

A MOLECULAR VIEW OF NEAR SURFACE BRINES ON MARS THROUGH MID-INFRARED SPECTRA OF MARTIAN ANALGS MIXED WITH CL SALTS. Merve Yeşilbaş^{1,2} and Janice L. Bishop^{2,3}, ¹Umeå University, (Umeå, SE 90187), ²SETI Institute (Mountain View, CA 94043; myesilbas@seti.org), ³NASA Ames Research Center (Moffett Field, CA 94035; jbishop@seti.org)

Summary: Cl-enriched regolith on Mars could liquefy at -30 to -50 °C in near surface environments. Investigating the spectral properties of Cl-bearing Mars analogs in the lab enables spectroscopic detection and characterization of Cl salts on Mars and will lead to understanding the conditions where liquid salty brines can exist on Mars. In this study, we used three volcanic samples as Mars analogs mixed with 40% CaCl₂ and 10% Mg(ClO₄)₂ salts to examine their hydration conditions from -90 to 25 °C using mid-IR spectra (4000-800 cm⁻¹) and to probe possible phase changes of liquid and frozen H₂O. Each of the martian analogs revealed varied responses to formation of water or ice in our experiments. This study highlights the complex relationships of Cl salts in low temperature soil/brine systems and the presence of liquid salty phases well below 0 °C.

Introduction: Chloride (Cl) bearing salts are distributed along the surface and near surface of Mars [1-3]. The salts depress the freezing point of water and favor salty liquid water in near surface environments, which has also been detected on Mars below the south polar ice caps using Radar data [4]. Previous studies pointed out that liquid salty brines could also be responsible for formation of recurring slope lineae (RSL) [5]. Each type of salt shows specific deliquescence/efflorescence features under different conditions; for instance, Mg-perchlorate reveals a lower eutectic temperature (~ -73 °C, 43.7%) [6], than CaCl₂ (~ -51 °C, 30%) [3]. The liquid salty brine quickly interacts with water in the environment, which can then be quickly released into the atmosphere through efflorescence [13].

Methods: The martian analogs used here include two natural volcanic samples collected from Mauna Kea (MK 91-16) [7], and Haleakala (JB399) [8] as well as the Mojave Mars Simulant (MMS) [9]. These samples were dry sieved to < 250 μm prior to the experiments and then mixed with chloride salts including aqueous 40% CaCl₂ solution, aqueous Mg(ClO₄)₂ suspensions at 1000 g/L, and 10% Mg(ClO₄)₂ solution.

Cryogenic-FTIR. We performed cryo-FTIR measurements using a Bruker Vertex 70/V FTIR spectrometer equipped with a DLaTGS detector. Prepared samples were directly applied on the precooled temperature-controlled Attenuated Total Reflectance (ATR) stage (Golden Gate, Serial Number N29328 by Specac) at -90 °C. The temperature was retained at -90 °C for 10 min to ensure the formation of a stable supercooled mixture at -90 °C. The heater was then set to increase at a rate of 10 °C/min up to 25 °C and time-resolved IR spectra (3

sec per scan) were taken in the spectral range 4000-600 cm⁻¹ to monitor phase changes of the brine solutions (40% CaCl₂, 10% Mg(ClO₄)₂) and super(cool)ed mixtures. The phase diagram of CaCl₂ (Fig. 1) illustrates the expected phase changes for CaCl₂ as a function of temperature and abundance.

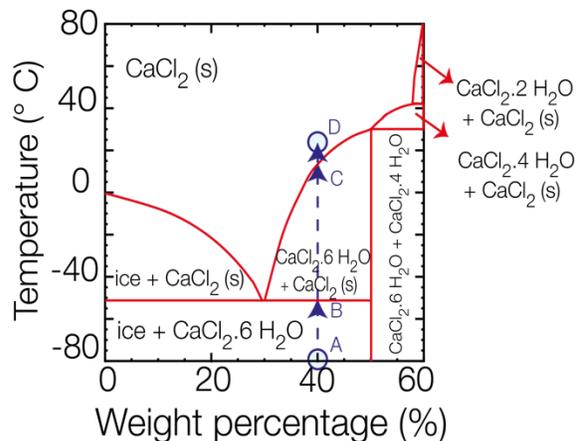


Fig 1. A classical phase diagram for CaCl₂. The letters A-D show possible phase changes corresponding to the spectral experiments of this study (Fig 2.)

Chemometric Analyses. The collected time-resolved IR spectra of supercooled mixtures were treated with the single-value decomposition (SVD) chemometric method [10] to reduce noise in the collected spectra.

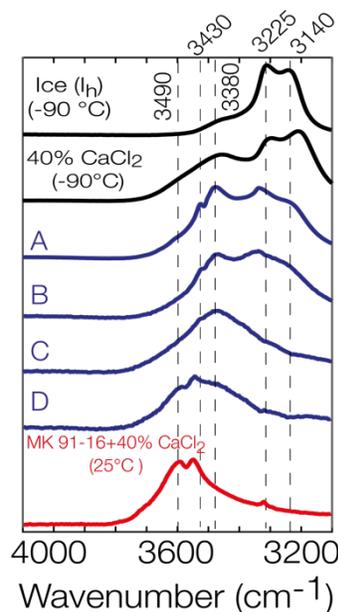


Fig 2. O-H stretching region of ice and frozen 40% CaCl₂ presented in black. The letters from A-D show the spectra of possible phase changes of MK 91-16 + 40% CaCl₂ mixtures following the experimental conditions in Fig 1. The dried spectrum of MK 91-16 + 40% CaCl₂ at 25°C is presented in red to compare with frozen mixtures.

Results: FTIR spectroscopy in the mid-IR region enabled determination of the vibrational modes of water, ice, and frozen aqueous solutions of CaCl_2 and $\text{Mg}(\text{ClO}_4)_2$ during hydration from -90 to 25 °C (Fig 3). Freezing of the aqueous solutions of 40% CaCl_2 and 10% MgClO_4 below -90 °C forms hexahydrates including $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ (antarcticite) [11] and $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ [6,11] and these hexahydrates coexist together with ice at -90 °C. In addition to ice bands, $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ presents a significant band at 3580 cm^{-1} , attributed to weak coordination of H_2O molecules to the ClO_4^- anion [12-13]. Antarcticite coexists with H_2O ice at -90 °C, and the spectra of this system include bands at ~ 3380 and 3225 cm^{-1} (Fig. 2); however, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ +ice at -90 °C coordinates stronger with liquid H_2O at ~ 3100 cm^{-1} than with H_2O ice (~ 3140 cm^{-1}) [10].

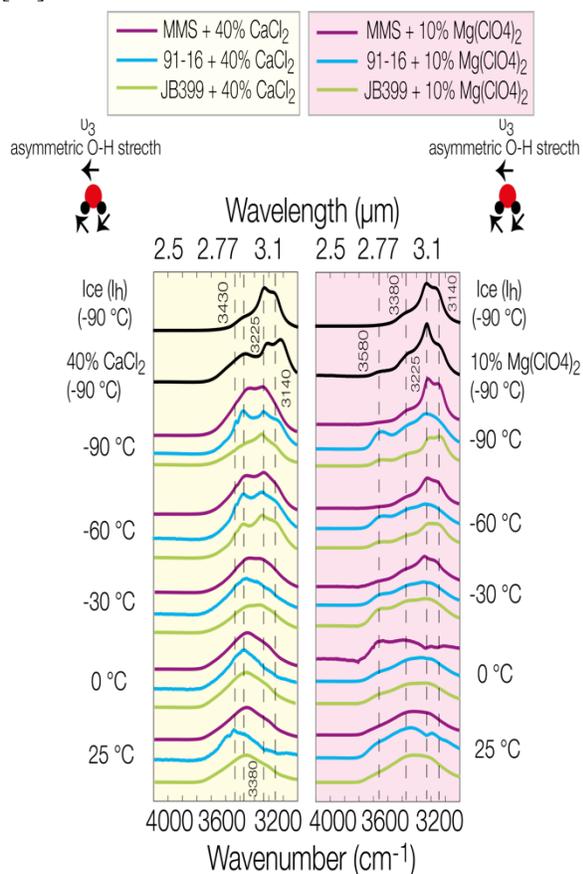


Fig 3. Hydration of samples mixed with Cl brine from -90 °C to 25 °C. While the *left* graph exhibits the results of samples mixed with CaCl_2 , the *right* graph presents hydration of samples mixed with $\text{Mg}(\text{ClO}_4)_2$.

In the case of brine mixtures with the samples at -90 °C, we observed that the spectra of MMS and MK 91-16 contain bands resembling ice and antarcticite. However, the spectrum of JB399 notably presents the

signatures of H_2O ice. We started to see the major changes when the temperature increased above the eutectic point of CaCl_2 at -51 °C, that ice bands at 3140 and 3225 cm^{-1} significantly decreased for MK 91-16 and the JB399 sample through melting at -30 °C. This could be explained by the presence of liquid salty water between -51 °C to 0 °C on Mars. Under further heating to 25 °C, water quickly effloresced for the MK 91-16 sample, while the water bound in the MMS and JB399 samples remained rather stable.

While the MMS and JB399 10% $\text{Mg}(\text{ClO}_4)_2$ mixtures exhibited similar spectra to those of ice plus $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ mixtures at -90 °C, the MK 91-16 mixture surprisingly produced spectra comparable to that of a 10% $\text{Mg}(\text{ClO}_4)_2$ solution at -40 °C, where the liquid phase of $\text{Mg}(\text{ClO}_4)_2$ and ice coexists according to its phase diagram [6]. The MK 91-16 sample may have more fine-grained particles that were able to provide surface area for the perchlorate. A previous study of MMS mixed with $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ found that MMS exhibited no significant role [14]. In our experiment, increasing the temperature to 25 °C resulted in elimination of the ice bands at 3225 and 3140 cm^{-1} and creation of bands at 3380 and 3220 cm^{-1} that are similar to the spectra of aqueous Mg -perchlorate suspensions, as expected from its phase diagram.

Conclusions and Future Studies: Our study observed varied hydration responses using mid-IR spectra for Mars analog samples containing different Cl-bearing salts. As the insoluble minerals also play a role in formation of crystalline H_2O below 0 °C [10, 14], further investigation is warranted on the role of the samples in affecting the conditions of transient liquid salty brines on Mars. Additionally, future VNIR spectra will complement the spectral database for analysis of CRISM at Mars and orbital spectrometers at icy bodies.

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