**INVESTIGATING THE HYSTERETIC BEHAVIOR OF MARS-RELEVANT SALTS.** K. M. Primm and D. E. Stillman, Dept. of Space Studies, Southwest Research Institute, 1050 Walnut St. #300, Boulder, CO 80302, USA (kprimm@boulder.swri.edu).

**Overview:** The existence of liquid water in the martian surface or subsurface appears to be absent because of the cold temperatures, a near zero daytime relative humidity, and low surface pressure. However, the discovery of perchlorate ($ClO_4^-$) and chloride ($Cl^-$) salts has increased the possibility of liquid brine on surface or subsurface of Mars today [1,2]. Here, we find that magnesium chloride $MgCl_2$ brines are metastable up to 18°C below its eutectic temperature of −32.2°. Additionally, how far metastable liquid solutions exist below the eutectic is dependent on the maximum temperature it was warmed too. Furthermore, this metastability is stable over at least 60 hours. Conversely, sodium chloride NaCl brines have small metastability (3°C). These findings along with those in the literature [3,4] suggest that salts with greater freezing point depressions (<–30°C) also have greater metastability when freezing. Thus, to understand when liquid brines could exist on Mars today, metastability of theses brines needs to be taken into account along with the full temperature profile that the brines undergo.

**Background:** Salts can significantly depressing the freezing point of liquid water [3-7]. When a salt hydrate and water ice mixture is warmed, it will melt at the eutectic temperature. Eutectic temperatures decrease with increasing solubility and van't Hoff factor (number of discrete ions dissolved in solution in a formula unit of the substance). However, when a brine is frozen, crystal inhibition allows the solution to remain in a metastable state below the eutectic temperature.

Toner et al. [4] used near eutectic concentrations of $MgCl_2$ and performed calorimetry to understand the metastability of Mars-relevant brines. Toner et al. [4] found that $MgCl_2$ brines were metastable at temperatures between 9-14°C below the eutectic temperature. Primm et al. [3] observed similar behavior with $MgCl_2$ seeing no freezing occur even at temperatures 20°C below the stable eutectic temperature.

The experimental studies in this abstract measure less concentrated solutions and measure the conductivity generated by brines that exist between ice grains known as called liquid vein networks (LVN). Furthermore, we examine the metastability of $MgCl_2$ brine over different starting concentrations, varying the time spent below the eutectic temperature, and varying the starting temperature to see if any of these factors change the metastability properties of these salts.

**Experimental Methods:** Several solutions of $MgCl_2$ and NaCl were prepared in high purity water. The solution was placed into a three electrode sample holder with a height of 5mm (enclosed in 31mm diameter Teflon cup), which was then loaded into an insulated box within an ultra-low freezer [8,9].

To determine the extent of metastability of the sample, the temperature was lowered by 0.25–10°C until −85°C. Such warming, recrystallization, and cooling cycles were repeated multiple times. To further investigate the metastability of the sample solution, the maximum temperature the sample was warmed to was changed. This would be performed by warming the temperature (after the previous freezing experiment) to various colder temperatures above the eutectic temperature (i.e. –5, –10, –15°C, etc.). At every temperature, the electrical properties of the sample are over a frequency range of 100mHz – 1MHz [see 9 for additional details].

**Results:** As the salt sample transitions from a solid to a partially briny phase there is a large change in DC conductivity as brine is significantly more conductive than an ice-salt hydrate mixture [8,9]. Thus, we can measure the eutectic and metastable eutectic temperature by identifying large changes in DC conductivity.

*$MgCl_2$*. For $MgCl_2$ our measurements yield a stable eutectic temperature of –32.2 ± 0.2°C, which is slightly higher than literature values of –33.0 [4]. **Figure 1a** shows a warming (dark blue) and consecutive freezing (cyan) experiment where the freezing experiment exhibits metastability down to –48°C. The warming and freezing experiment in yellow and red show and experiment where the temperature was only allowed to be warmed to –20°C and the temperature decreased from there. Here, we see that the extent of metastable liquid solutions in less when the temperature is warmed to only –20°C.

*NaCl.* The eutectic temperature of NaCl is higher than that of $MgCl_2$, –21.3°C, and seems to exhibit a smaller amount of metastability even when warming the sample to –0.5°C. This smaller metastability range was expected because Toner et al. [4] only saw metastability 6.6–8.3°C below the eutectic temperature, compared to 14°C for $MgCl_2$. **Figure 1b** shows the same DC conductivity vs. temperature as Figure 1, but for NaCl. Here we see less metastability with NaCl, 3°C below the eutectic.

*Varying Maximum Temperature Experiments.* These experiments show a different behavior when the sample was not warmed up to –0.5°C each time. **Figure 2** shows the result of the varying maximum temperature experiments with 7mM (blue) and 100mM (cyan) $MgCl_2$. At approximately –15°C, there is a distinct shift in the extent of metastability of $MgCl_2$ from –36°C to –47°C. This behavior is seen in both 7mM and 100mM over several experiments.

Our experiments show that the DC conductivity of an ice is a function of the brine conductivity, the volume of unfrozen water, and the tortuosity of the LVNs. The freezing measurements have a higher DC conductivity than the warming measurements (**Fig. 1**). Assuming there is not a large tortuosity difference in the warming and freezing samples, we suggest that the freezing measurements also possess more brine than the warming measurements.

**Conclusions:** Preliminary studies of metastable liquid solutions of $MgCl_2$ show that brine can exist as a liquid for at least 60 hours 6°C below the eutectic temperature. The metastability is also dependent on the temperature that the sample was warmed to before cooling. For $MgCl_2$, if the temperature is warmed below –15°C then the extent of metastability is less and the sample freezes at 3–4°C below the eutectic. However, if the temperature is warmed to above –15°C the extent of metastability is more and the sample freezes at 15°C below the eutectic. Conversely, NaCl solutions showed no temperature dependence. The metastability of salts could be dependent on the magnitude of warming related to the eutectic temperature, e.g. NaCl must be warmed above 0°C in order to experience large amounts of metastability. But, this could also be that salts with high eutectic temperatures (>–30°C) do not exhibit large metastability ranges. These studies could also have implications for the stability range of perchlorates on Mars. Chloride salts generally have higher eutectic temperatures than perchlorates, which could mean that perchlorate might have a larger range of metastability (i.e. >15°C below their eutectic temperature).

Therefore, metastable liquid solutions could be possible in the shallow subsurface or surface of Mars and could exist for extended periods of time. Thus, features that have been hypothesized to be caused by brines may be more stable due to the kinetics of phase changes. However, these findings call attention to a key issue with current models that model the possibility of brines on Mars, they do not consider metastability. Current models only consider where stable liquid solutions can exist using thermodynamics, but ignore any hysteretic effects. Thus, to fully understand when and where brines could exist on Mars today, metastability must be considered. Once we understand the extent of metastability of Mars-relevant brines, these findings could be included in models to more accurately map out the potential for liquid water on the surface and subsurface of Mars today.

**References:** [1] Hecht et al. (2009) *Icarus 233,* 36-47. [2] Osterloo et al. (2008) *Science, 319,* 1651-1654. [3] Primm et al. (2017) *GCA, 212,* 211-220. [4] Toner et al. (2014) *Icarus, 233,* 36-47. [5] Gough et al. (2011) *EPSL, 312,* 371-377. [6] Gough et al. (2014) *EPSL, 393,* 73-82.[7] Nuding et al. (2014) *Icarus, 243,* 420-428. [8] Grimm et al. (2008) *JPC-B, 112,* 15382-15390. [9] Stillman et al. (2010) *JPC-B, 114,* 6065-6073.

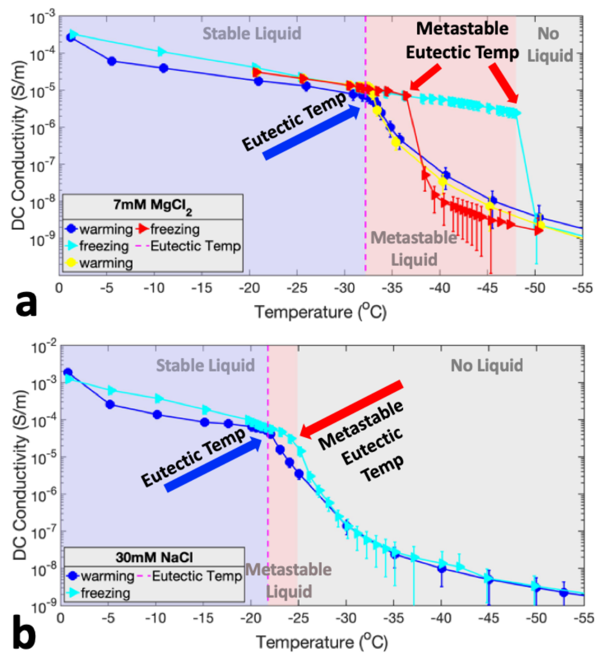


**Figure 1.** DC conductivity vs. temperature of warming and freezing experiments of 7mM $MgCl_2$ (a) and 30mM NaCl (b). The triangle markers indicate experiments where the temperature was decreased to observe the metastable eutectic temperature. The eutectic and metastable eutectic temperature are shown at –32.2°C, –36°C, and –48°C for $MgCl_2$ and –22.8°C and –25°C for NaCl, respectively.

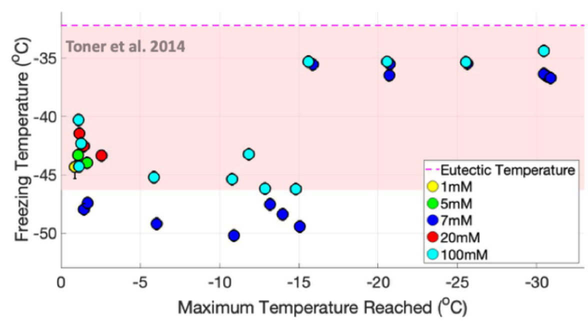


**Figure 2.** Freezing temperature vs. maximum temperature reached (°C) of various $MgCl_2$ concentrations where the starting temperature is the highest temperature that experiment reached before cooling again. The red box under the eutectic temperature is the region that Toner et al. [4] observed metastable liquid solutions of $MgCl_2$.