

## RESEARCH LETTER

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## Key Points:

- The formation of brines at Martian conditions was studied experimentally
- Bulk deliquescence from water vapor is too slow to occur diurnally on Mars
- Brines form in minutes when salts are placed in direct contact with ice

## Supporting Information:

- Readme
- Table S1
- Figure S1
- Figure S2

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## Experimental evidence for the formation of liquid saline water on Mars

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**Abstract** Evidence for deliquescence of perchlorate salts has been discovered in the Martian polar region while possible brine flows have been observed in the equatorial region. This appears to contradict the idea that bulk deliquescence is too slow to occur during the short periods of the Martian diurnal cycle during which conditions are favorable for it. We conduct laboratory experiments to study the formation of liquid brines at Mars environmental conditions. We find that when water vapor is the only source of water, bulk deliquescence of perchlorates is not rapid enough to occur during the short periods of the day during which the temperature is above the salts' eutectic value, and the humidity is above the salts' deliquescence value. However, when the salts are in contact with water ice, liquid brine forms in minutes, indicating that aqueous solutions could form temporarily where salts and ice coexist on the Martian surface and in the shallow subsurface.

### 1. Introduction

Our view of Mars has changed dramatically in the past two decades, from an inhospitable cold desert to a potentially habitable planet. Water ice was discovered in the shallow subsurface of areas ranging from polar latitudes to midlatitudes [Boynton *et al.*, 2002; Mitrofanov *et al.*, 2002; Feldman *et al.*, 2002; Smith *et al.*, 2009; Byrne *et al.*, 2009]; salts such as  $\text{Ca}(\text{ClO}_4)_2$ ,  $\text{Mg}(\text{ClO}_4)_2$ , and  $\text{NaClO}_4$ , capable of deliquescing and forming aqueous solutions at Martian temperatures were discovered in the polar and equatorial regions [Hecht *et al.*, 2009; Glavin *et al.*, 2013]. The idea that deliquescence (defined as the dissolution of a salt by the absorption of water vapor [Mirabel *et al.*, 2000]) is a slow process not capable of producing bulk aqueous solutions during the few hours of the diurnal cycle in which conditions are favorable for it is well established [Möhlmann, 2011] because Mars is extremely cold and dry [Lewis *et al.*, 1999; Meslin *et al.*, 2013]. This appears to contradict the discovery of observational evidence for deliquescence in Mars' polar region [Rennó *et al.*, 2009] and of possible flows of liquid brines in the equatorial region [McEwen *et al.*, 2011].

In an effort to shed light on this issue, we use Raman scattering spectroscopy [Zhang and Chan, 2003] to study the formation of liquid brines from bulk amounts of salt at Mars environmental conditions. Here we define "bulk" as a macroscopic collection of salt grains. First, we study the formation of liquid brines when water vapor is the only source of water (bulk deliquescence). Then, we investigate the formation of liquid brines when the salts are placed in direct contact with water ice like that observed in Mars' polar region [Martínez *et al.*, 2012; Smith *et al.*, 2009; Whiteway *et al.*, 2009]. Our results have important implications for the understanding of habitability because liquid water is essential for life as we know it, and halophilic terrestrial bacteria thrive in brines [Mikucki *et al.*, 2009; Boetius and Joye, 2009].

### 2. Methodology

#### 2.1. Environmental Chamber

All experiments reported in this letter were conducted in the Michigan Mars Environmental Chamber (MMEC), a cylindrical chamber with internal diameter of 64 cm and length of 160 cm. The MMEC is capable of simulating temperatures ranging from 145 to 500 K,  $\text{CO}_2$  pressures ranging from 10 to  $10^5$  Pa, and relative humidity ranging from nearly 0 to 100%.

We use salts from Sigma Aldrich with typical particle diameters  $< 300 \mu\text{m}$  (determined by visual inspection of images of the salt particles). Particles of this size are the most easily transported by saltation [Kok and Renno, 2009] and therefore can easily be accumulated in low topographical features and then buried. In our experiments the laser beam of the Raman spectrometer is focused on the thin layer of the salt being

investigated. We use layers of salt with a thickness of a few grains to ensure that it is within the penetration depth of the laser and thus to be able to detect the onset of the formation of liquid brines. Our results are not sensitive to particle size because deliquescence starts on defects on the surface of salt crystals, and Raman spectroscopy is capable of detecting the onset of deliquescence on the surfaces of the salt crystals. Once the salt particles start to absorb water, they start to coalesce, forming larger particles. Indeed, most particles are rough because they are aggregates of smaller particles.

We have conducted two sets of experiments, one to investigate deliquescence when the salt is exposed solely to water vapor and the other to investigate the formation of liquid brines when a thin layer of salt is placed in direct contact with a layer of water ice, like that found in the shallow Martian subsurface by the Phoenix lander [Smith *et al.*, 2009; Rennó *et al.*, 2009]. In both cases the CO<sub>2</sub> atmosphere was kept saturated with water vapor at a total pressure of 800 Pa. In the first set of experiments, the temperature of the sample was fixed at  $-50^{\circ}\text{C}$ , well above the  $-74^{\circ}\text{C}$  eutectic temperature of Ca(ClO<sub>4</sub>)<sub>2</sub> [Marion *et al.*, 2010]. In the second set of experiments, the salt was first placed on top of a layer of water ice at temperatures well below the salt's eutectic temperature. Then, the temperature was raised to values above the eutectic temperature at a rate of about  $6^{\circ}\text{C}/\text{h}$  to simulate the rate of the temperature increase in the shallow ( $\sim 1$  cm deep) Martian subsurface [Savijärvi and Määttä, 2010]. This rate was increased at temperatures well above the eutectic point to speed up the experiment.

## 2.2. Raman Spectroscopy

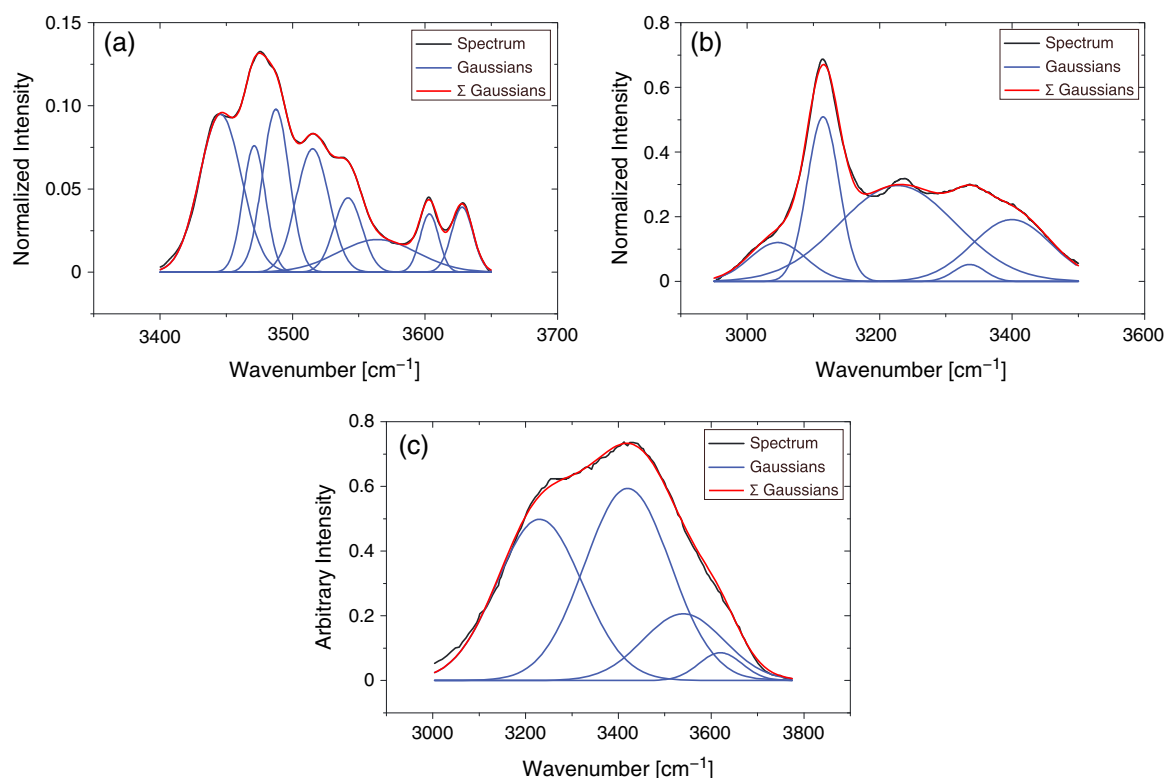
Raman spectroscopy is an excellent tool for studying hydration and deliquescence. For example, in Ca(ClO<sub>4</sub>)<sub>2</sub> vibrations of the tetrahedral perchlorate ion of the anhydrous crystalline salt produce a single Raman spectral peak at wave number  $\nu \sim 990\text{ cm}^{-1}$  [Nuding *et al.*, 2013], vibrations of perchlorate ions in hydrates produce spectral peaks at  $\sim 953$  and  $\sim 936\text{ cm}^{-1}$ , while vibration of perchlorate ion pairs in aqueous solutions also produces a spectral peak at  $\sim 936\text{ cm}^{-1}$ . The spectral peaks at  $\sim 953$  and  $936\text{ cm}^{-1}$  are ideal for detecting changes in the hydration state [Zhang and Chan, 2003], but they can also be used to detect the formation of a solution, in particular the shift of the 953 to the 936  $\text{cm}^{-1}$  spectral peak [Gough *et al.*, 2011]. Furthermore, changes in spectral peaks caused by O-H stretching can be used to detect a solution unambiguously. As shown below, stretching of O-H at Mars environmental conditions produces spectral peaks from around 3000 to 3600  $\text{cm}^{-1}$ . This portion of the spectrum shows distinct changes in the number, position, and width of spectral peaks when a solution forms. We argue that the O-H spectral region is more appropriate for studying the formation of liquid brines than the perchlorate spectral bands between  $\sim 930$  and  $\sim 1000\text{ cm}^{-1}$ . The main reasons for this are that some of the O-H spectral peaks depend directly on the presence of liquid water and that the perchlorate spectral peaks depend most strongly on the hydration state of the salts and the concentration of the solutions [Zhang and Chan, 2003; Miller and Macklin, 1985].

We use Raman spectroscopy to study the formation of liquid perchlorate brines at temperature, pressure, and humidity conditions of the Mars polar region. Our analysis focuses on Ca(ClO<sub>4</sub>)<sub>2</sub> because it has been detected at the Phoenix landing site, it has a low eutectic temperature ( $T_E$ ), and it is expected to be ubiquitous on Mars [Kounaves *et al.*, 2014]. First, we obtain separate spectra of water ice and crystalline hydrated perchlorate salt experimentally, while that of liquid water was taken from Zhang and Chan [2003]. Then, we use Gaussian decomposition to compare these single spectra to the spectra taken during the two sets of experiments described above. This technique is applied to all Raman spectra obtained to determine the wave number and full width half maximum (FWHM) of their decomposed spectral peaks. After subtracting a baseline, the measured spectrum is decomposed into Gaussians using the Origin<sup>®</sup> software package. The condition that every relative maximum and minimum of the relevant portions of the spectrum has to be resolved is imposed. This resulted in fits with  $\bar{R}^2 \geq 0.997$ . A summary of the properties of the Gaussian decompositions of the spectra in the O-H stretching region shown here is presented in Table S1 in the supporting information. Raman spectra were taken every 5 min and normalized by the amplitude of the perchlorate stretching band.

## 3. Results

### 3.1. Spectra of Single Components

Figure 1 shows the decomposed reference spectra for the single salt, water ice, and liquid water. Figure 1a shows that the Gaussian decomposition of Ca(ClO<sub>4</sub>)<sub>2</sub> • 4H<sub>2</sub>O at  $-50^{\circ}\text{C}$  contains spectral peaks



**Figure 1.** Decomposed Raman spectra of  $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ , water ice, and liquid water: (a) The decomposed O-H vibrational spectrum of hydrated  $\text{Ca}(\text{ClO}_4)_2$  at  $-50^\circ\text{C}$ , 800 Pa, and 100% RH shows eight Gaussian components, at 3446, 3471, 3487, 3515, 3542, 3564, 3603, and  $3628\text{ cm}^{-1}$ , with  $\bar{R}^2 = 0.999$ . (b) Water ice at  $-80^\circ\text{C}$  and 800 Pa indicating five Gaussian components, at 3046, 3115, 3227, 3336, and  $3399\text{ cm}^{-1}$ , with  $\bar{R}^2 = 0.997$ . (c) Decomposition of the O-H vibrational region of the spectrum of liquid water [Zhang and Chan, 2003], indicating four broad Gaussian components, at 3230, 3420, 3540, and  $3620\text{ cm}^{-1}$ , with  $\bar{R}^2 = 0.997$ .

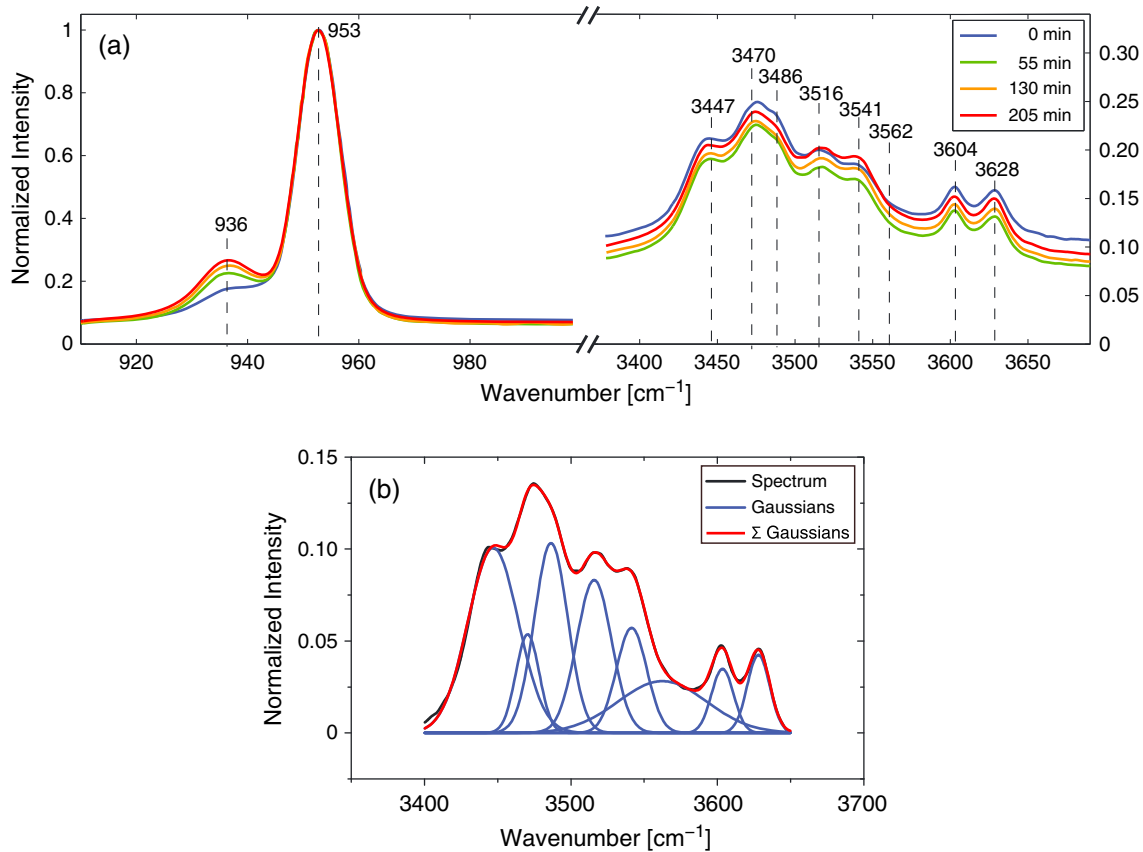
similar to those shown in literature [Nuding *et al.*, 2013]. It contains eight narrow peaks at 3446, 3471, 3487, 3515, 3542, 3564, 3603, and  $3628\text{ cm}^{-1}$ , with all peaks except for one exhibiting a full width at half maximum (FWHM)  $\leq 50\text{ cm}^{-1}$ . Figure 1b shows that the decomposition of the spectrum of pure water ice contains five peaks at  $\sim 3046$ ,  $\sim 3115$ ,  $\sim 3227$ ,  $\sim 3336$ , and  $3399\text{ cm}^{-1}$ , all with FWHM  $> 50\text{ cm}^{-1}$ . Figure 1c shows the Gaussian decomposition for liquid water with peaks at 3230, 3420, 3540, and  $3620\text{ cm}^{-1}$  from data obtained from literature [Zhang and Chan, 2003], indicating that all spectral peaks have FWHM  $> 50\text{ cm}^{-1}$ . These spectral features are summarized in Table 1. The 3230 and  $3420\text{ cm}^{-1}$  peaks for liquid water are ice-like components ( $\text{C}_1$  and  $\text{C}_2$ ), which explain their proximity to the 3227 and  $3399\text{ cm}^{-1}$  peaks in ice.

In a first set of experiments,  $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$  is exposed to a  $\text{CO}_2$  atmosphere saturated with water vapor. In a second set of experiments,  $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$  is placed in direct contact with ice. By comparing the number of decomposed spectral peaks, their wave number, and their width in both sets of experiments with those of the references summarized in Table 1, hydrated crystalline salts can be distinguished from solutions.

**Table 1.** Spectral Signatures of Calcium Perchlorate, Liquid Water, and Water Ice<sup>a</sup>

Substance	Spectral Peaks at $\nu$ ( $\text{cm}^{-1}$ )
$\text{Ca}(\text{ClO}_4)_2$ hydrates	3446 (37), 3471 (20), 3487 (24), 3515 (29), 3542 (25), 3564 (70), 3603 (17), 3628 (19)
Water ice	3046 (99), 3115 (57), 3227 (206), 3336 (56), 3399 (140)
Liquid water	3230 (217), 3420 (218), 3540 (206), 3620 (109)

<sup>a</sup>Values in parentheses are FWHM values for each peak.

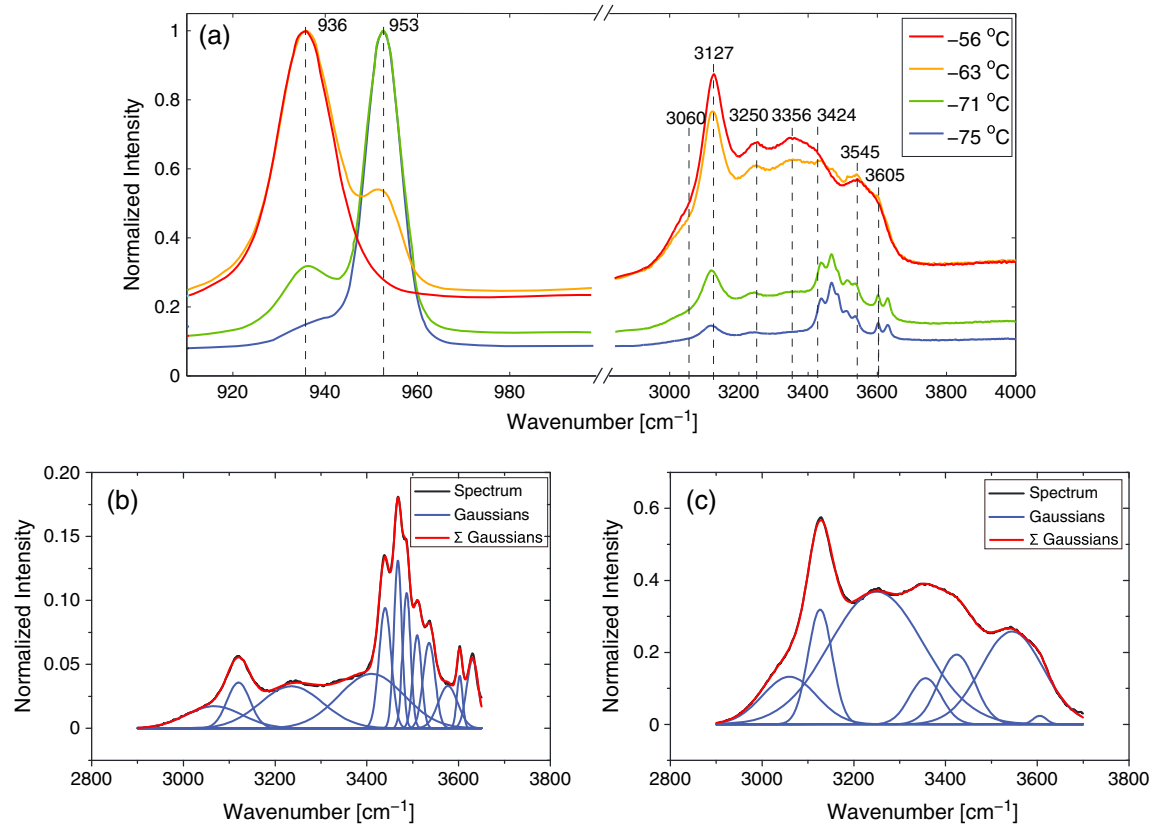


**Figure 2.** (a) Raman spectra of  $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$  exposed to saturated air. The spectra do not show evidence for deliquescence even after the sample has been kept at  $T = -50^\circ\text{C}$  (about  $25^\circ\text{C}$  above  $T_E \approx -74^\circ\text{C}$ ) and  $RH = 100\%$  for 205 min. The values shown in the figure correspond to the spectral peaks of the Gaussian decomposition of the 205 min curve. Analysis of this decomposition indicates that all significant spectral peaks in the O-H stretching region correspond to hydrates. The appearance of a small peak at  $936\text{ cm}^{-1}$  indicates a partial change to  $\text{Ca}(\text{ClO}_4)_2 \cdot 8\text{H}_2\text{O}$ . (b) Decomposed O-H vibrational spectrum of the 205 min curve. It shows eight Gaussian components at  $3447, 3470, 3486, 3516, 3541, 3562, 3604,$  and  $3628\text{ cm}^{-1}$ , all except one of them with  $\text{FWHM} \leq 50\text{ cm}^{-1}$ . Comparison with Figure 1a and Table 1 shows that these components indicate the presence of crystalline hydrated  $\text{Ca}(\text{ClO}_4)_2$ .  $\bar{R}^2 = 0.999$ .

### 3.2. Spectra of Brine Formation Experiments

Figure 2 shows results for the first set of deliquescence experiments.  $\text{Ca}(\text{ClO}_4)_2$  at a constant temperature of  $-50^\circ\text{C}$  (well above its eutectic point at  $-74^\circ\text{C}$ ) is exposed to a  $\text{CO}_2$  atmosphere at a pressure of 800 Pa saturated with water vapor. Figure 2a shows eight narrow peaks and shoulders in the O-H vibrational band, indicating the presence of hydrated crystalline salts throughout the experiment. Figure 2b shows the decomposition of the spectrum of the O-H vibrational band, taken 205 min after the beginning of the experiment whose results are shown in Figure 2a. It shows that the O-H spectrum can be decomposed into Gaussians representing the crystalline salt, with the same number of peaks and similar positions and widths (narrow) as the crystalline salt (Figure 1a). This indicates the presence of  $\text{Ca}(\text{ClO}_4)_2$  hydrates only. Indeed, spectral peaks in the O-H band indicating the occurrence of a solution were not detected within the limit of detection of the Raman spectrometer, even after the samples had been kept at  $T = -50^\circ\text{C}$  (about  $25^\circ\text{C}$  above  $T_E$ ) and  $RH = 100\%$  for almost 3.5 h. Since the O-H spectrum remains unchanged over the duration of the experiment, whereas a small peak appears in the perchlorate band at  $936\text{ cm}^{-1}$  (Figure 2a), and  $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$  is not stable under the above mentioned experimental conditions, we conclude that a partial change in the hydration state from tetrahydrate to octahydrate occurs.

Similar results are obtained for the Gaussian decomposition of the other curves shown in Figure 2a. The 3.5 h limit corresponds to an upper bound of the period of time during which conditions at the Phoenix landing site would meet the conditions necessary for deliquescence to occur [Möhlmann, 2011]. As shown next, this result indicates that liquid brines are much less likely to occur on Mars by the absorption of water vapor from the air than when salts are in direct contact with water ice.



**Figure 3.** (a) Spectra of  $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$  in contact with water ice. The values shown in the figure correspond to the spectral peaks of the Gaussian decomposition of the  $-56^\circ\text{C}$  curve. The blue and green curves contain spectral peaks indicating the presence of hydrated salt and water ice, similar to those shown in Figure 2 (see Table 1). The orange and red curves contain broad spectral peaks at  $\sim 3545$  and  $3605\text{ cm}^{-1}$ , indicating the formation of liquid brines by melting of the water ice within  $\sim 3$  h after the beginning of the experiment. (b) Decomposed O-H vibrational band of the spectrum of  $\text{Ca}(\text{ClO}_4)_2$  in contact with ice at  $-75^\circ\text{C}$ . It shows 12 Gaussians components: at  $3067, 3120, 3236,$  and  $3410\text{ cm}^{-1}$  indicating the presence of ice and at  $3440, 3468, 3487, 3510, 3536, 3577, 3602,$  and  $3630\text{ cm}^{-1}$  indicating the presence of crystalline hydrated salt.  $\bar{R}^2 = 0.999$ . (c) Decomposed O-H vibrational band of the spectrum at  $-56^\circ\text{C}$ . It shows seven Gaussians components at  $3060, 3127,$  and  $3356\text{ cm}^{-1}$  indicating the presence of ice, at  $3250$  and  $3424\text{ cm}^{-1}$  indicating the presence of liquid water or ice, and at  $3545$  and  $3605\text{ cm}^{-1}$  indicating the presence of liquid water, all except one with a width of  $\text{FWHM} > 50\text{ cm}^{-1}$ .  $\bar{R}^2 = 0.999$ .

Figure 3a shows the Raman spectra for  $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$  on top of water ice as the sample temperature is raised from below the eutectic temperature to values well above it, corresponding to those reached in the shallow subsurface during the warm season at the Phoenix landing site [Smith *et al.*, 2009; Rennó *et al.*, 2009]. Gaussian decomposition of the O-H vibrational spectrum of the blue curve, representing the spectrum just below the eutectic temperature, is shown in Figure 3b. It contains eight narrow peaks with  $\text{FWHM} \leq 50\text{ cm}^{-1}$  and similar positions as those in Figure 1a, indicating the presence of  $\text{Ca}(\text{ClO}_4)_2$  hydrates. It also contains four peaks with similar widths and positions as those in Figure 1b, indicating water ice. Spectral peaks indicating the presence of liquid water are not present in this spectrum.

In contrast, Figure 3c showing the Gaussian decomposition of the spectrum when the sample is about  $20^\circ\text{C}$  above the eutectic temperature (red curve in Figure 3a) contains the wider spectral peaks characteristic of liquid water. In particular, it shows peaks at  $3545$  and  $3605\text{ cm}^{-1}$  with widths of  $160$  and  $34\text{ cm}^{-1}$ , indicating that a solution has formed in less than  $\sim 1.5$  h. The spectral peaks at  $3060, 3127,$  and  $3356\text{ cm}^{-1}$  indicate that ice is still present below the solution.

Results of experiments with  $\text{NaClO}_4$  (shown in the supporting information) are qualitatively similar to those described above. Preliminary results for the O-H band of  $\text{Mg}(\text{ClO}_4)_2$  show similar Gaussians as in Figure 3c, indicating the presence of liquid water. Additionally, preliminary results of experiments with icy soil also indicate the formation of liquid brines but at a slower rate. These two cases are more complex and require a more detailed analysis. This will be addressed in a future publication.

#### 4. Discussion and Conclusion

The O-H vibrational band of the Raman spectra is excellent for studying the formation of liquid brines at Martian conditions. The change in the O-H spectrum from eight narrow peaks between  $\sim 3400$  and  $3600\text{ cm}^{-1}$  with nearly all of them having the widths of less than  $50\text{ cm}^{-1}$  typical of the hydrated perchlorate salts, to the four wide peaks between  $\sim 3200$  and  $3600\text{ cm}^{-1}$  with the widths greater than  $100\text{ cm}^{-1}$  typical of liquid water, is an unambiguous indicator of a solution. The changes in the O-H band provide a much clearer indication of the formation of the liquid phase than the changes in the perchlorate band (the  $\sim 930$  to  $\sim 1000\text{ cm}^{-1}$  region of the spectrum) because it is less sensitive to changes in the salt hydration and the concentration of the solution [Zhang and Chan, 2003; Miller and Macklin, 1985]. Thus, observations of changes in the O-H vibrational band could aid the search for liquid brines on Mars.

The results described above indicate that perchlorate salts in contact with ice can form liquid brines during the short periods of the diurnal cycle during which the ground temperatures are above the salts' eutectic temperatures, whereas when atmospheric water vapor is the only source of water bulk deliquescence is too slow to occur. We conclude that liquid brines are likely to form in the shallow subsurface where water ice exists, since the heating of the ground by solar radiation causes the temperature of the shallow Martian subsurface to exceed the eutectic temperature of many salts found on Mars, while the top regolith inhibits sublimation and evaporation. The formation of liquid brines in the shallow subsurface resolves the apparent inconsistency between observational evidence for liquid brines on Mars and the slow kinetics of deliquescence on a cold and dry planet.

The results of our experiments suggest that the spheroids observed on a strut of the Phoenix lander formed on water ice splashed during landing [Smith *et al.*, 2009; Rennó *et al.*, 2009]. They also support the hypothesis that "soft ice" found in one of the trenches dug by Phoenix was likely frozen brine that had been formed previously by perchlorates on icy soil. Finally, our results indicate that liquid water could form on the surface during the spring where snow has been deposited on saline soils [Martínez *et al.*, 2012; Möhlmann, 2011]. These results have important implications for the understanding of the habitability of Mars because liquid water is essential for life as we know it, and halophilic terrestrial bacteria can thrive in brines [Mikucki *et al.*, 2009; Boetius and Joye, 2009].

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