

**Combined Differential Scanning Calorimetric-Raman Spectral study of ion pairing in aqueous calcium perchlorate solution under Mars-relevant temperature.** S. Tu<sup>1</sup>, J. B. Parise<sup>1,2</sup>, E. Lars<sup>1,2</sup>, A. D. Rogers<sup>1</sup>, <sup>1</sup>Department of Geosciences, Stony Brook University, Stony Brook, NY, 11790-2100. <sup>2</sup>Brookhaven National Lab, National Synchrotron Light Source II, Upton, NY, 11973-5000.

**Introduction:** The recent detection of perchlorate ( $\text{ClO}_4^-$ ) in the Martian soil at both polar and equatorial regions [1] has significant implications for the habitability of Mars. The highly hygroscopic property [2] and the ability to depress the freezing point of water [3] make perchlorate a possible means for forming liquid water/brines at the Martian surface. Furthermore, near-eutectic perchlorate brines are reported to supercool into a glassy state under Martian-relevant conditions [4], which provides a potential route of cryopreservation for putative perchlorate-tolerant microorganisms [5] to survive the Martian winter [4].

These unique properties and astrobiology relevance have generated interest in how the  $\text{ClO}_4^-$  ion modifies the atomic arrangements associated with ion pairing, specifically how the structure of two positively-charged ions with 0 ~ 2 layers of solvent in between are held by the long-range, non-directional electrostatic force as a recognizable kinetic entity [6]. The concentration-dependence and temperature-dependence of ion pairing have important influence on the hygroscopicity and the eutectic point of electrolyte salts [7, 8]. However, among all potential candidates of perchlorate salts on Mars, only aqueous  $\text{NaClO}_4$  solution has been studied over wide ranges of composition regarding cation-anion-water association under Martian relevant temperature [9-12]. Given that various cations may interact differently with their counter ion ( $\text{ClO}_4^-$ ) in solution, this study is the first to examine the ion-pair formation in aqueous Ca-perchlorate solution upon supercooling into glass. The combination of a Differential Scanning Calorimeter-Raman microscope allows us to correlate thermal and structural changes of brine samples simultaneously while changing the temperature. The symmetric stretching  $\nu_1$  band of  $\text{ClO}_4^-$  (~933  $\text{cm}^{-1}$ ) contains overlapping signals of free ion and different ion pair species, thus providing important information of cation-anion-solvent association [9-12].

#### Experimental Methods:

**Sample Preparation.**  $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$  reagent (99%) was dissolved into deionized water to obtain the near-eutectic (5.0 molal) aqueous solution. The sample was freshly made just before the experiment to avoid further deliquescence.

**Differential Scanning Calorimeter-Raman Microscope (DSC-Raman microscope).** An *in situ* thermal and spectral data collection was accomplished by combining of Linkam Optical Differential Scanning Calorimeter

(DSC) 600 with a WITec alpha300 R confocal Raman microscope using 50× objective and 532 nm Nd:YAG laser. For studies of spectral changes of sample occurring upon transformation from glassy state to aqueous state, a continuous supply of liquid nitrogen rapidly cooled the sample from 20°C to -150°C (at ~60°C/min) to form a glass. The glass-transition was indicated by a heat capacity jump in the heat flow curve. After holding the sample at -150°C for ~10 minutes to ensure the glassy state was stable, the perchlorate glass was brought back to room temperature at a warming rate of 10°C/min. The structural changes were monitored by the Raman spectra every 10°C increment with an exposure time of 30s.

**Multi-peak Fitting.** All spectra were background-corrected and smoothed using the Savitzky-Golay technique. The high spectral resolution (1  $\text{cm}^{-1}$ ) allows further peak deconvolution analysis using a Matlab peak fitting program developed by O'Haver (2016) [13] based on an unconstrained non-linear optimization algorithm. A 40% Gaussian-Lorentzian sum function was performed iteratively on the ~933  $\text{cm}^{-1}$  band until the fitting in all solutions was mainly controlled by the changing height of each resolved-components with relatively invariant position and width. The quality of matching was judged by the goodness of fit and a display of the residual of the observed-calculated profile.

#### Results:

A glass-transition was observed in the 5.0 molal  $\text{Ca}(\text{ClO}_4)_2$  solution, indicated by a baseline shift of the DSC curve due to a heat capacity change (Fig 1). Below the glass-transition (-150°C ~ -120°C), the spectra are unchanged since the structure is “frozen in” the glassy state (Fig 2a). Above the glass-transition, perchlorate recovers into a mobile aqueous state, with the most pronounced difference occurring at the O-H stretching region from 3000  $\text{cm}^{-1}$  ~ 4000  $\text{cm}^{-1}$  (Fig 2a). This band contains four components: the two at lower frequency, C1 (3230  $\text{cm}^{-1}$ ) and C2 (3420  $\text{cm}^{-1}$ ), also called ice-like components, represent the water molecules constituting an extended tetrahedrally hydrogen-bonded network as observed in water ice. The other two at higher frequency, the C3 (3550  $\text{cm}^{-1}$ ) and C4 (3620  $\text{cm}^{-1}$ ), stand for the water molecules forming less or even no hydrogen bond. As the temperature goes up, the O-H stretching band starts to show a sequential damping of the ice-like components (3200  $\text{cm}^{-1}$  and 3420  $\text{cm}^{-1}$ ) towards higher temperature corresponding to the destruction of

tetrahedral hydrogen-bonding network that should exist massively in water ice (Fig 2a).

From the aqueous state to the glassy state, the symmetric stretching  $\nu_1$  band of  $\text{ClO}_4^-$  ( $\sim 933 \text{ cm}^{-1}$ ) expands asymmetrically on the high frequency side (Fig 2b). According to previous studies [9-12] and our multi-peak fitting analysis (Fig 3), this emerging asymmetry is assigned to a growing component at  $\sim 940 \text{ cm}^{-1}$  towards decreasing temperature related to the enhanced formation of solvent-shared ion pair (SIP) where the cation and anion share one layer of hydrated water in between. In this case, the  $T_d$  symmetry of perchlorate is perturbed as the newly formed  $\text{Ca}^{2+}(\text{H}_2\text{O})\text{ClO}_4^-$  species elongates one of the Cl-O bonds in the supercooling region. This observation is inconsistent with the accepted models that ion pairing is inhibited at lower temperature due to a parallel decline in the dielectric constant of water [14]. Fleissner et al. (1998) stated that the density maximum of water at  $\sim 4^\circ\text{C}$  prevents extrapolation of the population of contact ion pair (CIP) from room temperature into supercooled region [15]. This temperature of maximum density (TMD) implies the thermodynamic water anomalies, defined as the non-monotonic trend of thermodynamic functions upon changing temperature [16]. Similarly, our observation of increasing SIP towards glassy calcium perchlorate can be interpreted by this anomalous behavior of water. Above the TMD, the formation of ion pairing is weakened upon cooling due to the declining dielectric constant, while below the TMD, the restoration of a more open, fully hydrogen-bonded tetrahedral network in supercooled water enhances the ion pairing of solutes with decreasing temperature [15]. Besides, the interaction between the inner-shell water and calcium is too strong for perchlorate to penetrate [17]. Thus, CIP species in the form of  $\text{Ca}^{2+}\text{ClO}_4^-$ , which should generate a Raman signal centered at  $\sim 950 \text{ cm}^{-1}$  [11], is not detected even at the lowest temperature. Such extensive replacement of water-water hydrogen bonds by the cation-water-anion bonds could play an important role in the deep freezing-point depression of water upon addition of calcium perchlorate salt [8].

**Conclusion:** We have measured the formation of ion pair in aqueous Ca-perchlorate solution at different temperatures *in situ* using a DSC-Raman microscope set-up. Our study provides a more complete understanding of the how the addition of calcium perchlorate salts affects the structure of water under Martian-relevant temperature. Generally, increasing ion pairing with decreasing temperature probably reflects the water anomalies in supercooled region, with the water structure evolving towards a more open, fully hydrated tetrahedral network. The extensive replacement of strong hydrogen bonds between water molecules by the solvent-shared ion pairs in solution could contribute to the deep eutectic point of  $\text{Ca}(\text{ClO}_4)_2\text{-H}_2\text{O}$  system.

**Acknowledgement:** This work was supported by the NASA Solar System Workings award 80NSSC18K0535.

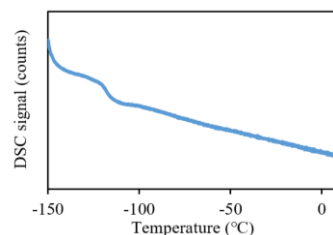


Fig. 1. DSC curve of warming 5.0m  $\text{Ca}(\text{ClO}_4)_2$  glass from  $-150^\circ\text{C}$  to  $20^\circ\text{C}$  at  $10^\circ\text{C}/\text{min}$

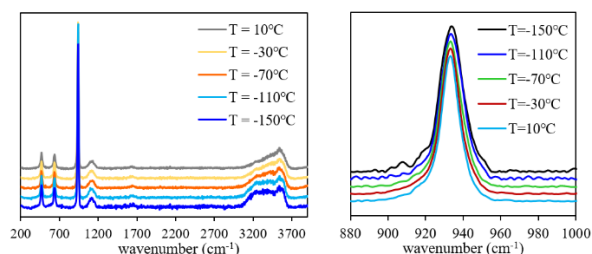


Fig. 2(a) Raman spectra of 5.0 m aqueous  $\text{Ca}(\text{ClO}_4)_2$  at different temperatures; (b) magnification of the  $\nu_1$  band ( $\sim 933 \text{ cm}^{-1}$ ) of  $\text{ClO}_4^-$

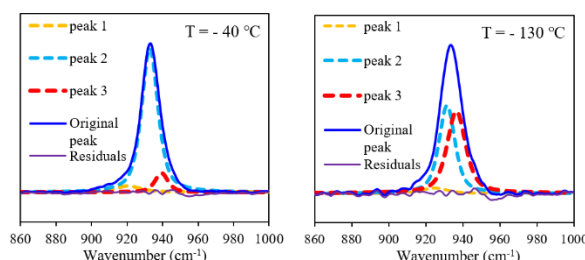


Fig. 3 Multi-peak fitting [13] of the  $\sim 933 \text{ cm}^{-1}$  band for 5.0 m  $\text{Ca}(\text{ClO}_4)_2$  spectra obtained at (a)  $-40^\circ\text{C}$ ; (b)  $-130^\circ\text{C}$  (glassy state)

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