

LIBS AND PIXL PREDICTION ACCURACIES FOR NI, MN, S, AND MAJOR ELEMENTS: A COMPARATIVE STUDY USING THE SAME STANDARDS. C. R. Ytsma¹, J. Harowitz², and M. D. Dyar¹

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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 Holyoke College ChemLIBS-analog instrument as well as 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 X-ray 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-Kwiaterek 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 dopants (Ni, Mn, S) and the major oxides (SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MgO, CaO, Na₂O, K₂O, P₂O₅) 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- α 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	XRF (keV)	LIBS (nm)
Ni	7.25–7.70	298–315
Mn	5.72–6.07	255–265, 290–300
S	2.2–2.42	no peaks
Si	1.64–1.86	245–300
Ti	4.3–4.7	245–460
Al	1.35–1.65	245–400
Fe	6.2–6.6	245–450
Mg	no peak	275–285
Ca	3.5–3.87	310–400
Na	no peak	325–335, 560–600, 815–825
K	3.1–3.5	760–775
P	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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Table of Contents Pixl Prediction Paper Nov 2014

1. Understanding the eBook Pixl Prediction Paper Nov 2014
 - The Rise of Digital Reading Pixl Prediction Paper Nov 2014
 - Advantages of eBooks Over Traditional Books
2. Identifying Pixl Prediction Paper Nov 2014
 - Exploring Different Genres
 - Considering Fiction vs. Non-Fiction
 - Determining Your Reading Goals
3. Choosing the Right eBook Platform
 - Popular eBook Platforms
 - Features to Look for in an Pixl Prediction Paper Nov 2014
 - User-Friendly Interface
4. Exploring eBook Recommendations from Pixl Prediction Paper Nov 2014
 - Personalized Recommendations

- Pixl Prediction Paper Nov 2014 User Reviews and Ratings
- Pixl Prediction Paper Nov 2014 and Bestseller Lists
- 5. Accessing Pixl Prediction Paper Nov 2014 Free and Paid eBooks
 - Pixl Prediction Paper Nov 2014 Public Domain eBooks
 - Pixl Prediction Paper Nov 2014 eBook Subscription Services
 - Pixl Prediction Paper Nov 2014 Budget-Friendly Options
- 6. Navigating Pixl Prediction Paper Nov 2014 eBook Formats
 - ePub, PDF, MOBI, and More
 - Pixl Prediction Paper Nov 2014 Compatibility with Devices
 - Pixl Prediction Paper Nov 2014 Enhanced eBook Features
- 7. Enhancing Your Reading Experience
 - Adjustable Fonts and Text Sizes of Pixl Prediction Paper Nov 2014
 - Highlighting and Note-Taking Pixl Prediction Paper Nov 2014
 - Interactive Elements Pixl Prediction Paper Nov 2014
- 8. Staying Engaged with Pixl Prediction Paper Nov 2014
 - Joining Online Reading Communities
 - Participating in Virtual Book Clubs
 - Following Authors and Publishers Pixl Prediction Paper Nov 2014
- 9. Balancing eBooks and Physical Books Pixl Prediction Paper Nov 2014
 - Benefits of a Digital Library
 - Creating a Diverse Reading Collection Pixl Prediction Paper Nov 2014
- 10. Overcoming Reading Challenges
 - Dealing with Digital Eye Strain
 - Minimizing Distractions
 - Managing Screen Time
- 11. Cultivating a Reading Routine Pixl Prediction Paper Nov 2014
 - Setting Reading Goals Pixl Prediction Paper Nov 2014
 - Carving Out Dedicated Reading Time
- 12. Sourcing Reliable Information of Pixl Prediction Paper Nov 2014
 - Fact-Checking eBook Content of Pixl Prediction Paper Nov 2014

- Distinguishing Credible Sources
- 13. Promoting Lifelong Learning
 - Utilizing eBooks for Skill Development
 - Exploring Educational eBooks
- 14. Embracing eBook Trends
 - Integration of Multimedia Elements
 - Interactive and Gamified eBooks

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web 2022 graphics devices simulia tests specific graphics devices to ensure adequate performance with abaqus cae and abaqus viewer the graphics devices that have been tested or scheduled for testing are listed in the tables below however we cannot certify that these devices are completely compatible with all possible hardware and software

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web abaqus is a suite of engineering analysis software packages used into create the physical response starting structures and solid bodies to load air request impact and other environmental conditions and is obtainable on standard engineering user systems complex materials include rubbers thermo plastics and human tissue