GRAIN SIZE EFFECTS ON LIBS MEASUREMENTS OF MINERAL POWDERS, EXPERIMENTAL RESULTS AND APPLICATIONS TO MARTIAN SANDS AND DRILLED MATERIALS
J. D. Henry[1], K. L. Siebach[1], M. D. Dyar[2], K. H. Lepore[2], and C. R. Ytsma[3] [1]Department of Earth, Environmental and Planetary Sciences, Rice University, Houston, TX (jdh18@rice.edu), [2]Department of Astronomy, Mount Holyoke College, South Hadley, MA, [3]Cai Consulting, Clyde Offices, 2nd Floor, 48 West George Street, Glasgow G2 1BP, UK.

Introduction: The ChemCam instrument onboard the *Curiosity* rover uses Laser-Induced Breakdown Spectroscopy (LIBS) to remotely measure the composition of diverse geologic materials [1]. This analytical technique involves ablating the surface of a target to produce a plasma of constituent elements in neutral to triply ionized sates. A spectrum is collected from this plasma and composition is quantified from characteristic emission lines [2]. Major elements are routinely quantified on materials including in-situ solid rock, active sand, and fine powdered materials drilled by the rover. The procedure for quantifying elements is identical regardless of the type of material shot by ChemCam.

The effects of grain size and porosity differences on emission line intensity or element quantification have not been investigated. Here, we explore them by comparing LIBS spectra of loose powders of pure minerals with a variety of grain sizes to spectra from pressed pellet standards to observe variations in emission line intensity and element quantification.

Experiment Design: The SuperLIBS instrument, located in the Mineral Spectroscopy Laboratory at Mount Holyoke College, is a benchtop analog to the ChemCam and SuperCam instruments on *Curiosity* and *Perseverance* respectively. SuperLIBS is equipped with a Nd:YAG laser that operates at a power and pulse width that is comparable to ChemCam, with slightly better spectral resolution in the UV, VIS, and VIS-NIR ranges. The SuperLIBS laser has an ablation spot size of ~110 µm, ~3× smaller than the average spot size of the ChemCam laser.

Powders of pure olivine, labradorite, and augite were chosen for this study based on their common occurrence in basaltic materials on Mars [3]. Loose grain sizes of <25, 25-38, 63-106, 300-500, and 710-1000 µm were analyzed for each mineral. Pressed pellets of all minerals at five grain sizes were also made.

Samples were loaded into aluminum cups and positioned with the incident laser 13° from normal to the sample surface. The chamber was pumped to a vacuum (<100 mTorr N_2) and backfilled with 7 Torr CO_2 to simulate the Martian atmosphere. Each sample was analyzed at up to four laser energies (2.4, 4.0, 5.6, and 7.2 mJ) to improve quantification [4]. The high resolution measured by this instrument was achieved by sampling two overlapping spectral ranges in the UV, VIS, and VIS-NIR regions. Spectra were concatenated during preprocessing, resulting in a total of thirty shots at each of five locations per laser energy [5]. For spectra collected on powder targets, the first shot was discarded to limit surface contamination effects, and spectra from shots 2 to 30 were averaged at each location. For pellet analysis, the first five shots were discarded and shots 6 to 30 were averaged at each location. Following a similar procedure to ChemCam spectra preprocessing, SuperLIBS spectra were dark-subtracted, wavelength aligned to a Ti standard, and corrected for instrument response [4,5]. Post-processing included baseline removal and L_1 normalization to each spectral range. Major elements were quantified using optimized multivariate partial least squares models [6] trained and tested on a compositionally diverse LIBS database of spectra collected on 2959 geochemical standards [7].

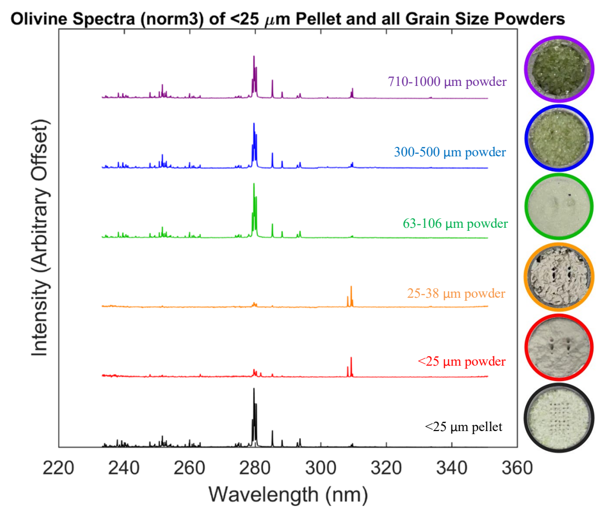

Figure 1. Normalized olivine spectra of the <25 µm pellet (black) and all powder grain sizes in the UV range (grain size increasing from red to purple).

Initial Results: Variations in overall intensity of a spectrum and of individual emission lines relevant to each element of interest are compared among spectra of pellets and powders across grain sizes (e.g., **Figure 1**). Spectra of pellets are found to be insensitive to grain size in this experiment; therefore spectra of pressed <25 µm pellets were used as a baseline to examine variations seen in the spectra of powders for each mineral.

In contrast, loose powder spectra across all three minerals are highly sensitive to grain size. The <25 µm and 25-38 µm powders form narrow, deep ablation pits and exhibit overall unnormalized spectral intensities approximately two orders of magnitude lower than their pellet counterparts. At the 63-106 µm grain size threshold (i.e., close to the beam size), the laser forms

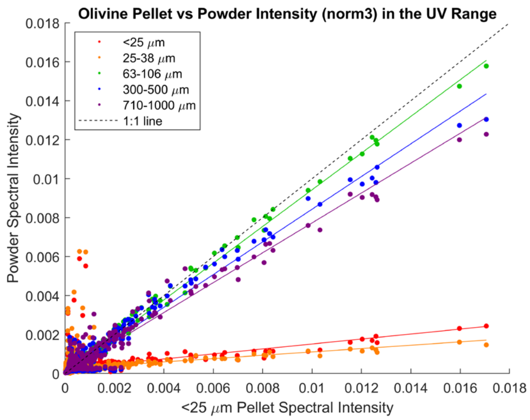

Figure 2. Normalized olivine intensity across the UV spectrum for powders of all five grain size fractions vs. the normalized intensity of the <25 μm pellet. Each data point represents one of the 3655 channels in the UV range. Both pellet and powder spectra represent averages of 7.2 mJ shots at one location. Simple linear regressions are fitted for each grain size.

wide, shallow ablation pits and spectral intensities are comparable (about half as intense) to pellet spectra. Larger grain sizes (300-500 μm and 710-1000 μm) have less prominent ablation pits; total spectral intensities are slightly less than that of 63-106 μm powders.

Normalization reduces some but not all of the spectral intensity differences. For example, UV spectra of olivine show normalized peak intensities similar to pellet spectra at the 63-106 μm grain size threshold (Figure 1). Note that the Mg peaks at ~280 nm and 310 nm account for most of the normalized intensity. Normalizing the finest grain size spectra, where those peaks are minimal, may amplify noise.

The effects of grain size on normalized spectra are observed by plotting the intensity of the powder spectra against the intensity of the <25 μm pellet spectrum for each wavelength channel in the UV range (**Figure 2**). Non-zero points that fall along a line represent wavelengths where either the pellet or the powder spectrum has a peak.

The slope of this line is shallow for fine powders where peak intensities are generally weaker compared to the pellet. The slope is close to 1 at the 63-106 μm grain size threshold, where the normalized intensities of the powder and pellet at certain peaks (in this case, Mg II) are similar. Lower slopes observed with coarser grain sizes reflect slightly decreased peak intensities at these grain sizes. The small cluster of points that exhibit high slopes (>1) represent Mg I (neutral, low energy) emissions and baseline spectral noise that is most intense in the finest powders due to poor laser-target coupling and noise distributed across all wavelengths. This dependence on grain size is seen across all spectral wavelength ranges that capture relevant emissions for all three tested mineral compositions. It is particularly apparent in the UV range shown in Figure 2 due to the high abundance of Mg in olivine.

Less-efficient Mg ionization in the finer olivine powers is interpreted to be indicative of poor laser-target coupling, which is in turn reflected in element quantifications (**Figure 3**). Predicted MgO wt% abundances for the <25 um and 25-38 μm powders are significantly lower than those for the pellets or any larger grain size fractions.

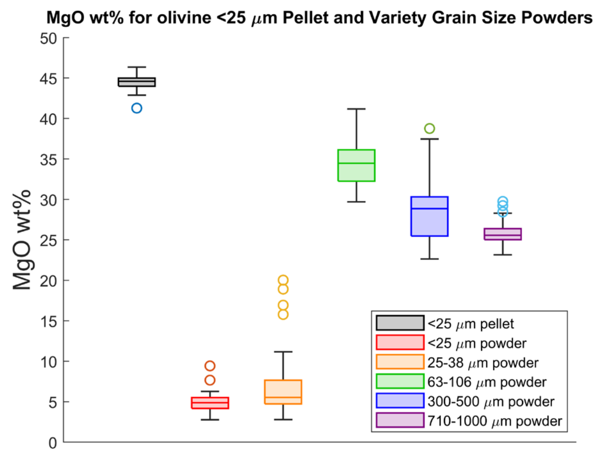

Figure 3. MgO wt% quantifications for one 7.2 mJ shot location taken on the <25 μm olivine pellet and all five grain size fractions.

Implications for Mars: Sand and drilled materials on Mars likely contain fine-grained components that could behave similarly to the finest powders tested in these experiments. For example, the Big Sky drill tailings, shot by ChemCam to measure bedrock composition at depth in the Stimson formation, are thought to have such fine components. The observation that fine grain size fractions are found to have significantly lower peak intensities, suggestive of poorer laser coupling efficiency, might lead to inaccurate element quantifications in such samples. Ongoing work is committed to understanding the nature of laser-target interactions, effects of plasma confinement in deep holes, and the geometry of the generated plasma relative to the detector at these grain sizes. This work will inform a better understanding of the predicted compositions of materials routinely analyzed and interpreted by ChemCam.

References: [1] Wiens, R.C. et al. (2012) SSR 170-227 [2] Clegg, S.M. et al (2016) SAB 5183 [3] Byrne, S. A. et al. (2015) *LPS XLVII* Abstr. #1499 [4] Lepore, K.H. et al. (2023) *GRL*, 50 [5] Lepore, K. H. et al. (2023) *Spectrochim. Acta B*, 211, 106839. [6] Dyar, M.D. and Ytsma, C.R. (2021), *Spectrochim. Acta B*, 177, 106073 [7] Dyar M. D. et al., (2019) LPS L, Abstr. #1396.