SOFTWARE TOOLS FOR EXPLORING AND ANALYZING CHEMCAM DATA. P. A. Dobosh[1] and M. D. Dyar[2], [1]Computer Science Dept., Mount Holyoke College, 50 College St., South Hadley, MA 01075 USA, pdobosh@mtholyoke.edu, [2]Astronomy Dept., Mount Holyoke College, South Hadley, MA 01075 USA.

Introduction: There are many geological scenarios in which microanalytical capabilities are not quite small enough to resolve and characterize individual mineral phases in intimate mixtures. In such situations, even microbeam analyses produce results representing mixtures of phases that cannot easily be untangled. The *in situ* analyses produced by ChemCam instrument on the Mars Science Lab *Curiosity* rover also suffer from this problem. The dominant rock type on the martian surface is basalt, with phenocrysts typically 200-700 μm in size, which is on the same scale as the 200-450 μm in diameter [1] LIBS beam. Thus the beam is too large to sample individual grains except in rare cases, and too small to obtain a representative bulk analysis suitable for input into normative calculations unless many locations on the rock are sampled [2]. Typical analyses sample multiple phases depending on the grain size and mineralogy of the rock. It is difficult to interpret chemical data of such a mixture.

However, knowledge of the minerals present and their stoichiometries can provide more than a glimpse into the compositions present. In most rock types, the compositions of the individual phases (minerals) remain roughly constant. Individual random spot analyses represent combinations of those phases in varying proportions. This software provides a framework for interpretation of the resultant mixed chemical analyses. This formulation provides an alternative to use of normative mineralogy. The results are immediately applicable to understanding of LIBS analyses on Mars [3].

Software and Data: Matlab was an obvious choice for a software development environment because of its ability to handle very large tables of data easily and quickly. Data for code development consisted of wt% oxide analyses of sanidine, pigeonite, andesine, ferrosilite, olivine, and hematite taken from webmineral.com compositions. Geochemical analyses expressed in the standard form of weight percent oxides are first converted to moles using constants that remove the contribution of oxygen from the oxide. The programs require as input a csv file of cation moles, target, location and shot number, as well as a list of target names.

Error Analysis: Because a critical part of this analysis involves use of slopes and intercepts, we propagated errors on reported RMSEP values from ChemCam analyses [4] using Deming regression, which fits a straight line to a data set where both *x* and *y* data have error (**Table 1**). Cantrell [5] presents equations for estimating the uncertainties in the slope and intercept. Those equations are for the general Deming regression with errors for each data point. We have used the equations with a single *x* error, a single *y* error, and assumed zero correlation between the errors.

Table 1. Deming Regression and Error Propagation

$$\bar{x} = \frac{1}{n}\sum x_i \text{ and } \bar{y} = \frac{1}{n} y_i$$

$$s_{xx} = \frac{1}{n-1}\sum (x_i - \bar{x})^2,$$

$$s_{xy} = \frac{1}{n-1}\sum (x_i - \bar{x})(y_i - \bar{y}),$$

$$s_{yy} = \frac{1}{n-1}\sum (y_i - \bar{y})^2$$

$$\hat{\beta}_1 = \frac{s_{yy} - \delta s_{xx} + \sqrt{(s_{yy} - \delta s_{xx})^2 + 4\delta s_{xy}^2}}{2s_{xy}} \text{ and}$$

$$\hat{v}_1 = \frac{-1}{\hat{\beta}_1} = \frac{-2\delta s_{xy}}{s_{yy} - \delta s_{xx} + \sqrt{(s_{yy} - \delta s_{xx})^2 + 4\delta s_{xy}^2}}$$

$$\hat{\beta}_0 = \overline{y - \hat{\beta}_1 \bar{x}}$$

$$\hat{x}_i^* = x_i + \frac{\hat{\beta}_1}{\hat{\beta}_1^2 + \delta}(y_i - \hat{\beta}_0 - \hat{\beta}_1 x_i)$$

where β_0 and β_1 are the intercept (b) and the slope (m). For error calculation, the relevant formulas are:

$$W_x = \frac{1}{\sigma_x^2} \text{ and } W_y = \frac{1}{\sigma_y^2} \text{ so } W = \frac{W_x W_y}{W_x + m^2 W_y}$$

$$Ui = x_i - \bar{x} \quad V_i = y_i - \bar{y}$$

$$\beta i = W\left(\frac{Ui}{Wy} + \frac{mVi}{Wx}\right) \text{ and } \sigma_m^2 = \frac{1}{W\sum(\beta i - \bar{\beta})^2}$$

$$\text{std err } m = \sqrt{\sigma_m^2}\sqrt{\frac{S}{n-2}} \text{ where } S = \sum[yi - (mxi + b)]^2$$

$$\sigma_b^2 = \frac{1}{nW} + (\bar{x} + \bar{\beta})^2 \sigma_m^2$$

$$\text{std err } b = \sqrt{\sigma_b^2}\sqrt{\frac{S}{n-2}}$$

Recognizing Single Phases: LIBS data are typically acquired using multiple laser shots on each location and, often, multiple locations on a target. Each shot ablates ~0.3-0.5 μm of material depending on its density and porosity [6]. ChemCam records these individual shots, so that chemical analyses can be calculated for each one. These point analyses are converted to moles and then individual phases are searched on the basis of their stoichiometry. For example, feldspar group minerals have molar $\frac{Si}{K+Na+Ca} = 2-3$, in keeping with solid solutions and coexisting combinations of albite ($NaAlSi_3O_8$), anorthite ($CaAl_2Si_2O_8$), and K-feldspar ($KAlSiO_4$). Our software searches for feldspar, pyroxene, olivine, and oxide stoichiometries using such stoi-

Table 2. Rules for Recognizing Single Phase Analyses

Mineral	Example Formula	Criterion
K-spar or Plagioclase	$K_{0.75}Na_{0.25}AlSi_3O_8$ or $Na_{0.6}Ca_{0.4}Al_{1.4}Si_{2.6}O_8$	$\sum Mg + Fe + Mn + Ti < 10\%^{*}\ and\ \frac{Si}{Na + K}$ or $\frac{Si}{Na + Ca} = 2 - 3$
Olivine	$Mg_{1.6}Fe^{2+}_{0.4}SiO_4$	$\sum Ca + Na + K + Al < 10\%^{*}\ and\ \frac{Si}{Mg + Fe} = 0.5$
Pyroxene	$Fe^{2+}MgSi_2O_6$ or $Mg_{1.35}Fe^{2+}_{0.55}Ca_{0.1}Si_2O_6$	$\sum Na + K + Al < 10\%^{*}\ and\ \frac{Si}{Mg + Fe}$ or $\frac{Si}{Mg + Fe + Ca + Mn + Ti} = 1.0$
Fe oxide	$Fe^{3+}{}_2O_3$	$Si < 10\%^{*}\ and \frac{Fe}{Fe + Mg} = 1$

*mole % calculated by summing all moles of all ten cations, setting any negative values to zero

chiometric criteria, and then outputs a list of shot numbers, location number, and rock target name for each single phase. Search criteria are shown in **Table 2**.

In a separate process, the software considers each location and computes the average measurement for each of the main cations. It determines if the measurement for each cation is within the error bars from the average. It then computes what percentage of the shots are within the error bars and records that value in an output file. Tabular output lists the percentage of shots for a location that fall within the error bars from the average value for each cation; the table also diplays a count of cations for which the value exceeds 95%. If all nine cations match this criterion, the location is likely a homogeneous phase, while for lower counts, judgments must be made. Single phase locations are easily seen in the graphical display program where any plot of one cation vs another shows as a cluster of points within the error bars of the *x* and *y* variables.

Mixtures of Phases: It is expected that a vast majority of LIBS shots will represent combinations of more than one mineral. If knowledge of mineralogy is desired, then it is necessary to take advantage of the data contained in individual shots at each location, because they represent varying combinations of data from two or more phases, each with a relatively constant composition. To enable inspection of catio ratios, a graphical program was created to plot combinations of cations versus other combinations, e.g., Ca/Ca+Na. The program allows the user to pick a target name, location, and/or shot number and displays whatever cation combination is needed. The user can also step through targets or locations. Two phase systems appear as collections of shot results arrayed in straight lines.

For every graph, the slope, intercept, Pearson correlation coefficient, and errors in the slope and intercept are displayed; these can also be output for all locations into a convenient ascii-formatted file.

As an example, **Figure 1** shows a plot of Ca vs. Na+Ca for a mixture of plagioclase plus any combination of Fe oxide, pyroxene, or olivine. Here only a single phase contains Na and Ca, so the line of possible sampled compositions passes through the origin. The composition of plagioclase modeled here would be its slope, or 0.4, which is the value of Ca/(Ca+Na) in the mineral andesine. The fact that the individual analyses plot on a line requires the presence of a second phase without Na or Ca, and the software allows investigation of other ratio plots to constrain the identity of the other phase.

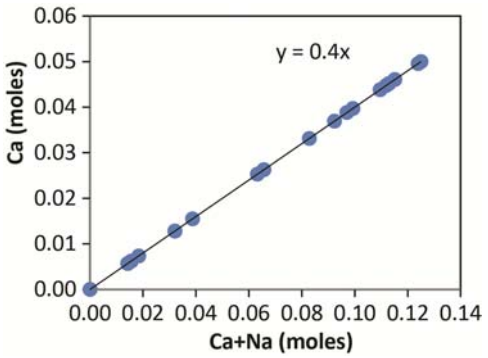

Figure 1. Plot of molar Ca vs. Na+Ca for a mixture of plagioclase plus any combination of Fe oxide, pyroxene, or olivine. Because Na and Ca both occur only in plagioclase, this line has an intercept at the origin. Thus the slope of this line is equal to the Ca/(Ca+Na) content of the plagioclase, which is 0.4 in the modeled andesine.

Applications: This software package allows users to quickly inspect and plot cation ratios for use in evaluating mineralogy of mixtures of phases. Its input files can be easily adapted to accommodate input files containing chemical analyses for which accuracies are also known. This package provides a simple way to inspect data from the ChemCam rover, and thus make mineralogical interpretations from LIBS data on Mars.

References: [1] Maurice S. et al. (2012) *Space Sci. Rev.*, *170*, 95-166. [2] McCanta M. C. (2013) *Planet. Space Sci.*, *81*, 48-54. [3] Dyar M.D. et al. (2013) *LPS XLV,* this volume. [4] Wiens R. C. (2013) *Spectrochim. Acta B*, *82*, 1-27. [5] Cantrell, C. A. (2008) *Chem. Phys.*, *8*, 5477-5487. [6] Lanza N. L. et al. (2013) *LPS XLIV,* Abstract #1723.