LIBS AND PIXL PREDICTION ACCURACIES FOR NI, MN, S. AND MAJOR ELEMENTS: A COMPARATIVE STUDY USING THE SAME STANDARDS, C. R. Yisma', J. Hurowitz', and M. D. Dyar' Dept. of Astronomy, Mount Holyoke College, 50 College St., South Hadley, MA 01075, yts-ma22c@mrholyoke.edu, 'Dept. of Geology, Stony Brook University, 100 Nicolls Rd, Stony Brook, NY 11794.

Introduction: Calibration models for detection and accurate quantification of elements on Mars are necessary to understand the composition of its surface. Mars 2020 will carry Planetary Instrument for X-ray Lithochemistry (PIXL), an x-ray fluorescence (XRF) instrument, and a laser-induced breakdown spectroscopy (LIBS) instrument as part of the SuperCam instrument for geochemical analyses. No comparison of prediction accuracies between these two techniques using identical standards has been undertaken to date, making it difficult to compare results from the two methods.

Another issue with Mars geochemical accuracies is that most calibration models are made using terrestrial geologic standards with concentrations that may be significantly lower than those of, especially, Ni, Mn, and S in Martian soils [1], where these elements may be enriched by contributions from meteorites and volcanic gasses. Accordingly, this study uses standards created from several different rock types doped with up to 1 wt% (10,000 ppm) of these elements to create appropriate calibration models.

Background: With XRF, samples are bombarded with high-energy X-rays, resulting in ejection of inner shell electrons. The resultant holes in the inner-shell orbitals are filled by electrons from outer shells, in the process ejecting a photon with energy diagnostic of each individual element. In contrast, LIBS uses energy from a laser pulse to excite electrons into higher energy orbitals. When electrons return to their ground state, they release photons detected by spectrometers from the UV to the NIR. These transitions occur at longer wavelengths and lower energies than those measured in XRF, due to differences in the energy of the two excitation sources (plasma heat and x-rays, respectively). So these two techniques are highly complementary, and each has its strengths and weaknesses.

Methods: Doped samples consisted of 7 matrices with different bulk compositions, including three basalts, one granite, one rhyolitic volcanic glass, sea sand, and a 50:50 mixture of diopside and forsteritic olivine. Standard preparation and analyses are described in [2]. These powders were pressed into pellets and a subset of the 84 samples was analyzed under Mars conditions with the Mount Holyoloc College Cheml.IBS-analog instrument as well as with the Stony Brook University PIXL-analog instrument in air.

Spectral Preprocessing: XRF spectra from three pellet locations were summed over a total dwell time of one or two hours using data from two spectrometers. X-axis resampling and baseline calculations for later removal were performed by PIQUANT, a software created specifically to analyze PIXL spectra [3-4]. To remedy temporal count differences, the spectra were normalized by the emission counts at 2.697 keV, which derive from Rh-anode L-emission lines in the PIXL Xray tube.

LIBS spectra were averages of 36 individual shots taken on 6 locations across the pellets' surfaces. Spectra were preprocessed using the same method as the ChemLIBS Curiosity team and normalized by the total intensity of each of the three spectrometers [5]. The baselines were removed using the Kajfosz-Kwiatek method (bottom width of 50 and top width of zero) [6].

Modeling and Analysis: Both datasets were uploaded to a web tool that utilizes the SciKit-learn library and allows for convenient multivariate analysis with partial-least squares (PLS) and the least absolute shrinkage and selection operator (lasso) regression methods [7]. Calibration models for the doponts (Ni, Mn. S) and the major oxides (SiO₂, TiO₃, Al₂O₃, Fe₂O₃, MgO, CaO, Na₂O, K₂O, P₂O₃) were made using both the entire available spectral range (0-40 keV for PIXL and -240-850 nm for ChemLIBS) as well as limited regions of the spectra that contain emission peaks specific to the element of interest (Table 1). XRF regions used each element's k-a fluorescence peak, while LIBS focused on regions with the most intense peaks or clusters of peaks found with the NIST LIBS spectral database [8]. PIXL calibrations for Na. and Mg were not possible because their XRF emissions are not measurable in air.

Table 1. Limited ranges used by calibration models.

Element	XIRF (logV)	LIBS (mm)
Ni	7.25-7.70	298-315
Man	5.72-6.07	255-265, 290-300
- 8	2.2-2.42	no peaks
58	1.64-1.86	245-300
T3.	4.3-4.7	245-460
AL	1.35-1.65	245-400
Fig	6.2-6.6	245-450
Mg	mo peak	275-285
Car	3.5-3.87	310-400
Non	mo pesik	325-335, 560-600, 815-825
IK.	3.1-3.5	760-775
Tr.	no visible peak	245-260

Root mean squared errors from cross-validation of the models (RMSECVs) were calculated with two methods: leave-one-out (LOO), which is similar to a simple calibration RMSE, and a more rigorous cross

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