

EVALUATING THE EFFECT OF SIGNAL DILUTION ON SILICATE GLASS-RAMAN SIGNATURES IN MIXED MATERIALS: IMPLICATIONS FOR MARS 2020 RAMAN INSTRUMENTS. B.O. LaDouceur¹, M.C. McCanta¹, M.D. Dyar², and E.C. Sklute², ¹University of Tennessee Knoxville: Department of Earth & Planetary Sciences (bladouce@vols.utk.edu), ²Mount Holyoke College: Department of Astronomy.

Introduction: Volcanic glasses and other associated amorphous phases are abundant materials on Mars, and have been recognized by spectroscopic investigations for decades [1]. Unaltered volcanic glasses can be used to constrain pre-eruptive melt properties such as viscosity, geochemical composition, and f_{O_2} – functions of glass structure pertinent to understanding system-wide igneous processes. In recent years, Raman spectroscopy has proven to be a reliable quantifier of such geochemical information for glassy Mars analogs [2,3,4] and has found use in the SuperCam and SHERLOC instruments onboarded *Perseverance* (Mars 2020). One particularly confounding issue with identifying individual glass species through various spectroscopic techniques (orbital NIR, UV-IR, rover Raman) has been the presence of other crystalline phases in the observed sample suite [5]. Minerals such as olivine and pyroxene, Fe-bearing sediments, and even partially crystalline glasses comprise intimate mixes in almost all exposures on the Martian surface, as pure-phase glasses do not often occur, and have been shown to hide glass spectral signatures within the collected profiles. In order to concretely understand the collected Raman data of any such phases that *Perseverance* may encounter in Jezero, an investigation on expected glass mixes must be conducted.

Methods: In an effort to discriminate between glass-unique Raman signatures and other phases in mixed sample suites, and identify key inflection points in sample dilution where these signals are no longer detectable, we have collected Raman data on 13 sediment-tephra mixes. A collection of natural Montserrat tephra powders and hemipelagic sediment were mixed on a paired scale where sample MC-1 contains 100% sediment and 0% tephra, and MC-13 contains 100% tephra and 0% sediment. Sample MC-8 is a 50/50 split sample, with equal amounts of tephra and sediment. MC-2 → MC-7 constitute samples with greater sediment concentrations, while MC-9 → MC-13 show the inverse trend. Tephra concentrations increase as sample number increases, while sediment decreases (Figure 1). Each sample has a calibrated coherent weight of 500 mg. Raman data were collected in the spectral range between 300 – 3198 cm^{-1} using a

handheld Bruker Raman spectrometer with two lasers, each with 2 minor shifts in laser position and 6 total channels. The channels are used together to perform an automated fluorescence removal on the data. Incident wavelengths for the spectrometer include 785 nm and 852 nm. Raw profiles were collected and baselined using Asymmetric Least Squares (ALS).

Results: Figure 1 shows the original data collected along all channels off of the handheld spectrometer truncated between 1200 – 2000 cm^{-1} . In this range, signal noise is minimized, and sample features become noticeable in the raw data prior to preprocessing. Tephra rich sample spectra are considerably more undefined and unevolved when compared with sediment-rich samples. When considering the raw data, the bands in samples containing more amorphous phases express only three major broad peaks, at ~1450, 1630, and 1920 cm^{-1} . Sediment-rich samples (MC-7 → MC-1) show greater variation in spectral shape and position, with narrower peaks and well-defined shoulders. These samples share the same peaks as the glass-rich spectra, however, with the increase in crystalline phase-presence – more spectral features are recognized in the spectra within these samples. Specifically, the peak around 1630 cm^{-1} is split into a doublet band with two major centroid positions. Along with this, strong shoulders develop at 1500 and 1840 cm^{-1} . Interestingly, MC-8, the sample split 50/50 between tephra-sediment concentration serves as the major inflection point for the shift in feature responses (Figure 1). The same trend is recognized for the preprocessed spectra (Figure 2), where an ALS baseline helps normalize the data relative to its channel collection. MC-8 also serves as a major inflection point for the loss of glass signal between 300 – 800 cm^{-1} in this data. However, samples between MC-13 → MC-6 preserve a broad peak arc at ~980 cm^{-1} , before the signal becomes extremely strong and narrow (Figure 2). This shows that glass-specific Raman features are present in a collected profiles in concentrations as low as ~40%. Preliminary analysis of these samples also suggests a shift to lower wavenumbers for almost all peak centroids as samples become more mixed with crystalline components (i.e. more sediment rich up to

100% sediment). The development of more defined and strong Raman features as samples lose glass is clearly evident, and those samples containing strong concentrations of glass are largely defined by unevolved, low intensity peaks over a wide range of wavelengths. By exploring separate collection channels, we allow the entire spectral range to be used in identifying key characteristics in the Raman data that result from glass phase presence in these mixed samples. In these samples, glassy phase signals are obscured in some regions once mixed with greater amounts of crystalline sediment up to roughly 50%, while in others these features are strengthened into more evolved narrow peaks with less flux (Figure 1, 2).

Discussion & Ongoing Work: This investigation presents a first order attempt to recognize glass-inherent features in a collected Raman spectrum when mixed sample suites are analyzed. By increasing the crystalline content, as expected, stronger Raman signals are collected due to the inherent vibrational nature of the technique. However, the retention of some glassy features helps encourage the notion that not all amorphous signal is lost in samples with higher crystallinity. The effects of sample mixing on these Raman features are highlighted in peak area, position, and shape changes – in which tephra-rich bands, though weak, yield distinct fingerprints that can still be attenuated down to an overall concentration of $\sim 40\%$. This could prove promising for *in-situ* Raman collections on the Martian surface using SuperCam, depending on collection distance. Preliminary results from the instrument to-date, predominantly express the ability to measure only the strongest Raman scatters when applied from a distance of a few meters. Though no glassy-phase material has yet been encountered, the opportunity exists to apply the first order results provided here if such mixed samples are encountered. It may be the case that highly evolved volcanic samples explored by the instruments may contain information beyond their crystalline matrices, and could be masking glass-phase signatures. These mixes will be investigated further using separate preprocessing procedures to explore the evolution of the Raman signals under varying conditions; and will also be the subject of paired Raman-machine learning modeling attempts to acquire glass phase percentages, similar to previous approaches [6]. To address the distance issue in relation to stand-off vs. laboratory Raman signals for glasses as a comparison to the rover more directly, a field campaign utilizing

handheld Raman measurements on mingled magma exposures in coastal Maine is planned for this year.

References: [1] Rampe E. et al. (2014) *Eight International Conference on Mars*, 1791, 1239 [2] Volovetsky M. et al. (2010) *Journal of Physics*, 217, 012050 [3] Di Muro A. et al. (2009) *Chem. Geology*, 259, 78 – 88 [4] Di Genova D. et al. (2015) *Journal of Raman Spectroscopy*, 46, 1235 – 1244 [5] Horgan et al. (2014) *Icarus*, 234, 132 – 154 [6] LaDouceur B. et al. (2021) *LPSC 2021 Conference Abs. Contrib.* No. 2548

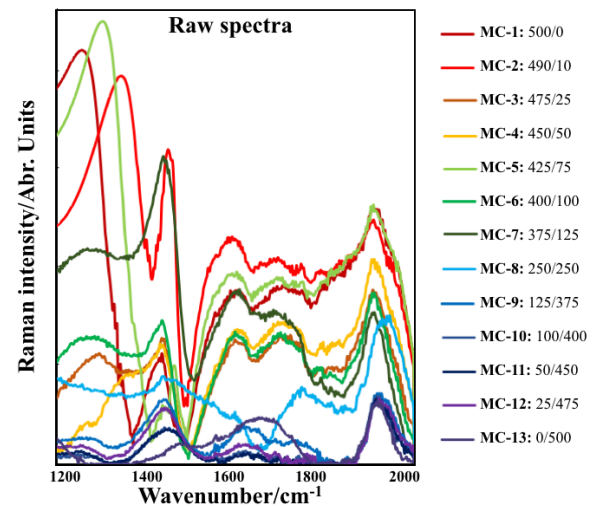


Figure 1. Raw Raman spectra for 13 tephra-sediment mixed samples. Samples are listed as \rightarrow Sample Name: Hemipelagic Sediment / Tephra Concentration (mg)

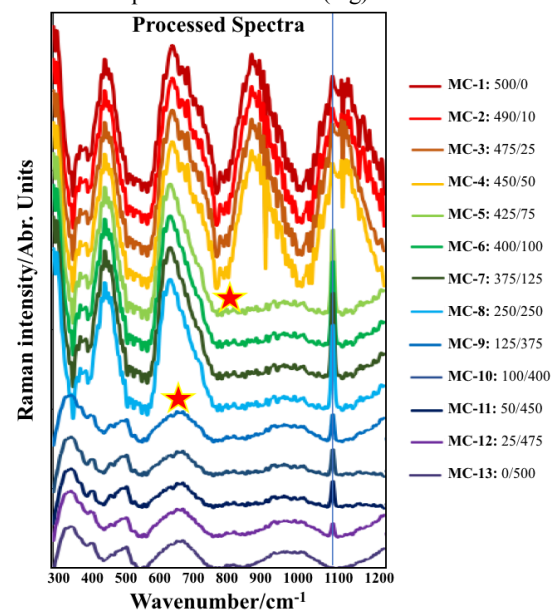


Figure 2. Processed Raman spectra for 13 tephra-sediment mixed samples (300 – 1200 cm^{-1}). Red stars highlight inflection points where glass signals are changed or lost