USING THE LIBSSIM PROGRAM TO CALCULATE ROCK COMPOSITION: TESTING THE POTENTIAL OF LIBS ANALYSES. M.C. McCanta[1], M.D. Dyar[2], P.A. Dobosh[3], and H.E. Newsom[4], [1]Dept. of Earth & Ocean Sciences, Tufts University, Medford MA 02155 (molly.mccanta@tufts.edu), [2] Dept. of Astronomy, Mount Holyoke College, South Hadley MA, [3]Computer Science Dept., Mount Holyoke College, South Hadley MA. [4]Inst. of Meteoritics, Univ. of New Mexico, Albuquerque, NM.

Introduction: The Laser-Induced Breakdown Spectrometer (LIBS) on the ChemCam instrument is part of the MSL science payload. ChemCam also includes a Remote Micro-Imager (RMI) with 90 µrad resolution (180 µm features just in front of the rover) [1,2]. The unique property of LIBS is that analysis can be performed remotely; LIBS can target samples up to 7 m away from the rover, with a spot diameter of 0.3-0.6 mm [1]. To interpret compositional data returned by LIBS, a clear understanding of which sampling procedures will optimize science return for a variety of rock types is required. This project examines the significance of sampling density using data from Mars-analog rocks.

LIBSSIM Program: The LIBSSIM program (www.mtholyoke.edu/~pdobosh/libssim/lasersimR5.html) was developed by P. Dobosh [3] to simulate LIBS sampling of Martian rocks or soils. Parameters such as grain size, beam size, and composition can be varied to determine their effects on the accuracy of bulk rock measurements. The program returns mineral and oxide percentages. Testing using the LIBSSIM program will result in better *in situ* sampling strategies on Mars and place constraints on the strengths and limitations of the resulting data.

Results: A natural terrestrial basalt composition with significant experimental phase equilibria data [4] was used in this study. User inputs to the program included varying phase proportions, densities, and compositions. Different phase proportions, compositions, and grain sizes were studied to investigate the effects on bulk compositions calculated from LIBS results.

Grain size. The program creates a 2D 1000×1000 pixel "rock"; the grain and beam sizes are pixel values within the array. A single beam size was considered (40 pixels) and grain sizes were varied to be significantly smaller, the same, or significantly larger than the beam to build the test rocks (Fig. 1). Both 10 and 50 sampling areas were investigated in each rock.

As expected, the bulk composition of the sample is best approximated when grain size << beam size (Fig. 1A, Fig. 2). Even when multiple phases are present random LIBS sampling among the fine-grained phases covers most grains, resulting in an accurate approximation of the sample's chemistry with a low standard deviation. As grain size increases, the correlation between true bulk composition and LIBS- predicted bulk composition decreases (Fig. 2) and the standard deviation increases to the point that the returned data were fairly meaningless for large grain sizes (Fig. 3). When grain size >> beam size (Figs. 1B,C), a single phase has the ability to disproportionately affect the analysis.

Interpretations: The larger the grain size in relation to the LIBS beam size, the more spots must be analyzed to generate meaningful data. As grain size increases relative to beam size, the standard deviation for the oxides increases to levels that result in meaningless data (Fig. 3). If grains are similar in size to or larger than the beam size, more analyses are needed to insure coverage of all rock components.

When a single minor phase controls the behavior of any oxide (e.g., FeTi oxides contain the majority of TiO_2 in an igneous rock), more analyses are required to make sure its contribution to bulk composition is

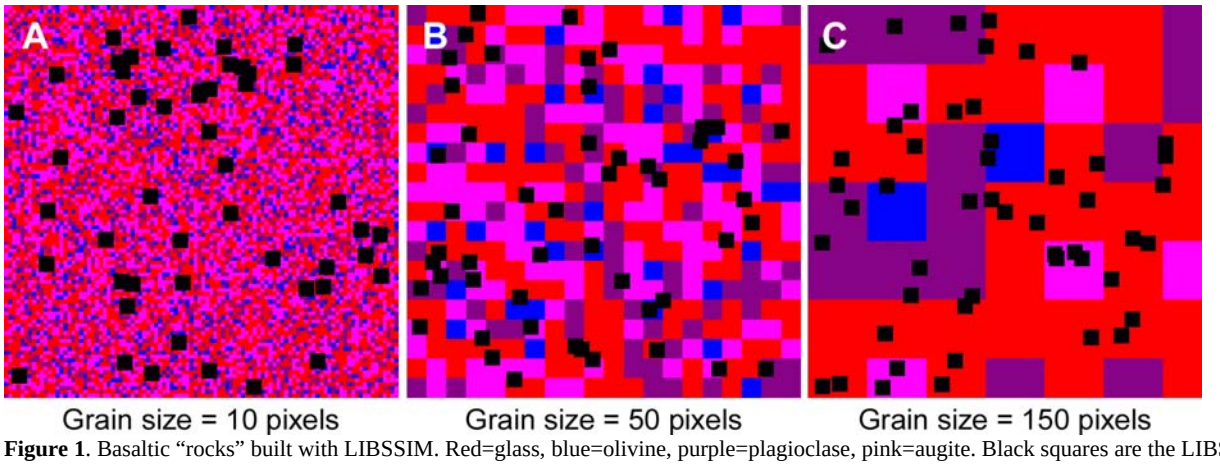

Figure 1. Basaltic "rocks" built with LIBSSIM. Red=glass, blue=olivine, purple=plagioclase, pink=augite. Black squares are the LIBS sampling areas (50 total sampling areas).

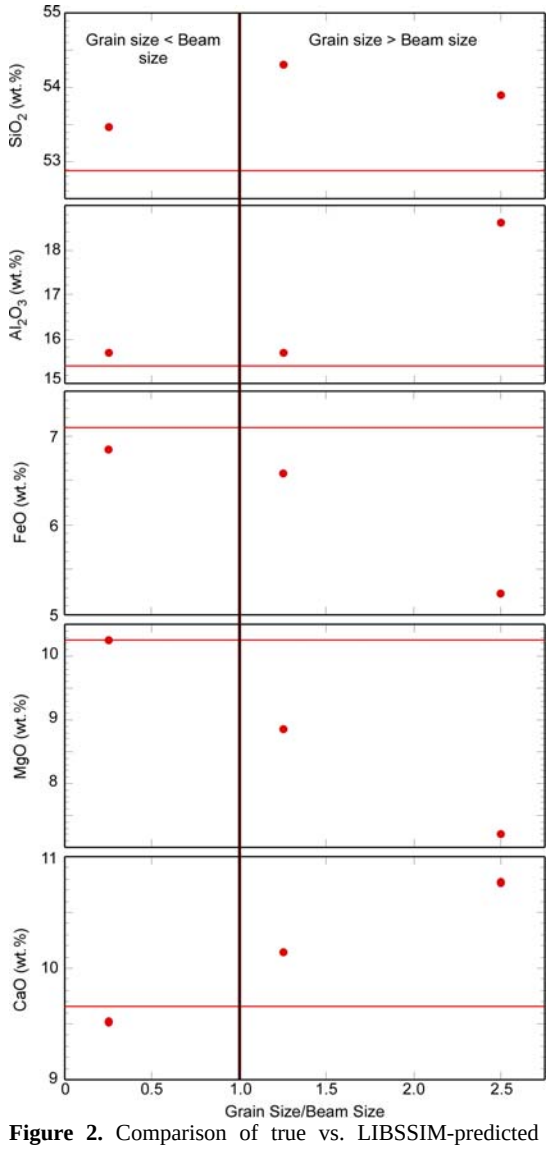

Figure 2. Comparison of true vs. LIBSSIM-predicted bulk composition as grain size increases relative to beam size. Red lines represent the experimentally determined bulk composition. Red circles are the LIBSSIM-predicted values.

recorded. This is clear in Fig. 3, where percentage of the oxide represented by the standard deviation is plotted as a function of grain size. This value skyrockets for MgO and FeO, which are dominantly held in olivine, a minor phase in this rock. In the coarse-grained rock, olivine is scarcely sampled, reducing its contribution to the bulk. This results in high standard deviations for MgO and FeO relative to the true bulk composition, and meaningless bulk data. Alternatively, when SiO_2 is considered, little change is seen as grain size increases because the wt% SiO_2 is roughly equal in the phases (glass, plagioclase, and augite). Thus SiO_2 is sampled with fairly high precision regardless of grain size.

The distribution of grains within the rock can affect LIBS analyses, causing significant problems in coarse-grained samples. For the randomly-generated "rocks" in LIBSSIM this is not an issue, although the standard deviations calculated for each oxide become prohibitively high in the large grain samples. For natural rocks that may exhibit grain preferred orientation, foliation, or layering, this could be present a sampling issue.

Finally, the number of phases present and their compositional similarities are important. If a single phase dominates the bulk rock (> ~80 vol.%) fewer LIBS analyses are needed to determine composition accurately, no matter the grain size. When multiple phases occur in subequal amounts more analyses are needed to insure that the contribution of each phase type is present in the calculated composition.

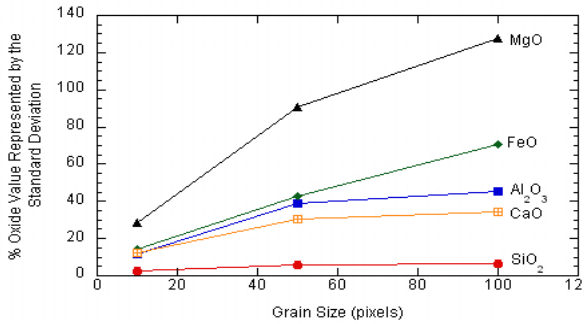

Figure 3. Comparison of the influence of grain size of different elements on the LIBSSIM-calculated oxide standard deviations.

Implications: On Mars, several issues must be considered to obtain representative bulk rock data from LIBS. Wherever possible, results from the MAHLI and RMI should be used to assess target grain size, preferential grain orientation, and heterogeneity to optimize LIBS sampling strategy [1] and minimize grain size issues. Sampling patterns that avoid straight lines and emphasize spatially-distributed analysis spots will be preferable for all but very fine-grained rocks. The number of LIBS analyses should be carefully selected to reduce the oxide standard deviations to acceptable levels for classification and interpretation. For fine-grained rocks or single phase rocks, LIBSSIM produces acceptable standard deviations with ~10 analyses. When the grain size >> beam size, 100 analyses still yield prohibitively high deviations. In this case, the LIBS data can provide an indication that a bulk analysis with the APXS is needed. This is important as the geology of Gale Crater is likely to contain both fine sediments and coarse clastic components [5].

References: [1] Wiens R.C. et al. (2012) Subm. to *Spa. Sci. Rev.* [2] Maurice S. et al (2012) Subm. to *Spa. Sci. Rev.* [3] Dobosh P.A.et al. (this vol.). [4] Baker M.B. et al. (1994) *CMP* 118, 111-129. [5] Thomson B.J. et al. (2011) *Icarus* 214, 413-432.