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 CaCl₂ salts. This study focused on transient liquid water formation in mixtures of three sediments with CaCl₂ using mid-IR spectra including H-O-H stretching (3000-3800 cm⁻¹) and H-O-H bending (1300-1900 cm⁻¹) vibrations to probe possible phase changes of liquid and frozen H₂O and CaCl₂. Notable spectral changes were observed for our mixtures, consistent with formation of liquid H₂O near -50 °C, following the CaCl₂ phase change to brine. The appearance of subzero liquid water in these Cl-bearing samples opens the door to potential subzero thin films of H₂O 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.% CaCl₂), transient liquid salty brines may occur in near surface environments on Mars through deliquesence 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 CaCl₂ and its hexahydrate form antarcticite (CaCl₂·6H₂O), a rare mineral 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/CaCl₂ mixtures at low temperatures using cryogenic FTIR spectroscopy in the mid-IR region.

Methods: A portion of each MDV sample was mixed with 5 µL of 1% CaCl₂ 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].

![Fig. 1](https://example.com/fig1.png)

**Fig. 1 a)** Phase diagram of CaCl₂. **b)** Spectral changes of JB1128+1% CaCl₂ mixture in the H₂O/O-H stretching region from -90 to 25 °C. **c)** H₂O/O-H stretching region of ice and frozen 1% CaCl₂ presented in black. The 1% CaCl₂ and JB1128/CaCl₂ mixture spectra at 25 °C are shown in red to compare with the frozen mixtures.
**Results:** As expected from the phase diagram of CaCl₂ (Fig. 1a), flash-frozen droplets of 1% CaCl₂ at -90 °C (Fig. 1c) form a mixture of ice and antarcticite, with a spectrum exhibiting 3220 and 3140 cm⁻¹ H₂O ice bands together with 3370 and 3430 cm⁻¹ antarcticite bands, similar to a previous cryogenic Raman spectroscopy study [9]. At 25 °C, the spectrum of the 1% CaCl₂ solution (Fig 1c) has a broader band shifted to higher wavenumbers compared to those of H₂O ice and antarcticite. This broad band occurs due to a distribution of H₂O vibrations for molecules surrounding the CaCl₂. At -90 °C, the CaCl₂/MDV mixtures exhibited a combination of H₂O ice and antarcticite features (Fig. 1b-c, Fig. 2).

Heating the mixture from -90 to -50 °C (A-B) resulted in a slight reduction in the JB1128/CaCl₂ mixture band intensity (Fig. 1b-c). After reaching the CaCl₂ eutectic point of -51 °C, spectra at -50 (B) to -40 °C, indicated progressive elimination of the ice bands, which continued until -20 °C (C). The JB1128/CaCl₂ mixture spectrum at -20 °C was not similar to spectra of H₂O ice, 1% CaCl₂ ice, or the liquid 1% CaCl₂ solution. The spectrum at (C) exhibits strong similarities to the spectrum of thin supercooled water films formed at the surface of micron-sized mineral grains at -10 °C [10]. Further heating from -20 to 25 °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 H₂O ice, liquid H₂O, and frozen mixtures of CaCl₂ in MDV samples including the H-O-H bending region. The H-O-H bending band for H₂O ice was broader and shifted to lower wavenumbers indicating stronger H-bonding than for the frozen and aqueous 1% CaCl₂. However, flash-frozen pastes of MDV/CaCl₂ mixtures at -90 °C presented distinct spectral bands at 1615-1665 cm⁻¹. While the 1637 and 1660 cm⁻¹ spectral bands are consistent with higher strength coordination between water molecules and were typically observed for the hexahydrate and tetrahydrate forms of CaCl₂, the 1614 cm⁻¹ band is attributed to H₂O associated with the Ca (including Ca-O attractions) [11]. As the temperature increased from -40 to 25 °C, the 1% CaCl₂ mixtures of the JB1127 and JB1128 samples revealed more liquid-like signatures due to the CaCl₂ solutions. It is noteworthy that the JB1126 sample retained distinct spectral bands through the experiment from -90 to 25 °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/CaCl₂ 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.](image)