Trace and Minor Element Quantification with SuperCam Laser Induced Breakdown Spectroscopy (LIBS).
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Introduction: Trace and minor elements are present in small quantities in most rocks and can provide important information about the formation and diagenesis of those rocks [e.g. 1]. The Mars 2020 SuperCam team has been working on accurately quantifying the trace and minor elements Li, Sr, Rb, Ba, Cr, and MnO using LIBS data. We evaluated a variety of preprocessing steps and regression methods to find the optimal solution for quantifying each element.

Data: This effort uses the same suite of LIBS spectra (collected prior to launch on samples of known composition) that is currently used for quantification of the major element oxides [2]. For each element the spectra were split into five "folds" with similar distributions of the element of interest in each fold. Four of these folds were designated as the "training set" and one was designated as the "test set" which is held out during model optimization. Afterwards, the test set is used to evaluate the performance of the regression models on novel data. All SuperCam calibration targets (SCCTs) were assigned to the test set. For several elements, a small number of samples had extremely high concentrations and were removed as outliers. Because targets with very high MnO have been detected on Mars, we evaluated MnO models trained and tested on several different concentration ranges (see Table 1).

Preprocessing: Several different preprocessing steps were evaluated. These included peak binning [2, 3], restricting the input spectra to a single spectrometer, using feature selection to reduce the number of spectral channels used as model input, normalizing the spectra on a per-spectrometer basis, and normalization to the amplitude of the O triplet near 777 nm. We found that peak binning and normalization to O generally did not improve the results, with the possible exception of MnO, which may benefit from binning. Using a single spectrometer and/or applying feature selection were beneficial in many cases.

We also applied a +/- 1 pixel shift in wavelength to the data. Models were trained and tested on the unshifted and shifted data to ensure robustness to slight variations in the wavelength calibration.

Quantification: We considered multiple regression models to relate LIBS spectra to abundance of each element. Prior work has shown good success with univariate models for trace and minor elements [e.g. 4], but we found that multivariate models performed better and focused most of our efforts on selecting the best model for each element. The algorithms considered included: Partial Least Squares (PLS), Elastic Net, Orthogonal Matching Pursuit (OMP), Random Forest (RF), Gradient Boosting Regression (GBR), eXtra Trees (XT), Support Vector Regression (SVR), and Gaussian Process Regression (GPR) (see [6]).

Model parameters were optimized using cross validation over the four training set folds. To select the best overall models, we first determined the lowest root mean squared error of cross validation (RMSECV) across all models and preprocessing permutations. Then, we found the standard deviation of the RMSE from the individual folds for that model. All models with RMSECVs that fell within one standard deviation of the minimum RMSECV were considered to have similar cross validation performance. We then selected the best model from among those based on the minimum root mean squared error of prediction (RMSEP) – the performance on the test set. We calculated the RMSEP for the test set spectra (including SCCTs) collected at 3 m, with wavelength shifts of -1, 0, and +1 pixels applied. Several team members performed this model selection process independently and their results were compared to identify the best models.

Results: Table 1 summarizes the current best models for the trace and minor elements. We found that the Cr performance was typically quite poor. Although some models appear to perform better on non-SCCT laboratory targets, more work is needed before we can be confident of Cr results. Most geologic targets have very low MnO, but high MnO has been detected on Mars. We are evaluating how best to handle the wide range of possible MnO values and sparsity of mid- to

	Li (ppm)	Sr (ppm)	Rb (ppm)	Ba (ppm)	MnO (wt.%)	MnO (wt.%)	MnO (wt.%)
Range	0-1000	0-2000	0-750	0-2500	0-2	0-5	0-50
Model	GBR	GBR	GBR	GBR	GPR	GPR	GPR
# Features	200	800	200	800	50	135	15
RMSEP	12	104	32	222	0.17	0.63	0.48

high-MnO training and test samples in the current data set. Initial MnO results that blend submodels trained on different composition ranges, similar to the approach used for ChemCam [5], are promising but more work needs to be done.

Line detection check: Multivariate regression methods can partially correct for "matrix effects" by utilizing emission lines from elements other than the element of interest [2]. However, this also introduces the risk of incorrect predictions when an unknown target does not follow the same correlations or anticorrelations that were present in the training data. For trace and minor elements, which tend to have weak emission lines compared to more abundant elements, it is not unusual for the diagnostic emission lines for the element to be absent when concentrations are very low. In this situation the model will still predict a concentration by using assumed correlations with major elements.

To avoid a situation where scientists unknowingly use predictions for undetected elements, we have developed a simple method for measuring the strength of diagnostic lines for each element. When no emission line is detected, we can choose to flag predicted abundances with a warning or refrain from reporting an abundance for the element altogether.

This method uses the maximum standard deviation of the shot-to-shot spectra in a pair of continuum locations near the line of interest as a proxy for the noise of the observation. It evaluates whether the intensity at the center of the emission line of interest is greater than a noise threshold (Figure 1). By visual inspection of many spectra, we found that the threshold at which a human identifies an emission line in the spectrum "by eye" is ~0.6 times the noise standard deviation. Predictions below this signal to noise threshold may still be accurate: the correlations identified by the models are real and hold true for many targets (Figure 2) However, such predictions should be used only with extreme caution. The "detection checker" will soon be implemented in the SuperCam quantification pipeline for both major and minor elements.

Future work: Before the regression models identified in Table 1 can be used in daily operations, their performance on Mars data to date must be evaluated. We are currently working on comparing the quantities predicted for spectra inferred to be pure minerals with the expected trace and minor element abundances for those minerals. This evaluation is ongoing at the time of writing and may lead to the selection of different final models than those currently listed in Table 1.

Concurrent with the efforts to quantify the trace and minor elements, the SuperCam team has been collecting a new, more extensive suite of LIBS data in the laboratory at Los Alamos National Laboratory with a clone of the SuperCam instrument. This new data is expected to improve quantification accuracy and robustness for both major and minor elements.

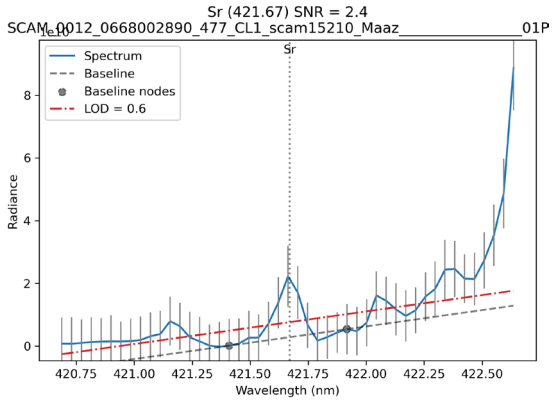

Figure 1: Illustration of the line detection check applied to the Sr 421.67 nm line on the first SuperCam target, Máaz. Baseline nodes are the two locations used to define the baseline and estimate noise. The gray error bars indicate the standard deviation of the shot to shot spectra. The dashed red line is the threshold for detection of 0.6 times the estimated noise. The target Máaz has a small but clearly visible Sr peak, with signal to noise of 2.4. Thus Sr is present and quantification is appropriate.

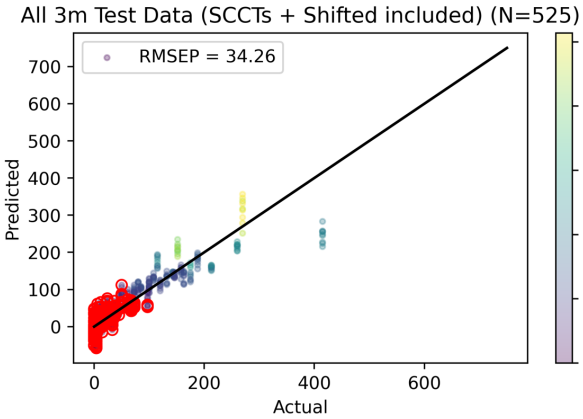

Figure 2: Example predicted vs actual Rb concentrations in the test set. Color corresponds to the signal to noise (SNR) calculated by the detection checker tool. Red points have SNR below the threshold of 0.6 and therefore have little or no detectable Rb line, but still follow the 1-to-1 line trend due to correlations with other elements in these terrestrial laboratory standards.

References: [1] Ollila, A. M., et al. (2014), *JGR* Planets, 119, 255– 285 [2] Anderson, R.B., et al. *Spectrochim. Acta B* (2021) 106347. [3] Clegg S.M. et al. (2020) 51st *LPSC,* #2561 [4] Payré, V., et al. (2017), *JGR Planets*, 122, 650– 679 [5] Gasda,P.J. et al. (2021) *Spectrochim. Acta B*, 181, 106223.