**Using Raman spectroscopy to detect and monitor freezing and melting processes in near-saturated water-salt mixtures at Mars-analogue temperatures.** D. P. Mason[1,2] and M. E. Elwood Madden[2], [1]University of New Mexico (danmason@unm.edu), [2]University of Oklahoma (melwood@ou.edu).

**Introduction:** Raman spectroscopy is an ideal tool to analyze the geochemistry and mineralogy of heterogenous mixtures of solids, liquid, and gases in-situ, while maintaining planetary protection protocols. Here we characterize saturated or near-saturated $CaCl_2$, $MgCl_2$, $MgSO_4$, $Na_2SO_4$, NaCl, and $NaClO_4$ brines, as well as ultrapure water, and mixed $MgSO_4$-NaCl, $MgSO_4$-$NaClO_4$, $Na_2SO_4$-NaCl, $Na_2SO_4$-$NaClO_4$, and NaCl-$NaClO_4$ brines from 200 K to 295 K to determine how changes in temperature affect spectral signatures of planetary analogue brines.

**Methods:** Raman spectroscopy is a vibrational spectroscopy technique that uses the interaction of laser light with covalently bonded electrons to identify the composition of materials. We used a Renishaw inVia High Resolution Raman microscope and spectrometer to collect Raman spectra from 200 K to 295 K using a Linkam THMS600 temperature-controlled stage. We used both a 785 nm and a 532 nm laser (45 watts each, Renishaw) at 1% laser power in streamline mode to gather data, using a 50x objective along with a 1200 l/cm grating. We collected data from twelve different solutions: ultrapure water, $CaCl_2$, $MgCl_2$, $MgSO_4$, $Na_2SO_4$, NaCl, and $NaClO_4$ endmember brines, and $MgSO_4$-NaCl, $MgSO_4$-$NaClO_4$, $Na_2SO_4$-NaCl, and $Na_2SO_4$-$NaClO_4$, NaCl-$NaClO_4$ mixed brines. The endmember brines were produced by saturating 18MΩ ultrapure water with each reagent grade salt at 295 K. Mixed brines were composed of a 50/50 volumetric mixture of the respective saturated endmember brines.

A 0.4 mL sample of each solution was placed in a quartz crucible within the Linkam stage with the temperature adjusted as follows-- at each observation point, we focused the laser just below the surface of the liquid brine or on the surface of the ice/solids once the brines froze. First, we collected spectra at 295 K, then lowered the temperature to 200 K at a rate of 100 K/min and proceeded to collect spectra at 10 K increments until the sample was 5 K below the melting point of the solution being tested. We then collected spectra at 1 K increments until the temperature was ~5 K above the melting point of the solution. During these smaller temperature adjustments around the melting point, the temperature changed at a rate of at least 20 K/min. We determined the phases present in the sample (liquid, solid, or a mix of the two) by both visually observing the sample to determine whether it looked more similar to ice or more similar to liquid, as well as spectrally by comparing the resultant spectrum to those taken when the sample was definitively ice (200 K) or definitively liquid (295 K). Once we collected the spectra, we used the WiRE 4.1 software to process and analyze the spectra, including curve fits.

**Results:** Sulfate and perchlorate brines produced clear, distinct peaks associated with each anion in both the solid and liquid phase. While chloride brines did not produce distinct anion peaks in the liquid phase, subtle changes were observed in the OH-stretching region, suggesting changes to the molecular water vibration states due to complexation (Figure 1).

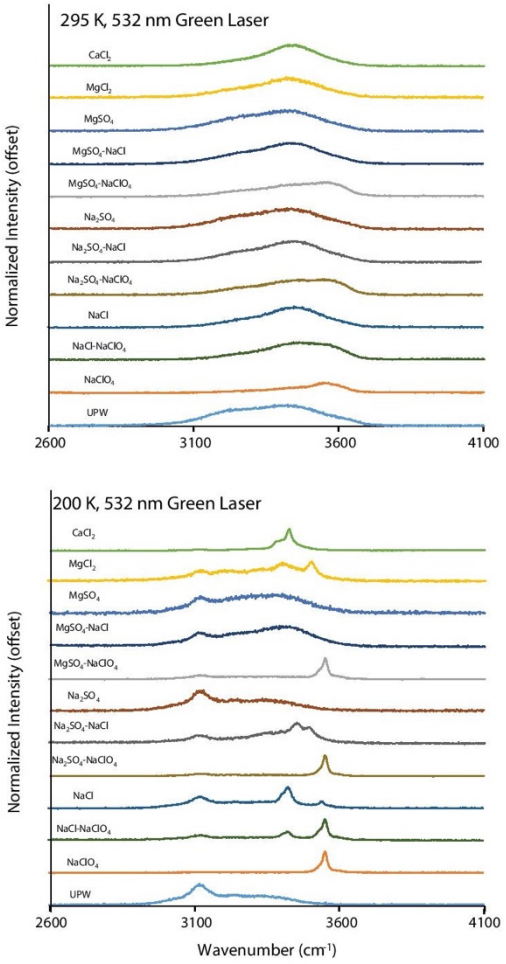


*Figure 1. Raman spectra (532 nm laser) of endmember and mixed brines at 295 K and 200 K.*

However, the presence of cations did not influence the spectral signature of the liquid brines in any meaning-

ful way when the anions were held constant. Indeed peak positions also match spectra collected for calcium and magnesium perchlorate solutions [1-4].

Peak intensity was variable within the mixed brines. In general, perchlorate peaks are more intense than sulfate peaks. This may lead to signals from perchlorate anions overshadowing the signals from sulfate anions in mixed brines.

*Solid-Liquid Transitions:* Solid-liquid phase transitions were clearly observed in each of the solutions using both 785 nm (red) and 532 nm (green) excitation lasers, particularly in the OH-stretching region between 3000-4000 $cm^{-1}$ with the 532 nm laser (e.g. $NaClO_4$ spectra shown in Figure 2).

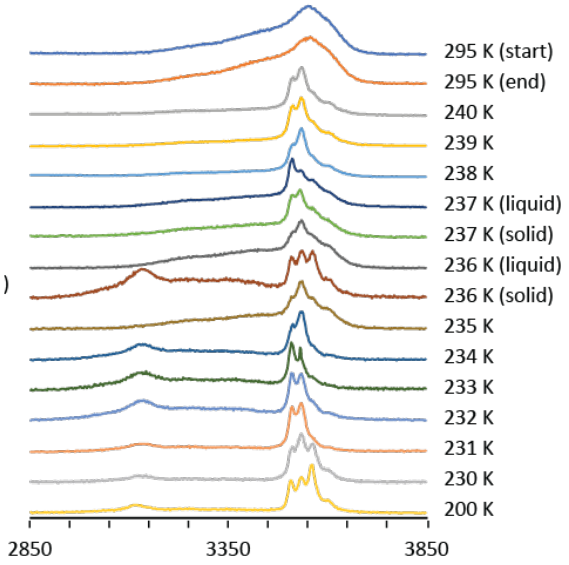


*Figure 2. $NaClO_4$ brine spectra (532 nm laser) show peaks indicative of both solid and liquid over a wide range of temperatures (235 K to 240 K). Therefore, Raman spectroscopy may be used to detect partial melting at Mars-relevant temperatures.*

We observed differences in the spectra of frozen sulfate brines when we changed the cooling rates, suggesting that subtle changes in environmental conditions may influence the hydration state and/or crystallinity of the solid magnesium and sodium- sulfate salts While we noted significant shifts in the sulfate peak position during freezing, we did not observe a similar magnitude of shift in the perchlorate peak position during freezing. Instead, the main perchlorate peak remains relatively fixed at approximately 938 $cm^{-1}$, regardless of the phase of the sample. This suggests that perchlorate anions do not interact as strongly with surrounding molecules, making them more immune to phase changes in the surrounding solution. Conversely, the shift in the sulfate peak suggests that sulfate ions are more strongly influenced by the surrounding water molecules in the hydration shell that forms in liquid aqueous solutions, making the sulfate spectra more sensitive to phase changes in the solution, as has also been observed in the Raman spectra of ion hydration shells [5].

**Implications:** The resulting reference dataset can be used to interpret spectra from future samples analyzed in-situ on planetary bodies. These experiments and the resulting spectral library will allow future researchers to use Raman spectroscopy to look for in-situ melting, freezing, evaporation, and deliquescence as well as identify the composition of high salinity brines and their frozen products in a range of planetary environments, including permafrost and recurring slope lineae on Mars, potential ice and salt-rich regolith on asteroids such as Ceres, and ice shells and possible seeps or geysers on icy moons and other bodies.

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**References:** [1] Fischer, E. (2016). *Física de la Tierra*, *28*, 181. [2] Nuding, D. L. *et al.* (2014) *Icarus*. 243, 420–428. [3] Nikolakakos, G. and Whiteway, J. A. (2015) GRL 42(19), 7899–7906. [4] Primm, K. M. *et al.* (2018) *JGR-P* 123(8),2076–2088. [5] Wang, Y. *et al.* (2016) *J Raman Spect.* 47(10), 1231–1238.