RAMAN ANALYSES OF WATER CHEMISTRY: DEVELOPING A SPECTRAL LIBRARY OF PLANETARY-ANALOG BRINES AND SOLUTES. M. E. Elwood Madden[1], J. Q. Colburn[1], M.N. Grubbs[1], D.P. Mason[1], and A. J. Rodriguez[1], School of Geosciences, University of Oklahoma, Norman, OK USA melwood@ou.edu.

Introduction: Bulk chemical analyses of *in situ* dust and rocks on Mars, as well as minerals observed in SNC meteorites and orbital spectra suggest that Mars hosts geographically widespread salt deposits. These salts likely formed through the evaporation and/or freezing of near-surface high salinity brines at various times in Mars history [1],[2]. Since adding salts decreases both the freezing temperature and vapor pressure of aqueous solutions, any liquid water on or near the surface of Mars today is likely very salty.

Liquid water in the outer solar system also likely exists as high salinity brines, protected from evaporation and freezing by ice crusts on Europa, Enceladus, Titan, and perhaps other icy bodies including Ganymede and Pluto [3]. Preliminary evidence of salts and hydrated mineral phases on Ceres [4], as well as similar phases in altered chondritic meteorites [5], suggest brines may also affect the near-surface mineralogy of some asteroids. Therefore, if we "follow the water" on other potentially habitable planetary bodies in our Solar System, including Mars, Ceres, Europa, Titan, and Enceladus, we will likely find a high salinity brine. Solutes observed in high salinity brines may provide key clues to determine the geochemical conditions, including habitability of the environments in which they are found, both on Earth and other planets.

However, brines are difficult to analyze using standard methods without significant dilution since high solute concentrations can overwhelm detectors and the brines themselves are often corrosive with relatively high density and viscosity which can clog traditional aqueous analytical tools and/or contaminate subsequent samples. However, Raman spectra can be collected remotely (no physical contact with sample) without sample preparation, preventing sample contamination, instrument clogging, and corrosion issues while preserving planetary protection protocols. Therefore, Raman may be the ideal technique for analyzing high salinity planetary fluids on potentially habitable worlds.

Raman spectroscopy can detect, and may in many cases quantitatively measure, covalently bonded species in high salinity brines [6]. In this project we have developed a robust Raman spectral database of common solutes, as well as calibration curves that can be used to interpret potential Raman spectra collected from aqueous samples and brine + matrix mixtures on Mars and other planetary bodies. These calibrated spectra can be used to employ Raman methods for detecting and measuring aqueous solutions in planetary environments, including the Mars 2020 and ExoMars missions, as well as future Raman-enabled missions to asteroids and icy moons.

Raman Analyses of Brines and Solutes: We used reagent grade NaCl, $CaCl_2$, $MgCl_2$, Na_2SO_4, $MgSO_4$, and $NaClO_4$ salts to synthesize saturated endmember brine matrix solutions. Solutions of Na_2CO_3, $NaHCO_3$, $NaNO_3$, NH_4Cl, Na_2PO_4, $NaHPO_4$, H_2PO_4, Na_2SO_4, $NaHSO_4$, NaCl, $NaClO_3$, $NaClO_4$, and NaF were also mixed using reagent grade salts and then serially diluted to create solute solutions with anion concentrations from 1 to 0.001 mol/kg. We then mixed 25 microliters of each solute standard into 75 ml of the endmember brine or deionized, ultrapure water in a multi-well ceramic paint pallet that allowed for rapid data collection, without inducing fluorescence from the substrate. Each anion, with the exception of Cl^-, produces unique

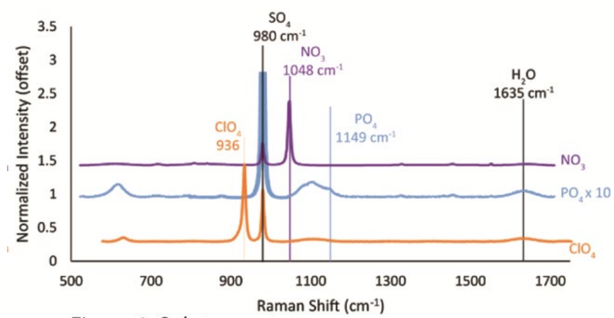

Figure 1. Solute spectra

spectra (Figure 1).

We collected two sets of spectra with a Renishaw InVia High Resolution Raman Microscope in streamline mode, using two different lasers- a 500 mW red Renishaw RL785 nm laser and a 500 mW green Renishaw RL532 nm laser. In each analysis we collect data for 100 seconds at 100% laser power over a predetermined spectral range (775-1850 cm^{-1} for the red laser and 400-2600 cm^{-1} for the green laser). Once the data were collected, we used the Wire 4.1 software package to remove any cosmic rays and subtract the baseline signal, then normalize the spectra based on the highest intensity peak. We compared the solute data using a stacked spectra plot (Figure 2a). We used the Wire 4.1 software to model the peak positions and heights using the curve fitting functions. Then we compared the target solute peak intensity with the major OH bending peak for water (1646 cm^{-1}) to develop calibration curves based on peak area and peak height ratios (Figure 2b). Efforts are underway to process and analyze all of the brine-solute data and then archive the data in the PDS.

Ongoing work includes brine freezing experiments to examine the effect of temperature from 200K to 295K endmember brine spectra, and experiments aimed at measuring brine spectra in saturated sediments [7] and Raman characterization of basalt-brine interactions [8].

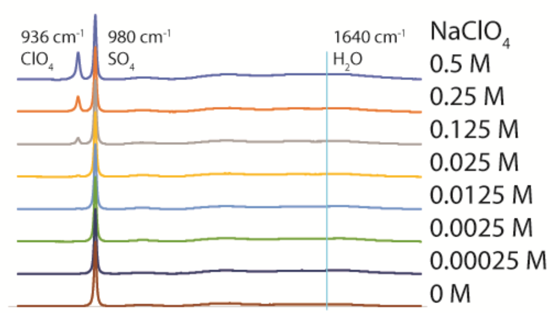

Figure 2a. $NaClO_4$ in Na_2SO_4 Brine

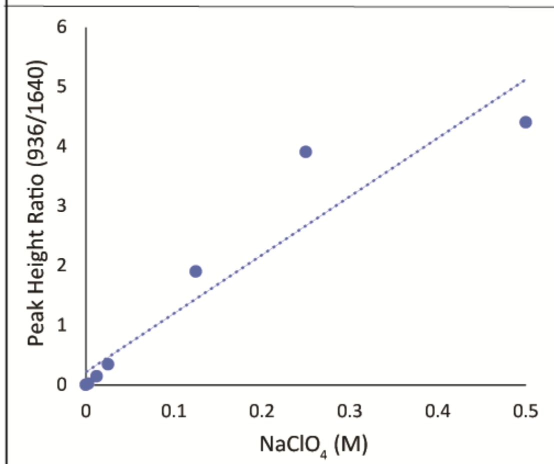

Figure 2b. Calibration curve

Acknowledgments: Thanks to Nina Webb, Charity Phillips-Lander, Lauren McGraw, and the 2017 Geo-Writing class for their assistance collecting preliminary data for this project.

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