

# 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-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 (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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12190 and 12191 constitutes the refereed proceedings of the 12th International Conference on Virtual Augmented and Mixed Reality VAMR 2020 which was due to be held in July 2020 as part of HCI International 2020 in Copenhagen Denmark The conference was held virtually due to the COVID 19 pandemic A total of 1439 papers and 238 posters have been accepted for publication in the HCII 2020 proceedings from a total of 6326 submissions The 71 papers included in these HCI 2020 proceedings were organized in topical sections as follows Part I design and user experience in VAMR gestures and haptic interaction in VAMR cognitive psychological and health aspects in VAMR robots in VAMR Part II VAMR for training guidance and assistance in industry and business learning narrative storytelling and cultural applications of VAMR VAMR for health well being and medicine      Advanced Machine Learning Technologies and Applications Aboul Ella Hassanien, Mohamed Tolba, Ahmad Taher Azar, 2014-11-04 This book constitutes the refereed proceedings of the Second International Conference on Advanced Machine Learning Technologies and Applications AMLTA 2014 held in Cairo Egypt in November 2014 The 49 full papers presented were carefully reviewed and selected from 101 initial submissions The papers are organized in topical sections on machine learning in Arabic text recognition and assistive technology recommendation systems for cloud services machine learning in watermarking authentication and virtual machines features extraction and classification rough fuzzy sets and applications fuzzy multi criteria decision making Web based application and case based reasoning construction social networks and big data sets      Advances in Physical Agents Raquel Fuentetaja Pizán, Ángel García Olaya, Maria Paz Sesmero Lorente, Jose Antonio Iglesias Martínez, Agapito Ledezma Espino, 2018-11-20 The book reports on cutting edge theories and methods aimed at the control and coordination of agents acting and moving in a dynamic environment It covers a wide range of systems including multiagent systems domestic agents robotic manipulators soccer robots autonomous and semiautonomous robots as well as systems for industrial applications Advances in software agents sensors computer visions and other related areas are also thoroughly discussed and presented in detail Based on the 19th edition of the International Workshop of Physical Agents WAF 2018 held on November 22 23 2018 in Madrid Spain this book offers a snapshot of the state of the art in the field of physical agents with a special emphasis on autonomous systems such as mobile robots industrial process or other complex systems      **Image and Video Technology** Manoranjan Paul, Carlos Hitoshi, Qingming Huang, 2018-02-15 This book constitutes the thoroughly refereed post conference proceedings of the 8th Pacific Rim Symposium on Image and Video Technology PSIVT 2017 held in Wuhan China in November 2017 The total of 39 revised papers was carefully reviewed and selected from 91 submissions The Pacific Rim Symposium on Image and Video Technology PSIVT is a high quality series of symposia that aim at providing a forum for researchers and practitioners who are being involved or are contributing to theoretical advances or practical implementations in image and video technology      **Data Mining and Big Data** Ying Tan, Yuhui Shi, 2023-01-19 This two volume set CCIS 1744 and CCIS 1745 book constitutes the 7th International Conference on Data Mining and Big Data DMBD 2022 held in Beijing China in November 21 24 2022 The 62

full papers presented in this two volume set included in this book were carefully reviewed and selected from 135 submissions. The papers present the latest research on advantages in theories, technologies and applications in data mining and big data. The volume covers many aspects of data mining and big data as well as intelligent computing methods applied to all fields of computer science, machine learning, data mining and knowledge discovery, data science etc.

**Environmental Science and Information Application Technology** David Chan, 2015-06-29. Environmental Science and Information Application Technology contains selected papers from the 2014 5th International Conference on Environmental Science and Information Application Technology ESIAT 2014 Hong Kong 7-8 November 2014. The book covers a wide variety of topics: Global Environmental Change and Ecosystems Management, Graphic and I, *Cognitive Systems and Signal Processing*. Fuchun Sun, Huaping Liu, Dewen Hu, 2017-07-07. This book constitutes the refereed proceedings of the Third International Conference on Cognitive Systems and Signal Processing ICCSIP 2016 held in Beijing, China, in December 2016. The 59 revised full papers presented were carefully reviewed and selected from 171 submissions. The papers are organized in topical sections on: Control and Decision, Image and Video, Machine Learning, Robotics, Cognitive System, Cognitive Signal Processing.

**Brain-image Based Computation for Supporting Clinical Decision in Neurological and Psychiatric Disorders** Lin Shi, Feng Feng, Weidong Cai, 2021-04-07. *Digital Forensics and Watermarking* Xianfeng Zhao, Alessandro Piva, Pedro Comesaña-Alfaro, 2022-01-20. This volume constitutes the proceedings of the 20th International Workshop on Digital Forensics and Watermarking IWDW 2021 held in Beijing, China, in November 2021. The 18 full papers in this volume were carefully reviewed and selected from 32 submissions. They are categorized in the following topical headings: Forensics and Security Analysis, Watermarking and Steganology. *Computer Vision - ACCV 2016 Workshops* Chu-Song Chen, Jiwen Lu, Kai-Kuang Ma, 2017-03-14. The three volume set consisting of LNCS 10116, 10117 and 10118 contains carefully reviewed and selected papers presented at 17 workshops held in conjunction with the 13th Asian Conference on Computer Vision ACCV 2016 in Taipei, Taiwan, in November 2016. The 134 full papers presented were selected from 223 submissions. LNCS 10116 contains the papers selected.

**Omics Data Integration towards Mining of Phenotype Specific Biomarkers in Cancer - Volume II** Liang Cheng, Lei Deng, Chuan-Xing Li, Yan Zhang, Mingxiang Teng, 2022-11-29. *Machine Learning Techniques Applied to Geoscience Information System and Remote Sensing* Hyung-Sup Jung, Saro Lee, 2019-09-03. As computer and space technologies have been developed, geoscience information systems, GIS and remote sensing, RS technologies which deal with the geospatial information have been rapidly maturing. Moreover, over the last few decades, machine learning techniques including artificial neural network (ANN), deep learning, decision tree and support vector machine (SVM) have been successfully applied to geospatial science and engineering research fields. The machine learning techniques have been widely applied to GIS and RS research fields and have recently produced valuable results in the areas of geoscience environment, natural hazards and natural resources. This book is a collection representing novel contributions.

detailing machine learning techniques as applied to geoscience information systems and remote sensing

**Recent Advances in Intelligent Information Hiding and Multimedia Signal Processing** Jeng-Shyang Pan, Akinori Ito, Pei-Wei Tsai, Lakhmi C. Jain, 2018-11-10 This book features papers presented at IIH MSP 2018 the 14th International Conference on Intelligent Information Hiding and Multimedia Signal Processing The scope of IIH MSP included information hiding and security multimedia signal processing and networking and bio inspired multimedia technologies and systems The book discusses subjects related to massive image video compression and transmission for emerging networks advances in speech and language processing recent advances in information hiding and signal processing for audio and speech signals intelligent distribution systems and applications recent advances in security and privacy for multimodal network environments multimedia signal processing and machine learning Presenting the latest research outcomes and findings it is suitable for researchers and students who are interested in the corresponding fields IIH MSP 2018 was held in Sendai Japan on 26-28 November 2018 It was hosted by Tohoku University and was co sponsored by the Fujian University of Technology in China the Taiwan Association for Web Intelligence Consortium in Taiwan and the Swinburne University of Technology in Australia as well as the Fujian Provincial Key Laboratory of Big Data Mining and Applications Fujian University of Technology and the Harbin Institute of Technology Shenzhen Graduate School in China

**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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