

## A MOLECULAR PERSPECTIVE FOR TRANSIENT LIQUID SALTY BRINE FORMATION IN SEDIMENTS FROM THE McMURDO DRY VALLEYS, ANTARCTICA, AND APPLICATIONS TO MARS.

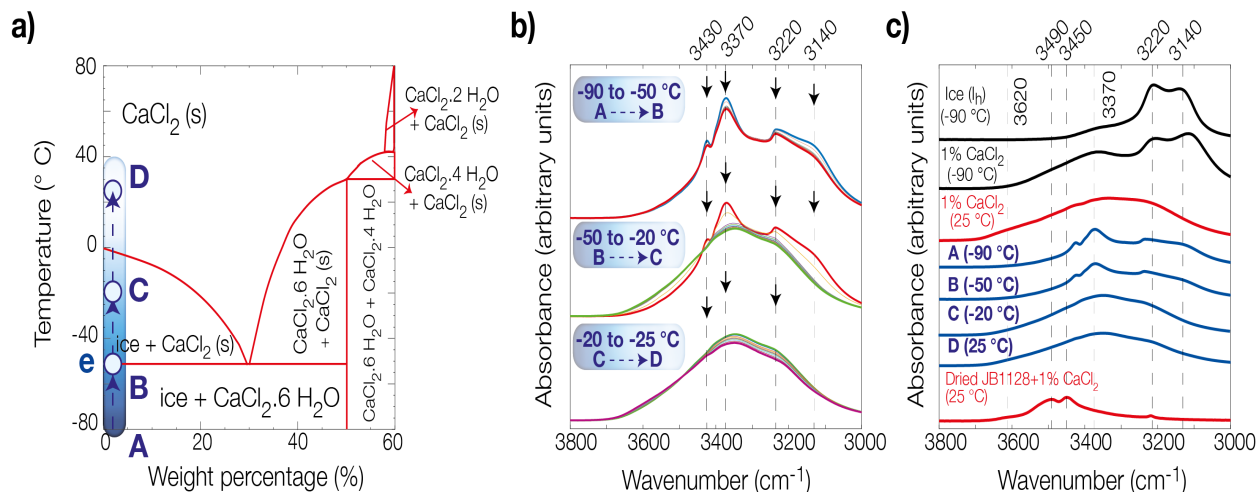
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**Summary:** The extreme environmental conditions of the McMurdo Dry Valleys (MDV) in Antarctica still allow for the formation of *transient liquid salty brines* near the surface with the help of CaCl<sub>2</sub> salts. This study focused on *transient liquid water* formation in mixtures of three sediments with CaCl<sub>2</sub> using mid-IR spectra including H-O-H stretching (3000-3800 cm<sup>-1</sup>) and H-O-H bending (1300-1900 cm<sup>-1</sup>) vibrations to probe possible phase changes of liquid and frozen H<sub>2</sub>O and CaCl<sub>2</sub>. Notable spectral changes were observed for our mixtures, consistent with formation of liquid H<sub>2</sub>O near -50 °C, following the CaCl<sub>2</sub> phase change to brine. The appearance of subzero liquid water in these Cl-bearing samples opens the door to potential subzero thin films of H<sub>2</sub>O in subsurface environments on Mars as well.

**Introduction:** The MDV region is characterized by an extremely cold and dry environment where liquid water is only present seasonally on the surface. Yet, liquid water can occur longer in its near surface environments due to the presence of chlorides and sulfates that allow depression of the freezing point of water well below 0 °C [1-4].

Advancing the specific *eutectic temperature* of each salt solution (e.g., -51 °C for 30 wt.% CaCl<sub>2</sub>), *transient liquid salty brines* may occur in near surface environments on Mars through deliquescence and/or by forming thin water films at mineral surfaces [5].

In this study, we used three MDV sediment encrustations (JB1126, JB1127 and JB1128) collected from the Don Juan Pond region of Wright Valley. This region is known as a shallow hypersaline lake enriched with CaCl<sub>2</sub>, and its hexahydrate form antarcticite (CaCl<sub>2</sub>·6H<sub>2</sub>O), a rare mineral first identified here [3, 4, 6]. Cl was detected by the Mars Odyssey Gamma Ray Spectrometer (GRS) at ~0.49 wt.% Cl in the upper tens of cm at equatorial and mid-latitude regions [7]. Considering the importance of *liquid salty brine* formation at the near surface of Mars for potential *habitability*, this study focused on *liquid salty brine* formation in MDV sediment/CaCl<sub>2</sub> mixtures at low temperatures using cryogenic FTIR spectroscopy in the mid-IR region.



**Fig. 1 a)** Phase diagram of CaCl<sub>2</sub>. **b)** Spectral changes of JB1128+1% CaCl<sub>2</sub> mixture in the H<sub>2</sub>O/O-H stretching region from -90 to 25 °C. **(c)** H<sub>2</sub>O/O-H stretching region of ice and frozen 1% CaCl<sub>2</sub> presented in black. The 1% CaCl<sub>2</sub> and JB1128/CaCl<sub>2</sub> mixture spectra at 25 °C are shown in red to compare with the frozen mixtures.

**Methods:** A portion of each MDV sample was mixed with 5 μL of 1% CaCl<sub>2</sub> aqueous solution and equilibrated ~15 min. Then, the mixtures were applied directly on the pre-frozen Attenuated Total Reflectance (ATR) stage at -90 °C. The temperature was held constant at -90 °C for 10 min to form a stable

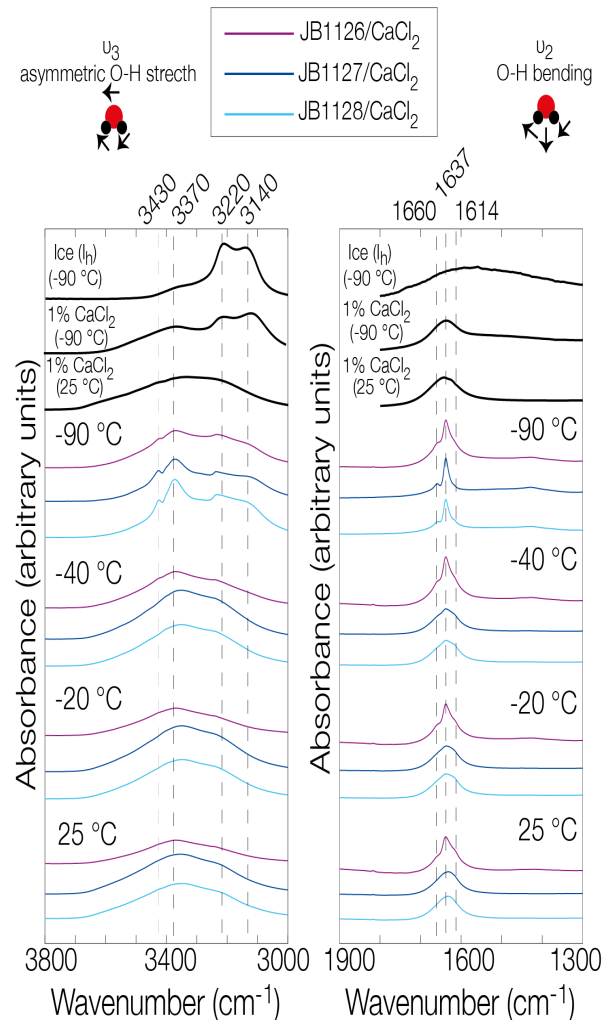
supercooled mixture at -90 °C. Then, the temperature was increased at a rate of 10 °C /min up to 25 °C. We applied the same spectral parameters and data analysis procedures from our previous study to detect transient liquid salty brines in volcanic soils [8].

**Results:** As expected from the phase diagram of  $\text{CaCl}_2$  (Fig. 1a), flash-frozen droplets of 1%  $\text{CaCl}_2$  at  $-90^\circ\text{C}$  (Fig. 1c) form a mixture of ice and antarcticite, with a spectrum exhibiting  $3220$  and  $3140\text{ cm}^{-1}$   $\text{H}_2\text{O}$  ice bands together with  $3370$  and  $3430\text{ cm}^{-1}$  antarcticite bands, similar to a previous cryogenic Raman spectroscopy study [9]. At  $25^\circ\text{C}$ , the spectrum of the 1%  $\text{CaCl}_2$  solution (Fig. 1c) has a broader band shifted to higher wavenumbers compared to those of  $\text{H}_2\text{O}$  ice and antarcticite. This broad band occurs due to a distribution of  $\text{H}_2\text{O}$  vibrations for molecules surrounding the  $\text{CaCl}_2$ . At  $-90^\circ\text{C}$ , the  $\text{CaCl}_2/\text{MDV}$  mixtures exhibited a combination of  $\text{H}_2\text{O}$  ice and antarcticite features (Fig. 1b-c, Fig. 2).

Heating the mixture from  $-90$  to  $-50^\circ\text{C}$  (A-B) resulted in a slight reduction in the JB1128/ $\text{CaCl}_2$  mixture band intensity (Fig. 1b-c). After reaching the  $\text{CaCl}_2$  eutectic point of  $-51^\circ\text{C}$ , spectra at  $-50$  (B) to  $-40^\circ\text{C}$ , indicated progressive elimination of the ice bands, which continued until  $-20^\circ\text{C}$  (C). The JB1128/ $\text{CaCl}_2$  mixture spectrum at  $-20^\circ\text{C}$  was not similar to spectra of  $\text{H}_2\text{O}$  ice, 1%  $\text{CaCl}_2$  ice, or the liquid 1%  $\text{CaCl}_2$  solution. The spectrum at (C) exhibits strong similarities to the spectrum of thin super(cooled)water films formed at the surface of micron-sized mineral grains at  $-10^\circ\text{C}$  [10]. Further heating from  $-20$  to  $25^\circ\text{C}$  slightly decreased the spectral band intensities, but no spectral shifts were presented.

Fig. 2 revealed further insights for comparison of varied phase formations of  $\text{H}_2\text{O}$  ice, liquid  $\text{H}_2\text{O}$ , and frozen mixtures of  $\text{CaCl}_2$  in MDV samples including the H-O-H bending region. The H-O-H bending band for  $\text{H}_2\text{O}$  ice was broader and shifted to lower wavenumbers indicating stronger H-bonding than for the frozen and aqueous 1%  $\text{CaCl}_2$ . However, flash-frozen pastes of MDV/ $\text{CaCl}_2$  mixtures at  $-90^\circ\text{C}$  presented distinct spectral bands at  $1615$ - $1665\text{ cm}^{-1}$ . While the  $1637$  and  $1660\text{ cm}^{-1}$  spectral bands are consistent with higher strength coordination between water molecules and were typically observed for the hexahydrate and tetrahydrate forms of  $\text{CaCl}_2$ , the  $1614\text{ cm}^{-1}$  band is attributed to  $\text{H}_2\text{O}$  associated with the Ca (including Ca-O attractions) [11]. As the temperature increased from  $-40$  to  $25^\circ\text{C}$ , the 1%  $\text{CaCl}_2$  mixtures of the JB1127 and JB1128 samples revealed more liquid-like signatures due to the  $\text{CaCl}_2$  solutions. It is noteworthy that the JB1126 sample retained distinct spectral bands through the experiment from  $-90$  to  $25^\circ\text{C}$ , possibly due to higher amounts of Cl in this sample. To resolve this, we will expand our experiments using cryogenic XRD to confirm the possible phase changes obtained through our experiments.

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**Fig. 2** Comparison of the MDV/ $\text{CaCl}_2$  mixture spectra in the H-O-H stretching and bending regions. Spectra of the JB1127 and JB1128 sediment mixtures were similar, while the JB1126 mixture spectra followed different trends.

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