

LIBS ANALYSIS OF MINOR ELEMENTS IN GEOLOGIC SAMPLES. J. M. Tucker¹, M. D. Dyar², S. M. Clegg³, M. W. Schaefer⁴, R. C. Wiens³, J. E. Barefield II³. ¹Department of Astronomy, Amherst College, Amherst, MA 01002, jtucker09@amherst.edu, ²Department of Astronomy, Mount Holyoke College, 50 College St., South Hadley, MA 01075, mdyar@mtholyoke.edu, ³Los Alamos National Laboratory, P.O. Box 1663, Los Alamos, NM 87545, sclegg@lanl.gov, rwiens@lanl.gov, jbarefield@lanl.gov, ⁴Department of Geology and Geophysics, E235 Howe-Russell, Louisiana State University, Baton Rouge, LA 70803, mws@lsu.edu.

Introduction: LIBS (Laser-induced Breakdown Spectroscopy) will be used by ChemCam on the Mars Science Laboratory rover for remote elemental identification and quantification in rock and soil samples. LIBS uses a laser pulse focused onto a sample, creating a plasma of excited atoms and ions whose emissions give rise to spectroscopic features characteristic of specific ions and molecules.

Previous work on geological samples [1-3] has focused on quantification of major elemental abundances, e.g. Al, Ca, Fe, K, Mg, Mn, Na, Si, and Ti. These elements (with oxygen) typically account for >99% of the mass of the sample. This study investigates the detection and quantification of minor elements, whose abundances are typically less than a few hundred parts per million. These elements are important for ChemCam because quantifying them will facilitate detailed geochemical studies using methods heretofore employed only on terrestrial rocks. Thus, we would hope to move beyond total alkali silica classification [4] into standard methods used by geochemists to understand the origins of igneous rocks. For example, quantitative minor element analyses (routinely measured in terrestrial XRF and ICP labs) allow subdivision of weathered and altered volcanics into rock types and volcanic series like Pearce plots [5] and discrimination diagrams based on minor and trace elements [e.g. 6].

Experimental: Samples for this study are the same as those used in [2] and [3], which were analyzed for major and minor elements in Michael Rhodes' XRF lab at the Univ. of Massachusetts using standard operating procedures [7]. Rock types represent a range of common igneous compositions and also include a metamorphosed gabbro and basalt [2]. Samples were chosen because their broad range of compositions and rock types would create extended calibration curves.

The LIBS experimental conditions are chosen to mimic ChemCam operating conditions as closely as possible. Samples were placed in a vacuum chamber filled with 7 Torr CO₂. An Nd:YAG laser pulsing at 10 Hz produces the LIBS plasma. The laser energy was set to 17±1 mJ per pulse. The plasma emission was collected by an 89 mm aperture telescope situated 9 m distant from the sample. Spectra were obtained using three Ocean Optics HR2000 spectrometers covering

the spectral ranges 223-326 nm (UV), 382-471 nm (VIS), and 495-927 nm (VNIR) with resolutions of 0.1, 0.09, and 0.42 nm, respectively. The exposure time was set to 1 second to record the cumulative emissions of 10 laser shots. For each sample, five such spectra were recorded with the sample moved slightly between each exposure to account for inhomogeneities in the sample. Spectra were normalized to total intensity of each spectral region and then all spectra for a sample

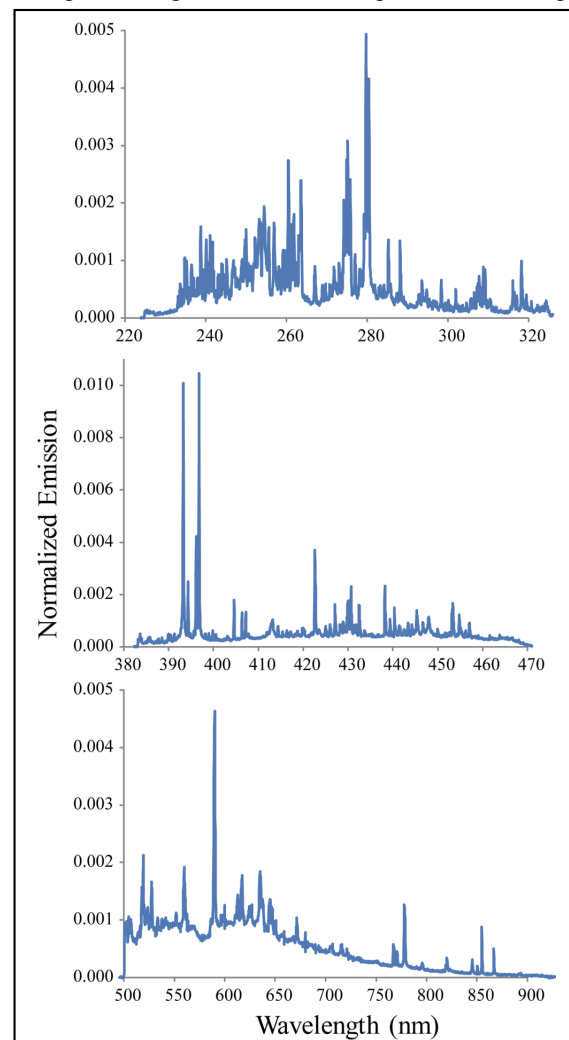


Figure 1: UV, VIS, and VNIR spectra from sample BWQC-1, a coarse-grained basaltic andesite, Westfield, MA. Each spectral channel has been normalized to the total emission intensity of its spectral region.

are averaged together. A typical LIBS spectrum is shown in Figure 1. Peaks were fit using Lorentzian lineshapes by an iterative algorithm [8], as in [3].

For a given element, a correlation coefficient is determined between each peak area and elemental concentration in all samples. The highest correlation coefficients indicate the wavelengths of the peaks whose areas are most highly correlated with concentration. High correlations do not, however, imply that the emission line is caused by the element, as explained below.

Table 1: The highest correlation coefficient (R^2) and corresponding wavelength for several trace elements, along with possible emissions taken from the NIST Atomic Spectra Database using their listed precision.

Element	R^2	Peak (nm)	NIST Database Possible Matches (nm)
Ba	0.72	245.6	Ba I: 245.24
Cr	0.96	311.3	Cr I: 310.934, 311.086
	0.96	312.4	Cr I: 311.925, 311.971
	0.96	420.9	Cr I: 420.937, Fe I: 420.03
Nb	0.59	239.5	V I: 239.290, 239.778
	0.59	386.4	Nb I: 386.338, Fe I: 386.55, V I: 386.49
Ni	0.95	311.3	Ni I: 311.412
	0.95	312.4	Mn I: 312.2874, Ni I: 312.9305
	0.95	420.9	Ni I: 420.0454, Mn I: 420.7937
V	0.92	258.7	V II: 258.9103, Fe I: 258.45
Y	0.61	419.0	Sc I: 419.3528, La I: 418.732
Zn	0.72	457.3	Fe I: 457.2860

Results: This type of statistical analysis chooses the peak with a centroid best correlated with each trace element (Table 1). However, this association does not necessarily imply causality, and may in fact lead to incorrect interpretations. For example, Th (with a maximum abundance of 5 ppm) is correlated at an R^2 of 0.56 with the area of a peak at 667.8 nm, very close to a known Th peak at 667.4697 nm in the NIST database. However, 5 ppm is well below the detection limit of the 12-bit Ocean Optics spectrometers, assuming elements like U and Th have similar irradiance as the major elements for a given concentration. This reality serves as a reminder that use of statistics is "blind," and geochemical and scientific good sense must always prevail in interpretation of the results.

However, in some cases (e.g., Ba, Ce, Cr, La, etc.), there are obvious strong lines in the NIST database associated with that particular element, and this result bodes well for possible quantification of those elements. In others, there is no known emission line for that element in the nearby wavelength range. It is then apparent that the trace element is being camouflaged or captured by another element of similar size and charge or one having a higher ionic potential (cf. Goldschmidt's Rules of Substitution). This can be seen, for example, in the case of Nb being camouflaged by V,

which is directly above it on the periodic chart. Another good example is the camouflage of Y by Sc and La. Such geochemical substitutions are not unexpected in igneous samples like those studied here.

Discussion: As noted above, many lines do not precisely correspond to those in the NIST database. The acquisition conditions of those reference spectra are likely very different from LIBS. Our results highlight the need for careful studies of emission lines in both simple systems (pure elements, elemental oxides, binary compounds, etc.) and geological samples in a LIBS setup similar to ChemCam. In order for quantitative analyses relating peak areas to element-specific emissions to be made in geological samples, rigorous statistical analyses will be needed to find multiple peaks unambiguously associated with each element. This task is complicated by the fact that elements in the NIST database have hundreds of associated emissions. These issues alone make it difficult to develop calibration procedures for LIBS lines based on first principles, and they will be complicated by the need to correct for matrix effects [2,3]. In short, it is clear that quantitative analysis based on traditional univariate analytical chemistry approaches will not be viable in our geological samples with complicated compositions. However, this work shows that for many trace elements, useful lines corresponding to emission from minor elements do exist and may be used for *qualitative* identifications and abundances.

Fortunately, empirical statistical methods that do not presume to assign specific emissions to particular elements provide an attractive alternative to traditional spectroscopic methods. This study lays the foundation for and is a crucial first step toward more detailed studies with more sophisticated statistical techniques which utilize more spectral information than a single peak area. The PLS [2] and PASRA [3] methods have been shown to overcome the problems raised here in studies of major elements, and show promise for development of more quantitative methods for measuring these minor elements.

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