values less than 1.40-1.55 depending on the temperature (Koop et al., 2000). Although the focus of this paper is to study the ice nucleation conditions of Martian brines and not the nucleation mechanisms of the particles, we do believe that we are observing heterogeneous ice nucleation because in all but one case, the $S_{\text{ice}}$ values observed are lower than the threshold of homogeneous freezing (Koop et al., 2000).

It is clear that supersaturation with respect to ice occurs under the temperature range studied here; therefore, Mg(ClO$_4$)$_2$ would be expected to remain in the aqueous phase over a larger range of RH than if this supersaturation did not occur. Figure 3-3 contains shading to illustrate the stable and metastable aqueous phases of Mg(ClO$_4$)$_2$. The region where aqueous Mg(ClO$_4$)$_2$ is stable is indicated by the dark blue shading and metastability is indicated by light blue. The right-most light blue region is due to the hysteresis between deliquescence and efflorescence. These supersaturated solutions can persist at low RH when the crystalline solid is the predicted, thermodynamically-stable phase. The left-most light blue region is due to the supersaturation with respect to ice that is the focus of this
work. These supersaturated solutions can persist at high RH when a solid ice/salt mixture is the predicted stable phase.

3.3.3 MgCl₂

Shown in Fig. 3-4 is stability diagram and data for MgCl₂ performed here with overlaid stable and metastable liquid solution regions. The modeled deliquescence lines of the different hydrates for MgCl₂ were calculated using the same model explained above in section 3.2 (Altheide et al., 2009; Chevrier et al., 2009).

Altheide et al. (2009) calculated a eutectic temperature for MgCl₂ of 239.5K and is derived from data taken from Bernard 1958. This value is within the typical error due to Pitzer parameters and thus marginally different than the previously reported eutectic of 237K (Marion and Grant, 1994). Each experiment began with crystalline MgCl₂•4H₂O and upon raising the RH, the sample behaved in one of two ways: it either transitioned to the hexahydrated crystalline salt (MgCl₂•6H₂O) or it persisted as the tetrahydrate. This solid-solid phase transition (i.e., hydration) is not fully understood, but the formation of higher hydration states is generally favored at colder temperatures (Chevrier et al., 2009; Wise et al., 2012). These observations are very similar to that seen for CaCl₂ by Gough et al. (2016). In that study, CaCl₂ was observed to undergo solid-solid phase transitions from the dihydrate to the hexahydrate prior to deliquescence in some cases, while undergoing direct deliquescence from the dihydrate into brine in others. Each of the two MgCl₂ hydrates that were observed exhibited different DRH values, but in neither case did the phase transition have a temperature dependence.
Figure 3-4. Stability diagram and experimental data for DRH, ice RH, and ERH for MgCl₂ with overlaid stable and metastable liquid solution regions. Two hydrates are observed, tetra- and hexahydrate, with different DRH. Modeled RH and T boundary for the deliquescence of the hexa-, octa, and dodecahydrates (red, purple, and pink, respectively) are plotted using the model from Chevrier et al. 2009. The dotted continuation of these modeled lines are the metastable deliquescence lines of the hydrates. The line between liquid and ice represents $S_{\text{ice}}=1$ (Murphy and Koop 2005). A Mars diurnal cycle at the Phoenix landing site at 3cm depth is also plotted (solid black line) on top to show the RH and temperature fluctuations that correlate with the liquid solution regions (Nuding et al. 2014). The DRH of MgCl₂•6H₂O from Gupta et al. 2015 is reported as a range and thus plotted as a range.
The DRH for MgCl$_2$•4H$_2$O was found to be 12.8-12.3% RH in the temperature range studied (261-242K) while the DRH for MgCl$_2$•6H$_2$O was 37.6-31.2% RH in the temperature range studied (253-220 K). The DRH values for the two hydrates, MgCl$_2$•4H$_2$O and MgCl$_2$•6H$_2$O are plotted in Fig. 3-4 (orange and red symbols respectively). As seen in Fig. 3-4, the eutectic calculated here and Altheide et al. 2009 for MgCl$_2$•12H$_2$O of 239.5 K is not consistent with our experimental results; deliquescence of the hexahydrate is observed below the eutectic, where aqueous solutions are not predicted to be present. Although our experimental data points for MgCl$_2$•6H$_2$O are offset from the model, our values are consistent with several other studies using different techniques along with the observation of only two hydrates (Cziczo and Abbatt, 2000; Greenspan, 1977; Gupta et al., 2015; Schindelholz et al., 2014).

After deliquescence occurred, the RH was increased far above the DRH until ice formation was observed. The RH at which ice formation occurred ranged from 80-100% RH for temperatures between 221 and 252K. This corresponds to $S_{ice}$ values ranging from 1.3 to 1.35. Again, the nucleation of ice was observed to require supersaturation; the MgCl$_2$ remained aqueous over a much larger RH range than would be predicted purely by thermodynamic equilibrium models. After ice was formed, the relative humidity was lowered, leading to the melting of ice into an aqueous droplet, followed by efflorescence into a crystalline hydrate (always as MgCl$_2$•4H$_2$O). The open black circles plotted in Figure 3-4 as “ERH Upper limit,” are defined where the experiment was stopped due to experimental limitations but efflorescence was not yet observed, while the black circles are experiments where complete efflorescence was observed. As in Fig. 3-3, the darker and
lighter blue shading in Fig. 3-4 indicates the stable and metastable regions, respectively, of aqueous liquid solutions of MgCl₂.

### 3.4 Martian Implications

The two salts studied here, Mg(ClO₄)₂ and MgCl₂, exhibit different regions of liquid solution stability and metastability, illustrated in Figs. 3-3 and 3-4. These figures allow prediction of the phase of salt (crystalline hydrate, deliquesced brine, solid ice + salt mixture) that would be present under any given set of relative humidity and temperature conditions. A modeled subsurface (depth = 3 cm) diurnal cycle at the Phoenix landing site is plotted in as a solid black line (Nuding et al. 2014) in Figs. 3-3 and 3-4 to illustrate the brine stability and metastability that could occur in the case of a magnesium perchlorate or chloride brine on Mars.

Figure A-1 shows the Mars subsurface diurnal cycle (Nuding et al. 2014) plotted over the Mg(ClO₄)₂ stability diagram with corresponding Raman spectra and optical images of the phase changes. This diurnal cycle has been replicated throughout a compressed Martian Sol where 10 minutes equals every hour and each hour is labeled with the matching value. Experimental hour 1 corresponds to 5PM on Mars, while hour 12 corresponds to 6AM on Mars. Fig. A-1b shows the Raman spectra when the RH was increased (hours 1-12) and the images adjacent to the spectra show a particle of Mg(ClO₄)₂ at hour 1, when it is dry and crystalline, and hour 8 (bolded) when it has deliquesced into a liquid droplet. This same procedure is done when decreasing RH, hours 13-24. The optical images are at hour 13 when the particle is liquid and at hour 20 (bolded) when the particle has effloresced into a crystalline solid. The same phase transitions in Fig. A-1 have been observed in Figs. 3-3 to 3-5.
Under the environmental conditions present in the shallow subsurface during this particular diurnal cycle, it can be seen that Mg(ClO$_4$)$_2$ could exist in the aqueous phase over a wider range of RH values (and thus a longer portion of the Martian sol) if supersaturation with respect to ice is considered compared to if it is not. Overall, it is clear that the consideration of only stable aqueous solutions (dark blue shaded region) of Mg(ClO$_4$)$_2$ would significantly underestimate the fraction of the time that a liquid water phase could be present. Similarly, it can be seen that MgCl$_2$ would be expected to be aqueous for large portions of this sol, and that these liquid solutions are often metastable liquids.

The predictions of phase for Mg(ClO$_4$)$_2$ and MgCl$_2$ as a function of time of day (noon to noon, local time) are shown in Fig. 3-5. For these two salts, the DRH of the hexahydrate was used because according to Ojha et al. 2015, MgCl$_2$$\cdot$6H$_2$O and Mg(ClO$_4$)$_2$$\cdot$6H$_2$O were inferred from CRISM data to possibly be present in association with RSL. Fig. 3-5 a and b show the duration of liquid aqueous salt solutions present during a sol (Martian day). These plots were created using experimental data from the current study and diurnal subsurface RH and temperature cycles relevant to the Phoenix landing site on Mars (Nuding et al., 2014). In Fig. 3-5a, dark blue regions for Mg(ClO$_4$)$_2$ represent time periods when liquid brines are stable, formed via deliquescence or melting. The regions of metastable solution (light blue) are present due to either ice supersaturation (due to the difference between our experimentally determined RH values needed for ice to form and a value of $S_{\text{ice}} = 1$) or salt supersaturation (due to the difference between previous experimentally determined ERH values and DRH values).
Figure 3-5. a) Liquid stability regions of Mg(ClO$_4$)$_2$•6H$_2$O for a Martian subsurface diurnal cycle of RH and temperature (Nuding et al. 2014). b) Liquid metastability regions of MgCl$_2$•6H$_2$O over the same Martian diurnal cycle plotted in a). For this salt, any liquid formed is metastable, and so each region is labeled to note the particular type of metastable liquid solution that can form.
Figure 3-5b for MgCl\textsubscript{2}, shows the same subsurface temperature and RH diurnal cycle, but the stable and metastable liquid solution regions are of different durations. We find that MgCl\textsubscript{2} does not effloresce into a crystalline salt phase under these Martian conditions. The left-most light blue region represents a metastable liquid solution that exists due to MgCl\textsubscript{2} losing liquid water but not fully efflorescing. The left-most dark blue region represents a stable liquid solution when MgCl\textsubscript{2} absorbs more water vapor as the RH is increased. As in Figure 3-5a, the middle light blue region labeled “Ice Supersaturation” is a metastable liquid solution due to the supersaturation of ice. The right-most dark blue region represents a stable liquid solution due to melting, and the right-most light blue region represents the same metastable liquid solution (left-most light blue region) when MgCl\textsubscript{2} loses water. The supersaturation required for ice formation extends the metastable liquid solution for an additional 1-2 hours (left-most light blue region labeled ‘Ice Supersaturation’) for both salts.

3.5 Conclusion

There have been several studies of salt deliquescence and efflorescence since the detection of perchlorates and chloride salts on Mars (Gough et al., 2014, 2011; Nuding et al., 2014). However, few have examined the metastability region of these salts in the low temperature, high humidity region of in which supercooling and ice formation occur (Stillman and Grimm, 2011; Toner et al., 2014). Using only equilibrium thermodynamics to predict stability of these aqueous phases leads to an underestimation of liquid stability. Through this study we have shown that metastability is not restricted to salt supersaturation at low RH, but includes supercooling (supersaturation with respect to ice) at high RH.
The DRH and ERH of MgCl$_2$ were studied here. Two MgCl$_2$ hydrates were observed in this work (tetrahydrate and hexahydrate), each exhibiting different DRH values. MgCl$_2$ also demonstrates hysteresis upon decreasing RH, with an ERH value much lower than the DRH value. While two hydrates for MgCl$_2$ are seen upon increasing RH, aqueous MgCl$_2$ brines effloresce solely into the tetrahydrate. This behavior has been observed previously at room temperature by Schindelholz et al. (2014). The data for MgCl$_2$ collected in this paper is also consistent with (Cziczo and Abbatt, 2000) who also observed deliquescence of MgCl$_2$ around 33%. They hypothesized that only one hydrate was observed at low RH because they saw no change in the Raman spectra. Presumably the hydrate observed in both studies is MgCl$_2$•6H$_2$O based on previous spectral analyses (Greenspan 1977; Gough et al. 2014). Although the MgCl$_2$•12 H$_2$O and MgCl$_2$•8 H$_2$O are calculated to be stable in these conditions (Marion et al., 2010), these salts could be spectrally indistinguishable from MgCl$_2$•6H$_2$O (Cziczo and Abbatt 2000) or may simply not form under our experimental conditions.

Our experimental determination of the relative humidities and temperatures required for ice formation by perchlorate and chloride salt brines provides a more complete study of liquid brine stability and metastability on current Mars. Considering solution supercooling, Mg(ClO$_4$)$_2$ and MgCl$_2$ could be in an aqueous state up to 2 hours longer than predicted using equilibrium ice formation.

**Acknowledgements**

This material is based upon work supported by the National Aeronautics and Space Administration under grant No. NNX14AJ96G, NNX14AJ96G, a NASA Earth and Space
Science Fellowship No. NNX15AT6OH, and Mars Fundamental research grant No. NNX13AG67G.
4 Relative Humidity with respect to Liquid and Ice

*A majority of text in this chapter is identical to the published version of the cited paper.*

4.1 Introduction

A discussed in section 2.2.1, relative humidity is the defined as the percentage of water vapor pressure in the air compared to that of the saturated water vapor pressure (liquid or ice). Although these two values are with respect to the same molecule (different phase), the values of relative humidity can be drastically different. This difference is due to the value of the saturated water vapor pressure over liquid water or ice. Figure 4-1 shows a plot of the differences of RH with respect to liquid (RH\(_L\)) and RH with respect to ice (RH\(_i\)). Ice and liquid refer to the different relative humidities with respect to either ice or liquid and is plotted on a temperature vs. relative humidity with respect liquid plot. The ice and liquid line use the same temperatures and shows that the difference can be 50% as the RH\(_i\) (ice) line is at 200% while RH\(_L\) (liquid) line is 100% at the same temperature. This is because the difference between RH\(_L\) and RH\(_i\) is from the denominator of the following relative humidity equation:

\[
RH = \frac{VP_{H_2O}}{VP_{s,H_2O}}
\]

Where RH is the relative humidity, \(VP_{H_2O}\) is the actual vapor pressure of water in the air, and \(VP_{s,H_2O}\) is the equilibrium saturated vapor pressure of water which can either be over ice or over liquid. Table B-1 show the values in Figure 4-1 using this difference in denominator. This difference can be over looked when comparing different relative humidities when the values are not specified with respect.
Figure 4-1. Comparison of RH$_{i}$ (blue trace) and RH$_{L}$ (grey trace). These values are plotted on a RH$_{L}$ plot and used the same temperatures showing that at 180K the difference is 50%.
The main hypothesis for the possibility of liquid solution being present on Mars today is through the deliquescence of salts. When determining the conditions in which these liquid solutions via deliquescence are present, the relative humidity and temperature conditions on Mars must be known, thus understanding if the value is relative humidity with respect to liquid or ice is important.

4.2 Results

Liquid production through deliquescence has been suggested to be constrained to a select few regions on Mars (Kossacki and Markiewicz, 2014; Martínez and Renno, 2013). However, recently, surface meteorological conditions derived from the Rover Environmental Monitoring Station (REMS) were compared with the phase diagram of calcium perchlorate, suggesting that surface and shallow subsurface brines are possible at Gale crater (Martín-Torres et al., 2015). REMS data, though, has undergone several calibrations (Martínez et al., 2017), the last of which was on June 2015. The latest calibrations have led to drier conditions, but, more importantly, previous investigations have compared relative humidity w.r.t. ice (RH_{i}) as measured by REMS to a phase diagram w.r.t. liquid water (e.g., Gough et al., 2016; Martín-Torres et al., 2015; Martínez et al., 2017; Pál and Kereszturi, 2017; Rummel et al., 2014). Indeed, MSL REMS measures air relative humidity at a height of 1.6 m using a capacitance based hygrometer calibrated to RH_{i} (Harri et al., 2014). The difference between RH_{L} and RH_{i} could drastically alter interpretation of potential brine formation events through deliquescence. In addition to MSL REMS data, the Phoenix lander also measured relative humidity with the Thermal and Electrical Conductivity Probe (TECP) where several studies have compared the RH_{i} in
RH_{L} space (Gough et al., 2016; Nuding et al., 2014; Primm et al., 2017). Here I correct the mistakes I have made in Figures 3-3 and 3-4 to compare the same relative humidities, which in this case will be RH_{L}.

Figure 4-2 shows the corrected Mars diurnal cycle plotted on phase diagrams for Mg(ClO\textsubscript{4})\textsubscript{2} and MgCl\textsubscript{2} from Figures 3-3 and 3-4, respectively. The grey trace in both Fig.4-2a and b is the original diurnal cycle plotted in Primm et al. (2017) and is incorrect because the RH values are with respect to ice plotted on an RH with respect to liquid axis. The black trace in Figure 4-2 represents the correct Mars diurnal cycle, where the values in grey were converted to RH with respect to liquid.

4.3 Conclusions

To understand if deliquescence of Mars-relevant salts can occur on the surface of Mars today greatly relies on plotted experimental and modeled data in a temperature vs. relative humidity space to compare that to conditions on Mars. However, if the data is plotted incorrectly in relation to RH_{L} and RH_{i}, it can give false positives on the conditions in which liquid solutions via deliquescence is possible on Mars. This incorrect equating of RH_{L} and RH_{i} (e.g. plotting RH_{i} in RH_{L} space) will show higher relative humidities at higher temperatures, which is favorable for deliquescence of most perchlorates (e.g. Mg(ClO\textsubscript{4})\textsubscript{2} and Ca(ClO\textsubscript{4})\textsubscript{2}). Recognizing the difference between RH_{L} and RH_{i} and conveying the discrepancy in current published work is important for further research in correctly explaining the extent at which liquid solutions via deliquescence can be present on Mars today.
Figure 4-2. a) Mg(ClO$_4$)$_2$ and b) MgCl$_2$ phase diagram adapted from Primm et al. (2017) with corrected Mars diurnal cycle in black with the previous diurnal cycle in grey to show the difference.
5 The Effect of Mars-relevant soil analogs on the Water Uptake of Magnesium Perchlorate and Implications for the Near-Surface of Mars

*A majority of text in this chapter is identical to the published version of the cited paper.*

5.1 Introduction

Several recent studies have examined the deliquescence, efflorescence or freezing of pure perchlorate salts or brines (Fischer et al., 2016, 2014; Gough et al., 2011; Nikolakakos and Whiteway, 2015; Nuding et al., 2014; Primm et al., 2017). The low temperature phase transition behavior of many perchlorates is therefore fairly well established. However, because the surface of Mars is primarily (~99%) sparingly soluble minerals and dust (Ehlmann and Edwards, 2014), it is conceivable that the presence of sparingly soluble minerals in contact with, or in the interior of, a salt grain would affect the interactions of the salt with water. The mineral could affect the uptake of atmospheric water vapor by the salt due to competition for water molecules. In contrast to deliquescence, efflorescence, and ice formation are nucleation processes and thus may be affected when insoluble nuclei provide a nucleation seed and prevent supercooling or supersaturation. No studies have examined the effect of the Martian regolith on perchlorate phase transitions involving nucleation. However, Nikolakakos and Whiteway (2017) studied the deliquescence of magnesium perchlorate mixed with chabazite (Mars-relevant mineral) and quartz sand and found that the DRH of the magnesium perchlorate was not affected by the adsorption of water by the mineral. Here we experimentally test the full range of phase transitions (deliquescence, efflorescence, and ice formation) to understand the complete interaction between water vapor, hygroscopic salts, and sparingly soluble minerals on Mars and the potential for small scale liquid brines.
Two Mars-relevant soil analogs have been chosen for these studies, sodium montmorillonite and Mojave Mars Simulant (MMS). Clay minerals are widespread on the surface of Mars and dioctahedral smectites such as montmorillonite have been detected (Bristow et al., 2017; Carter et al., 2015; Ehlmann and Edwards, 2014). Montmorillonite can absorb water and incorporate $\text{H}_2\text{O}$ molecules into the interlayer spaces of the clay. Frinak et al. (2005) studied the water uptake of montmorillonite and found it took up a considerable amount of water, similar to that of very hygroscopic ammonium sulfate. The swelling nature of montmorillonite makes it an interesting candidate for studying the competition for water between the minerals and magnesium perchlorate. The second soil analog chosen to study, the Martian regolith simulant MMS, was first identified and characterized by Peters et al. (2008). MMS was used as a simulant for Mars global regolith simulant because it is a good geochemical and mineralogical match to the Rocknest sample investigated by MSL and has low organic and water content. Ladino and Abbatt (2013) studied the ice nucleating ability of simulants MMS and JSC Mars-1 with relevance to Martian water ice clouds. That study found that MMS was a better ice nuclei than JSC Mars-1, a property that makes MMS an interesting candidate to mix with perchlorate salts and brines. In our studies, perchlorate brine will be supercooled or supersaturated in the presence of a soil analog to determine the effects of these soil analogs on the DRH, ice formation, and ERH of pure perchlorate brines.
5.2 Experimental Methods

5.2.1 Sample preparation

Equal masses of magnesium perchlorate hexahydrate and either montmorillonite or MMS were mixed in HPLC (High Performance Liquid Chromatography) grade water. This ratio was selected because it gave the most reliable Raman spectral signal of each component (Figure C-1 in Appendix C). Magnesium perchlorate hexahydrate was obtained from Sigma Aldrich (99% purity), sodium montmorillonite (SWy-2) from the Clay Mineral Society, and MMS from NASA Jet Propulsion Laboratory (G. Peters). Montmorillonite has a bimodal spherical diameter of 60 nm and 250 nm (Assemi et al., 2015) and the MMS that was used here was MMS dust with a grain size of ≤0.4mm (Peters et al., 2008) and a unimodal diameter of 30.21 μm was determined.

These soil/salt solutions were nebulized using nitrogen gas and the resulting particles were deposited onto a hydrophobically coated fused silica disc. The particles typically ranged from 5 to 50 μm in diameter. We assume that all particles were internally mixed and had the same salt: soil ratio as the solution from which they were generated. The sample was placed into an environmental cell within the Raman microscope and particles were allowed to dry in a ~0%RH environment prior to beginning an experiment.

5.2.2 Raman microscope, environmental cell, and flow system

A Raman microscope outfitted with an environmental cell was used for this analysis. This instrument is discussed in section 2.2.
5.3 Results

5.3.1 Spectral analysis

Montmorillonite and MMS have strong fluorescence signals in Raman spectra and are thus challenging to study using Raman spectroscopy. Here we treat the fluorescence itself as a spectral signature unique to the mineral and therefore we can identify a mixture of mineral and perchlorate based on the presence of a strong fluorescence background that raises the baseline (indicating a mineral) and a Raman stretch at 931 cm\(^{-1}\) (indicating magnesium perchlorate). Figure 5-1 shows Raman spectra of pure crystalline Mg(ClO\(_4\))\(_2\)\(\cdot6\)H\(_2\)O, pure montmorillonite, and pure MMS as well as the 1:1 mixtures of Mg(ClO\(_4\))\(_2\)\(\cdot6\)H\(_2\)O with either montmorillonite or MMS. The OH stretch from the crystalline phase water in the hydrated magnesium perchlorate and also the perchlorate stretch from the salt are visible through the fluorescence from the mineral phase, confirming that the mixture particles indeed contain both species.

After the composition of a particle was analyzed at room temperature and RH\(_L\)~0\%, the RH\(_L\) was increased and the temperature was decreased until the particles were confirmed to have deliquesced visually and spectrally. These conditions were achieved by keeping the water vapor constant and decreasing the temperature. After a brine was formed the temperature was further decreased to increase RH\(_L\) until ice nucleation occurred and at least one of the brine droplets froze into a solid ice particle. This freezing could also be observed both visually and spectrally.
Figure 5-1. Raman spectra of pure Mg(ClO₄)₂•6H₂O, pure montmorillonite, pure MMS, and 1:1 mixtures of perchlorate with montmorillonite or with MMS. The blue shaded region highlights the O-H stretch of water and the brown shaded region highlights the ClO₄⁻ stretch.
After ice nucleation occurred, the temperature was increased to lower the RH until melting occurred and then further lowered until efflorescence was observed. This entire procedure was repeated at least three times at 10-15K temperature intervals within the range of 215 and 277 K.

5.4 Comparison of pure Mg(ClO$_4$)$_2$$\cdot$6H$_2$O to the mixtures of Mg(ClO$_4$)$_2$$\cdot$6H$_2$O with montmorillonite and MMS

Figure 5-2 shows dry crystalline phase of pure Mg(ClO$_4$)$_2$$\cdot$6H$_2$O particle (left panel, red curve) and that of a 1:1 Mg(ClO$_4$)$_2$$\cdot$6H$_2$O: montmorillonite mixture particle (right panel, red curve) deliquescing (blue curve), forming ice (green curve), and efflorescing (black curve). Raman spectra and corresponding microscope images are shown. While the particles and spectra look different with and without mineral, the features in the OH region (shaded in blue) 2900-3600 cm$^{-1}$, still clearly shows the OH stretch of condensed-phase H$_2$O independent of composition of the particle. Before deliquescence (top red curve), the mixture particle has intense fluorescence as well as a visible O-H stretch of Mg(ClO$_4$)$_2$$\cdot$6H$_2$O. When the mixture particle deliquesces, the peak in the O-H stretching region broadens due to the formation of liquid water, similar to the spectral changes observed when pure Mg(ClO$_4$)$_2$$\cdot$6H$_2$O deliquesces.

In Figure 5-2 at 223 K (blue curves), the pure Mg(ClO$_4$)$_2$$\cdot$6H$_2$O particle deliquesced at 56% and the 1:1 Mg(ClO$_4$)$_2$$\cdot$6H$_2$O: montmorillonite mixture particle also deliquesced at 56%.
Figure 5-2. Spectra and images showing the phase transitions of pure Mg(ClO$_4$)$_2$•6H$_2$O (left panel) compared to 1:1 Mg(ClO$_4$)$_2$•6H$_2$O: montmorillonite (right panel). The following colors correspond to the phase either of Mg(ClO$_4$)$_2$•6H$_2$O (left panel) and 1:1 Mg(ClO$_4$)$_2$•6H$_2$O: montmorillonite: dry crystalline phase (red curve), deliquescence (blue curve), ice formation (green curve), and efflorescence (black curve) The images above the spectra correspond to the Raman spectra. The values above each spectrum are temperature and RH$_L$. It can be seen that all perchlorate phase transitions - deliquescence, efflorescence and ice formation - happen at under similar conditions in the presence and absence of montmorillonite.
When the RH$_L$ was increased further by decreasing the temperature to 222(±1) K, ice formation occurred at 79(±1) % RH$_L$ for pure Mg(ClO$_4$)$_2$$\cdot$6H$_2$O and 83(±1) % RH$_L$ for the Mg(ClO$_4$)$_2$$\cdot$6H$_2$O: montmorillonite mixture. After ice formed, the RH$_L$ was decreased by increasing the temperature to 233(±1) K.

The particle melted and finally effloresced into a crystalline particle at 19(±1) % RH$_L$ for pure Mg(ClO$_4$)$_2$$\cdot$6H$_2$O and 21(±1) % RH$_L$ for the Mg(ClO$_4$)$_2$$\cdot$6H$_2$O: montmorillonite mixture. The three phase transitions (DRH, ice formation, and ERH) between the pure Mg(ClO$_4$)$_2$$\cdot$6H$_2$O and Mg(ClO$_4$)$_2$$\cdot$6H$_2$O: montmorillonite mixture occurred within 4% RH$_L$ of each one another, and thus no significant difference was found between the behavior of the pure magnesium perchlorate particle and that of the mixture of perchlorate and montmorillonite. In all cases, the combination of images and spectra allowed for confident determination of the conditions for DRH, RH of ice formation, and ERH for the Mg(ClO$_4$)$_2$$\cdot$6H$_2$O/montmorillonite mixtures.

A similar analysis was performed using the 1:1 mixture of Mg(ClO$_4$)$_2$$\cdot$6H$_2$O and MMS. Raman spectra of this mixture were not obtained because the MMS strongly absorbs 532 nm light (the excitation laser in the Raman spectrometer). We found that when a Raman spectrum was collected, the particle would absorb the laser light, heat up, and evaporate any liquid water. Unlike montmorillonite, which is white in color, the reddish MMS strongly absorbs 532nm laser light. Because of this strong absorption, experiments were performed using only visual analysis. Crystalline dry particles have a structured, heterogeneous, light-colored visual appearance, while liquid particles are dark, homogeneous, and round. When the particle appeared rounder and darker, it had taken up
water, and once all of the crystalline phase was dissolved, deliquescence had occurred. Once deliquescence is observed and the RH$_L$ is increased further, the particle started to nucleate ice when it appeared crystalline again and crystals started to grow outward. These visual clues also apply as the particle loses water. An example of this visual determination experiment for MMS is shown in Figure C-2 in the supporting information.

5.5 DRH, ERH, and freezing results for mixtures of Mg(ClO$_4$_2)•6H$_2$O with montmorillonite and MMS.

Figure 5-3 shows the results of all deliquescence, ice formation, and efflorescence experiments performed on mixtures of 1:1 Mg(ClO$_4$_2)•6H$_2$O: montmorillonite (part a) and 1:1 Mg(ClO$_4$_2)•6H$_2$O: MMS (part b), as well as the individual pure components (perchlorate or mineral) for comparison. The experimental data is plotted on the magnesium perchlorate-water stability diagram. The blue dotted deliquescence line is from a thermodynamic calculation (Chevrier et al., 2009) while the blue dashed efflorescence line is a best fit line. The blue symbols in both figures represent the experimentally determined deliquescence, efflorescence or ice formation of pure perchlorate salt or brine (Gough et al., 2011; Primm et al., 2017) with standard deviations of the different experimental values. Because pure montmorillonite and MMS are insoluble materials, they have no DRH or ERH values. The ice nucleating ability of both montmorillonite and MMS has been studied (Ladino and Abbatt, 2013; Welti et al., 2009) and these S$_{ice}$ values are shown as gold markers in both Figure 5-3a and 5-3b, where the squares represent experimental values performed in this study and the triangles represent literature values.
Figure 5-3. Plots showing the DRH, ice RH ($S_{\text{ice}}$), and ERH of pure Mg(ClO$_4$)$_2$·6H$_2$O and of 1:1 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.
These ice formation values are plotted as RH$_L$ and not S$_{ice}$ in order to reasonably plot them with DRH and ERH values. For reference, the black “ice” line is S$_{ice} = 1$. Both montmorillonite and MMS are efficient ice nuclei, nucleating ice when S$_{ice}$ is close to one.

Because Welti et al. (2009) studied ice nucleation by montmorillonite in a primarily N$_2$ atmosphere, we repeated this measurement in our Raman microscope with a CO$_2$ atmosphere (gold triangles). Ladino and Abbatt (2013) studied the ice nucleation of MMS only at temperatures below 223 K (gold triangles), and so we repeated the measurement of S$_{ice}$ at a wider range of temperatures (gold squares).

In Figure 5-3a, the green symbols represent the observed phase transitions of Mg(ClO$_4$)$_2$$\cdot$6H$_2$O-montmorillonite mixtures and in Figure 5-3b the green symbols represent the observed phase transitions of Mg(ClO$_4$)$_2$$\cdot$6H$_2$O-MMS mixtures. It can be seen that neither montmorillonite nor MMS have an effect on the water uptake of pure Mg(ClO$_4$)$_2$$\cdot$6H$_2$O, within experimental standard deviation. For example, the DRH of pure Mg(ClO$_4$)$_2$$\cdot$6H$_2$O at 233 K is 54.5 ± 2.3%, the DRH of the salt mixed with montmorillonite at the same temperature is 55.8 ± 1.1%, and the DRH of the salt mixed with MMS at 227 K is 54.4 ± 2.5%. To further analyze the differences in these number, we used a student’s t-test at 95% confidence and found that the difference is not significant. Similarly, beyond experimental uncertainty there is no difference in ERH values between the pure salt and the salt-mineral mixture. The RH$_L$ values at which ice was formed due to freezing of a brine had more scatter and experimental standard deviation. This is likely due to the random nature of ice nucleation, and also because often only one particle on the entire sample would freeze initially. Despite this scatter, pure perchlorate brines and mixed perchlorate-mineral brines generally experienced the same extent of supercooling prior to freezing. The
complete experimental data set plotted in Figure 5-3 is given in Table C-1 in Appendix C, with the ice formation conditions reported as both RH\textsubscript{L} and S\textsubscript{ice}.

### 5.6 Discussion

S\textsubscript{ice} values as high as 1.45 were reached for the salt-mineral brine particles prior to freezing. This high value is surprising given that the S\textsubscript{ice} values for either pure mineral on its own close to 1.0. We found that the presence of the sparingly soluble minerals, which are excellent ice nuclei, does not hinder the supercooling of the brine phase under high RH\textsubscript{L} and low T conditions that are predicted to form ice. Additionally, the minerals do not hinder supersaturation of the salt brine (ERH). When RH\textsubscript{L} values are lowered below the DRH, efflorescence of the salt-mineral mixture does not occur any more readily if mineral is present. This is also a surprising observation, as it is often assumed that the presence of a seed crystal or nuclei will initiate precipitation of the solid salt. Our results suggest that not all potential nuclei will cause crystallization of a supersaturated salt solution.

Bryant et al. (1960) proposed that the molecular level structures of the ice nuclei and of the salt can be correlated using the lattice mismatch between the two species. A lower lattice mismatch will theoretically result in nucleation occurring more readily, allowing less supersaturation of the brine phase. Davis et al. (2015) applied this theory to salt crystal efflorescence specifically. Here we use the methods of Davis et al. to calculate lattice mismatch values between Mg(ClO\textsubscript{4})\textsubscript{2}•6H\textsubscript{2}O and montmorillonite. The lattice mismatch equation is described in detail in Davis et al. (2015), but briefly the equation is,

\[
\delta = \frac{1}{2} \left( \frac{\alpha_{\text{mineral}} - \alpha_{\text{MP}}}{\alpha_{\text{MP}}} + \frac{b_{\text{mineral}} - b_{\text{MP}}}{b_{\text{MP}}} \right)
\]
where $\delta$ is the lattice mismatch value and $a$ and $b$ are cell parameters of the unit cell for a given species (mineral = montmorillonite; MP = Mg(ClO$_4$)$_2$·6H$_2$O). The comparison between Mg(ClO$_4$)$_2$·6H$_2$O and MMS was not calculated because MMS is a combination of minerals and not one mineral would give an accurate representation of the unit cell of MMS, thus only the comparison with montmorillonite was calculated. The value of $\delta$ is calculated for each of the three different unit cell parameters, $a$, $b$, and $c$, and then these values can be compared between Mg(ClO$_4$)$_2$·6H$_2$O and montmorillonite (Davis et al., 2015; Kihara, 1990; Robertson and Bish, 2011). The cell parameters used for the calculation of $\delta$ is shown in Table C-2 in Appendix C. The lowest value is used to determine if there is a weak or strong lattice match. As stated in Davis et al., when $\delta \leq 0.12$ there is little lattice mismatch and so the mineral species is predicted to be effective at nucleating the supersaturated aqueous species, in this case Mg(ClO$_4$)$_2$. The lowest mismatch value with montmorillonite between the unit cell parameters was $\delta = 0.140$. This value suggests that Mg(ClO$_4$)$_2$·6H$_2$O and montmorillonite have different lattice structures, which could explain the ineffectiveness of recrystallization of the Mg(ClO$_4$)$_2$ solution by montmorillonite. We can conclude that montmorillonite is a poor lattice match for crystalline perchlorate and therefore is not an effective nucleus for recrystallization. This mismatch can potentially explain why the ERH values of Mg(ClO$_4$)$_2$·6H$_2$O were unchanged even when the salt was mixed with these soil analogs. These soil analogs are therefore expected to have no effect on the conditions over which magnesium perchlorate can exist as a liquid brine, and also no effect on the water activity of these brines.

The two soil analogs studied here are different in several ways. One is a swelling clay of singular mineralogy (montmorillonite) and the other is a mixture of several minerals
that is not known to adsorb water vapor to a great extent (MMS). Despite these differences, they both had no effect on the phase transitions of magnesium perchlorate. According to Kiselev et al. (2017), ice nucleation occurs in defects on the surface of minerals, e.g. steps, cracks, and cavities. In this study, when the perchlorate and minerals were mixed together, the perchlorate might have filled in these defects known to nucleate ice efficiently. This hindering of the nucleation ability of the soil analogs is one possible reason why the soil analogs did not nucleate ice in the supercooled perchlorates as might have been expected. If other Martian minerals and salts behave similarly, then previously published DRH and ERH values of pure Mars-relevant salts are likely relevant to the real Martian environment, where salts and minerals are closely intermixed.

5.7 Martian Implications: Potential for deliquescence at Gale Crater (MSL) and Vastitas Borealis (PHX)

The experimental data plotted in Fig. 5-3 confirms that the three major regions present in the T vs. RH\textsubscript{L} stability diagram – crystalline hydrate, aqueous brine, and ice-salt mixture, are valid even when the perchlorate salt is mixed with other minerals. Assuming this stability diagram is also unaffected by other minerals on Mars, this allows one to predict the likely phase of perchlorate in any environment with known meteorology data (RH\textsubscript{L} and temperature at the surface). Here we perform this exercise for the surface using in-situ data and shallow subsurface using numerical modeling for Gale Crater, the landing site of the MSL and PHX landing sites.
At Gale Crater, the Rover Environmental Monitoring Station (REMS) has measured environmental conditions such as air temperature, ground temperature, relative humidity with respect to ice, wind speed, and atmospheric pressure along Curiosity’s traverse. Measurements are nominally taken during the first five minutes of each hour for more than two and a half Martian years at the time of this writing. Here, we specifically use the ground temperature \((T_g)\) measured by the ground temperature sensor, the air temperature measured at 1.6 m \((T_{1.6m})\) measured by multiple air temperature sensors, and the relative humidity measured at 1.6 m \((RH_{1.6m})\) measured by a Vaisala relative humidity sensor. \(T_{1.6m}\) and \(RH_{1.6m}\) are used to find the water partial pressure at 1.6 m. This is assumed to be constant down to the surface, and then \(T_g\) is used to calculate the relative humidity at the surface, \(RH_g\).

Among all REMS relative humidity measurements, we only consider here those taken during the first four seconds after the sensor has been turned on after at least \(\sim 5\) minutes of inactivity. This is because after four seconds, the local RH\(_{(i)}\) values are affected by the heater effect of the sensor (Martínez et al., 2016). Reliable values include RH\(_{(i)}\) measurements taken during the nominal and the so-called high-resolution interval mode (HRIM), which consists of alternately switching the sensor on and off at periodic intervals to minimize heating and is only used on selected one or two hour observation blocks (Martínez et al., 2017). The average of the \(RH_{1.6m}\) and \(T_{1.6m}\) values measured during these four seconds is then calculated (measurements stay stable). To calculate \(RH_g\), we consider quasi-simultaneous \(T_g\) values of the highest confident measured over a 5-minute interval centered at the time at which RH measurements of the highest confidence are measured. This is done to avoid the noise in REMS \(T_g\) measurements and ensure a statistically robust
$T_g$ values. The data analysis strategy typically results in 24 hourly values of $RH_{1.6m}$ and $T_{1.6m}$, $T_g$ and $RH_g$ per sol.

The Thermal and Electrical Conductivity Probe, or TECP, on the Phoenix lander measured the temperature, thermal conductivity, and volumetric heat capacity of the regolith (Zent et al., 2010). The TECP was mounted near the end of the 2.3 m Robotic Arm where it was able to measure the H$_2$O content of either the regolith or the air, depending on where it was positioned at the time. However, some in-soil measurements only measured temperature in-soil while relative humidity was measured in-air due to the location of the sensors. Furthermore, temperature was measured along the 15 mm length of the TECP needle, which is a non-negligible fraction of the diurnal skin-depth (~ 5 cm), and therefore strongly affected by the temperature gradient in the regolith.

Subsurface temperature and relative humidity conditions for both PHX and MSL were modeled using a 1-D, fully coupled, heat and mass transfer model with a vertical resolution of 0.01 m and small (180 s) temporal resolution that has been previously vetted for Mars (Chevrier and Rivera-Valentin, 2012; Kereszturi and Rivera-Valentin, 2012; Nuding et al., 2014; Rivera-Valentin et al., 2011). In the case of Gale crater, fits to REMS derived water vapor pressure are applied as a boundary condition at the surface-atmosphere interface. The REMS measures, among other quantities, ground temperature and relative humidity with respect to ice ($RH_{(i)}$) at 1.6 m (Hamilton et al., 2014; Harri et al., 2014). From these two quantities, the water vapor pressure can be derived. The Thermal and Electrical Conductivity Probe (TECP) onboard PHX measured relative humidity at various heights, but not consistently at the surface making it difficult to integrate into the model (Zent et al., 2016, 2010). For PHX, the simulation includes an ice table at a depth of 0.1 m.
(Smith et al., 2009) that exchanges water vapor with the atmosphere. Thermal inertia for the regolith is consistent with site measurements at Gale Crater (Vasavada et al., 2017) and at the PHX landing site (Zent et al., 2010). Furthermore, perturbations to the water vapor mass flux through the regolith, such as adsorption or ice formation, are not considered.

Figure 5-4 shows measured and modeled relative humidity and temperature data at Gale Crater (MSL) up to sol 1527 and Vastitas Borealis (PHX) overlaid on the Mg(ClO$_4$)$_2$ stability diagram. The data points representing the deliquescence, efflorescence, and freezing of Mg(ClO$_4$)$_2$, both pure and mixed with soil analogs, are included as grey points. Figure 5-4a shows all REMS $RH_g$ and $T_g$ data as black circles, and then modeled conditions at 1 cm depth (red line). In the case of these subsurface modeled conditions, the solar longitude ($L_s$) = 90°, which is shown here because the simulated diurnal cycle permits for the deliquescence of Mg(ClO$_4$)$_2$. Figure 5-4b shows all in-air data from the Phoenix TECP instrument averaged over 1-hr intervals (Zent et al., 2016). The measurement height varied, as the robotic arm of PHX was moved up and down over the course of the measurements. In Figure 5-4b, the modeled conditions at 1 cm depth are shown by the red line. Figure 5a shows that the conditions at MSL are too cold during high RH$_L$ periods for liquid Mg(ClO$_4$)$_2$ solutions to be possible, as the conditions do not cross the threshold of deliquescence of magnesium perchlorate (even mixed with minerals). Figure 5b shows that during some high RH$_L$ periods, the warm temperatures in the subsurface of the Phoenix landing site may allow for the deliquescence of magnesium perchlorate-soil analog mixtures.
Figure 5-4. a) MSL REMS data (black circles) and Gale Crater subsurface model results from different depths (red line, Ls = 90°, 1cm depth) overlaid on a magnesium perchlorate stability containing all experimental data from this paper (grey markers). b) Phoenix TECP data (black circles) and Phoenix subsurface model results (red line, Ls=90°, 1cm depth) overlaid on same stability diagram and data as a).
These findings are consistent with Cull et al. (2010) suggesting that the PHX landing site has had or currently has aqueous environments or thin liquid water films, which explains the transportation of perchlorate from the surface to the subsurface.

5.8 Conclusions

Experiments were performed investigating the potential effect on soil analogs on the deliquescence, efflorescence, and ice formation by the hygroscopic salt Mg(ClO$_4$)$_2$•6H$_2$O. Particles of equal masses magnesium perchlorate and either sodium montmorillonite or Mojave Mars Simulant experienced deliquescence, ice formation, and efflorescence by varying temperature and relative humidity. We observed that the mineral had no detectable effect on any phase transitions of magnesium perchlorate. Particularly surprising is the inability of the soil analog to affect the supersaturation of the salt that is observed when a brine is dehydrated or the supercooling of brine that occurs when ice is theoretically predicted to form. Our lattice mismatch calculations show that magnesium perchlorate and these soil analogs are not a good match for nucleation, thus these soil analogs are not expected to efficiently nucleate crystallization of magnesium perchlorate.

Furthermore, we have compared the stability diagrams of magnesium perchlorate mixed with Mars-relevant soil analogs to conditions found at the MSL and Phoenix landing sites. We find that the MSL landing site is not likely to have magnesium perchlorate brines because the ground temperatures during high relative humidity periods are always below the eutectic temperature of the salt. At the Phoenix landing site, though, high relative humidity periods during the summer are accompanied by temperatures above the eutectic
temperature in the subsurface and are able to potentially generate a liquid phase if magnesium perchlorate is present, even if mixed with mineral soil analogs. These findings are consistent with several other studies on the presence of liquid at the Phoenix landing site (Cull et al., 2010; Fischer et al., 2016, 2014; Zorzano et al., 2009). The results found in this paper demonstrate that if small-scale liquid solutions ever form on Mars due to the deliquescence of perchlorate salts on the surface or in the subsurface, this brine may persist as a stable or metastable solution even if perchlorate is a minor species in the soil.

Acknowledgements

The data used are listed in the references, tables, figures, and Appendix C. This material is based upon work supported by the National Aeronautics and Space Administration under grant No. NNX14AJ96G, and a NASA Earth and Space Science Fellowship No. NNX15AT6OH. The authors would also like to thank Greg Peters at JPL for providing the MMS. E. G. Rivera-Valentin acknowledges support from the National Aeronautics and Space Administration under grant No. NNX15AM42G from the Mars Data Analysis Program.
6 Hydration and Dehydration of Mars-relevant Chloride and Perchlorate Salts at Gale Crater

6.1 Introduction

Many perchlorate and chloride salts can potentially absorb water vapor and turn into liquid solutions (i.e., deliquesce) under some Mars-relevant conditions, such as those at the Phoenix landing site; however, drier locations on Mars, such as Gale Crater, are less likely to permit the formation of liquid brines. At these drier locations, perchlorate could still be interacting with water vapor via hydration-dehydration cycles. This hydration and dehydration of crystalline salts could be at least partially responsible for the diurnal variations in near-surface atmospheric water vapor observed at both the Phoenix (Zent et al., 2010) and Curiosity (Savijärvi et al., 2016, 2015) landing sites.

This nighttime decrease in water vapor could be due to frost formation at the surface (Chevrier and Rivera-Valentin, 2012). Other potential processes include diffusion and adsorption of water in subsurface soil (Savijärvi et al., 2015), soluble salt deliquescence, or salt hydration changes. Many salts found at these landing sites and elsewhere on Mars (sulfates, perchlorates and chlorides) have multiple potential hydration states, suggesting that phase transitions may be possible. It is important to understand if transitions between two or more hydration states of a salt can occur under Mars-relevant conditions and time scales. If so, such salts can provide a diurnal sink for atmospheric water vapor.
The possibility of humidity-induced salt hydration is also relevant to recurring slope lineae (RSL), the dark, recurring streaks that are proposed by some to be formed by liquid (Martinez et al., 2016). Hydrated perchlorate and chloride salts were spectrally detected at several RSL locations, prompting the suggestion that the hydrated salts were likely precipitated from a liquid brine (Ojha et al., 2015). Here we question if the salts could have hydrated via a solid-solid phase transition involving the incorporation of atmospheric H₂O vapor into its crystal structure. If hydration can occur due to changes in relative humidity (RH) or temperature, then liquid water is not required to produce hydrated salts in RSL.

We perform experiments to understand the conditions needed for hydration and dehydration of five different Mars-relevant salts: NaCl, NaClO₄, CaCl₂, Ca(ClO₄)₂, and MgCl₂. In order to understand the role of solid-solid salt hydration on Mars, we compare the results to the environmental conditions observed by the Curiosity rover in Gale Crater.

6.2 Experimental Methods

Aqueous solutions of NaCl, NaClO₄, CaCl₂, Ca(ClO₄)₂, and MgCl₂ in HPLC grade water were nebulized using N₂ gas onto a hydrophobic quartz disc. The resulting particle diameters were between 5 and 50 μm. The sample was placed into an environmental chamber within a Raman microscope (see section 2.2) while pure CO₂ flows through the system. The sample was allowed to dry in a ~0% RH environment prior to beginning an experiment to ensure it was dry (not liquid).

The particles were analyzed by Raman spectroscopy (see Section 2.2) to determine the phase of H₂O. Figure 6-1 shows MgCl₂ hydrating from 4H₂O to 6H₂O. Because chloride
does not have a Raman signature, only the O-H stretching region of the Raman spectrum (3000-3800 cm\(^{-1}\)) is shown in Fig. 6-1.
Figure 6-1. Hydration of a MgCl₂•4H₂O particle to MgCl₂•6H₂O is shown spectrally (upper panel) and optically (lower images). In all cases, the spectra color and the image frame color correspond to the same RH and T conditions.
The stable hydrate for MgCl$_2$ at room temperature and ~0% RH is MgCl$_2$$\cdot$4H$_2$O (red trace). As the humidity increases to 12.8% RH, a solid-solid hydration phase transition occurs from MgCl$_2$$\cdot$4H$_2$O (3438 cm$^{-1}$) to MgCl$_2$$\cdot$6H$_2$O (3513, 3390, and 3349 cm$^{-1}$) (Gough et al., 2014) The images below the spectral series in Fig. 6-1 show the particle brightened at 12.8% RH as the 6H$_2$O forms.

This hydration procedure was attempted for all salts at a variety of temperatures. If hydration occurred, a dehydration experiment was then performed. The RH was decreased while the temperature was increased in order to see if any spectral changes indicative of dehydration occurred.

### 6.3 Results

Although NaCl and NaClO$_4$ do have stable hydrates (Chevrier et al., 2009; Gough et al., 2011), no hydration was observed after exposing the anhydrous salts to 65% RH for 8 hours (Gough et al., 2011; Wise et al., 2012). In contrast, hydration was observed for CaCl$_2$, Ca(ClO$_4$)$_2$, and MgCl$_2$ salts (Gough et al., 2011; Nuding et al., 2014; Primm et al., 2017).

Figure 6-2 shows the observed RH and temperature of hydration and dehydration of these three salts: (a) CaCl$_2$, (b) Ca(ClO$_4$)$_2$, and (c) MgCl$_2$. In each plot in Fig. 6-2, MSL Rover Environmental Monitoring Station (REMS) ground relative humidity (RH$_g$) and temperature (T$_g$) up to sol 1527 (grey circles) and modeled subsurface conditions at four L$_s$ values (62-cyan, 151-orange, 241-gold, 330-pink) are plotted. The hydration and dehydration of MgCl$_2$ was performed at both Earth pressure (630 Torr) and Martian
pressure (5 Torr) and no discernable difference was detected. Each symbol represents a single hydration or dehydration experiment.
Figure 6-2. RH and temperature conditions under which (a) CaCl$_2$, (b) Ca(ClO$_4$)$_2$, and (c) MgCl$_2$ hydrate (solid circles) and dehydrate (open circles). MSL REMS RH$_g$ and T$_g$ through sol 1527 (grey circles) and modeled subsurface conditions (10 cm depth) at L$_s$ = 62, 151, 241, and 330. MgCl$_2$ experiments were performed at Earth atmospheric pressures and Mars atmospheric pressures; no difference was observed.
Figure 6-2 shows that all three salts can hydrate by exposure to water vapor. Often only very low humidity (RH < 20%) is required. The only salt studied here that was observed to hydrate at the surface at Gale Crater is Ca(ClO₄)₂, which can hydrate from the anhydrous phase to Ca(ClO₄)₂•4H₂O (red symbols). However, Gale Crater does not appear to be warm enough to allow for dehydration. In the case of Ca(ClO₄)₂•4H₂O as well as MgCl₂•6H₂O, dehydration only occurred at 298 K despite waiting for 5-8 hours at 280 K at low RH (<0.1%). These salts will likely remain in the hydrated state throughout the year. The only salt observed to dehydrate under conditions found at Gale Crater is CaCl₂; however, hydration is not predicted at the surface.

The subsurface conditions at Gale Crater are quite different (colored lines in Fig. 6-2) and future studies will simulate these conditions to see if any candidate salts can both hydrate and dehydrate under Martian conditions.

6.4 Conclusion

Even though multiple hydration states of Martian salts are possible and even predicted theoretically (Nuding et al., 2014), the phase transitions are not always possible in practice and experiments must be performed to determine the feasibility of phase transitions of salts at the surface or in the shallow subsurface. We were unable to hydrate either NaCl or NaClO₄ at all. Under Gale Crater conditions, hydration is possible for Ca(ClO₄)₂ and MgCl₂•4H₂O but unlikely for CaCl₂; however, dehydration is observed only for CaCl₂ under Gale Crater conditions and is unlikely to occur for Ca(ClO₄)₂ and MgCl₂•4H₂O unless the conditions reach 298 K. Therefore, none of these salts are likely to be involved with the diurnal (or even seasonal) water cycle on Mars today. However, warmer
conditions on Mars could support the hydration and dehydration of salts potentially triggering RSL formation.
7 Dissertation Summary

7.1 Dissertation Summary

The preceding work will comprise my dissertation. It shows the water uptake and release for pure salts, \( \text{Mg(ClO}_4\text{)}_2 \cdot 6\text{H}_2\text{O} \) and \( \text{MgCl}_2 \cdot 6\text{H}_2\text{O} \). This dissertation is the first study to show that these two salts undergo supercooling and quantifies the ice supersaturation conditions. The supercooling of these salts will help the Mars community to understand the extent of ice supersaturation for the surface of Mars, which has not been studied previously. Both salts were predicted to transition into liquid solutions under the Phoenix landing site conditions on Mars.

While studying the surface salts and regolith analogs, a discrepancy between using relative humidity with respect to ice and liquid was found. The two values (\( \text{RH}_\text{L} \) and \( \text{RH}_\text{i} \)) can be a difference of 50% depending on the temperature and were found to be plotted incorrectly, i.e. \( \text{RH}_\text{i} \) values plotted on a \( \text{RH}_\text{L} \) axis. This has been addressed and previous plots have been corrected, some locations on Mars are now not predicted to support liquid solution stability (for \( \text{Ca(ClO}_4\text{)}_2 \)).

In addition, we show that adding insoluble (or sparingly soluble) minerals, e.g. MMS and montmorillonite, does not affect the water uptake and release for pure \( \text{Mg(ClO}_4\text{)}_2 \cdot 6\text{H}_2\text{O} \), thus suggesting that the surface of Mars behaves similarly to studies on pure mars-relevant salts. When comparing to Mars data, it is predicted that liquid solutions of \( \text{Mg(ClO}_4\text{)}_2 \) mixed with mars regolith analogs could be found in the subsurface of the Phoenix landing site, but not at Gale Crater (location of the Curiosity rover). Finally, the hydration of mars-relevant salts was studied and we found that salts do not need to undergo
or be exposed to a liquid phase in order to hydrate (incorporate $\text{H}_2\text{O}$ into its crystal structure). Our studies show that the hydration depends on the atmospheric relative humidity surrounding the salt. Although all salts were able to hydrate and dehydrate with only atmospheric humidity increase and decrease, none were observed to hydrate and dehydrate under conditions recorded at Gale Crate. In locations on Mars that are warm enough (~298K), the salts are able to dehydrate and a complete cycle of hydrate and dehydrate could lead to a change in the surrounding humidity.

The following first and co-author publications resulting from this dissertation are as follows:

1-Chapter 3 has been accepted and published in Geochimica et Cosmochimica Acta


2-Chapter 4 (along with other analysis and results that the author of this dissertation did not contribute to) has been accepted to *Journal of Geophysical Research: Planets* and is in press.

**Title:** Constraining the potential liquid water environment at Gale Crater, Mars

**Author List:** E.G. Rivera-Valentin$^1$, R.V. Gough$^2$, V.F. Chevrier$^3$, K.M. Primm$^2$, G.M. Martinez$^4$ and M.A. Tolbert$^2$.
$^1$Arecibo Observatory, Universities Space Research Association, Arecib, PR 00612, USA and Lunar Planetary Institute, USRA, Houston TX 77058, USA
$^2$Cooperative Institute for Research in Environmental Sciences and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309, USA
$^3$Arkansas Center for Space and Planetary Sciences, University of Arkansas, Fayetteville, ER 72701, USA
$^4$Department of Climate and Space Sciences and Engineering, University of Michigan, Ann Arbor, MI, USA

3-Chapter 5 has been submitted to *Journal of Geophysical Research: Planets* and under revisions.

**Title:** The Effect of Mars-relevant soil analogs on the Water Uptake of Magnesium Perchlorate and Implications for the Near-Surface of Mars

**Author List:** K.M. Primm$^{1,2}$, R.V. Gough$^{1,2}$, J. Wong$^2$, E. G. Rivera-Valentin$^{3,4}$, G. M. Martinez$^5$, J. V. Hogancamp$^6$, P. D. Archer$^7$, D. W. Ming$^8$, and M.A. Tolbert$^{1,2*}$.
 Chapter 5 is currently composed of unpublished results that will be published following the publication of this dissertation.
8 Future Directions

The work presented in this thesis explores the possibility for liquid solutions on the surface of Mars today, but the work serves as a basis for future studies.

First, the experimental setup was originally suited for atmospherically Earth-relevant studies. In this thesis, the setup was modified for Mars-relevant studies by flowing CO$_2$ through the system to mimic the atmospheric composition of Mars. However, preliminary studies to match the atmospheric pressure of Mars (6mbar) have been performed and should be explored further. The difference (if any) of deliquescence, efflorescence, and ice formation under low pressure could be quantified, along with any time delays in the phase transitions.

Second, the ice formation conditions of two salts were studied here, but only the deliquescence and efflorescence of other Mars-relevant salts and mixtures of these salts have been studied. Further studies on mixtures of Mars-relevant salts and their ice formation conditions could give a more accurate explanation of the possibility of liquid solutions and duration on the surface of Mars today.

Lastly, the mixture of mars-relevant minerals and regolith analogs at a 1:1 wt% ratio, while the surface is more closely related to a 100 (regolith):1 (salt). The high regolith to salt ratio was not able to be studied here because of experimental limitations. But, a different laser on the Raman microscope (780nm) or using an FTIR (Fourier Transform Infrared) could be used to be able to identify the amount of regolith in the particles. In addition, several Mars-relevant salts could be mixed with regolith analogs for the most representative sample of the Martian surface.
A future robotic mission to Mars, ExoMars 2020, will have onboard HABIT
(Habitability: Brine, Irradiation, and Temperature) which has two instruments: BOTTLE
(Brine Observation Transition to Liquid Experiment) and ENVPACK (Environmental
Package). BOTTLE will expose Mars-relevant salts to the Martian atmosphere to monitor
if deliquescence of these salts is observed, while ENVPACK will monitor UV radiation,
ground temperature, and atmospheric temperature. This mission and their findings will help
the Tolbert’s laboratory study direction and potentially confirm or deny if deliquescence is
possible on Mars today (in the area and conditions where ExoMars lands).
References


Hoose, C., Möhler, O., 2012. Heterogeneous ice nucleation on atmospheric aerosols: a review of results from laboratory experiments. Atmos. Chem. Phys. 12, 9817–9854. doi:10.5194/acp-12-9817-2012


Appendix A

The following figure is supplementary to Chapter 3: Freezing of Perchlorate and Chloride Brines under Mars-relevant Conditions of this dissertation.

Figure A-1. a) Mars subsurface diurnal cycle (3cm) (Nuding et al. 2014) plotted over modeled deliquescence (Chevrier et al. 2009) and water ice lines of Mg(ClO$_4$)$_2$. Each point on the line represents the conditions for every hour on Mars. This experiment was performed under a compressed Martian Sol where every hour was compressed to 10 minutes. Each hour is labeled on the diurnal cycle and corresponds to the same numbered spectra. Experimental hour 1 corresponds to 5PM on Mars, while hour 12 corresponds to 6AM on Mars. (b) Shows when the RH is increased and the images show where the deliquescence phase change occurs, and (c) shows when the RH is decreased and the images show where the particle effloresced. The spectrum that is bolded is where the phase change occurred.
Appendix B

The following table is supplementary to Chapter 4: Relative Humidity with respect to Liquid and Ice.

**Table B-1.** Calculated values of $RH_i$ from $RH_L$ and Temperature to show the difference in value at lower temperatures. These values are plotted in Figure 4-1.

<table>
<thead>
<tr>
<th>$RH_i$ (%)</th>
<th>$RH_L$ (%)</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>208.23</td>
<td>100</td>
<td>180</td>
</tr>
<tr>
<td>192.129</td>
<td>95</td>
<td>185</td>
</tr>
<tr>
<td>176.953</td>
<td>90</td>
<td>190</td>
</tr>
<tr>
<td>162.578</td>
<td>85</td>
<td>195</td>
</tr>
<tr>
<td>148.877</td>
<td>80</td>
<td>200</td>
</tr>
<tr>
<td>135.724</td>
<td>75</td>
<td>205</td>
</tr>
<tr>
<td>122.999</td>
<td>70</td>
<td>210</td>
</tr>
<tr>
<td>110.62</td>
<td>65</td>
<td>215</td>
</tr>
<tr>
<td>98.5702</td>
<td>60</td>
<td>220</td>
</tr>
<tr>
<td>86.9032</td>
<td>55</td>
<td>225</td>
</tr>
<tr>
<td>75.724</td>
<td>50</td>
<td>230</td>
</tr>
<tr>
<td>65.1442</td>
<td>45</td>
<td>235</td>
</tr>
<tr>
<td>55.2457</td>
<td>40</td>
<td>240</td>
</tr>
<tr>
<td>46.0666</td>
<td>35</td>
<td>245</td>
</tr>
<tr>
<td>37.6071</td>
<td>30</td>
<td>250</td>
</tr>
<tr>
<td>29.842</td>
<td>25</td>
<td>255</td>
</tr>
<tr>
<td>22.7331</td>
<td>20</td>
<td>260</td>
</tr>
<tr>
<td>16.2373</td>
<td>15</td>
<td>265</td>
</tr>
<tr>
<td>10.311</td>
<td>10</td>
<td>270</td>
</tr>
<tr>
<td>4.91186</td>
<td>5</td>
<td>275</td>
</tr>
</tbody>
</table>
Appendix C

The following 2 Figures and 2 tables are supplementary to Chapter 5: Effect of Mars-relevant soil analogs on the Water Uptake of Magnesium Perchlorate and Implications for the Near-Surface of Mars

Figure C-1. Raman spectra of the perchlorate region (934 cm$^{-1}$) of magnesium perchlorate and montmorillonite mixtures. The range is from 1:1 to 1:50 magnesium perchlorate: montmorillonite. The spectra show that the perchlorate peak is the strongest in the 1:1 mixture and completely disappears at 1:10, thus the reason for choosing a 1:1 mixture of salt to mineral.
Figure C-2. Optical images of pure Mg(ClO$_4$)$_2$·6H$_2$O undergoing phase transitions (left) compared to images of the same phase transitions for the mixture of 1:1 Mg(ClO$_4$)$_2$·6H$_2$O: MMS (right). Although Raman spectra was unable to be obtained due to laser absorption of MMS, the following images show the visual changes while the mixture particle took up and released water. These images were taken where 25°C ≥ T ≥ -53°C.
### 1:1 Mg(ClO$_4$)$_2$:Mont.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>% RH of Ice formation</th>
<th>S$_{Ice}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>255.6 ± 0.1</td>
<td>101.4 ± 0.5</td>
<td>1.20 ± 0.01</td>
</tr>
<tr>
<td>246.5 ± 1.7</td>
<td>99.9 ± 1.1</td>
<td>1.30 ± 0.01</td>
</tr>
<tr>
<td>233.4 ± 1.7</td>
<td>89.7 ± 4.5</td>
<td>1.32 ± 0.05</td>
</tr>
<tr>
<td>224.9 ± 0.6</td>
<td>81.2 ± 2.9</td>
<td>1.28 ± 0.03</td>
</tr>
<tr>
<td>214.1 ± 1.5</td>
<td>89.3 ± 1.2</td>
<td>1.53 ± 0.01</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>T(K)</th>
<th>DRH</th>
</tr>
</thead>
<tbody>
<tr>
<td>265.0 ± 0.5</td>
<td>46.7 ± 0.5</td>
</tr>
<tr>
<td>252.3 ± 0.6</td>
<td>49.4 ± 0.6</td>
</tr>
<tr>
<td>245.0 ± 0.4</td>
<td>49.9 ± 0.9</td>
</tr>
<tr>
<td>232.1 ± 0.3</td>
<td>55.8 ± 1.1</td>
</tr>
<tr>
<td>222.4 ± 1.0</td>
<td>61.5 ± 5.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>T(K)</th>
<th>ERH</th>
</tr>
</thead>
<tbody>
<tr>
<td>273.7 ± 0.8</td>
<td>24.4 ± 0.7</td>
</tr>
<tr>
<td>262.5 ± 0.6</td>
<td>21.0 ± 1.0</td>
</tr>
<tr>
<td>254.3 ± 1.5</td>
<td>22.9 ± 1.8</td>
</tr>
<tr>
<td>243.2 ± 1.0</td>
<td>21.0 ± 0.6</td>
</tr>
</tbody>
</table>

### 1:1 Mg(ClO$_4$)$_2$:MMS

<table>
<thead>
<tr>
<th>T(K)</th>
<th>% RH of Ice formation</th>
<th>S$_{Ice}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>256.6 ± 1.4</td>
<td>96.1 ± 3.3</td>
<td>1.13 ± 0.03</td>
</tr>
<tr>
<td>241.2 ± 1.6</td>
<td>95.3 ± 1.6</td>
<td>1.30 ± 0.02</td>
</tr>
<tr>
<td>223.8 ± 2.2</td>
<td>82.4 ± 1.9</td>
<td>1.31 ± 0.02</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>T(K)</th>
<th>DRH</th>
</tr>
</thead>
<tbody>
<tr>
<td>266.8 ± 0.7</td>
<td>42.0 ± 0.4</td>
</tr>
<tr>
<td>249.1 ± 2.0</td>
<td>46.2 ± 0.8</td>
</tr>
<tr>
<td>227.0 ± 2.8</td>
<td>54.4 ± 2.5</td>
</tr>
<tr>
<td>T(K)</td>
<td>ERH</td>
</tr>
<tr>
<td>------------</td>
<td>------------</td>
</tr>
<tr>
<td>277.0 ± 0.2</td>
<td>20.0 ± 1.1</td>
</tr>
<tr>
<td>258.8 ± 2.5</td>
<td>21.4 ± 1.6</td>
</tr>
<tr>
<td>237.2 ± 2.2</td>
<td>22.2 ± 0.7</td>
</tr>
</tbody>
</table>

*Table C-1. Complete data set of DRH, ERH, and ice formation RH of pure Mg(ClO$_4$)$_2$•6H$_2$O, 1:1 Mg(ClO$_4$)$_2$•6H$_2$O: montmorillonite, and 1:1 Mg(ClO$_4$)$_2$•6H$_2$O:MMS.*
### Table C-2. Unit cell constants for crystalline compounds.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Mg(ClO$_4$)$_2$·6H$_2$O$^a$</th>
<th>Montmorillonite$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>7.775</td>
<td>5.17</td>
</tr>
<tr>
<td>b</td>
<td>13.49</td>
<td>8.94</td>
</tr>
<tr>
<td>c</td>
<td>5.27</td>
<td>9.95</td>
</tr>
</tbody>
</table>

$^a$Robertson and Bish 2011

$^b$Values taken from [www.mindat.org](http://www.mindat.org); the online mineral and locality database