END-TO-END MODELS FOR EFFECTS OF SYSTEM NOISE ON LIBS ANALYSES OF IGNEOUS ROCKS. M. L. Carmosino[1], S. Bender[2], E. A. Speicher[1], M. D. Dyar[1], S. M. Clegg[2], R. C. Wiens[2]. [1]Dept. of Astronomy, Mount Holyoke College, 50 College St., South Hadley, MA 01075, mdyar@mtholyoke.edu; [2]Los Alamos National Laboratory, P.O. Box 1663, MS J565, Los Alamos, NM 87545.

Introduction: The ChemCam instrument on Mars Science Laboratory [1] will be the first extra-terrestial deployment of laser-induced breakdown spectroscopy (LIBS) for remote geochemical analysis. LIBS instruments are also being proposed for future missions. Understanding the effects of key instrument parameters and their variability on the elemental predictions is essential to such LIBS applications.

Baseline experiments were run on a laboratory instrument in conditions reproducing ChemCam performance on Mars [1]. These experiments employed a Nd:YAG laser producing 17 mJ/pulse on target with a 200 μm FWHM spot size on the surface of a sample. The emission was collected by a telescope, imaged on a fiber optic, and then interfaced to a demultiplexer capable of >40% transmission into each spectrometer.

We report here on an integrated end-to-end system performance model that simulates the effects of output signal degradation that might result from the input signal chain (Table 1) on multivariate model predictions. There are two approaches to modifying signal to noise (SNR): degrade the signal and/or increase the noise. Ishibashi [2] used spectra of nine silicate rocks to show that the addition of noise had a significantly greater impact on precision and accuracy compared to degradation of spectral resolution. Here, we use a larger data set to assess LIBS instrument performance by degrading spectra, either by increasing peak widths (simulating misalignment) or decreasing the spectral amplitude (decreases in SNR).

Data Reduction: Elemental compositions were predicted using variably-degraded laboratory spectra from a suite of 50 igneous rocks. PLS techniques and a training set created from another 50 related spectra [3], acquired under optimal laboratory conditions at 9 m standoff distances, were used. Compositions of the entire 100-sample data set (in wt.% oxide ±standard deviation) are SiO_2: 52.53±9.69, Al_2O_3: 12.92±3.43, TiO_2: 2.04±1.40, Fe_2O_3: 10.79±4.23, MgO: 8.91±7.40, MnO: 0.17±0.06, CaO: 8.12±3.66, K_2O: 1.35±1.60, Na_2O: 2.56±1.15, and P_2O_5: 0.34±0.56. Data processing included wavelength-registration to create even *x* axis increments, background/baseline subtraction, and averaging of five spectra from each sample.

Multivariate analyses used PLS-2, which regresses multiple responses against the predictors, to explain variance in **X** and **Y**. Tests used only the major elements Si, Al, Ti, Fe, Mg, Mn, Ca, Na, P, and K for **Y** variables; **X** variables were the 6144 channels of the three detectors. Internal validation was used to tune parameters of each model. Root mean square error predictions (RMSEP) were used to compare results. The number of components to be used in the models was individually chosen for each element using the first local or global minimum value of RMSEP.

Treatment #1: This treatment simulates throughput losses by selectively reducing the amplitude of the spectra. If a pixel is greater than the median of its ±31 neighbors, then its intensity is multiplied by an amplitude reduction factor, ARF (1, 0.9, 0.8, down to 0.1, with 1 being the same as untreated data), and then added back to the median; otherwise, the pixel value is left untouched. This procedure keeps the baseline fixed and reduces relative signal amplitude. Results (Fig. 1) show that some elements are robust to detector noise, while projections of others immediately get worse. We hypothesize this may occur because the total area/intensity of emission peaks from each element is quite variable; perhaps elements with larger peaks are less vulnerable to these amplitude degradations.

Treatment #2: Here, photon noise limit performance is emulated by reducing the optical throughput linearly while reducing the the noise by the root of the reduction factor. The treatment is thus the same as in

Table 1. Summary of Simulations Undertaken

Instrument Issue	#	Treatment
SNR degradation resulting from throughput loss with fixed detector noise (dark current, read-out noise, etc.); i.e. detector-limited performance	**1**	Decrease amplitude of all pixels with magnitudes above the local median baseline
Through-put losses in the optical train: transmission loss, demux alignment, telescope alignment, etc.; also, reductions in laser energy; i.e. photon-limited performance	**2**	Same as #1, except every pixel equal to or below the median is multiplied by the square root of the amplitude reduction factor
Resolution and signal loss due to misalignment or focus errors	**3**	Resolution analysis applied to raw spectral distribution
Resolution loss only due to misalignment or focus errors; amplitude restoration with intensifier	**4**	Same as #3, but also multiply each spectrum by a constant until the peak amplitudes are comparable to the raw data

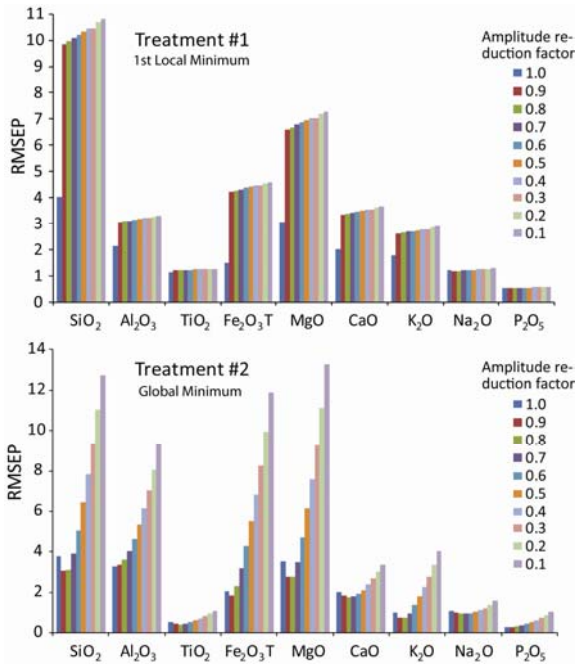

Fig. 1. Comparison of RMSEP values for Treatments #1 (simulating detector-limited performance resulting from throughput loss with fixed detector noise) and #2 (photon-limited performance resulting from through-put losses in the optical train), as described in Table 1. The 1st (top) treatment shows an immediate worsening of prediction errors even at ARF=0.9, with all degraded RMSEP values being similar. The 2nd (bottom) treatment shows a dramatic change in RMSEP over the range of ARF from 0.8-0.1.

Treatment #1, except that every pixel with a value ≤ median is multiplied by the square root of the ARF. Results show a very slight initial improvement in RMSEP errors at ARF = 0.9 and 0.8. There are rapid increases in error that triple the RMSEP at reductions of 0.7-0.1 (Fig. 1). Clearly, quantitative analyses are highly sensitive to signal degradation resulting from through-put losses, particularly in the optical train.

Treatment #3: In this treatment, we simulate misalignment or focus errors by applying various resolution curves to the transformed raw spectra, then taking the inverse transform without applying a subsequent gain correction (Fig. 2). This is a worst-case scenario for LIBS spectra because the resolution loss is accompanied by a nominal 50% amplitude degradation. A slight reduction in RMSEP at increased error is initially observed when the signal is degraded *before* being averaged in the processing pipeline; it appears to be related to averaging-out of the changes made to the signal. If the resolution curve is applied *after* averaging of the data, then trends similar to those in Treatment #1 result. The Fourier process is somewhat imperfect by nature (due to the lack of infinite points and a replicating series), and thus, applying it multiple times before averaging may compound the limitaions. Note that RMSEP values here are nearly half those caused by through-put losses (Treatments #1 and 2).

Treatment #4: In this test, the spectra were treated as in #3 above, then multiplied by a gain factor of 2.0 to approximately replicate amplitudes of the raw spectra. This step simulates use of detector gain such as with an intensified CCD, which is commonly included in LIBS systems. Using gain reduces (improves) prediction errors ~¼-⅓ lower than those for Treatment #3, with the comparable trends within each element.

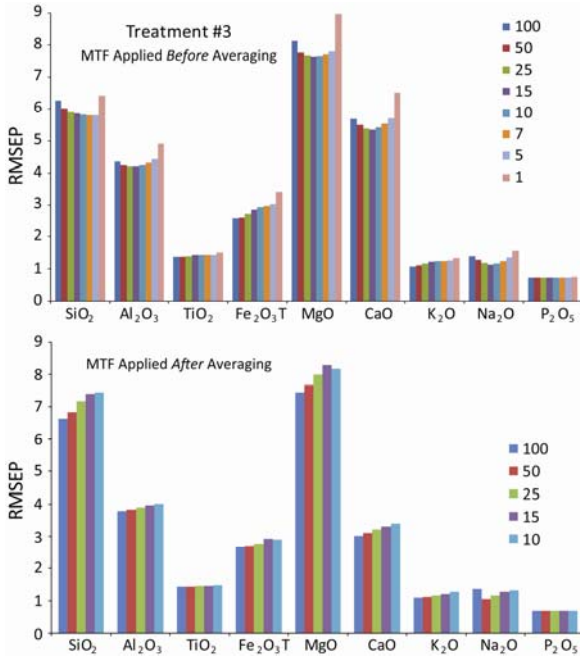

Fig. 2. Comparison of RMSEP values for treatment #3 with the resolution curve applied *before* (top) and *after* (bottom) averaging the five spots on each sample. Results are produced by application of a resolution curve to each of 50 spectra of igneous samples from [3].

Implications for In-Situ Planetary Exploration: Each of the four treatments above produced a set of RMSEP errors that demonstrate how elemental predictions are affected by instrument degradations. Overall, this work demonstrates that remote LIBS analyses should be less vulnerable to misalignment or focus errors than to through-put losses [2]. To appreciate the impact of these errors on geochemical interpretations, note that measurement requirements on the ChemCam instrument are ±10 relative wt.% for each of these major elements. These can be compared toRMSEP values determined in this study (using 9 m standoff data) that are expressed in units of absolute ±wt.% error.

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References: [1] Maurice, S. (2005) *LPSC XXXVI*, Abstract #1735. [2] Ishibashi, K. et al. (2010) *LPSC XLI*, Abstract #1719. [3] Tucker J. M. et al. (2010) *Chem. Geol.*, 277, 137-148.