

UNREPORTED EMISSION LINES OF Ce, La, Pb, Rb, Se, Sr, Y, AND Zr DETECTED USING LASER-INDUCED BREAKDOWN SPECTROSCOPY. K. H. Lepore¹, J. Mackie², M. D. Dyar¹, C. Ytsma³, and C. I. Fassett⁴, ¹Mount Holyoke College, Dept. of Astronomy, 50 College St., South Hadley, MA 01075 klepore@mtholyoke.edu, ²Dept. of Geology, Amherst College, 220 South Pleasant St., Amherst, MA 01002, ³Dept. of Chemistry, Smith College, Ford Hall, 100 Green Street, Northampton, MA 01063, ⁴NASA Marshall Space Flight Center, Huntsville, AL 35805.

Introduction: Information on emission lines for major and minor elements is readily available from the National Institute of Standards and Technology (NIST) as part of the *Atomic Spectra Database* [1]. However, tabulated emission lines are scarce for some minor elements and wavelength ranges given in the NIST database are limited to those included in existing studies. Previous work concerning minor element calibration curves measured using laser-induced breakdown spectroscopy found evidence of Zn emission lines that were not documented on the NIST database [2]. In this study, rock powders were doped with Rb, Ce, La, Sr, Y, Zr, Pb and Se in concentrations ranging from 10% to 10 ppm. The difference between normalized spectra collected on samples containing 10% dopant and those containing only 10 ppm were used to identify all emission lines that can be detected using LIBS in a ChemCam-like configuration at the Mount Holyoke College LIBS facility [3]. These emission spectra provide evidence of many previously undocumented emission lines.

Sample preparation and analysis: Four geochemically-diverse sample matrices were doped with 10%, 1%, 0.5%, 0.1%, 500 ppm, 250 ppm, 100 ppm, 50 ppm and 10 ppm of Rb, Ce, La, Sr, Y, Zr, Pb and Se [4]. They include a weathered basalt from Holyoke, MA, a rhyolitic volcanic glass from Mexico (locality unknown, but likely from Tequila Volcano), a Hawaiian basalt collected from Kīlauea by Tim Orr (USGS, HVO), and sea sand from Fisher Scientific.

At the higher concentrations of 10%, 1% and 0.5%, only a single dopant was used in each matrix in order to minimize interactions between the dopant and the matrix. At lower concentrations, all dopants were mixed into the same matrix. Further information on sample preparation is given in [4]. Samples were pressed into pellets for LIBS analysis and aliquots were analyzed for major and minor elements by x-ray fluorescence and inductively coupled plasma mass spectrometry by Bureau Veritas Mineral Laboratories (Vancouver BC, Canada) using standard procedures [4].

LIBS spectra were collected at Mount Holyoke in the Mineral Spectroscopy Laboratory [3] under Mars atmospheric conditions using a Quantel Ultra 100 laser operating at 1064 nm and 2.5 mJ. Spectra were recorded during 1-s integration times by three Ocean Optics HR2000+ spectrometers at wavelength ranges of 247-338 nm, 388-469 nm, and 496-848 nm. To account for heterogeneity in our powdered samples, six locations on

each pressed pellet were sampled with 50 shots per location, then all 300 shots were averaged together.

Difference spectra: To identify the emission lines for each dopant in the sampled wavelength ranges, spectra collected from a matrix with the lowest dopant concentration (10 ppm) were subtracted from spectra of the same matrix containing the highest dopant concentration (10%). Any residual emission lines remaining on this calculated “difference spectra” indicate the presence of an emission line for the dopant (**Figure 1**, column A). Difference spectra are shown with the wavelengths of reported NIST emission lines, as well as the emission lines that best correlate with dopant concentration according to r^2 values calculated at each wavelength for the entire dataset. Not only are there many emission peaks present in LIBS spectra that are not listed on the NIST database [1], but often the spectral regions with the most dopant information (identified by high r^2 values) are not represented in the NIST lines. This discrepancy can be seen for all dopants, but is especially pronounced for Ce, Y, La and Zr.

Emission lines: To verify that difference spectra represent emission lines of the dopants, spectra at each concentration were examined to ensure that difference peaks and regions of high correlation (r^2) correspond with peaks that diminish with decreasing concentrations of the dopant. Spectral regions of interest are highlighted in Figure 1, column A, and are shown for each matrix in columns B through E. Dopant peaks were identified by comparing the maximum peak for the 10% concentration with the same peak at successively lower concentrations.

Spectra of Ce, La, Y and Zr contain numerous peaks in the difference spectra, and also display many measureable peaks that decrease in magnitude with dopant concentration. LIBS spectra for these elements are rich in predictive information, and can likely be used to provide reliable quantitative information useful for geochemical analysis.

Acknowledgments: Research supported by NASA grants NNX14AG56G and NNX15AC82G and NSF grants IIS-1564083, CHE-1306133 and CHE-1307179. We thank Tim Orr for collecting the Hawaiian sample used as a matrix.

References: [1] Kramida A. et al. (2015) *NIST Atomic Spectra Database* (ver. 5.3), [online]. <http://physics.nist.gov/asd>. NIST, Gaithersburg, MD. [2] Lepore K. H. et al. (in press) *Appl. Spectrosc.* [3] Dyar M. D. et al. (2016) *LPS XLVIII*, Abstract #2205. [4] Mackie, J. et al. (2017) this volume.

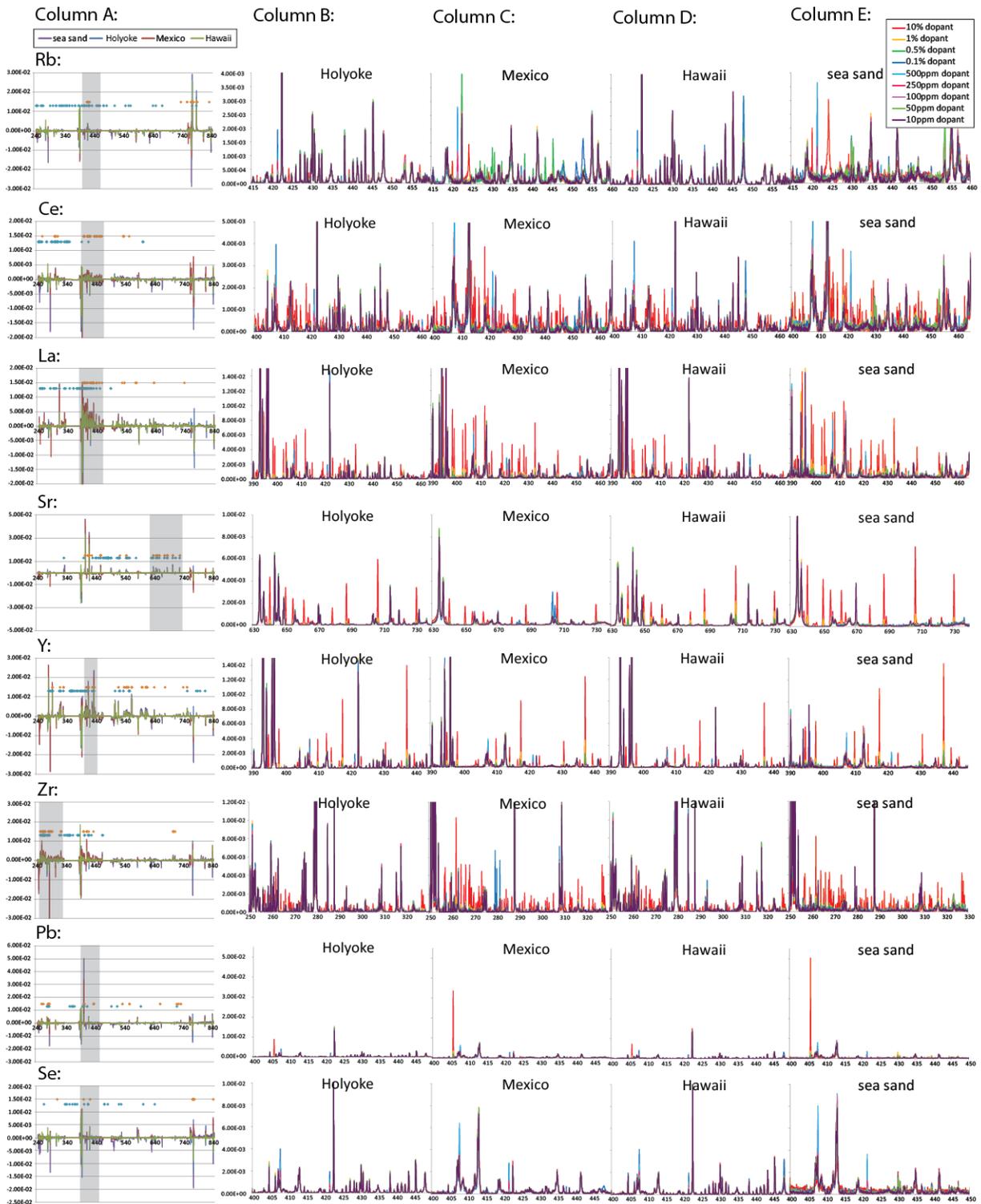


Figure 1. Column A: Difference spectra for each matrix and each dopant. The locations of NIST-reported emission lines (blue diamonds) and wavelengths with a high correlation between emission line and dopant concentration (r^2 ; orange circles) are shown. Columns B, C, D, and E: LIBS spectra for each dopant concentration in spectral regions containing the most peaks relevant to each dopant.