A MULTI-PARAMETER LIBS REFERENCE DATABASE OF GEOLOGICAL MATERIALS: OPPORTUNITIES FOR THE PLANETARY SCIENCE COMMUNITY. K. Lepore[1], K. Bickford[1], I. Belkhodja[1], and M. D. Dyar[1,2] [1]Dept. of Astronomy, Mount Holyoke College, 50 College St., South Hadley, MA 01075, klepore@mtholyoke.edu, [2]Planetary Science Institute, 1700 E. Fort Lowell Rd Suite 106, Tucson, AZ 85719.

Introduction: Demand for high-quality LIBS spectral databases has grown over the past decade due to use of LIBS-derived elemental predictions in geochemical studies on Earth and Mars [1,2,3]. To this end, the Mineral Spectroscopy Laboratory at Mount Holyoke College (MHC) has collected a large, geochemically diverse database of LIBS spectra on four different instruments over a range of laser energies and atmospheric conditions. Dissemination of this dataset to the broader community via the NASA Planetary Data System will provide access to an invaluable resource to the planetary science community and enable improvements to the accuracy of LIBS-derived predictions.

This reference database provides spectra collected under diverse conditions analogous to those encountered by in-situ instruments on planetary surfaces. Included spectra cover a range of laser energies to mimic the effect of changing target distances as well as different ambient conditions germane to conditions on Earth, Mars, and lunar or asteroid surfaces. These data will be made publicly available on the NASA PDS Geosciences node in the near future. This database provides calibration support for LIBS flight instruments and in general for all studies that lack the range and quantity of targets needed to generate reliable models for major, minor, and trace element prediction.

Reference targets: The sample suite at MHC includes 2951 rock powders with a ≪10 µm grain size pressed into 1.6 cm diameter pellets for LIBS analysis [4]. Samples represent a diverse collection of igneous (70%), sedimentary (25%), and metamorphic (5%) rocks (**Figure 1**). Included in this database are a series of rock powders (from low-Si, high Mg-Fe basalts up to nearly pure SiO_2 sea sands) doped with trace elements [5,6]. These standards ensure that rock compositions encompass the range of concentrations in surface materials anticipated on extraterrestrial bodies. Doped elements include Ba, C, Ce, Co, Cr, Cs, Cu, Ga, La, Li, Mn, Mo, Nb, Ni, Pb, Rb, S, Sc, Se, Sn, Sr, Y, Zn, and Zr in concentrations ranging from 100 ppm to 10 wt. %.

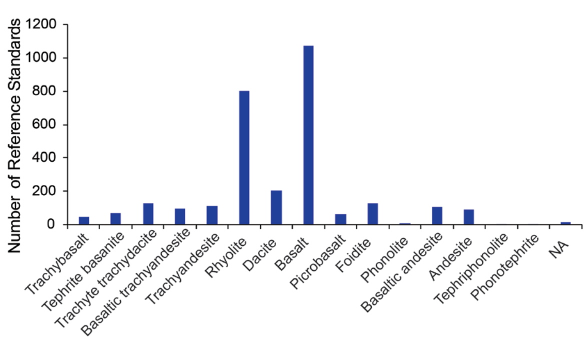

Figure 1. Distribution of rock types included in the reference target database at MHC.

Instruments: Spectra were collected using four instruments: benchtop instruments ChemLIBS and SuperLIBS, and hand-held LIBS instruments pLIBSZ300 and pLIBSZ903. The ChemLIBS instrument was originally built to provide calibration support for the ChemCam instrument onboard *MSL Curiosity*. Wavelength resolution and ranges were selected accordingly (**Table 1**). The SuperLIBS instrument is a high-sensitivity LIBS instrument built using 2D CCD detectors identical to those on SuperCam on the *Perseverance* rover. SuperLIBS was designed to collect both low- and high-resolution spectra in the VIS-NIR (VNIR) region (10K and 18K, respectively) to directly mimic SuperCam LIBS data collection. Both ChemLIBS and SuperLIBS utilize a Nd:YAG laser operated at 1064 nm, 10 Hz, with an eight ns pulse width. Laser energies for spectra in the new database range from 1.6 to 7.2 mJ. Both instruments are equipped with vacuum chambers for target analysis. These chambers facilitate collection of spectra at ambient (Earth) atmosphere, vacuum (50-200 mTorr), and 7 Torr CO_2 to mimic conditions on Mars.

The portable LIBS instruments are SciAps models Z300 and Z903. These instruments offer fewer opportunities to customize sample collection, and operate at a fixed laser energy and target distance but are becoming commonly used in terrestrial field studies.

Table 1. Instrument configurations and settings for LIBS reference database.

	Resolution (nm)			Atm.	Laser Energy
	UV	VIS	VNIR		(mJ)
SL 10K	0.08	0.08	0.41	M, E, V	2.4, 4.0, 5.6, 7.2
SL 18K	0.08	0.08	0.08	M	2.4, 4.0, 5.6, 7.2
CL	0.14	0.14	0.55	M, E, V	1.6, 2.5, 3.5
Z300	0.03			E	-
Z903	0.07-0.20			E	-

Atmospheres: M = Mars under CO_2, E = Earth in air, V = vacuum (Moon)

Instrument resolutions, laser energies, and atmospheric conditions are reported in Table 1.

Datasets: Spectra were collected on all reference targets for the ChemLIBS Mars dataset. Subsequent datasets (ChemLIBS Earth and Vacuum, all SuperLIBS, and both pLIBS) contained fewer standards because sample pellets were sometimes destroyed during analysis. The number of reference targets sampled for each dataset are reported in **Table 2**.

Table 2. Number of reference targets sampled in each instrument configuration.

Instrument/Atmosphere	Reference Targets #
SuperLIBS 10K MARS	2676
SuperLIBS 10K EARTH	2644
SuperLIBS 10K VACUUM	2858
SuperLIBS 18K MARS	2872
ChemLIBS MARS	2951
ChemLIBS EARTH	2767
ChemLIBS VACUUM	2695
pLIBS Z300	2849
pLIBS Z903	2686

Spectra vary in peak shape and distribution according to the instrumentation and atmospheric conditions of collection (**Figure 2**). The Martian atmosphere provides optimal conditions for LIBS analysis because atmospheric pressure is high enough to constrain plasma expansion, but low enough to reduce the density, and therefore optical opacity, of the plasma [7]. Spectral changes with atmosphere are readily apparent in the VNIR region (**Figure 3**). Peak widths generally increase in Earth conditions, and the peak areas and amount of material ablated are lowest under vacuum.

Spectra posted to the PDS Geosciences node will be separated and searchable according to instrument, resolution, atmosphere, and laser energy.

Objectives: The primary objective of this reference database is to provide calibration support for quantitative LIBS analyses. Few research groups have

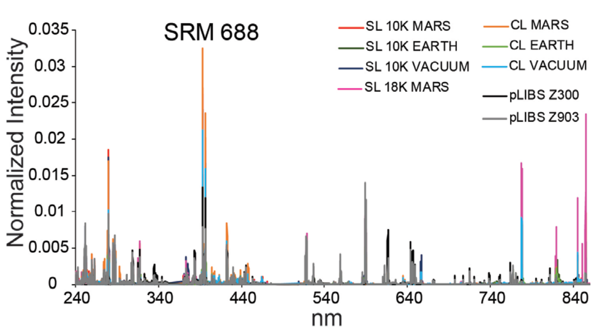

Figure 2. Full wavelength range of spectra collected on all instruments in all atmospheric conditions on reference target SRM688.

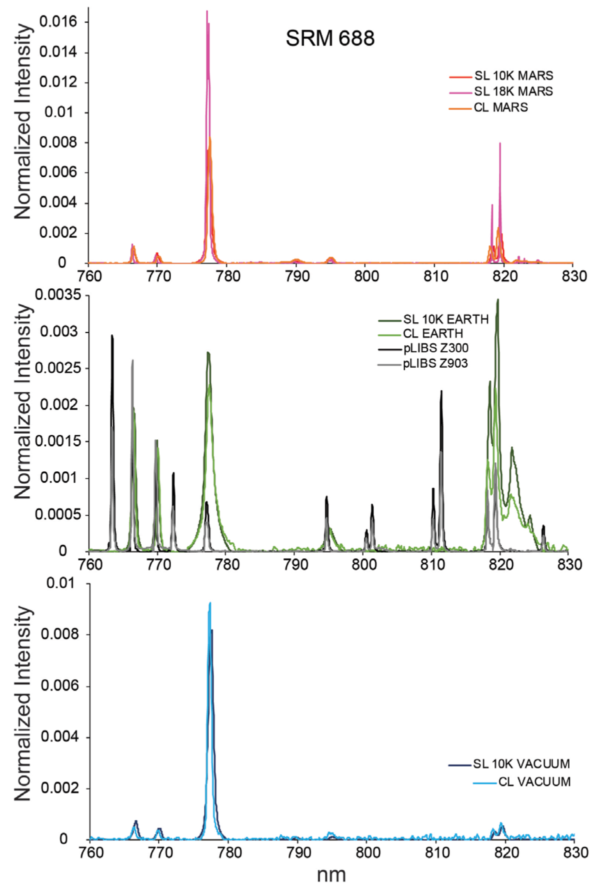

Figure 3. VNIR region of spectrum separated by atmosphere.

access to the quantity and geological diversity of calibration targets reported here. In addition, the time and effort involved in collecting such a large database under so many different conditions is beyond the scope of most projects. By publicly posting these spectra with all relevant metadata, it is our hope that researchers will be able to identify spectra that match the collection conditions and geological compositions of their unknown targets. These spectra can be used to generate robust calibrations and improve the accuracy of quantitative predictions necessary to advance the use of LIBS in planetary exploration.

Acknowledgments: This work was supported by NASA [80NSSC21K0888].

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