

# LIBS AND PIXL PREDICTION ACCURACIES FOR NI, MN, S, AND MAJOR ELEMENTS: A COMPARATIVE STUDY USING THE SAME STANDARDS. C. R. Ytsma<sup>1</sup>, J. Harowitz<sup>2</sup>, and M. D. Dyar<sup>1</sup>

<sup>1</sup>Dept. of Astronomy, Mount Holyoke College, 50 College St., South Hadley, MA 01075, ytsma22c@mholyoke.edu, <sup>2</sup>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 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-Kwiatkiewicz 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 (SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, CaO, Na<sub>2</sub>O, K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>) 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- $\alpha$  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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detailing machine learning techniques as applied to geoscience information systems and remote sensing

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**Emerging zoonoses: eco-epidemiology, involved mechanisms and public health implications** Rubén Bueno-Marí, A. Paulo Gouveia Almeida, Juan Carlos Navarro, 2015-07-06 Zoonoses are currently considered as one of the most important threats for public health worldwide Zoonoses can be defined as any disease or infection that is naturally transmissible from vertebrate or invertebrate animals to humans and vice versa Approximately 75% of recently emerging infectious diseases affecting humans are diseases of animal origin approximately 60% of all human pathogens are zoonotic All types of potential pathogenic agents including viruses parasites bacteria and fungi can cause these zoonotic infections From the wide range of potential vectors of zoonoses insects are probably those of major significance due to their abundance high plasticity and adaptability to different kinds of pathogens high degrees of synanthropism in several groups and difficulties to apply effective programs of population control Although ticks flies cockroaches bugs and fleas are excellent insects capable to transmit viruses parasites and bacteria undoubtedly mosquitoes are the most important disease vectors Mosquito borne diseases like malaria dengue equine encephalitis West Nile Mayaro or Chikungunya are zoonoses with increasing incidence in last years in tropical and temperate countries Vertebrates can also transmit serious zoonoses highlighting the role of some carnivorous animals in rabies dissemination or the spread of rodent borne diseases in several rural and urban areas Moreover the significance of other food borne zoonoses such as taeniasis trichinellosis or toxoplasmosis may not been underestimated According to WHO FAO and OIE guidelines an emerging zoonotic disease can be defined as a zoonosis that is newly recognized or newly evolved or that has occurred previously but shows an increase of incidence or expansion in geographical host or vector range There are

many factors that can provoke or accelerate the emergence of zoonoses such as environmental changes habitat modifications variations of human and animal demography pathogens and vectors anomalous mobilization related with human practices and globalization deterioration of the strategies of vector control or changes in pathogen genetics To reduce public health risks from zoonoses is absolutely necessary to acquire an integrative perspective that includes the study of the complexity of interactions among humans animals and environment in order to be able to fight against these issues of primary interest for human health In any case although zoonoses represent significant public health threats many of them still remain as neglected diseases and consequently are not prioritized by some health international organisms      **State-of-the-art**

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