INVESTIGATION OF REFINEMENT OF HIGH SODIUM AND POTASSIUM CALIBRATIONS FOR CHEMCAM. R. Anderson[1], P. J. Gasda[2], J. Frydenvang[3], R. C. Wiens[2], S. Maurice[4], O. Forni[4], S. Clegg[2], [1]United States Geological Survey, Astrogeology Science Center Flagstaff, AZ [2]Los Alamos National Laboratory, NM, [3]U. Copenhagen Natural History Museum, [4]IRAP

Introduction: High-alkali materials discovered in Gale crater, Mars by the NASA Mars Science Laboratory (MSL) rover have important implications for Mars igneous and fluvial history. A wide range of evolved igneous materials, including those that are high in Na and K, have been identified by ChemCam [1,2], and APXS [3] instruments. These compositions range from basalts to trachytes [4–10]. These materials have been identified primarily during the first ~800 sols as float rocks, conglomerate clasts, or identified as a likely endmember component [e.g., 10–12] and also as float rocks near Ireson Hill (sol 1608) [8]. Igneous float rocks in Gale crater that were found during the first ~800 sols, in the Bradbury formation, were likely erosional detritus transported by mass wasting, by fluvial action in valley networks along the crater rim (e.g., Peace Vallis [13]), or emplaced by impact processes. Recent measurements of lacustrine mudstone have detected high alkali materials, possibly indicative of evaporitic minerals such as halite [e.g., 14].

The large variety and range of possible alkali compositions on Mars has compelled us to revisit the ChemCam calibration for high-alklai materials. The current Major-element Oxide Composition (MOC) algorithm for ChemCam uses a database of 408 rock powder standards and uses a combination of Independent Component Analysis (ICA) and Partial Least Squares (PLS) regression [15] to yield Na_2O and K_2O compositions with an RMSEP accuracy of ~0.3 wt. % or greater for Na_2O and ~0.9 wt. % or greater for K_2O, with the exact accuracy varying with abundance [15]. The goal of this project is to refine and improve the accuracy when identifying high-alkali abundances with ChemCam using an expanded training set of alkali-rich standards and new regression methods.

Methodology: *Calibration Data Set.* ChemCam is a combination remote laser-induced breakdown spectroscopy (LIBS) and micro imager (RMI) instrument [2–3]. All laboratory measurements used for this study were performed using the ChemCam engineering unit located at Los Alamos National Laboratory (LANL). For each target, data were collected at 5 points on the sample with 50 laser shots per point. Samples were analyzed at a range of 1.6 m in a chamber that simulates the martian atmosphere. An "Earth-to-Mars" correction [15] was applied to these spectra to make them comparable to the LIBS spectra taken with the flight unit on Mars.

In an effort to improve the calibration for high-alkali targets, we analyzed an additional 35 Al-, Na-, and K-rich standards (Brammer) and 25 salt-basalt mixtures [16] to expand the ChemCam database to a total of 470 samples (**Fig. 1**). These samples cover a range of compositions that encompasses feldspars, feldspathoids, clays, zeolites, and salts (approximately up to 25 wt.% K_2O, 45 wt.% Na_2O, 40 wt.% Al_2O_3).

We used the Isolation Forest algorithm [17] as implemented in the Python Spectral Analysis Tool (PySAT) [18] to identify and remove possible outliers in the training database, including high-Mn and high-Ti samples. We also removed mixtures of KCl and $CaSO_4$ with >25 wt.% KCl because these samples showed an unusual broadening of the K emission lines not observed in other high-K samples.

Multivariate Model. We used PySAT to sort spectra on either Na_2O or K_2O and divide them into five folds, each with a similar distribution of compositions. One fold was used as an independent test set, and the remaining folds were used as the training set. We ran cross validation to optimize the parameters for the following regression methods: Bayesian Ridge Regression (BRR), Least Angle Regression (LARS), Least Absolute Shrinkage and Selection Operator (LASSO), Elastic Net (ENet), Ordinary Least Squares (OLS), Orthogonal Matching Pursuit (OMP), Ridge regression, PLS, and Gaussian Process regression (GP). Cross validation calculations were run on spectra normalized to the total signal ("norm 1") and to the signal for each of the three spectrometers ("norm 3"). In addition, cross validation was run for three "sub-models" with restricted compositional ranges.

Based on the cross validation results (Table 1), we trained optimized regression models and blended their estimates following the procedure described in [19]. To estimate the accuracy of the final optimized and blended submodels, we calculated the compositions for the test set and report the errors as RMSEP (Figure 2).

Results and Discussion: Our cross validation results indicate that a combination of Elastic Net, LASSO, and PLS regression models give the lowest error for K_2O and Na_2O calibration. The overall RMSEP for the blended K_2O models is 0.83 wt.%, and for the blended Na_2O models it is 0.97 wt.%.

Work is ongoing to validate these optimized models by evaluating their performance on feldspars and alkali-rich rocks analyzed in the laboratory, the calibration targets on the rover, and suspected feldspar observations on the martian surface. Due to the sparse nature of the regression coefficients for LASSO and Elastic net models, we will also investigate the model sensi-

tivity to slight shifts in wavelength calibration. The end result of this effort will be an improved calibration that is more accurate for high concentrations of Na_2O and K_2O than the currently implemented calibration.

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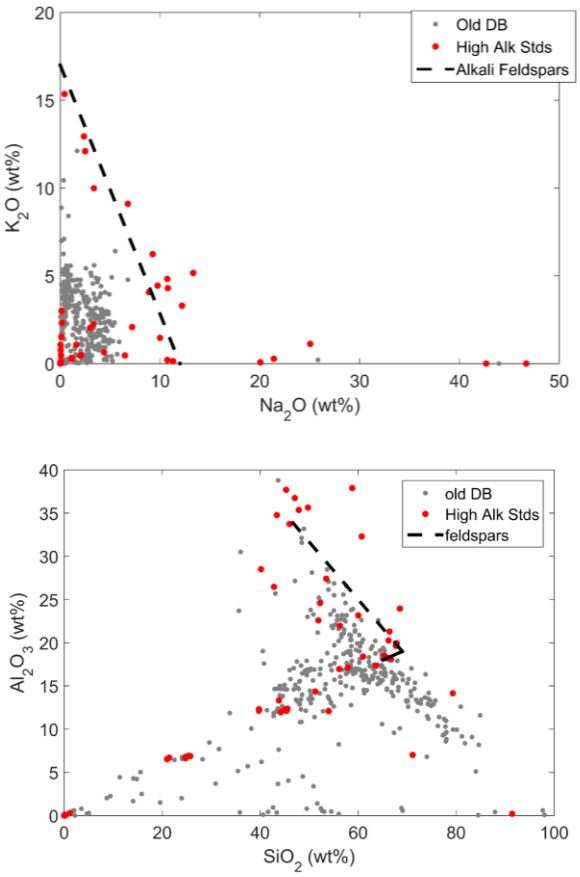

Figure 1: Compositions of the ChemCam database (grey dots) and new standards used in this study (red dots). Dashed line represents ideal feldspar compositions.

Table 1: Optimal Cross Validation Results

Training Range (wt.%)	Regression Method	Normalization	RMSECV (wt.%)
Na_2O			
0-100	Elastic Net	Norm 3	1.00
0-1.5	Elastic Net	Norm 1	0.19
1-6	Elastic Net	Norm 1	0.57
5-100	PLS	Norm 3	2.32
K_2O			
0-100	LASSO	Norm 3	0.91
0-1.5	LASSO	Norm 1	0.24
1-6	LASSO	Norm 1	0.67
5-100	LASSO	Norm 1	1.54

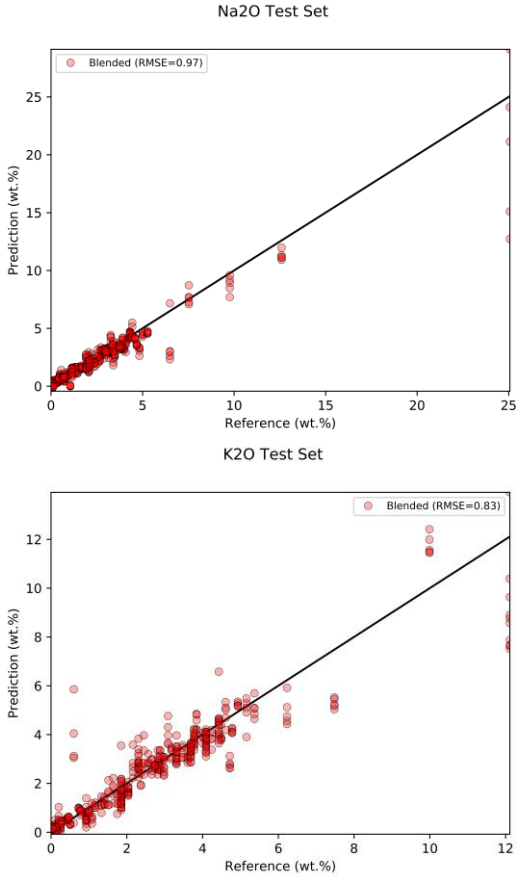

Figure 2: Plot of test set modeled compositions vs. known compositions for the optimized, blended Na_2O and K_2O models.