

**Thermal and structural changes during supercooling of eutectic perchlorate solutions.** S. Tu<sup>1</sup>, J. B. Parise<sup>1,2</sup>, E. Lars<sup>1,2</sup>, A. D. Rogers<sup>1</sup>, J. Gregerson<sup>1</sup>, B. Paul<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:** Perchlorate ion ( $\text{ClO}_4^-$ ) has been detected in Martian soil at both polar [1] and equatorial regions [2], and is believed to exist ubiquitously on Mars [3] in the form of  $\text{Mg}(\text{ClO}_4)_2$ ,  $\text{Ca}(\text{ClO}_4)_2$ ,  $\text{NaClO}_4$  and  $\text{KClO}_4$  salts [1, 4]. The highly hygroscopic property [5-7] and the ability to depress the freezing point of water [8] enable perchlorate to sporadically deliquesce into aqueous solution and mobilize other soluble salts to sporadically flow across the Martian surface. Additionally, these perchlorate brines can form into a series of hydrated salts [5-8] to sequester a specific amount of water under Mars-relevant temperature and relative humidity (RH). In this way, perchlorate salts are suggested to be a possible repository of the liquid water on present-day cold and dry Mars. The transformation between their aqueous phases and different hydrated solid phases impacts the hydrologic activity and the potential habitability on the (sub)surface of Mars.

However, the behavior of  $\text{ClO}_4^-$ - $\text{H}_2\text{O}$  system at low-temperature is not fully understood. Supercooling effects are commonly observed in salt solutions due to kinetic inhibition of nucleation [9], which can be decreased by slower cooling rates or the existence of external particles. Previous studies showed that magnesium perchlorate and calcium perchlorate solutions at eutectic concentration could deeply supercool into glassy material near  $-120^\circ\text{C}$ , even at small cooling rates of  $<1^\circ\text{C}/\text{min}$  with the addition of Martian regolith simulant [8]. Meanwhile, the analysis of the Rocknest soil from CheMin and APXS suggests the presence of  $\text{SO}_3^-$  and Cl-bearing amorphous components [10]. Given the wide temperature ranges on Mars, the glass transition of perchlorate is likely to occur to stabilize liquid water in the Martian soil periodically. However, this perchlorate glass, and its thermodynamic as well as structural relationships to the crystalline forms, is unknown. In this study, we aimed at investigating the thermal and structural changes during supercooling of perchlorate solutions using both differential scanning calorimeter (DSC) and a High-energy X-ray diffraction.

#### Experimental Methods:

**Sample preparation.** Eutectic magnesium perchlorate solution (3.4m) and calcium perchlorate solution (4.2m) were prepared by dissolving  $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$  reagents into deionized water. All solutions were freshly made just before the experiment to avoid further deliquescence.

**Differential Scanning Calorimeter (DSC).** A Linkam DSC 600 was used to trace the phase changes

by recording the heat flux across the sample while decreasing temperature. Each solution sample was deposited into an aluminum sample pan and then enclosed into the main interface of the DSC. With a continuous flow of liquid nitrogen, the sample inside the DSC was cooled at  $3^\circ\text{C}/\text{min}$  from  $20^\circ\text{C}$  to  $-150^\circ\text{C}$ . If any crystallization or melting event occurs, an exothermic peak or an endothermic peak will appear in the DSC curve, while glass transition will be indicated by a kink.

**Temperature-resolved High-energy X-ray diffraction (XRD).** The *in situ* XRD experiment was conducted at the NSLS-II on the 28-ID-2 beamline. Each solution sample was sealed in a 2mm capillary and then brought from room temperature to  $-150^\circ\text{C}$  at  $5^\circ\text{C}/\text{min}$  using a flow of cold  $\text{N}_2$  gas. After reaching the lowest temperature, the sample was held at  $-150^\circ\text{C}$  for another 30 min to ensure the stability of phases, and then warmed back at the same rate. XRD patterns were continuously collected simultaneously with an exposure time of 300s for each pattern. The high energy X-ray beam ( $>30\text{keV}$ ) can provide a low background and a wide range of Q-space for Pair Distribution Function (PDF) and Rietveld studies, which cannot be achieved by lab x-ray sources.

**Results:** Our results from both  $\text{Mg}(\text{ClO}_4)_2$  solution (Fig 1) and  $\text{Ca}(\text{ClO}_4)_2$  solution (Fig 2) show a baseline drift in DSC curves around  $-130^\circ\text{C}$ , which is absent in the blank curve. Note that the vitrification point of either  $\text{Mg}(\text{ClO}_4)_2$  or  $\text{Ca}(\text{ClO}_4)_2$  is around  $-120^\circ\text{C}$ . Given that the cooling rate of  $3^\circ\text{C}/\text{min}$  is not enough to avoid severe supercooling effect that commonly occurs in perchlorate system, the DSC curve shift probably reflects the abrupt heat capacity change due to a glass transition.

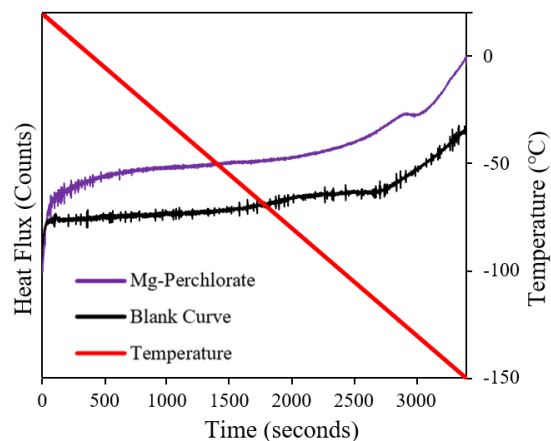


Fig. 1. DSC curve of cooling Mg-Perchlorate solution (3.4m) from  $20^\circ\text{C}$  to  $-150^\circ\text{C}$  at  $3^\circ\text{C}/\text{min}$

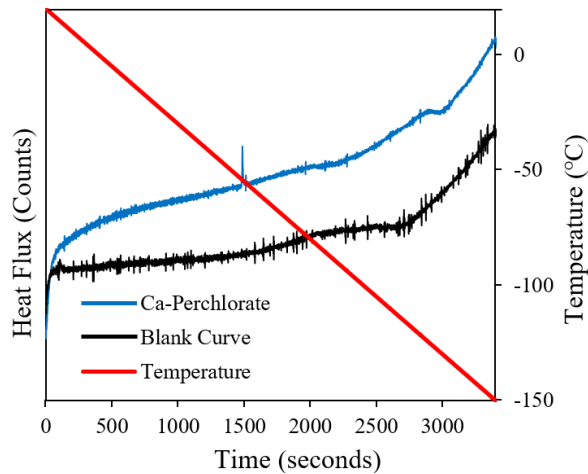


Fig. 2. DSC curve of cooling Ca-Perchlorate solution (4.2m) from 20°C to -150°C at 3°C/min

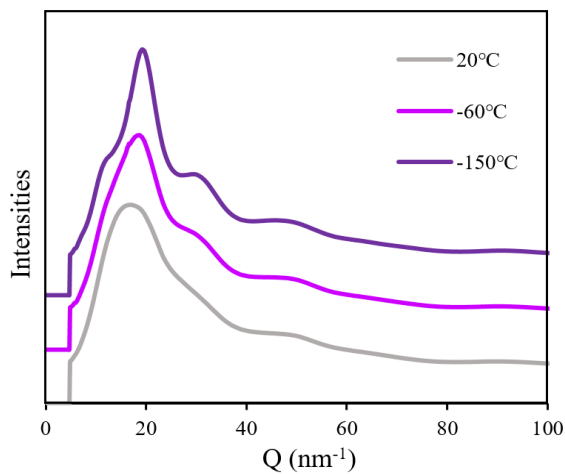


Fig. 3. In situ XRD patterns while cooling Mg-Perchlorate solution (3.4m) from 20°C to -150°C at 5°C/min

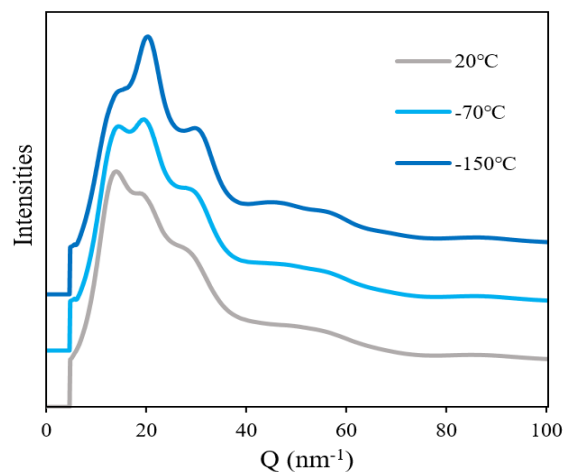


Fig. 4. In situ XRD patterns while cooling Ca-Perchlorate solution (4.2m) from 20°C to -150°C at 5°C/min

Fig 3 and Fig 4 show the results of *in situ* high-energy XRD of  $\text{Mg}(\text{ClO}_4)_2$  and  $\text{Ca}(\text{ClO}_4)_2$  solutions, respectively. During cooling, no sharp peaks emerge in either diffraction pattern, indicating the absence of crystallization, even after staying under their freezing points for 30 min. However, the relative intensity of the “broad peak” at  $20 \text{ nm}^{-1}$  gradually grows up compared to other “broad peaks” in both samples, which probably imply a liquid-liquid/liquid-amorphous transition or a pre-nucleation event.

**Conclusion:** We have measured phase changes in 3.4m Mg-perchlorate solution and 4.2m Ca-perchlorate solution, both at eutectic concentration, via DSC and *in situ* High-energy XRD. The drift in DSC curves around  $-120^\circ\text{C}$ , together with the sharpening of the “broad peak” at  $20 \text{ nm}^{-1}$  in XRD patterns probably imply a phase transition from brines rather than crystallization. Our future work will focus on ascertaining the phase transformation and constraining the formation and stability of this new phase using the obtained thermal and structural information. Our study provides a more complete understanding of the behavior of perchlorate salts/brines on the surface of the Mars.

**References:** [1] Hecht, M. H., et al. (2009) *Science*, 325, 64-67. [2] Ming, D. W., et al. (2014) *Science*, 343, 1245-1267. [3] Kounaves, S. P., et al. (2014) *Icarus*, 229, 206-213. [4] Kounaves, S. P., et al. (2010) *JGR*, 115, E1 [5] Gough, R. V., et al. (2011) *EPSL*, 312, 371-377. [6] Nuding, D. L., et al. (2014) *Icarus*, 243, 420-428. [7] Gough, R. V., et al. (2014) *EPSL*, 393, 73-82. [8] Toner, J. D., et al. (2014) *Icarus*, 233, 36-47. [9] Angell, C. A. (2002) *Chemical Reviews*, 102, 2627-2650. [10] Bish, D. L., et al. (2013) *Science*, 341, 1238-1242.