PREDICTION ACCURACIES OF MAJOR ELEMENT COMPOSITIONS DERIVED FROM SPECTRA COLLECTED UNDER A RANGE OF ATMOSPHERIC CONDITIONS RELEVANT TO PLANETARY EXPLORATION.
K. Lepore[1], I. Belkhodja[1], K. Bickford[1], and M. D. Dyar[1,2], [1]Dept. of Astronomy, Mount Holyoke College, 50 College St., South Hadley, MA 01075, [2]Planetary Science Institute, 1700 E. Fort Lowell Rd Suite 106, Tucson, AZ 85719.

Introduction: The development of elemental analyses on Earth and Mars derived from laser-induced breakdown spectroscopy (LIBS), and the potential for LIBS exploration of lunar and asteroid surfaces, has accelerated the use of LIBS as a geochemical tool for earth-based and planetary exploration [1,2,3,4,5,6]. However, quantitative predictions derived from LIBS spectra are plagued by uncertainties related to matrix effects, which are changes in emission spectra that cannot be attributed to differences in sample composition. The atmospheric pressure and composition during LIBS plasma formation have profound effects on plasma characteristics such as temperature and electron density [7,8], and thus contribute to matrix effects observed in LIBS spectra. To understand this, there is a demand for geochemically diverse, high-quality LIBS spectral databases that can be used under a range of environmental conditions including variable atmosphere.

In this project spectra were collected under Earth, vacuum, and Mars-like atmospheric conditions to compare and contrast the accuracy of LIBS predictions in different environments. In addition, prediction uncertainties were quantified for cases where models trained under one set of conditions were used to predict major element compositions using spectra collected in a different atmosphere.

Reference targets: The database of rock standards includes 2503 rock powders with a $\ll 10$ μm grain size pressed into 1.6 cm diameter pellets [9]. Samples represent a diverse collection of igneous (70%), sedimentary (25%), and metamorphic (5%) rocks.

Spectra collection: Spectra were collected using SuperLIBS, a high-sensitivity LIBS instrument built with 2D CCD detectors identical to those used by SuperCam on the *Perseverance* rover. SuperLIBS employs a Nd:YAG laser operated at 1064 nm, 10 Hz, with an eight ns pulse width. Laser energies ranged from 2.4 to 7.2 mJ. Sample ablation was conducted in a sealed chamber to facilitate collection of spectra under varying conditions: ambient (Earth) atmosphere, vacuum (50-200 mTorr), and 7 Torr CO_2 (Mars). After collection, spectra were dark-subtracted, wavelength-aligned to a Ti standard, corrected for instrument response, baseline-corrected, and normalized.

Models: Spectra were stratified into training and test sets that represent the composition range of each major element. For all spectra acquired in all atmospheres, targets allocated to training and test sets were identical, ensuring consistency among datasets. Cross-validation
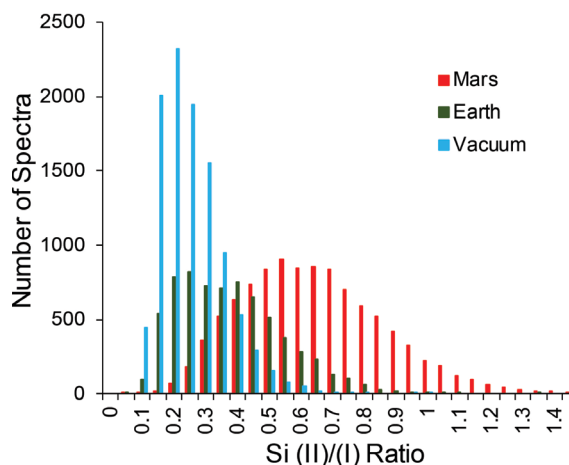

Figure 1. Si (II)/(I) ratios of spectra collected at a range of laser energies under earth, vacuum, and Mars conditions.

of partial least squares (PLS) models was used to identify the ideal number of components for training (between 2 and 30), and compositions of test set spectra were predicted using these optimized models. Model results were reported as the accuracy (RMSE-P wt. % oxide) and variance (r^2) of predictions.

Results: The ratio of the Si(II) peak at 634.7 nm to the Si(I) peak at 288.2 nm is often used as a proxy for
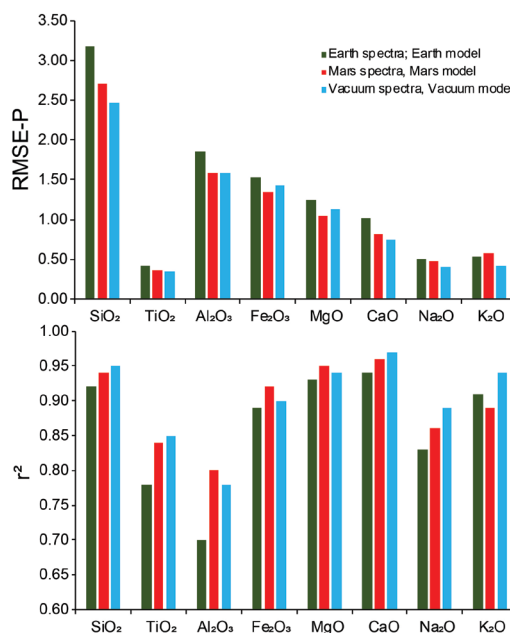

Figure 2. RMSE-P and r^2 values reported for spectra collected under Earth, vacuum, and Mars conditions.

plasma temperature [10]. This temperature is a function of sample composition, laser energy on target, and ambient atmosphere. Si(II)/(I) ratios in spectra collected under Earth, vacuum, and Mars-like conditions exhibit a wide range of values among the three atmospheres
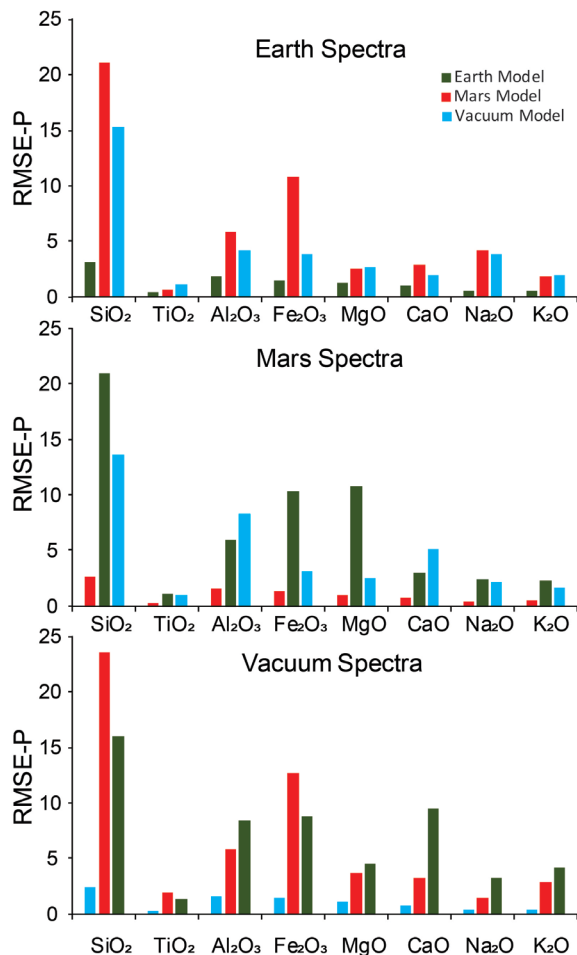
Table 1. Average RMSE-P and r^2 values for all major elements when training and test sets do not match.

Average	RMSE-P	r^2
Earth model predicting Vacuum and Mars	7.1	0.30
Mars Model predicting Vacuum and Earth	6.6	0.50
Vacuum Model predicting Earth and Mars	4.5	0.66

and Mars spectra (**Table 1**). Vacuum-based models are more robust when predicting spectra collected under Earth and Mars-like conditions, but prediction accuracies for mis-matched training and test sets are clearly suboptimal.

Conclusions: High-quality quantitative predictions of major elements calculated under ambient, vacuum, and Mars-like atmospheres yield similar accuracies for major elements. Results show that LIBS holds great potential as an analytical tool for remote operations on Earth, Mars, lunar, and asteroid surfaces.

Importantly, a model trained using spectra collected in one atmosphere should not be used to predict spectra collected in another. Differences in emission line distribution observed with Si(II)/Si(I) ratios indicate that plasma characteristics are too disparate to pair training and test spectra collected in different environments. The extremely high uncertainty of major element predictions when atmospheres do not match indicate that calibrations must be specifically tailored to the conditions expected during in-field analyses.

The process of generating a large (>2000 standards), geochemically diverse spectral database is not always feasible due to constraints on time and funding. Therefore, the LIBS database presented here will be made available on the NASA Planetary Data System Geosciences node [9]. These spectra can be used to generate large-scale calibrations collected under a range of atmospheric conditions appropriate for use in Earth-based, Mars, lunar, and asteroid applications.

Figure 3. Prediction accuracies (RMSE-P) reported for models trained and tested using spectra collected under a range of atmospheric conditions.

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(**Figure 1**). Clearly, spectra reported here represent diverse plasma characteristics that influence the models trained under each type of atmosphere.

Despite substantial differences in plasma characteristics observed using Si(II)/Si(I) ratios, prediction accuracies reported for models trained under Earth, vacuum, and Mars-like conditions are very similar (**Figure 2**), demonstrating the power of the PLS algorithm. Model results demonstrate reliable major element predictions in all three atmospheres.

In contrast, when models trained in one atmosphere are used to predict spectra collected under different conditions, prediction accuracies decline substantially (**Figure 3**). Prediction accuracy and variance are worst when Earth-based models are used to predict vacuum