

# Multi-Parameter LIBS Reference Database of Geological Materials

## PDS User Guide

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## 1. Purpose

The purpose of this user guide is to provide an overview of the spectra included in a multi-parameter LIBS reference database of geological materials that is archived on the Planetary Data System. This document describes how to access spectra collected at the Mineral Spectroscopy Laboratory at Mount Holyoke College (MHC) on a series of four laser-induced breakdown spectroscopy (LIBS) instruments. It explains the instrument configuration and sample collection protocols used to collect spectra using these instruments. It also briefly describes the reference targets included in the database, as well as analytical tools that might be helpful for data analysis. It does not explain how to apply post-processing or calibration modeling to these datasets. For more information on the application of these data products, we direct the user to a series of publications from the Mineral Spectroscopy Laboratory at MHC. [1-10], as well as a Zenodo page with processing and modeling recommendations (10.5281/zenodo.8377071).

## 2. Introduction

The Mineral Spectroscopy Laboratory at MHC utilized four different LIBS instruments to collect spectra on a reference database of 2951 unique calibration targets [11, 12]. These targets have known concentrations of all 10 major element oxides as well as up to 64 minor and trace elements. Spectra were collected using two benchtop instruments (ChemLIBS and SuperLIBS), as well as two handheld instruments (pLIBS Z-300 and pLIBS Z-903).

ChemLIBS is a benchtop instrument that was built to provide calibration support to ChemCam on *MSL Curiosity* [13, 14]. ChemLIBS has three Ocean Optics HR2000+ user-configured spectrometers for the UV, VIS and VNIR ranges, each with 25  $\mu\text{m}$  slit widths. Ranges covered by ChemLIBS are 241-340 nm, 382-469 nm, and 473-905 nm in the UV, VIS, and VNIR regions, respectively. Ablation was performed using a Quantel Ultra100 laser operating at 1064 nm, up to 15 mJ/pulse, 10 Hz, with a 6-ns pulse width. The diameter of the focused laser beam at the target surface is approximately 133  $\mu\text{m}$ . An attenuator is permanently integrated into the laser, allowing power density to be varied to obtain data that match those acquired on Mars ( $\sim 2 \text{ GW}/\text{cm}^2$ ). The laser beam is passed through a 50/50 cubic beamsplitter to monitor pulse energy and focused using a plano-convex lens with a 200 mm effective focal length. A 12-inch cube vacuum chamber houses a sample tray that holds up to 16 targets. Spectra archived on PDS were collected at three different laser energies under Earth ( $\sim 760 \text{ Torr}$ ), vacuum ( $\sim 100\text{-}300 \text{ mTorr}$ ), and Mars-like (7 Torr  $\text{CO}_2$ ) conditions.

pLIBS Z-903 is a portable, hand-held instrument made by SciAps. Spectra were collected on all reference targets on a 4x3-spot grid at a single laser power and under ambient atmospheric conditions. Spectra cover a continuous wavelength range from 180 to 960 nm. Immediately prior to ablation, the pLIBS instrument releases a pulse of Ar gas to clean the target surface and remove potential contaminants.

pLIBS Z-300 is a portable, hand-held instrument made by SciAps. Spectra were collected on all reference targets on a 4x3-spot grid at a single laser power and under ambient atmospheric conditions. Spectra cover a continuous wavelength range from 180 to 961 nm. Immediately prior to ablation, the pLIBS instrument releases a pulse of Ar gas to clean the target surface and remove potential contaminants.

SuperLIBS was designed and built by Princeton Instruments using 2D CCD detectors identical to those fabricated for the SuperCam LIBS on the *Perseverance* rover [15,16]. It employs three Princeton Instruments IsoPlane-160 spectrographs for the UV, VIS and VNIR regions and uses stacked fiber

bundles to deliver light to the spectrographs and cameras. PIXIS cameras are used in the UV and VIS regions, while a PI-MAX4 camera with a gated intensifier is used in the VNIR region. High-resolution gratings in the spectrographs enable spectral resolutions up to 0.08 nm in the UV, VIS, and VNIR regions. A lower-resolution grating can also be used in the VNIR grating, with a wavelength resolution of 0.43 nm. Spectral ranges are 233-353 nm and 369-479 nm for the UV and VIS regions, respectively; high resolution VNIR spectra are collected from 496-872 nm, and low resolution NVIR spectra are collected from 499-888 nm. Ablation optics and laser are similar to ChemLIBS, with a Quantel Ultra100 laser operating at 1064 nm, up to 15 mJ/pulse, 10 Hz, with an 8 ns pulse width. The diameter of the focused laser beam at the target surface is approximately 110  $\mu\text{m}$ . The laser beam is passed through a 20/80 cubic beamsplitter to monitor pulse energy and focused using a plano-convex lens with a 300 mm effective focal length. A 24 $\times$ 24 $\times$ 18" vacuum chamber includes an automated XY translation stage to increase sample throughput to up to 100 individual targets in a single run. Spectra archived to PDS were collected at three to four different laser energies under Earth ( $\sim$ 760 Torr), vacuum ( $\sim$ 100-300 mTorr), and Mars-like (7 Torr CO<sub>2</sub>) conditions.

**2a. ChemLIBS Data Overview** LIBS spectra were collected using the ChemLIBS instrument during six 1-second integrations at each of six locations per target. Because integration times are long relative to the pulse frequency of the laser, ten plasmas are sampled during each integration. This signal is divided by the number of shots per integration (10) during spectra preprocessing so that each integration represents an average of ten shots. The first integration is always discarded in order to mitigate any surface contamination of the reference targets. "Dark" spectra were collected at identical operating conditions, but without a target surface. These were collected every fourth target, for a total of 30 integrations per dark measurement. Dark spectra consist primarily of electronic noise from the spectrometers, and are subtracted from spectra during preprocessing.

ChemLIBS spectra are preprocessed by dark subtraction, wavelength alignment to a titanium standard, correction for instrument response, and masking regions with poor instrument sensitivity. Unlike the ChemCam and SuperCam instruments, baseline removal is not performed during preprocessing [13, 14, 17]. A single file of ChemLIBS spectra contains header information, a column for wavelength, and five columns of spectral data. These data represent the average of ten shots for each 1 s integration at a single location.

**2b. pLIBS Z-903 Data Overview** pLIBS Z-903 spectra were collected using the handheld SciAps Z-903 instrument. Spectra were collected under ambient atmospheric conditions, although a pulse of compressed Ar gas was released prior to ablation. Spectra were collected on a 4 $\times$ 3 raster grid. Spectra were resampled onto a standard wavelength axis and all 12 datapoints were averaged into a single measurement prior to data export from the instrument. A single file of pLIBS Z-903 spectra contains a column for wavelength, and one column of spectral data.

**2c. pLIBS Z-300 Data Overview** pLIBS Z-300 spectra were collected using the handheld SciAps Z-300 instrument. Spectra were collected under ambient atmospheric conditions, although a pulse of compressed Ar gas was released prior to ablation. Spectra were collected on a 4 $\times$ 3 raster grid. Spectra were resampled onto a standard wavelength axis and all 12 datapoints were averaged into a single measurement prior to data export from the instrument. A single file of pLIBS Z-300 spectra contains a column for wavelength, and one column of spectral data.

**2d. SuperLIBS Data Overview** LIBS spectra were collected using the SuperLIBS instrument at three to four laser energies at up to five locations each on a single reference target. Single-shot spectra were collected during thirty 10 ms integrations at each location. During high-resolution (18K) Mars and

vacuum spectra collection, the first shot was always discarded in order to remove any contamination on the target surface due to dust present in the chamber during ablation. For low-resolution (10K) Mars and Earth spectra, the first five shots were discarded due to the possibility of increased sample mass ablation and cross-contamination among reference targets under these conditions.

SuperLIBS 18K spectra were collected using a high-resolution grating in the VNIR region. These spectra were collected in order to match or exceed the resolution of any instruments used in current or future field studies. In order to collect spectra across the entire VNIR region, ten wavelength ranges of approximately 45 nm each were sampled at one location per range. Ranges overlapped by up to ~5 nm to allow concatenation at points within the overlapping ranges that did not contain visible peaks. Similarly, two overlapping ranges were employed in the UV and VIS regions for all spectra, and in the VNIR region for 10K spectra (Earth, Vacuum, and Mars). These ranges covered approximately 50 nm (UV and VIS) and 150 nm (VNIR). Lower resolution spectra (10K) are likely to match spectra collected by most benchtop or handheld instruments with respect to peak shape and resolution.

A total of ten locations were sampled at each laser energy on each target. For spectral regions with two overlapping ranges (UV, VIS, and low-resolution VNIR), five locations were sampled at each range; for the ten high-resolution VNIR ranges, one location was sampled for each range. Spectra were concatenated during preprocessing to produce a continuous spectrum in each region (UV, VIS, and VNIR) for each target.

“Dark” spectra were collected every 25 targets under identical conditions, but without a laser pulse. As with ChemLIBS, these dark spectra consist primarily of electronic noise from the cameras, and are subtracted from spectra during preprocessing.

SuperLIBS spectra are preprocessed by dark subtraction, wavelength alignment to a titanium standard, correction for instrument response, masking regions with poor instrument sensitivity, and concatenation of wavelength ranges. Unlike the ChemCam and SuperCam instruments, baseline removal is not performed during preprocessing [13, 14, 17]. A single file of SuperLIBS spectra contains header information, a column for wavelength, and 25-29 columns of spectral data. Each column of data represents a single laser shot at one location.

### 3. Applicable Documents

1. Boucher, T.F., Ozanne, M.V., Carmosino, M.L., Dyar, M.D., Mahadevan, S., Breves, E.A., Lepore, K.H., Clegg, S.M. (2015) A study of machine learning regression methods for major elemental analysis of rocks using laser-induced breakdown spectroscopy. *Spectrochim. Acta B*, 107 (2015) 1-10, doi:10.1016/j.sab.2015.02.003
2. Giguere, S., Carey, C., Dyar, M.D., Boucher, T.F., Parente, M., Tague, T.J., Mahadevan, S. (2015) Baseline removal in LIBS and FTIR spectroscopy: optimization techniques. *Lunar Planet. Sci. XLVI*, Lunar Planet. Inst., Houston, #2775 (abstr.)
3. Dyar, M.D., Giguere, S., Carey, C.J., and Boucher, T. (2016a) Comparison of baseline removal methods for laser-induced breakdown spectroscopy of geological samples. *Spectrochim. Acta B*, 126, 53-64. doi/10.1016/j.sab.2016.10.018
4. Dyar, M.D., Fassett, C.I., Giguere, S., Lepore, K., Byrne, S., Boucher, T., Carey, C.J., and Mahadevan, S. (2016b) Comparison of univariate and multivariate models for prediction of major and minor elements from laser-induced breakdown spectra with and without masking. *Spectrochim. Acta B*, 123, 93-104. doi/10.1016/j.sab.2016.07.010
5. Lepore, K.H., Fassett, C.I., Breves, E.A., Byrne, S., Giguere, S., Boucher, T., Rhodes, J.M., Vollinger, M., Anderson, C.H., Murray, R.W., and Dyar, M.D. (2017) Matrix effects in

- quantitative analysis of laser-induced breakdown spectroscopy of rock powders doped with Cr, Mn, Ni, Zn, and Co. *Appl. Spectros.*, 71, 600-626. doi/10.1177/0003702816685095
6. Ytsma, C.R., Knudson, C.A., Dyar, M.D., McAdam, A.C., Michaud, D.D., Rollosso, L.M. (2020) Accuracies and detection limits of major, minor, and trace element quantification in rocks by portable laser-induced breakdown spectroscopy. *Spectrochim. Acta B*, 171, 105946. Doi/10.1016/j.sab.2020.105946
  7. Dyar, M.D., and Ytsma, C.R. (2021) Effect of data set size on geochemical quantification accuracy with laser-induced breakdown spectroscopy. *Spectrochim. Acta B*, 177 (2021) 106073, doi:10.1016/j.sab.2021.106073
  8. Lepore, K.H., Ytsma, C.R., and Dyar, M.D. (2022) Quantitative prediction accuracies derived from laser-induced breakdown spectra using optimized multivariate submodels. *Spectrochim. Acta B*, 191 (2022) 106408, doi:10.1016/j.sab.2022.106408
  9. Ytsma, C.R., Dyar, M.D. (2022) Calculations of and effects on quantitative limits for multivariate analyses of geological materials with laser-induced breakdown spectroscopy. *Spectrochim. Acta B*, 191, 106395. doi/10.1016/j.sab.2022.106395
  10. Lepore, K.H., Dyar, M.D., and Ytsma, C.R. (2023) Effect of plasma temperature on major element prediction accuracy from laser-induced breakdown spectroscopy. *Geophys. Res. Lett.*, 50, e2023GL102919. doi:10.1029/2023GL102919
  11. Dyar, M.D., Breves, E.A., Lepore, K.H., Boucher, T.F., Bender, S., Tokar, R., Berlanga, G., Clegg, S.M., and Wiens, R. (2015b) Calibration suite for Mars-analog laser-induced break-down spectroscopy. *Lunar Planet. Sci. XLVI*, Lunar Planet. Inst., Houston, #1510 (abstr.)
  12. Dyar, M.D., Ytsma, C.R., and Lepore, K. (2019) Standards for geochemical analysis of major, minor, and trace elements in rock powders. *Lunar Planet. Sci. L*, Lunar Planet. Inst., Houston, (abstr.#1396)
  13. Wiens, R.C., Maurice, S., Lasue, J., Forni, O., Anderson, R.B., Clegg, S., et al. (2013) Pre-flight calibration and initial data processing for the ChemCam laser-induced breakdown spectroscopy instrument on the Mars Science Laboratory rover. *Spectrochimica Acta Part B*, 82 (2013) 1-27, doi:10.1016/j.sab.2013.02.003
  14. Clegg, S., Wiens, R. C., Anderson, R., Forni, O., Frydenvang, J., Lasue, J., et al. (2017) Recalibration of the Mars Science Laboratory ChemCam instrument with an expanded geochemical database. *Spectrochimica Acta, Part B*, 129, 64-85, doi:10.1016/j.sab.2016.12.003
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  16. Wiens, R.C., et al. (2021) The SuperCam instrument suite on the NASA Mars 2020 rover: body unit and combined system tests. *Space Sci Rev* (2021) 217:4, doi:10.1007/s11214-020-00777-5
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  18. Rhodes, J.M. (1988) Geochemistry of the 1984 Mauna Loa eruption: implications for magma storage and supply. *J. of Geophys. Res.*, 93(85), 4453-4466
  19. Rhodes, J.M. and Vollinger, M.J. (2004) Composition of basaltic lavas sampled by phase-2 of the Hawaii Scientific Drilling Project: Geochemical stratigraphy and magma types. *G<sup>3</sup>*, 5(3), Q03G13, doi:10.1029/2002GC000434
  20. Laura, J. R., Gaddis, L. R., Anderson, R. B., & Aneece, I. P. (2022) Introduction to the Python Hyperspectral Analysis Tool (PyHAT), In *Machine Learning for Planetary Science*, Elsevier. doi: [10.1016/B978-0-12-818721-0.00012-4](https://doi.org/10.1016/B978-0-12-818721-0.00012-4)

#### 4. PDS Location

The LIBS Reference Database is organized into one PDS bundle with five collections. The Logical Identifier (LID) for the bundle is urn:nasa:pds:libs\_reference\_database. Collection products include: ChemLIBS Reference Spectra, pLIBS Z-903 Reference Spectra, pLIBS Z-300 Reference Spectra and SuperLIBS Reference Spectra archived in four collections: data\_chemlibs, data\_plibs\_z903, data\_plibs\_z300 and data\_superlibs, respectively. Users will mostly likely want to separate data within a collection by laser energy and/or atmosphere when applicable. In addition, there is a document collection containing this user's guide, a metadata spreadsheet, and release notes. The bundle may be located online at: <https://doi.org/10.17189/b2aj-cz96>.

#### 5. LIBS Reference Spectra

The spectra obtained using the ChemLIBS and SuperLIBS instruments have undergone similar preprocessing steps to those applied to ChemCam and SuperCam spectra, with the notable exception of baseline removal. ChemLIBS and SuperLIBS spectra available on the PDS repository have undergone removal of dark spectra, correction for instrument response, alignment to a Ti wavelength standard, and masking of regions of low instrument sensitivity. These spectra are reported in units of spectral radiance (photons\*cm<sup>-2</sup>\*λ<sup>-1</sup>\*sr<sup>-1</sup>\*pulse<sup>-1</sup>). The spectra collected on the two pLIBS instruments are resampled onto a standard wavelength axis; however, the information needed to apply a correction for instrument response is not available. Therefore, these spectra are reported in arbitrary units of intensity.

**5a.** File names for spectra collected on all instruments are related to the reference target identification and sampling conditions (for ChemLIBS and SuperLIBS). Naming conventions are given in tables 5a. 1-4; file name components are listed in **bold**.

<b>5a. i.</b> Table 1. ChemLIBS File Naming Scheme		
Characters	Field	Contents
1-3	Product type	<b>mh6</b> indicates preprocessed spectra collected at MHC
4		Underscore for readability
5-12	Date	Date of analysis and run number (R) (YYMMDDRR)
13-15	<b>ccs</b>	Clean Calibrated Spectra <sup>1</sup>
16		Underscore for readability
MARS spectra:		
17-20	Atmosphere	<b>mars, earth, or vacuum</b> identification of atmosphere
21		Underscore for readability
22-27	Target and Location	Target and location information for spectrum
28		Underscore for readability
29-end	Target ID	Reference target identification followed by <b>_spect</b>
EARTH spectra:		
17-21	Atmosphere	<b>mars, earth, or vacuum</b> identification of atmosphere
22		Underscore for readability
23-28	Target and Location	Target and location information for spectrum
29		Underscore for readability
30-end	Target ID	Reference target identification followed by <b>_spect</b>
VACUUM spectra:		
17-22	Atmosphere	<b>mars, earth, or vacuum</b> identification of atmosphere
23		Underscore for readability
24-29	Target and Location	Target and location information for spectrum
30		Underscore for readability

31-end	Target ID	Reference target identification followed by <b>_spect</b>
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<sup>1</sup> **ccs** does not correlate directly to ChemCam or SuperCam because ChemLIBS spectra are not corrected for baseline removal.

Example Filename for ChemLIBS:

**mh6\_16080201ccs\_mars\_t02105\_iah250\_spect.csv**

<b>5a. ii.</b> Table 2. pLIBS Z-903 File Naming Scheme		
Characters	Field	Contents
1-5	Instrument ID	<b>plibs</b>
6		Underscore for readability
7-10	Instrument ID	<b>z903</b> to distinguish between pLIBS instruments
11		Underscore for readability
12-end	Target ID	Reference target identification

Example Filename for pLIBS Z-903:

**plibs\_z903\_1d13.csv**

<b>5a. iii.</b> Table 4. pLIBS Z-300 File Naming Scheme		
Characters	Field	Contents
1-5	Instrument ID	<b>plibs</b>
6		Underscore for readability
7-10	Instrument ID	<b>z300</b> to distinguish between pLIBS instruments
11		Underscore for readability
12-end	Target ID	Reference target identification

Example Filename for pLIBS Z-300:

**plibs\_z300\_04g029b.csv**

<b>5a. iv.</b> Table 3. SuperLIBS File Naming Scheme		
Characters	Field	Contents
1-3	Product type	<b>mh6</b> indicates preprocessed spectra collected at MHC
4		Underscore for readability
5-12	Date	Date of preprocessing and run number (R) (YYMMDDRR)
13-15	<b>ccs</b>	Clean Calibrated Spectra <sup>1</sup>
16		Underscore for readability
MARS spectra:		
17-20	Atmosphere	<b>mars, earth, or vacuum</b> identification of atmosphere
21		Underscore for readability
22-27	Target and Location	Target and location information for spectrum
28		Underscore for readability
29-end	Target ID	Reference target identification followed by <b>_spect</b>
EARTH spectra:		
17-21	Atmosphere	<b>mars, earth, or vacuum</b> identification of atmosphere
22		Underscore for readability

23-28	Target and Location	Target and location information for spectrum
29		Underscore for readability
30-end	Target ID	Reference target identification followed by <b>_spect</b>
VACUUM spectra:		
17-22	Atmosphere	<b>mars, earth, or vacuum</b> identification of atmosphere
23		Underscore for readability
24-29	Target and Location	Target and location information for spectrum
30		Underscore for readability
31-end	Target ID	Reference target identification followed by <b>_spect</b>

<sup>1</sup> **ccs** does not correlate directly to ChemCam or SuperCam because SuperLIBS spectra are not corrected for baseline removal.

Example Filename for SuperLIBS:

**mh6\_20092402ccs\_vacuum\_t00101\_rvw862\_spect.csv**

**5b.** File formats are nearly identical between ChemLIBS and SuperLIBS, and between pLIBS Z-903 and pLIBS Z-300. The ChemLIBS and SuperLIBS instruments were used under a range of experimental conditions, all of which must be reported in spectra files. Therefore, the file formats for these instruments are more detailed than the formats used for the two pLIBS instruments.

<b>5b. i.</b> ChemLIBS Header and Data Unit (HDU) contents		
Row:	Relevant HDU section	Content
1	Header	Date and time
2	Header	Carousel number; corresponds to analysis date and run number (R) (YYMMDDRR)
3	Header	Sample ID
4	Header	Target number
5	Header	Location on sample
6	Header	Rock type
7	Header	Atmosphere type
8	Header	Distance to target (mm)
9	Header	Locations per sample
10	Header	Integrations per location
11	Header	Pulses per integration
12	Header	Laser attenuation
13	Header	Laser repetition rate (Hz)
14	Header	Integration time (s)
15	Header	Integrations averaged
16	Header	UV trigger delay (ns)
17	Header	VIS Trigger delay (ns)
18	Header	VNIR trigger delay (ns)
19	Header	Dark subtracted (yes or no)
20	Header	Boxcar smoothing
21	Header	Pulses discarded
22	Header	Spectral columns discarded
23	Header	Saturated integrations
24	Header	Wavelength (nm)   Integration number (1-5)

25-end	Data	Wavelength (nm)	Spectral intensity
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<b>5b. ii. pLIBS Z-903 Header and Data Unit (HDU) contents</b>			
Row:	Relevant HDU section	Content	
1	Header	Wavelength (nm)	Intensity
2-end	Data	Wavelength (nm)	Intensity (arbitrary units)

<b>5b. iii. pLIBS Z-300 Header and Data Unit (HDU) contents</b>			
Row:	Relevant HDU section	Content	
1	Header	Wavelength (nm)	Intensity
2-end	Data	Wavelength (nm)	Intensity (arbitrary units)

<b>5b. iv. SuperLIBS Header and Data Unit (HDU) contents</b>			
Row:	Relevant HDU section	Content	
1	Header	Date and time of spectra collection	
2	Header	Carousel numbers; correspond to date and run number (R) for each analysis (YYMMDDRR); two numbers for 10K spectra; ten for 18K spectra	
3	Header	Sample ID	
4	Header	Target number	
5	Header	Location on sample	
6	Header	Rock type	
7	Header	Atmosphere type	
8	Header	Distance to target (mm)	
9	Header	Locations per sample	
10	Header	Integrations per location	
11	Header	Pulses per integration	
12	Header	Laser attenuation	
13	Header	Laser repetition rate (Hz)	
14	Header	Integration time (s)	
15	Header	Integrations averaged	
16	Header	UV trigger delay (ns)	
17	Header	VIS Trigger delay (ns)	
18	Header	VNIR trigger delay (ns)	
19	Header	Dark subtracted (yes or no)	
20	Header	Boxcar smoothing	
21	Header	Pulses to discard	
22	Header	Spectral columns discarded	
23	Header	Saturated integrations	
24	Header	Wavelength (nm)	Integration number (1-up to 29)
25-end	Data	Wavelength (nm)	Spectral intensity

## 6. Reference Target Metadata

Reference targets utilized in this spectral database include 2951 unique geochemical samples, including 484 rock powders doped with minor and trace elements ranging in concentration from 10 wt. % to 10 ppm. The distribution of rock types is approximately 70% igneous, 25% sedimentary, and 5% metamorphic. Within the dataset, there are also seven pure metal standards and seven calibration targets from the *MSL Curiosity* calibration dataset. Concentrations of major and minor elements, sample location and provenance, material type and rock type are all listed in the data labels for each spectrum available on the PDS database.

Element compositions in doped standards were measured by ICP-ES after lithium borate fusion at Bureau Veritas Minerals ([www.bureauveritas.com/um](http://www.bureauveritas.com/um)). These standards are identified with the term “mix” in the sample name.

The sample collection provided by Michael Rhodes at the University of Massachusetts, Amherst (UMass) comprises approximately one third of all standards. These were analyzed at the UMass X-Ray Fluorescence (XRF) facility according to procedures described in Rhodes et al., 1988 and Rhodes and Vollinger, 2004 [18,19]. Precision of major element analyses were calculated from duplicate analyses and ranged from <1% (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, and K<sub>2</sub>O) to ~2-4% (MnO, Na<sub>2</sub>O, and P<sub>2</sub>O<sub>5</sub>) of the average concentration.

Prior to LIBS analysis, rock powders with a <<10 μm grain size were pressed into 1.6 cm diameter pellets under four tons pressure for three minutes, forming a flat, uniform sample surface. A more detailed description of reference targets can be found elsewhere [10,11].

## 7. Target Name

All reference targets have a unique target name and are listed in the metadata spreadsheet located in the document collection of this bundle, LID:  
urn:nasa:pds:libs\_reference\_database:document:libs\_metadata.

## 8. Software and Tools

Spectral analysis can be conducted by means of a range of computational programs (Matlab, Python, etc.). One tool specifically designed for use with LIBS spectra is the PyHAT program developed by the USGS [20].

## 9. Spectra Collection and Datasets

Spectra collected on all instruments vary slightly, although every attempt was made to maintain consistency among the datasets for each instrument. Reference targets were sampled in approximately the following order: ChemLIBS Mars, ChemLIBS Earth, ChemLIBS Vacuum, pLIBS Z-300, SuperLIBS 18K Mars, SuperLIBS 10K Vacuum, pLIBS Z-903, SuperLIBS 10K Mars, and SuperLIBS 10K Earth. The number of spectra collected using each instrument under each set of collection protocols are listed in Table 5.

ChemLIBS and SuperLIBS collect spectra at a range of laser energies, determined by adjusting the attenuation of a 100 mJ ablation laser. Values for laser attenuation are listed in spectra labels and are used for spectra organization. However, the presence of a beamsplitter in both instruments (50/50 and 80/20 for ChemLIBS and SuperLIBS, respectively) alters the actual laser energy on target (listed in Table 5). ChemLIBS laser attenuation settings were 3.2, 5, and 7 mJ, which correspond to laser energies on

target of 1.6, 2.5, and 3.5 mJ. SuperLIBS laser attenuations settings were 3, 4, 5, 7, and 9 mJ, which correspond to laser energies on target of 2.4, 3.2, 4.0, 5.6, and 7.2 mJ.

Table 5. Spectra collected at each instrument configuration.

Instrument/Atm	Resolution (nm)			Laser Energy								
	UV	VIS	VNIR	1.6mJ	2.4mJ	2.5mJ	3.2mJ	3.5mJ	4.0mJ	5.6mJ	7.2mJ	unkn
SuperLIBS 10K MARS	0.08	0.08	0.41	-	334500	-	-	-	334500	334500	334500	-
SuperLIBS 10K EARTH	0.08	0.08	0.41	-	330500	-	281625	-	330500	48250	48250	-
SuperLIBS 10K VACUUM	0.08	0.08	0.41	-	414410	-	-	-	414410	414352	414265	-
SuperLIBS 18K MARS	0.08	0.08	0.08	-	83317	-	-	-	83317	83288	83317	-
ChemLIBS MARS	0.14	0.14	0.55	88215	-	86950	-	90685	-	-	-	-
ChemLIBS EARTH	0.14	0.14	0.55	78530	-	83025	-	78690	-	-	-	-
ChemLIBS VACUUM	0.14	0.14	0.55	78975	-	80850	-	80760	-	-	-	-
pLIBS Z-903	.07 to .20					-	-	-	-	-	-	-
pLIBS Z-300	0.03					-	-	-	-	-	-	-

Due to differences in the focusing optics of SuperLIBS and ChemLIBS, identical laser energies would not exactly correspond to the same energy density on target. This is a primary reason why we chose to sample up to four different laser energies for all datasets. With a range of laser energies, we can hope to find common ground among different instruments.

As spectra collection progressed, some reference targets became unusable. For this reason, more targets are sampled for the earlier runs (ChemLIBS and SuperLIBS 18K Mars and 10K Vacuum). When direct comparisons are made among instruments, we recommend using a subset of data collected on all instruments (2503 unique targets). The number of reference targets sampled under each instrument configuration are listed in Table 6.

Table 6. Reference Targets sampled under 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 Z-903	2686
pLIBS Z-300	2849

LIBS spectra collected under Earth atmospheric conditions cause more damage to the target surface. After analyzing some targets with the four laser attenuation settings used for Mars and vacuum conditions, we chose to sample three lower laser energies (3, 4, and 5mJ) in order to mitigate damage done to the targets. Therefore, all samples were analyzed in Earth conditions at laser attenuation settings of 3 and 5 mJ, most were analyzed at 3, 4, and 5 mJ, and approximately 380 were analyzed at 3, 5, 7, and 9 mJ.

## **10. Additional Resources**

Additional help can be found on [zenodo.org](https://zenodo.org) at doi: [10.5281/zenodo.8377071](https://doi.org/10.5281/zenodo.8377071). These resources include post processing steps used by our research group to improve data performance. It also includes a series of protocols for using these spectra within the PyHAT program developed by the USGS [20].