

Study of micro-laser-induced breakdown spectroscopy (μ LIBS) for applications in planetary exploration.

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Abstract

Laser-induced breakdown spectroscopy (LIBS) is a type of atomic emission spectroscopy which uses a laser to create a plasma on the surface of a target material. Light collected from the plasma will show characteristic emission lines coming from unique deexcitation transitions within the atoms comprising the sample. LIBS is particularly useful for remote planetary exploration because it requires relatively simple components and has the ability to perform measurements of any type of target without the need for sample preparation. Micro-LIBS (μ LIBS) is a variant of LIBS using μ J laser pulse energies and μ m spatial sampling scales. An investigation of μ LIBS for geologic samples has only been performed twice before, on the minerals hematite and ilmenite. The Canadian Space Agency (CSA), in partnership with MDA, Institut nationale d'optique/National Optics Institute (INO) and York University, are combining μ LIBS with two similar analytical techniques – Raman and fluorescence spectroscopy – to develop the LIBS/Raman sensor (LIRS). The performance of the LIRS instrument was characterized, and was found to be competitive with other single-mode instruments, including ChemCam, and others. An investigation into the capabilities and limitations of μ LIBS was extended to include 38 geologic standard materials. Concurrently, a separate μ LIBS system was designed and constructed with the intent to further explore feasibility of μ LIBS on specific sample types in various environmental conditions.

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Contents

Abstract	ii
Acknowledgements	iii
Table of Contents	iv
List of Tables	viii
List of Figures	x
List of Abbreviations	xv
List of Symbols	xvi
1 Introduction	1
1.1 Laser-Induced Breakdown Spectroscopy	1
1.2 Research Motivation	3
1.3 Research Goals	4
1.4 Thesis Overview	5
2 Background	6
2.1 LIBS Systems in the Context of Space Exploration	6
2.1.1 Brief history of elemental analysis instruments in space	6
2.1.2 Curiosity rover: ChemCam instrument	7
2.1.3 Future LIBS instruments	8
2.2 Physics of LIBS	9
2.3 Obtaining quantitative information from LIBS	16
2.4 Techniques similar to LIBS	17
2.5 μ LIBS	18
2.5.1 μ LIBS in the literature: metal alloys	20
2.5.2 μ LIBS in the literature: geologic-type standards	21

3	μLIBS System	22
3.1	μLIBS system design	22
3.1.1	Paraxial ray tracing	30
3.1.2	Using gaussian beam optics	32
3.1.3	Modelling in optical design software	34
3.2	Verification of performance	34
4	The LIBS/Raman Sensor (LIRS)	38
4.1	LIRS Concept	38
4.2	LIBS mode	41
4.3	Raman mode	41
4.4	Laser-induced fluorescence (LIF) mode	44
4.5	Science Team at York University	45
5	LIRS Performance Characterization Strategy	47
5.1	LIBS, Raman, and fluorescence objectives	47
5.2	Samples and sample preparation	48
5.3	LIBS characterization methods	52
5.4	Raman characterization methods	54
5.5	Fluorescence characterization methods	54
5.6	Combined methods	55
5.7	Performance and sensitivity test summary	55
6	LIRS Characterization Results: Phase 1	59
6.1	Raman mode Results	59
6.2	μLIBS mode Results	62
6.3	LIF mode Results	62
6.4	Breadboard upgrades	62
7	LIRS Characterization Results: Phase 2	63
7.1	Samples and Sample Preparation	63
7.2	Instrument Calibration	68

7.3	Raman Characterization	74
7.3.1	Comparison to previous breadboard	74
7.3.2	Optimal acquisition parameters	75
7.3.3	Results at 35 cm	76
7.3.4	Organic Limits of Detection (LODs)	81
7.3.5	Multivariate analysis	85
7.3.6	Comparison at other sensing distances	87
7.3.7	Other measurements: size of focus	88
7.4	μ LIBS Characterization	88
7.4.1	Comparison to previous breadboard	88
7.4.2	Optimal acquisition parameters	90
7.4.3	Spectral pre-treatment	91
7.4.4	Results at 35 cm	93
7.4.5	Elemental Limits of Detection (LODs)	102
7.4.6	Multivariate analysis	113
7.4.7	Comparison at other sensing distances	121
7.4.8	Other Measurements	122
7.5	LIF Characterization	125
7.5.1	Results at 35 cm	125
7.5.2	Time-resolved fluorescence	130
7.6	Passive reflectance measurements	131
7.7	Combined characterization	134
7.8	Implications for LIRS flight concept	136
7.9	LIRS flight concept	137
8	μLIBS Experiments	139
9	Conclusion	148
10	Future Work	150
	Bibliography	153

Appendices	160
A ICA and PLS algorithms	160
B LIRS: μ LIBS whole rock spectra	165
C Polishing SMA-905 fiber connectors	167

List of Tables

2	Elementary interactions between atoms and light (* denotes an excited state). Adapted from [57]	10
3	Performance of some μ LIBS instruments.	20
4	Validation of system parameters for the 532 nm μ LIBS system.	29
5	LIRS instrument requirements.	40
6	Certified major element compositions (in oxide wt%) for selected geological standards	50
7	Organic compounds for Raman/LIF analysis	51
8	Summary of Phase 1 Raman measurement results.	60
9	Summary of Phase 1 LIBS measurement results.	61
10	Certified concentrations of all geological standards used in LIRS characterization. . .	66
10	Table 9 Continued.	67
11	Typical acquisition parameters for Raman measurements. Each spectrum in this report was acquired using parameters following these guidelines.	74
12	Summary of Phase 2 Raman measurement results for (a) geologic standards and (b) organic samples.	79
13	Summary of RSD and average intensity values from both Phase 1 and Phase 2 of the characterization plan for four different lines in ilmenite and manganese ore. . . .	89
14	Typical acquisition parameters for LIBS measurements. Each spectrum in this report was acquired using parameters following these guidelines.	90
15	Summary of Phase 2 LIBS measurement results.	97
16	Line parameters for those lines selected for calibration curve analysis. A_{mn} is the Einstein coefficient and g_m and E_m are the degeneracy and energy of the upper energy level, respectively.	104
17	Limits of detection (LODs) for major elements determined using primitive calibration curves.	107
18	Prediction of elemental concentrations of granite including errors in prediction. . . .	111
19	Limits of detection (LODs) for major elements calculated from calibration curves created using internal normalization.	114

20	Comparison of LODs from LIRS with similar instruments.	117
21	Comparison of prediction capabilities between LIRS and ChemCam using advanced PLS algorithm.	118
22	Mean LIBS crater sizes on each standard from 5 pulses.	125
23	Typical acquisition parameters for LIF measurements. Each spectrum in this report was acquired using parameters following these guidelines.	126
24	Summary of Phase 2 LIF measurement results for (a) geologic standards and (b) organic samples.	129
25	Prediction of elemental concentrations of quartz latite including errors in prediction using advanced PLS model.	136
26	Comparison of laser parameters for this study and for ChemCam and SuperCam. . .	136
27	1064 nm reflectance before and after a LIBS measurement for geologic standards and aluminum. $\Delta\%R$ is the change in reflectance. Bolded entries are those samples which produce a successful single-shot μ LIBS spectrum.	141

List of Figures

1	Graphical representation of characteristic atomic emissions.	2
2	Number of papers found with both key words “LIBS” and “space” per year (via Google Scholar).	8
3	Visualization of a LIBS event.	9
4	Temporal evolution of a typical LIBS event. Early after the laser pulse spectra are dominated by continuum emission, and only later are characteristic emissions visible. Adapted from [41].	12
5	Atomic processes occurring during a LIBS event.	15
6	An example of a LIBS spectra (turkey skin). Taken from [12].	15
7	Example of a calibration curve.	16
8	Laser peak irradiance versus beam waist radius for various peak powers. The ablation threshold given throughout LIBS literature is 1 GW/cm^2 . See Section 3.1, page 26 for a thorough explanation of focusing Gaussian beams.	19
9	Internal components of the ME5000 (Credit: Andor).	23
10	Arrangement of orders in the focal plane of the ME5000.	24
11	Simplified schematic of the μ LIBS instrument design (in Configuration 1).	25
12	Flowchart of the optical design process.	26
13	Propagation of a Gaussian beam in air. The radius of the beam $w(z)$ is at the smallest value at the <i>beam waist</i> w_0 and expands outwards based on the full angle divergence Θ and the radius of curvature R	26
14	Power of Gaussian beam transmitted past an edge as it is translated across, perpendicular to the optical axis.	27
15	Characterization of laser performance. Top: measurement of beam waist size and laser quality (M^2). Bottom: measurement of spot size formed using a $f = 35 \text{ mm}$ lens. 28	
16	Schematic of the optical system used to collimate and focus the beam from the fiber (FI) to the sample surface (far right).	33
17	Beam waist radius at the target in Configuration 1.	35
18	The μ LIBS system in configuration 1.	36

19	An example of a LIBS spectra of aluminium using the 532 nm μ LIBS instrument. . .	36
20	Schematic overview of the LIRS concept instrument. The blue and red lines represent the paths of the UV and IR lasers, respectively, and the yellow represents the collected light from the sample (either characteristic emissions from a plasma, Raman scattered photons, or a fluorescence signature).	39
21	Overview of the data products available from the LIRS instrument.	42
22	Molecular energy level diagram depicting Stokes Raman scattering, where emitted photons have lower energy (and therefore, longer wavelength) than the incoming radiation.	43
23	Molecular energy level diagram depicting laser-induced fluorescence. The de-excitations through vibrational states are non-radiative transitions.	45
24	Overview of the elemental composition range for the geologic standard sample set used to test the performance of LIRS.	49
25	Comparison of calibration curves for Si with a) non-normalized spectra and b) internally normalized spectra.	53
26	Equipment for sample preparation.	64
27	Context camera images. From left to right, top: andesite, coulsonite, flint clay, bottom: ilmenite, pyroxenite, wollastonite.	65
28	Spectra of required calibration sources: (a) HG-1 mercury-argon lamp, (b) DH-3p-BAL-CAL tungsten-halogen-deuterium lamp (230-1100 nm). Source: Ocean Optics.	68
29	Overview of the relative efficiency correction (REC) process.	70
30	Examples of uncorrected and corrected spectra (REC correction) for (a) LIBS, (b) Raman, and (c) LIF on ilmenite, gypsum, and alanine, respectively.	71
30	Figure 29 continued	72
31	Calibration and brief overview of basic data processing for each measurement mode.	73
32	Timing and duration of the 1017 cm^{-1} band of anhydrite at four different laser frequencies. Each point on the curve is an integrated peak intensity at a different gate delay.	75
33	Raman spectra of (a) anhydrite, (b) aragonite, (c) dolomite, (d) gypsum, and (e) quartz taken with their optimal parameters. Spectra are vertically offset for clarity.	77

34	Raman spectra of pure organics, (a) alanine, (b) lysine, (c) octacosane, (d) serine, (e) stearic acid, and (f) tyrosine taken with their optimal parameters. Spectra are vertically offset for clarity.	78
35	Observable and identifiable molecular vibrations in LIRS Raman results.	81
36	Raman spectra of organic doped gypsum at different concentrations: (a) alanine, (b) octacosane, (c) serine, and (d) stearic acid.	82
37	Calibration curves for amino acids created from the ratios of integrated peak intensities of the organic to the integrated peak intensity of gypsum: (a) alanine, (b) octacosane, (c) serine, and (d) steric acid.	83
38	Signal versus concentration calibration curve emphasizing the relationship between $k\sigma$ to the LOD. Adapted from [36].	84
39	Workflow for the advanced algorithm similar to that found in Wiens et al. [62]. . . .	86
40	Predicted versus reference plot for alanine using spectra taken of the 2.5%, 10%, and 25% alanine doped gypsum samples.	86
41	Percent error of prediction of alanine using multivariate analysis techniques.	87
42	SNR with number of total laser shots for three lines in ilmenite.	91
43	Example of baseline correction for LIBS spectra. The baseline correction both corrects the baseline height and the leftover instrument response.	92
44	Result of the algorithm that aligns and resamples LIBS spectra taken on different days (with slightly different wavelength calibrations).	92
45	Overview of LIBS spectra for samples which LIBS in the μJ regime works well. . . .	94
46	Overview of LIBS spectra for samples that do not work in the μJ regime.	95
47	Standards which do not produce a good μLIBS spectrum under typical, single spot conditions do produce a successful μLIBS spectrum when the target is continuously sampled during the measurement, i.e., when the sample is kept in motion over the 0.5 s measurement.	96
48	Overview of LIBS spectra with major peaks identified (268-315 nm).	98
49	Overview of LIBS spectra with major peaks identified (318-365 nm).	99
50	Overview of LIBS spectra with major peaks identified (365-412 nm).	99
51	Overview of LIBS spectra with major peaks identified (412-468 nm).	100

52	Overview of LIBS spectra with major peaks identified (469-516 nm).	100
53	Overview of LIBS spectra with major peaks identified (516-563 nm).	101
54	Overview of LIBS spectra with major peaks identified (563-850 nm).	101
55	Example of line fitting for potassium peaks in various geologic standards.	102
56	Visual representation of the reduced data set used in calibration curve analysis. . .	103
57	Primitive elemental calibration curves.	105
57	Primitive elemental calibration curves (continued).	106
58	Visual representation of large and small variation within a set of spectra.	108
59	Example spectra from the ChemCam instrument.	109
60	QAP turnery diagram for the identification of igneous rocks (adapted from R.W. Le Maitre 2002. Igneous Rocks: A Classification and Glossary of Terms).	110
61	Calibration curves created using normalized peak intensities.	112
61	Calibration curves created using normalized peak intensities (continued).	113
62	Predicted vs known plots from elemental MVA.	115
62	Predicted vs known plots from elemental multivariate analysis (continued).	116
63	Various LIBS spectra of iron ore with degraded resolution used to test prediction capabilities at varying resolutions.	119
64	RMSEP (wt%) versus Lorentzian profile line widths for all elements.	120
65	Comparison of LIBS spectra of aluminum at different sensing distances.	121
66	Comparison of LIBS spectra of ilmenite at different sensing distances.	122
67	Craters left over after LIBS measurement with 5000 laser pulses at 10 kHz.	124
68	Raman spectra of (a) andesite, (b) anhydrite, (c) anorthosite, (d) aragonite, (e) dolomite, (f) flint clay, (g) granite, (h) quartz, (i) syenite, (j) pyroxenite, and (k) wollastonite, taken with optimal parameters.	127
69	LIF spectra of pure organics: (a) alanine, (b) β -carotene, (c) cystine, (d) lysine, (e) octacosane, (f) phenylalanine, (g) serine, (h) stearic acid, (i) thymine, (j) tryptophan, and (k) tyrosine, taken with their optimal parameters.	128
70	Time resolved measurement of lysine. Each time slice corresponds to a measured spectrum at a different time delay.	130

71	Examples of time-resolved fluorescence for (a) dolomite, (b) β -carotene, and (c) thymine. Organic compounds usually exhibit fluorescence with shorter lifetimes. . .	131
72	Passive reflectance: (a) measurements of spectralon standards and (b) reflectance calibration curve.	132
73	Passive reflectance spectra of various samples: (a) andesite, (b) anorthosite, (c) flint clay, (d) wollastonite, (e) ilmenite, (f) pyroxenite, (g) basalt, (h) manganese ore, (i) granite, and (j) syenite.	133
74	LIF (top), Raman (middle), and LIBS (bottom) measurements of quartz latite. The Raman range is 0–4000 cm^{-1}	135
75	Time-resolved LIF spectrum of quartz latite standard.	135
76	Reflectance experiment geometry.	139
77	Spectral response from standard reflectance materials using the laser at 50%, and measured with the IS.	140
78	Comparing (a) melting point, (b) hardness, (c) thermal conductivity, (d) density, (e) electron density, and (f) photoelectric effect (or work function) for all most original samples.	143
78	Figure 77 Continued.	144
79	Evolution of the μ LIBS plasma on aluminium from 10 ns after the laser pulse arrival, to $\sim 20 \mu\text{s}$	145
80	Evolution of the μ LIBS plasma on manganese ore from 10 ns after the laser pulse arrival, to $\sim 20 \mu\text{s}$	145
81	Evolution of the μ LIBS plasma on andesite from 10 ns after the laser pulse arrival, to $\sim 20 \mu\text{s}$	147
82	Whole rock samples.	165
83	Single shot spectra of whole rock samples.	166
84	Examples of fiber polishing for (a) superficial burning and (b) direct core damage. .	169

List of Abbreviations

APXS	Alpha Particle X-ray Spectrometer
CCD	Charged Coupled Device
CF	Correction Factor
CSA	Canadian Space Agency
DDG	Digital Delay Generator
ESA	European Space Agency
FOV	Field of View
FWHM	Full-Width Half Maximum
ICA	Independant Component Analysis
ICCD	Intensified Charged Coupled Device
ICP	Inductively Coupled Plasma
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectrometry
INO	Institut Nationale d'Optique/National Optics Institute
IUPAC	International Union of Pure and Applied Chemistry
JEM	Joint Europa Mission
LIBS	Laser-Induced Breakdown Spectroscopy
LIF	Laser-Induced Fluorescence
LIPS	Laser Induced Plasma Spectroscopy
LIRA	Laser Induced Remote Analyzer
LIRS	LIBS/Raman Sensor
LOD	Limit of Detection
LTE	Local Thermal Equilibrium
MCP	Multi-Channel Plate
MDA	MacDonald, Dettwiler and Associates
MEPAG	Mars Exploration Program Analysis Group
MSL	Mars Science Laboratory
MVA	Multivariate Analysis
NASA	National Aeronautics and Space Administration
NIST	National Institute of Standards and Technology
PCA	Partial Component Analysis
PE	Photoelectric Effect
PLS	Partial Least Squares
REC	Relative Efficiency Correction
RMSEP	Root-Mean-Square Error of Prediction
RSD	Relative Standard Deviation
SHERLOC	Scanning Habitable Environments with Raman & Luminescence for Organics & Chemicals
SNR	Signal-to-Noise Ratio
TR-LIF	Time-Resolved Laser-Induced Fluorescence
XRF	X-ray Fluorescence
μLIBS	Micro-Laser Induced Breakdown Spectroscopy

List of Symbols

A	Einstein coefficient, coefficient in ABCD matrix
α	absorption coefficient
B	coefficient in ABCD matrix
C	coefficient in ABCD matrix
c	speed of light, concentration
D	diffusion coefficient for electrons, coefficient in ABCD matrix
d	distance travelled along optical axis (analogous to z)
d_0	beam waist diameter
δ_h	heat penetration depth
δ_{opt}	optical penetration depth
Δ	denotes a change or difference
E	energy
ϵ	line emission coefficient
f	focal length
$f/\#$	f-number
g	degeneracy
h	Planck constant
I	irradiance, intensity
i	imaginary unit
k	confidence factor
k_B	Boltzmann constant
κ	thermal conductivity
λ	wavelength
M^2	beam quality factor
m	slope of linear regression
μ	mean
NA	numerical aperture

n	number density, index of refraction, number
n_e	electron number density
∇	gradient
ν	frequency
P	power
π	pi (3.1415926...)
q	complex radius of curvature, q-parameter
R^2	coefficient of determination
R	reflectance, radius, radius of curvature
r_c	LIBS crater radius
σ	standard deviation
T	temperature
t_{pulse}	laser pulse width
θ	ray angle with respect to optical axis
Θ	beam divergence angle
v	impact ionization, recombination, attachment rates
W_m	multiphoton ionization rate coefficient
w	beam radius
w_0	beam waist radius
x_L	smallest measure that can be detected with reasonable certainty
$\overline{x_B}$	mean background signal
y	ray height
Z	partition function
z	position along optical axis
z_R	Rayleigh range
$*$	denotes excited state
$+/-$	denotes ionized state

1 Introduction

The research presented in this thesis addresses micro-laser-induced breakdown spectroscopy (μ LIBS) and its potential for in-situ investigations of geological samples for planetary science. The focus of this work is on the ability of μ LIBS to analyze Mars relevant minerals using multivariate analysis (MVA) methods while characterizing the performance of a concept instrument called the LIBS/Raman sensor. The Canadian Space Agency (CSA), in partnership with MDA, the Institut nationale d'optique/National Optics Institute (INO), and York University, are developing the LIBS/Raman sensor (LIRS) which combines μ LIBS with complimentary analytical techniques called Raman and laser-induced fluorescence (LIF) spectroscopy. Knowing both elemental and molecular information, from LIBS and Raman respectively, can definitively identify rocks and minerals [9], and fluorescence signatures can aid in identifying organics. Since these techniques utilize similar equipment such as a laser, spectrograph, and a camera, the combination of LIBS, Raman, and fluorescence spectroscopy into one unit is attractive for planetary exploration missions where mass, volume, and power are greatly restricted. The science team at York University is responsible for characterization of the capabilities of the system and to determine the novelty of combining LIBS, Raman, and LIF into the same instrument. A large portion of the project includes the optical design and assembly of a separate μ LIBS instrument, which could eventually be integrated into an environmental chamber.

1.1 Laser-Induced Breakdown Spectroscopy

LIBS is a plasma-based atomic emission spectroscopy technique that permits rapid multi-elemental analysis both qualitatively and quantitatively. It relies on ablating and evaporating material by focusing radiation from a pulsed laser onto the surface of a target, forming a plasma. Within the hot plasma, atoms and ions are excited and characteristic emission lines can be seen when plasma emissions are analyzed spectroscopically. Elemental information is obtained via specific atomic or ionic transitions and the associated emanating photons (Figure 1).

LIBS has many advantages over other methods for remote environments of planetary bodies, including instrument simplicity, rapid simultaneous analysis of multiple elements, dust or surface removal and depth profiling, high spatial resolution measurements (depending on laser spot size), low power consumption, both close-up and stand-off capabilities, and most importantly, sample

preparation is not required [12]. LIBS is also robust – there is no limitation on the species of element LIBS is able to detect, and measurements can be acquired from a target in any form (i.e., solid, liquid, or gas). The technique is a relatively simple one whose small number of components make it ideal for remote exploration on planetary bodies, where mass and size restrictions are a dominant part of payload selection. For these reasons, LIBS is preferred to other established laboratory techniques like inductively coupled plasma (ICP) mass spectrometry (ICP-MS), or ICP atomic emission spectroscopy (ICP-AES) for remote exploration. When developing an instrument for planetary exploration, a LIBS device would be an attractive option if surface geochemistry is a mission objective. An atomic emission instrument that analyzes elemental compositions could be useful to (i) characterize the surface geochemistry of the planetary body, (ii) provide information pertaining to past habitability, (iii) assess potential for living organisms, and (iv) assess conditions for future manned missions (especially for Mars) [43].

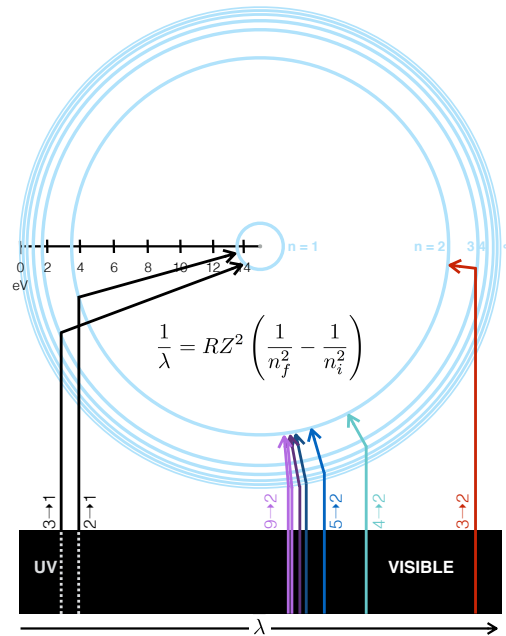


Figure 1: Graphical representation of characteristic atomic emissions. An atom contains electrons which can occupy many energy levels (represented by blue concentric circles), and transitions of electrons between these levels create emissions at specific wavelengths. These transitions are well characterized for each element.

1.2 Research Motivation

Although the LIBS technique has already been utilized for elemental composition analysis on the surface of Mars (via the ChemCam instrument on the Curiosity rover), there is still room to extend this technique to other planetary bodies as well as improving these methods for future missions to Mars. Most of what is known about LIBS comes from experimental studies, and ongoing research looks to improve stand-off capabilities, laser-matter interaction in different ambient environments, or mineral and organic detection and mapping, to name a few. Senesi et al. [53] has the most recent review for LIBS studies with applications to planetary science.

Micro-LIBS (μ LIBS) is a relatively new subset of LIBS that utilizes μ J laser pulse energies for excitation of plasma emission, carrying out analysis of materials with spatial resolutions approaching micron scales [59]. With a decrease in pulse energy comes the need for tighter focusing to surpass the threshold needed for ablation; the smaller sample areas achieved allow the probing of much smaller features. The Mars Exploration Program Analysis Group (MEPAG) specifies in their Mars Science Goals, Objectives, Investigations and Priorities document, the need for microanalysis instruments [24]. Because typical LIBS has flight heritage, the jump to making a similar instrument but with high-resolution sampling scales is not a big one, and is advantageous since LIBS is superior to other methods in instrument and sampling simplicity. Also, since lasers typically scale with pulse energy, μ LIBS instruments could be more compact than other payloads. There has been only two studies, Dreyer et al. [17] and Lefebvre et al. [35], which use the μ LIBS technique on geologic materials, but an investigation of μ LIBS techniques for other materials has yet to be performed.

Some LIBS/Raman combined systems exist (see SuperCam and others [11, 26, 42, 48, 55]), but the best concept for combining Raman and LIBS technologies in a way that maximizes flight potential is uncertain. There are four major differences between the LIBS/Raman sensor (LIRS) instrument and others which make this instrument a novel concept:

- 1) LIRS utilizes 266 nm laser excitation for both Raman and LIF modes,
- 2) a high repetition rate laser with μ J pulse energy for LIBS measurements (i.e., μ LIBS),
- 3) a single echelle spectrograph, whose spectral resolution is greater than, for example, ChemCam by a factor of four [62],

- 4) a single intensified CCD (ICCD) to measure time-resolved fluorescence with a small temporal resolution (~ 1 ns), and,
- 5) measurements are taken at a very high spatial resolution (≤ 60 μm) but still in a standoff configuration (20–50 cm).

Full characterization and testing of the LIRS instrument is critical in order to progress towards a complete flight concept for future Canadian contributions to planetary missions. Specifically, there are major advantages of the μLIBS mode, but the abilities of this particular technique are relatively unexplored.

1.3 Research Goals

The goals of this research are two-fold:

- 1) Characterize the performance of the LIRS breadboard to investigate the feasibility of a highly integrated LIBS/Raman/LIF instrument for Mars.
- 2) Design and build a separate μLIBS system for future investigations of μLIBS in environments mimicking different planetary bodies.

Characterization and testing of LIRS involves optimization of acquisition parameters and determining compositional detection limits, among others, for each analysis mode of the instrument. The second goal is to have a fully functional μLIBS system available at York to then use in investigations regarding other planetary bodies or applications (such as asteroids, the Moon, and icy bodies like Europa, etc.). The standalone instrument could eventually be integrated into an environmental chamber. The LIBS plasma, and therefore the information available from a plasma, depends highly on both the ambient temperature, pressure, and composition. Dreyer et al. looks at the dependence of μLIBS specifically on ambient pressure, while a more general review of effects of ambient environment properties on LIBS spectra is found in Cremers & Radziemski [12, 17].

The ultimate aim of this research is to investigate the applicability of μLIBS for geologically relevant materials, both contributing to the LIRS project and extending LIBS techniques for space exploration applications.

1.4 Thesis Overview

Section 2 will describe the background behind laser induced breakdown spectroscopy. This includes an overview of instruments that have performed elemental analysis in space, including the ChemCam instrument on the Mars Science Laboratory (MSL) or Curiosity rover, and future missions that could include a LIBS instrument. Section 2 further introduces what is known about the physics of a LIBS plasma and how the technique is used to determine quantitative information about a sample. The same section includes a description of μ LIBS and how it differs from “typical” LIBS. The typical requirements for any LIBS system along with the design and initial testing of a 532 nm μ LIBS instrument is detailed in Section 3. The testing presented here is cursory, because characterization of the LIRS instrument took precedence.

The concept behind the LIRS instrument is introduced in Section 4, and is immediately followed by Section 5 which details the characterization strategy. A synopsis of characterization performed in two phases, Phase 1 and 2, is presented in Sections 6 and 7, respectively, the latter including an overview of the future of the LIRS concept instrument.

Section 8 overviews initial attempts to explain the inadequacies encountered with the μ LIBS mode and the differences between μ LIBS and “typical” LIBS. This is meant as a starting point for future work, which is discussed in Section 10.

2 Background

The first recorded observation of a LIBS-type plasma was from a 1962 abstract from Breech and Cross [7]. The study used a ruby laser to produce a vapour plume on the surface of a sample, and created a plasma with an auxilliary spark source. This allowed for characteristic emission detection, and was essentially the birth of LIBS. Since then, LIBS has found applications in many areas including art dating, forensic science, hazard detection and avoidance, soil sampling, analyzing the quality of meat, and most recently, the analysis of geologic materials and matter on the surface of Mars [12].

2.1 LIBS Systems in the Context of Space Exploration

2.1.1 Brief history of elemental analysis instruments in space

The first instrument to provide elemental surface analysis was Surveyor 5, which landed on the Moon in 1967 carrying the alpha-scattering surface analyzers [43]. Alpha particles would irradiate the surface directly underneath the lander, and major elements could be detected via the energy spectrum of the scattered radiation. Data from this mission and Surveyors 6 and 7 – the last two lunar robotic landers in the Surveyor program – definitively identified the major components of lunar regolith: $\sim 57\%$ oxygen, $\sim 20\%$ silicon, and $\sim 7\%$ aluminium [43]. Following up the Moon missions, the Venera series of missions to Venus included an X-ray fluorescence (XRF) instrument and a gamma ray spectrometer, which were both able to determine elemental compositions on the surface of Venus. In 1975, Viking 1 and 2 successfully landed on Mars with similar instrumentation; each lander incorporated an XRF instrument, along with a gas chromatograph-mass spectrometer into its scientific analysis suite.

The first elemental analysis instrument to utilize a laser was flown over a decade later. In 1988 Russian space probes Phobos 1 and 2 were launched to the Mars moons Phobos and Deimos with an instrument called LIMA-D, the first space-based laser instrument for chemical analysis [12, 43]. These lasers were designed to ablate the surface of the Mars moons from a distance of 30 m, but the mission was ultimately unsuccessful because of an unrelated computer malfunction.

The next visit to the surface of Mars was accomplished by the small Sojourner rover (part of the

Mars Pathfinder mission) in 1997. The rover included the alpha proton x-ray spectrometer, similar to the instrument flown on the Surveyor spacecraft, to analyze rock and soil composition. A similar instrument, the alpha particle x-ray spectrometer (APXS), which only differs in its inability to detect protons, was used on the Mars Exploration Rovers Spirit and Opportunity and MSL/Curiosity, as well as on Philae, the lander studying the comet 67P/Churyumov-Gerasimenko. The Sample Analysis at Mars instrument, which can determine chemical compositions via a mass spectrometer is also on the MSL rover, along with the first-ever LIBS instrument in space, ChemCam, which is the focus of Section 2.1.2.

Although these instruments were and are successful in their analyses, the fact remains that LIBS, typified by ChemCam, has major benefits over other elemental analysis techniques in space exploration. For example, the technique used by APXS is limited by the number of elements it can detect (only those heavier than sodium¹), even at high concentrations, while LIBS can theoretically detect all elements as long as they are above the detection limits of the instrument. A measurement from APXS is also very slow; while a LIBS measurement is typically a fraction of a second, an APXS measurement requires hours of integration time.

2.1.2 Curiosity rover: ChemCam instrument

The most recent (and only) successful demonstration of the LIBS technique used in space exploration was part of the ChemCam instrument on board the MSL/Curiosity rover. The LIBS instrument on ChemCam utilizes a 1067 nm Nd:KGW laser with >30 mJ, 8 ns pulse illuminating a 0.6–1.2 mm spot diameter on the target over a 1.5–7 m range [12, 38, 43]. The ChemCam instrument was activated for the first time on August 19, 2012, firing at a rock (deemed ‘Coronation Rock’) 2.7 m from the rover’s mast unit [43]. This was the first rock to be interrogated by a laser on another planetary body. The ability of the ChemCam instrument to detect elements in a stand-off configuration has allowed the science team to use their limited time for surface analysis wisely. Targets can be analyzed from a distance, and when something looks interesting, the rover can approach and interrogate a sample more thoroughly. ChemCam has and continues to provide chemical composition data of Mars geology and, because of its success, has pushed LIBS and other

¹Although APXS cannot measure these light elements directly, it can obtain information about the atmosphere through indirect measurements.

laser spectroscopy methods for space applications forward.

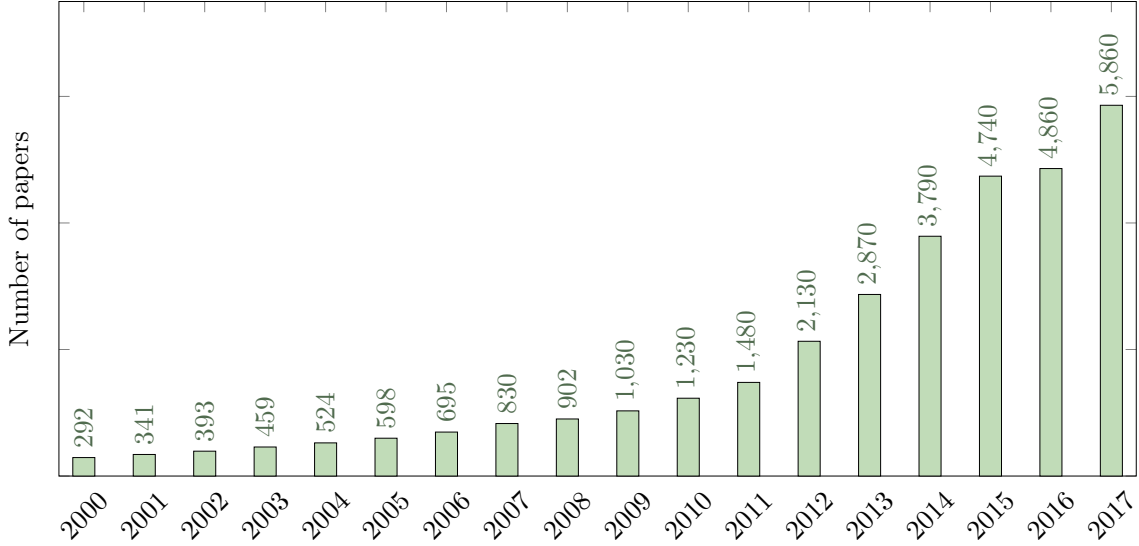


Figure 2: Number of papers found with both key words “LIBS” and “space” per year (via Google Scholar).

2.1.3 Future LIBS instruments

Because of the overwhelming success of the ChemCam instrument, many missions propose the use of a compact LIBS instrument for elemental analysis. Figure 2 shows the increase in papers discussing the applicability of LIBS for space exploration from 2000–2017. For reference, LIBS was selected for the MSL/Curiosity in 2004, and the first successful spectrum returned by ChemCam was in August 2012. Since 2004, the number of publications looking at LIBS for space exploration has grown almost exponentially.

NASA’s follow-up mission to the surface of Mars, Mars2020, includes an updated version of ChemCam called SuperCam, which incorporates LIBS with Raman, fluorescence, and infrared spectroscopy. LIBS is also being used on the Chandrayaan-2 rover (Indian Space Research Organization) launching to the Moon late 2018 [43], and is being considered for an ESA Moon lander and a NASA/ESA Europa lander called JEM [5, 47]. LIBS was considered for the Hayabusa2 (Japan Aerospace Exploration Agency) mission to asteroid 162173 Ryugu, and ESA’s Exomars rover (where it was originally also combined with Raman spectroscopy). Although no longer slated for flight on these specific missions, LIBS is still a popular competitor when aiming for fast surface

geochemistry analysis of a planetary body.

An exhaustive overview of past, current, and future robotic missions that include elemental analysis instrumentation is found in Chapter 10 of [43].

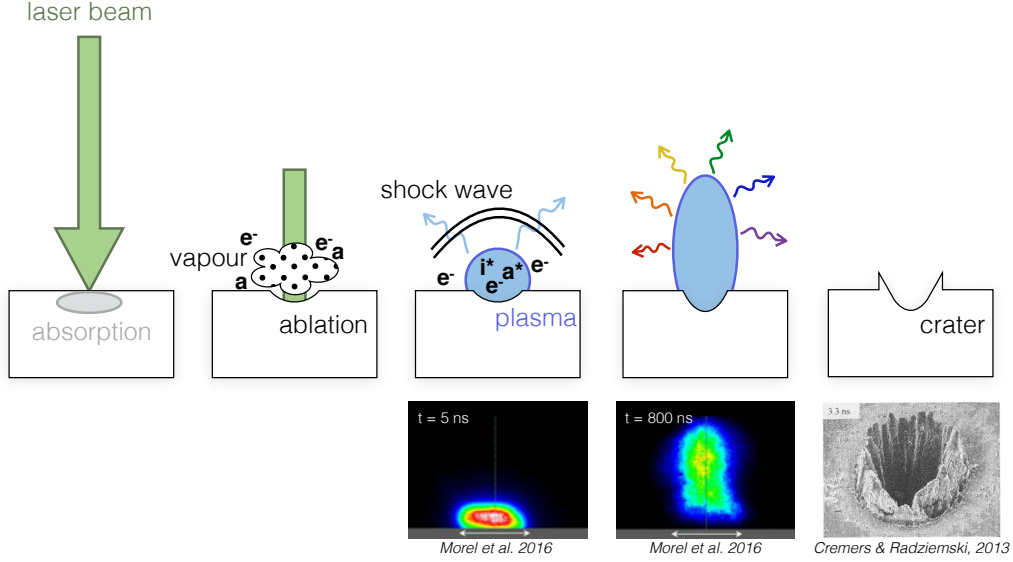


Figure 3: Visualization of a LIBS event. Adapted from [45] with additions from Morel et al. [41] and Cremers & Radziemski [12].

2.2 Physics of LIBS

Understanding the physics behind the plasma created during the laser-matter interaction is key to determining the optimal parameters of the instrument. Although the physics behind the formation and evolution of a LIBS plasma is not fully understood, there are some known fundamentals. Here the focus is on descriptions of the result – the relationship between the observed spectra and the plasma. An overview of the LIBS process is shown in Figure 3.

Consider a high-power laser pulse incident onto a target. Assuming homogeneity, absorption of radiation from the beam is described by the Beer-Lambert law,

$$I(z) = (1 - R)I_0 e^{-\alpha z} = (1 - R)I_0 e^{-\frac{z}{\delta_{opt}}}, \quad (1)$$

where $I(z)$ is the irradiance at distance z from the sample surface along the axis of propagation, R is the reflectivity (and the factor $1 - R$ describes the part of the irradiance which enters the

Table 2: Elementary interactions between atoms and light (* denotes an excited state). Adapted from [57]

Process	Scheme
Excitation as a result of photon absorption	$h\nu + A \rightarrow A^*$
Spontaneous radiation	$A^* \rightarrow h\nu + A$
Stimulated emission	$h\nu + A^* \rightarrow 2h\nu + A$
Atomic photoionization	$h\nu + A \rightarrow A^+ + e^-$
Photodetachment of a negative ion	$h\nu + A^- \rightarrow A + e^-$
Photodissociation of a molecule	$h\nu + AB \rightarrow A + B$
Photorecombination of an electron to an atom	$e^- + A^+ \rightarrow A + h\nu$
Radiative attachment of an electron to an atom	$e^- + A \rightarrow A^- + h\nu$
Atomic photorecombination	$A + B \rightarrow AB + h\nu$
Bremsstrahlung	$e^- + A \rightarrow e^- + A + h\nu$

sample), I_0 is the irradiance at the sample surface, $\alpha = 1/\delta_{opt}$ is the absorption coefficient, and δ_{opt} is the optical penetration depth. Both R and α depend on the laser wavelength via dependence on the complex index of refraction of the material [12]. If the kinetic energy imparted by the beam is higher than the potential well depth, then particles can escape. Here potential well depth is used to refer to the amount of energy needed for the structure to hold onto a single particle (similar to bond strength). Ablation (removal) of sample constituents occurs due to the impact pressure of the laser beam. Whereas in slower processes, material is vaporized once the temperature surpasses a threshold which depends on the material properties, ambient environment, surface morphology, the presence of defects, and laser parameters such as wavelength and pulse duration [45], ablation is an extremely fast process that does not depend on any thermal effects. Ablation decouples atoms and ions from the bulk into a vapour plume above the sample surface that travels at supersonic speeds along the axis of propagation [12].

A plasma is hot gas characterized by strong Coulomb (or electrostatic) interactions, where ionization has stripped electrons from atoms, balancing positive and negative charges in a quasi-neutral state. Recall that an ion is an atom or molecule that has a different number of electrons than protons, and the process by which an electron is lost or gained is called ionization. There are two requirements for breakdown; there must be some initial free electrons in the beam path available to absorb energy from photons, then rapid ionization must occur [12, 45]. The high-

temperature plume will induce thermionic emissions, generating free electrons above the surface. Simply put, the thermal energy overcomes the work function of the material, and plasma formation is initiated [45]. These free electrons will absorb energy from collisions with photons through inverse bremsstrahlung (IB) processes, and some neutral atoms may be ionized by photoionization or multiphoton ionization. At high irradiances, multiphoton absorption (of m photons) can occur

$$A + mh\nu \rightarrow A^+ + e^-, \quad (2)$$

producing more electrons. As the electron energies grow by absorption of beam energy, collisions with neutral atoms produce ionization,

$$e^- + A \rightarrow 2e^- + A^+, \quad (3)$$

creating more free electrons which absorb more energy from photons and ionize more atoms, and so on, initiating plasma formation [45]. The change in electron density occurring during these processes is governed by

$$\frac{dn_e}{dt} = n_e(v_i - v_a - v_r) + W_m I^m n + \nabla(D\nabla n_e), \quad (4)$$

where W_m is the multiphoton ionization rate coefficient, D is the diffusion coefficient for electrons, I^m is the irradiance necessary for an m -photon process to occur, n is the number density of species being irradiated, and v_i , v_a , and v_r are the impact ionization, attachment (combinations of electrons with neutral atoms to form negative ions), and recombination rates respectively [12]. This cascading process which creates an exponential increase in the number of free electrons is called *avalanche ionization*. Once the density of free electrons surpasses some value (which depends on material and beam factors) a hot plasma visible to the naked eye is formed. Table 2 lists the many elementary collisional processes between atoms and light that could occur within a plasma. The typical energy deposition needed for ablation and breakdown is on the order of 1 GW/cm² [12, 38, 45], though this varies greatly for differing target materials and their state of matter, along with the surrounding air pressure.

Although the initiation of the laser-induced plasma varies greatly depending on sample type

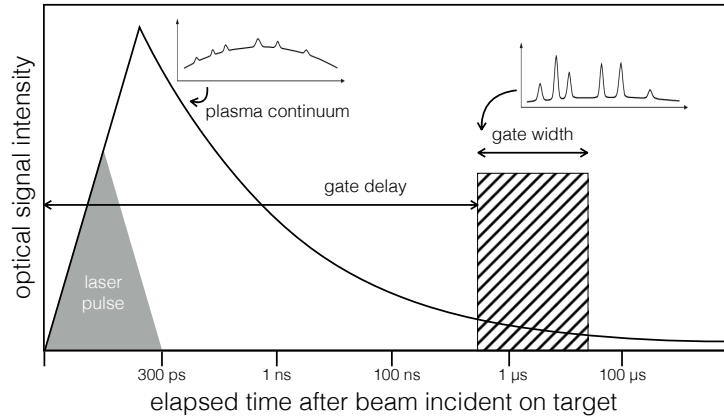


Figure 4: Temporal evolution of a typical LIBS event. Early after the laser pulse spectra are dominated by continuum emission, and only later are characteristic emissions visible. Adapted from [41].

and laser properties, the evolution of the plasma is similar for many target types [45]. Expansion of the plasma plume along the direction of beam propagation slows due to collisions with the surrounding gas. During expansion, after the plasma has cooled a “significant” amount, the continuum emission decreases and characteristic emissions can be detected [12,45]. The initial period of bright continuum emission is caused by Bremsstrahlung emission (free-free transitions of electrons, when photons are emitted from electron-ion interactions). At later times, radiative recombination of ions to bound states (free-bound transitions of electrons) dominates [45]. Characteristic lines will become apparent after highly excited species with electrons bound in upper energies decay to lower energy levels via spontaneous emission. Ions and electrons will recombine to form neutrals and some neutrals will recombine to form molecules (detection of molecules becoming possible at these later times) [12]. If light is collected during this entire phase the spectra could be dominated by the continuum. For this reason, LIBS measurements are usually gated for detection after continuum emission decay (Figure 4).

The light from the laser-induced plasma is collected into a detection system (spectrometer and camera) where the light can be split into its constituent wavelengths and recorded. Since the 1800’s scientists have known that elements can emit different wavelengths or frequencies of light, which makes the spectra – a plot of the collected light’s intensities at specific wavelengths – a chemical fingerprint of a material [12]. Atoms have a specific, discrete (or quantized) set of known energy levels and electrons that transition between these bound states will emit photons that are

characteristic of the species. These characteristic photons make up the element's spectrum, allowing the identification of species in a more complicated material by looking for these known emission lines. Energy conservation gives the wavelength of the line

$$\lambda_{mp} = \frac{ch}{E(m) - E(p)} \quad \text{or} \quad \nu_{mp} = \frac{E(m) - E(p)}{h}, \quad (5)$$

where m and p represent the m^{th} and p^{th} energy level. The decay is proportional to the density $n_a(m)$ of the species a with electrons in the upper state, $-dn_a(m)/dt|_{m \rightarrow p} = A_{mp}n_a(m)$, where the constant A_{mp} describes the probability of the electron transitioning from the m^{th} to p^{th} energy level (also called the Einstein coefficient) [45]. The line emission coefficient, ϵ (essentially the emitted local radiance at the surface of the plasma, analogous to line intensity) resulting from the emitted photons is given by

$$\epsilon(m \rightarrow p) = \frac{h\nu_{mp}}{4\pi} A_{mp} n(m). \quad (6)$$

This assumes the plasma is emitting isotropically [45]. If it is assumed that the laser-induced plasma is in local thermodynamic equilibrium (LTE), the density of energetic levels can be represented by the Boltzmann distribution $n^* = n^o(g/Z) \exp[-E^i/k_B T]$ (where $*$ denotes an excited state and o is a ground state), then the spectral line radiant intensity is given by

$$I_{mp} \propto \epsilon(m \rightarrow p) = \frac{h\nu_{mp} g A_{mp}}{4\pi Z} n^o \exp[-E^*/k_B T], \quad (7)$$

$$= \frac{hc g A_{mp}}{4\pi \lambda Z} n^o \exp[-E^*/k_B T], \quad (8)$$

where Z is the partition function, g is the degeneracy of the upper energy level, and k_B is the Boltzmann constant. Equation 8 reveals the nature behind the technique – that the population densities of the atomic species are the quantities obtained from a measurement of the plasma light [45]. The atomic processes governing the plasma radiation are shown visually in Figure 5. The state of thermal equilibrium of the plasma can be determined by confirming that the intensities of two lines with similar upper level energies of the same species follow Equation 8. Specifically, the

ratio of two lines of the same species is

$$\frac{I'}{I} = \frac{hcg'A'_{mp}}{4\pi\lambda Z} \frac{4\pi\lambda'Z}{hcgA_{mp}} \frac{n^o}{n^o} \exp[-(E' - E)/k_B T], \quad (9)$$

$$\frac{I'}{I} = \frac{g'A'_{mp}\lambda'}{\lambda gA_{mp}} \exp[-(E' - E)/k_B T]. \quad (10)$$

As long as you choose lines for which parameters are known, T can be calculated from the relative intensities of these lines [12, 14]. Instead of just using two lines of the same species, the estimation of plasma temperature can be improved using many pairs of measurements. We can rearrange Equation 8 into the form of a straight line with slope of $-1/k_B T$,

$$\frac{4\pi\lambda Z I}{hcn^o gA_{mp}} = \exp[-E^*/k_B T], \quad (11)$$

$$\ln\left(\frac{4\pi\lambda Z I}{hcn^o gA_{mp}}\right) = -\frac{E^*}{k_B T}, \quad (12)$$

$$\ln\left(\frac{I\lambda}{gA_{mp}}\right) = -\frac{E^*}{k_B T} - \ln\left(\frac{4\pi Z}{hcn^o}\right). \quad (13)$$

If $\ln(I\lambda/gA_{mp})$ is plotted versus E^* for multiple species, and the resulting plot is linear, a Boltzmann distribution (and condition for LTE) can be inferred to be correct and the temperature can be determined from the slope. This is called a Boltzmann plot [14].

It is worth noting that this technique is sometimes referred to as LIPS (laser-induced plasma spectroscopy) in the literature. The modern consensus is to instead use the acronym used here (LIBS), omitting any reference to a plasma. The main reason for this is the fact that LIBS is not always characterized by *ideal* plasma formation, that is to say, the Debye length condition (which considers the ion interaction scales within a plasma) isn't satisfied.

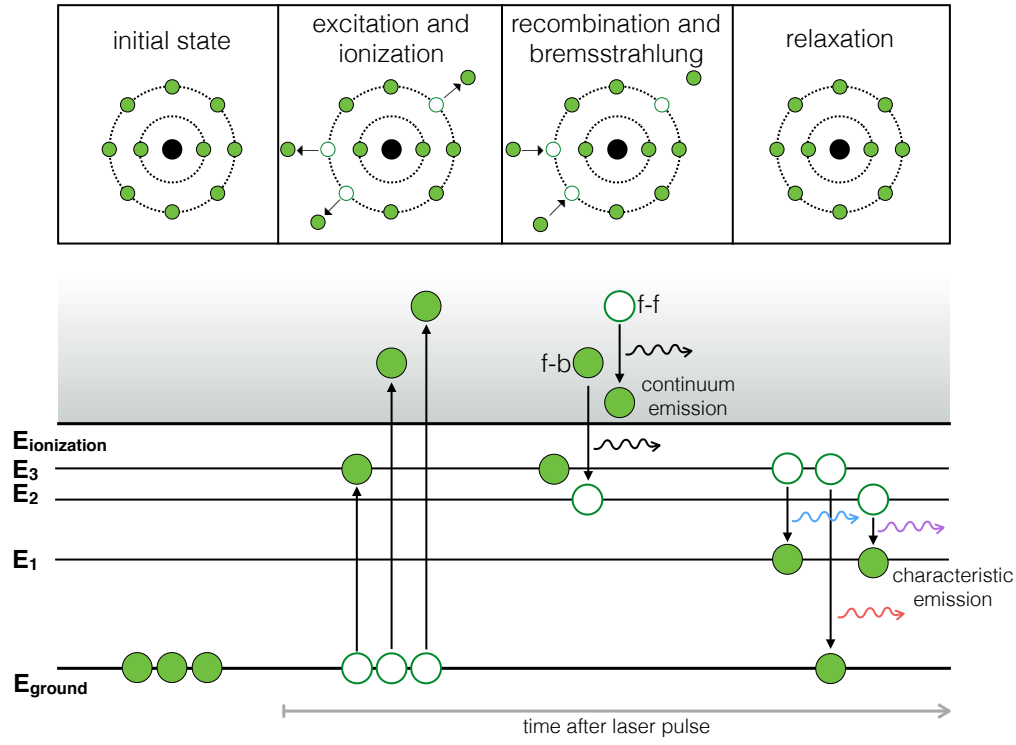


Figure 5: Atomic processes occurring during a LIBS event (evolving from left to right). The black circles represent the nucleus of the atom, the green circles represent electrons, and the white circles represent holes (the absence of an electron). Characteristic emissions occur during relaxation of excited electrons to lower states.

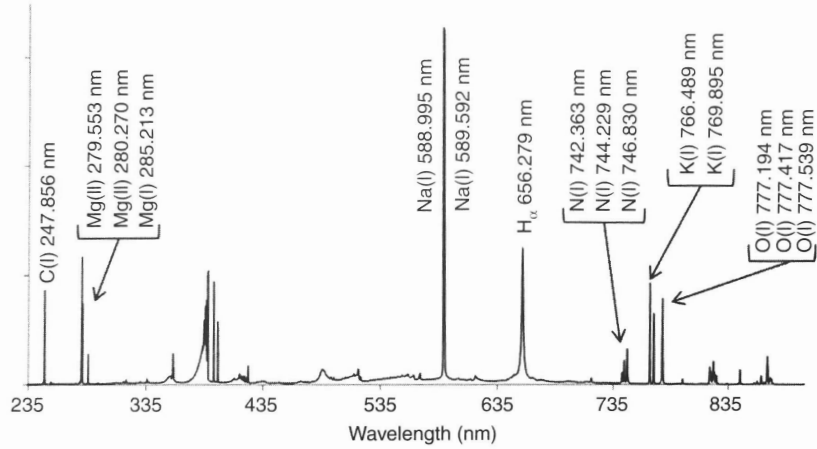


Figure 6: An example of a LIBS spectra (turkey skin). Taken from [12].

2.3 Obtaining quantitative information from LIBS

An example of a spectrum resulting from a LIBS measurement is shown in Figure 6. With sufficient resolution, obtaining qualitative information about the sample is possible by matching peaks to their known wavelengths using the National Institute of Standards and Technology (NIST) Spectral Line Database [30]. Obtaining quantitative information from LIBS spectra is possible if a predictive model is created. The most basic type of predictive model is a calibration curve (a plot of peak measurement verses concentration) created using samples of known concentrations (i.e., standard materials). To create a calibration curve for an element within a material, a representative line (at a specific wavelength λ_j) must be chosen from the spectrum. The measured quantity is the integrated peak intensity I_j at the chosen wavelength. The intensity of a spectral line should have a linear relationship with concentration of the element, however, quantitative LIBS analyses of complex matrices (like geological samples) are hampered by matrix effects that can result from shot-to-shot variations in the vaporized mass and/or in the excitation temperature of the plasma resulting from fluctuations in laser intensity, coupling efficiency of the laser with the target material, and other instrumental variations [12]. Using an internal standard for normalization of peak intensities is a common approach for correction of matrix effects in LIBS studies [12, 45]. Instead, calibration curves are created using intensity *ratios* I_j/I_r where the normalization intensity I_r is usually the major element of the matrix, and preferably an element that occurs in all samples [45]. In the case of geologic materials, the preferred normalization element is either Si, Fe, or O [12, 31].

Standards are used which have a varying amount of the relevant element, a spectrum is measured from each sample, and intensity ratios at each concentration are plotted. A calibration curve is

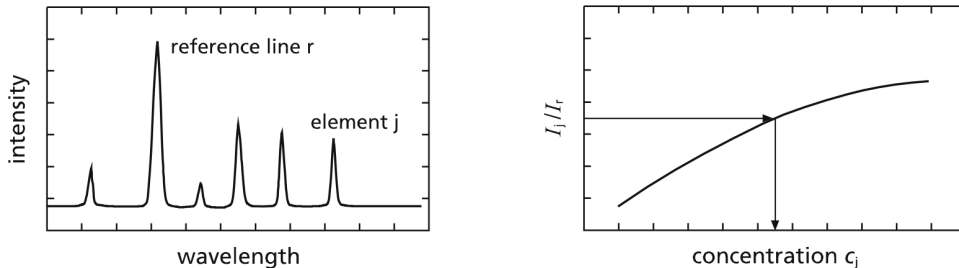


Figure 7: Left: resulting spectrum with element j of interest and reference peak r labeled. Right: ratioed intensity (j/r) versus concentration calibration curve. Taken from [45].

determined by linear regression analysis [45]. An example of a calibration curve is shown in Fig. 7 (right), where each point along the fitted line is the integrated peak intensity from a different sample containing the element of interest. For an unknown sample, the integrated intensity of the considered element peak is measured, and the concentration of the analyte is found via the working curve which is the inverse function of the calibration curve, i.e., the calibration curve is used in reverse, matching a measured intensity to a concentration (following the arrows in Figure 7) [45]. A calibration curve can be created for all elements that are visible within a spectrum (given they are present within the selected sample suite).

In recent years, multivariate analysis (MVA) techniques have been used for LIBS analysis, specifically partial least squares (PLS) regression techniques which are useful when a linear regression is desired but the number of variables is large, which is the case with spectral data [12]. Chapter 7 of Cremers & Radziemski compares the different MVA techniques for LIBS analyses [12]. These techniques are useful because dependence of the emission of an element j is not only on the concentration of the element j , but also on the concentrations of a number of other elements through plasma temperature (which depends on chemical composition), laser fluence, and overlapping of spectral lines.

2.4 Techniques similar to LIBS

There are three general types of atomic spectroscopy: atomic absorption spectroscopy, atomic fluorescence spectroscopy, and atomic emission spectroscopy (AES). The latter, which utilizes emission and detection of characteristic electromagnetic radiation produced after excitation and decay of atomic or ionic species, is the most common approach to elemental analysis [63]. Different excitation techniques are used such as a spark or flame, an inductively-coupled plasma (ICP), or a laser beam (LIBS), among others. ICP-AES is frequently used for chemical analysis in a laboratory setting, and similar to LIBS, utilizes plasma emissions. Because the plasma is created using principles of electromagnetic induction the measured species must be conductive, leaving out H, C, O, N, and the halogens. LIBS has no restrictions of this kind. Some of these established techniques require initial target preparation that might be tedious, may introduce errors into the analytical process, and limit the remote capabilities of the technique. For example ICP-AES techniques typically require samples that are in liquid form, making it unideal for remote use where preparation would

not be available and the ability to sample all matter types would be desired. LIBS does not require sample preparation of any type.

2.5 μ LIBS

Many “typical” LIBS systems use pulse energies of 20–50 mJ and low laser repetition rates (few 10s of Hz), resulting in average powers of ~ 0.5 W. While traditional systems have been proven effective, there is a desire to adapt this relatively simple system to perform higher spatial resolution measurements, and to make more compact, adaptable instruments.

Although μ LIBS technically refers to the condition on laser pulse energy (10s or 100s of μ J), beams normally have very small pulse widths to increase peak power, and have to be focused down to <100 μ m scales to overcome the ablation and breakdown threshold of the material (Figure 8). In this sense, μ LIBS has been also used to describe ablation at micron scales [59]. In most cases the definitions are equivalent. The spatial scale of the crater left over by a μ LIBS measurement is small, but the volume is also small. In aluminium, μ LIBS has allowed for sampling of volumes on the order ~ 10 – 1000 μm^3 , and masses ~ 10 pg–ng [59]. Though microanalysis is possible, there could be a large tradeoff with sensitivity because of the inhomogeneity of the sample on the 10s of microns scale.

μ LIBS also allows for more flexibility when designing a flight instrument. Lasers in the typical regime are reasonably compact (see ChemCam [38]), though because the size of a laser usually scales with pulse energy, lasers used for μ LIBS analysis can be relatively small. These are typically microchip, or recently, fiber lasers. Since μ LIBS requires tighter focusing, the plasma created at the sample surface is smaller and the evolution progresses on a faster timeline. Characteristic emissions occur very quickly after the laser pulse arrives (100s of ns after, e.g. 100 ns for 200 μ J pulse energy as in [25], compared to >1 μ s for ~ 1 ns pulse widths). It has been found that the broadband continuum emission emitted in early stages is reduced compared to typical LIBS (see [12, 22, 59]), therefore an un-gated detector *could* be used. The former weakens mass and size constraints, while the latter simplifies detector requirements and lowers cost.

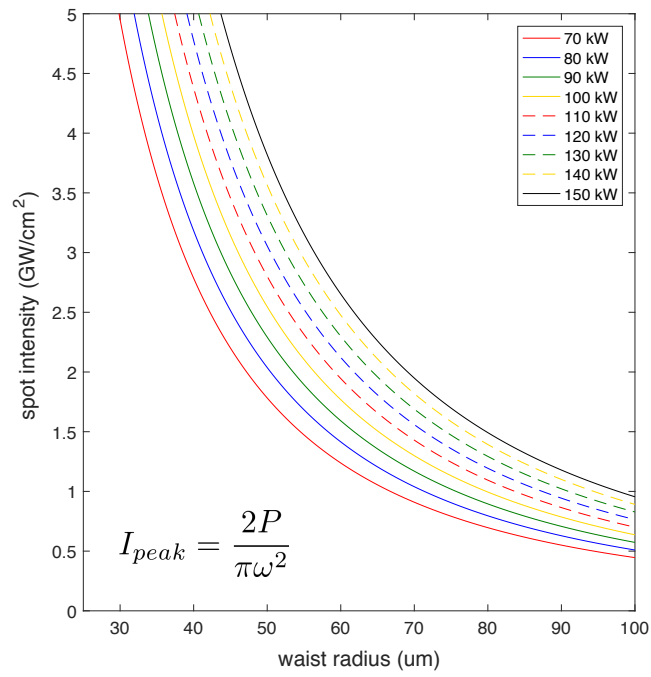


Figure 8: Laser peak irradiance versus beam waist radius for various peak powers. The ablation threshold given throughout LIBS literature is 1 GW/cm². See Section 3.1, page 26 for a thorough explanation of focusing Gaussian beams.

2.5.1 μ LIBS in the literature: metal alloys

The μ LIBS technique has been used mostly for metal alloy analysis and micro-machining. A great review is presented in [59]. There are some μ LIBS systems that are “laboratory” systems, which are those that are high-precision but often large and would not be able to make the leap to a flight instrument. There are however, some μ LIBS systems that are portable (or could easily become portable). These are found in Cristoforetti et al. [13], Gravel et al. [23], Lopez-Moreno et al. [37], and Freedman et al. [21]. Table 3 compares the instrumental parameters and results for these four studies. All of these studies use metal alloy samples as is typical for μ LIBS. One of the major figures of merit in LIBS studies is the limit of detection (LOD), which quantifies the smallest amount of a compound that an instrument can positively detect. LODs from these μ LIBS studies are lower than other typical LIBS studies. For example, ChemCam’s LODs for major elements are on the order of 1 wt% or 10,000 ppm, while μ LIBS LODs reach 10s or 100s of parts per million. There is a thorough discussion of LODs in Section 7.3.4.

Table 3: Performance of some μ LIBS instruments.

	Lopez-Moreno et al. 2005 [37]	Cristoforetti et al. 2006 [13]	Gravel et al. 2011 [23]	Freedman et al. 2005 [21]
Laser type	Nd:YAG Powerchip	Nd:YAG prototype	Fiber laser	Nd:YAG Microchip
Wavelength	1064 nm	1064 nm	1064 nm	1064 nm
Repetition rate	1 kHz	8 kHz	25 kHz	7.8 kHz
Pulse energy	50 μ J	80 μ J	800 μ J	14 μ J
Pulse duration (FWHM)	0.5 ns	9 ns	30 ns	0.5 ns
Spot size ($1/e^2$ waist)	10 μ m	5 μ m	40 μ m	20 μ m
Target material	Steel	Aluminium	Aluminium	Aluminium
Elements analyzed	Cr, Mn, Mo Ni, Si	Cu, Fe, Mn Ni, Si, Ti, Mg	Cr, Cu, Fe Mg, Mn, Si	Fe, Mg, Mn Ni, Si, Zn
Typical LOD	30–200 ppm	2–490 ppm	1–210 ppm Si: 520 ppm Fe: 1300 ppm	500–1400 ppm

2.5.2 μ LIBS in the literature: geologic-type standards

There are only two pieces of literature which detail the use of μ LIBS on geologic-type standards. These are Dreyer et al. [17] and Lefebvre et al. [35]. The former tests the μ LIBS technique in different ambient pressures using hematite, an iron oxide mineral that is commonly found on Mars (fine-grained hematite gives Mars its red colour). The focus of this study was the combination of μ LIBS with Raman spectroscopy using a Nd:YLF laser operating at 523 nm, with 170 μ J pulse energy, 10 ns pulse width, and 4 Hz repetition rate. The latter tests the applicability of lasers with low pulse energy and high repetition rates for μ LIBS analysis of ilmenite and brass plates. Three lasers were tested with pulse energies ranging from 100 to 189 μ J, pulse widths of 8–10 ns, and repetition rates ranging from 1–400 Hz. Resulting spectra of both ilmenite and aluminium had higher signal-to-noise ratios than those found in a previous study from a co-author (Koujelev et al. [31]). Lefebvre et al. acknowledges the potential for portability and mass and power savings using this type of laser (and the μ LIBS technique). The use of μ LIBS on geologic standards has not been investigated since, and there is a large number of samples for which μ LIBS is untested.

3 μ LIBS System

3.1 μ LIBS system design

LIBS instruments are attractive for use in space exploration because they are typically very simple. The main components of any LIBS system are:

- 1) high peak power laser to induce plasma on sample surface,
- 2) focusing optics to bring the beam to a small spot size at the sample,
- 3) plasma emission collection optics,
- 4) and a light detection system which consists of both a spectrograph to disperse light into its constituent wavelengths and a device to record the spectra.

The laser, spectrograph, and an intensified charge-coupled device (ICCD) were selected first. In most LIBS experiments a common solid state Nd:YAG (Nd^{3+} ions in a yttrium aluminum garnet crystal) laser is used either at the fundamental 1064 nm or one of the harmonics (532 nm, 355 nm, 266 nm), mainly because they are generally reliable and compact sources. Since all elements emit somewhere in the 200–980 nm range a 1064 nm laser is used most commonly [53], though with gated detectors, any wavelength can be used without much consequence. Laser parameters affect both plasma formation and the resulting spectral signature. The wavelength dependence on LIBS takes place during ionization of particles in the vapour, and depends also on the surrounding pressure, though LIBS has been achieved at the fundamental and all harmonics of the Nd:YAG [11, 38, 49, 53]. In order to get the large peak power required to ablate the target, *Q-switched* pulsed lasers are used, which use either an active (e.g. electro-optical switch) or passive (e.g. an absorber with a low saturation intensity) switch to create a pulse with the highest possible intensity. The switch is used in the optical cavity to block lasing until the population inversion has increased past its continuous threshold to a maximum, then opened, releasing the light and depopulating much of the laser medium all at once [12]. This process allows for an intense, short laser pulse. The laser chosen for this μ LIBS device was the 532 nm Teem Photonics passively Q-switched microchip laser (PNG-M04005) with 45 μJ per pulse and a 300 ps pulse width, supplying a 150 kW peak power (according to the specifications). Assuming zero loss in transmission, to achieve the required irradiance at the target (1 GW/cm^2) the laser spot size should be around 100 μm in diameter.

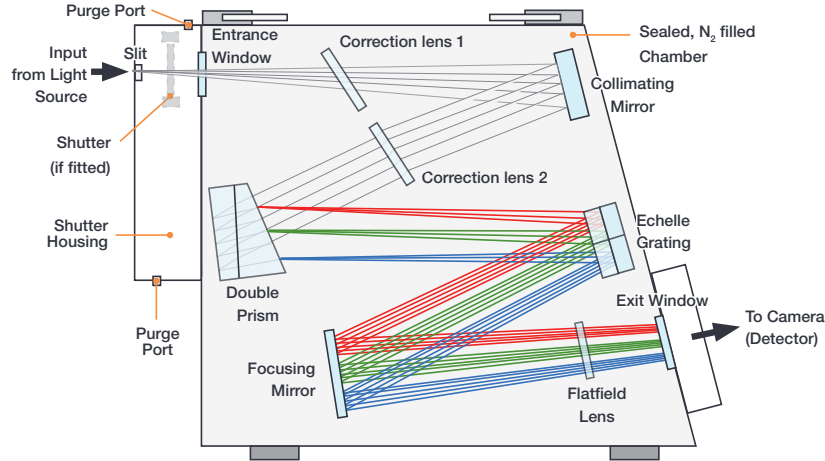


Figure 9: Internal components of the ME5000 (Credit: Andor).

The plasma emission covers a large spectral range and a spectral resolution of at least 0.1 nm is required for good line selectivity. The Andor Mechelle echelle spectrograph (ME5000) was chosen to meet these requirements. Although a large spectral range is achievable using multiple, smaller spectral band Czerny-Turner monochromators (e.g. those used in ChemCam [38]), the echelle spectrograph covers the same range in a single system. The large spectral range is accomplished using a series of dispersion elements, spreading out spectral components in two directions to fill the 2D focal plane of the detector (Figure 9). A blazed diffraction grating is used to disperse light into a large number of overlapping orders each covering a small range of wavelengths, followed by a prism which spatially separates the orders [12]. Czerny-Turner spectrographs, on the other hand, only have one dispersive element. The major benefits to using an echelle spectrometer over a Czerny-Turner set are the compactness, spectral range, and the number of lines observed in a LIBS measurement (because of the higher resolution). Figure 10 shows how the orders are arranged across the entire area of the detector. The information from the *echelleogram* (Fig. 10) is converted to a more familiar spectral representation using a proprietary algorithm embedded into the Andor Solis software package which allows for data collection and export.

Charged coupled devices (CCDs) are solid-state systems that are used to transform light patterns (photons) into electrical patterns (electrons). Detectors are made up of square arrays of charge collecting elements (or pixels) which act as wells, collecting electrons, until the entire detector is read out and reconstructed as an image. The Andor iStar ICCD was recommended along

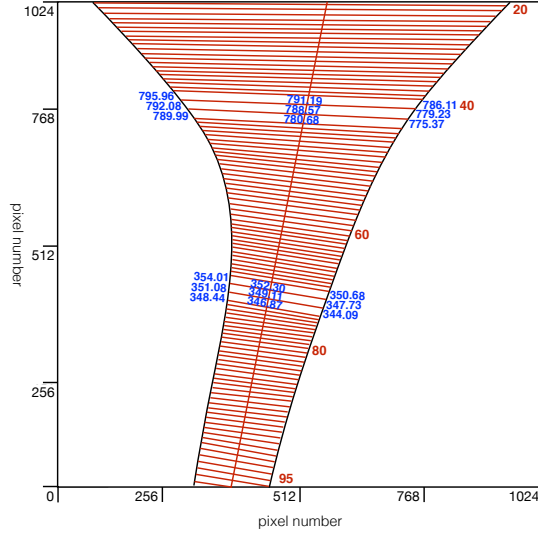


Figure 10: Arrangement of orders in the focal plane of the ME5000. The red lines represent the 80 orders covered by the spectrograph. The majority of order spacings are even, and the wider spaces are simply to allow demonstration of the order overlap. Wavelength (examples shown in blue) decreases nonlinearly down the central line.

with the ME5000 spectrograph and was selected here. An ICCD (intensified CCD) is a CCD that includes an image intensifier, which works to amplify the intensity of an image. Specifically, the intensifier includes a photocathode, micro channel plate (MCP), and a phosphor screen. Photons are converted into electrons at the cathode, accelerated to the MCP near the positive voltage anode, multiplied by the MCP, and then converted back into photons at the phosphor screen. A major advantage of this camera is its fast response: the camera can be gated very quickly by switching on/off the anode voltage. For LIBS the camera can be programmed to only allow light to reach the CCD during the characteristic emission phase, removing almost all unwanted background (e.g. continuum emissions).

A schematic of the 532 nm μ LIBS instrument designed here is shown in Figure 11. The design is similar to that used by Rai et al. [49]. The instrument was designed to use an optical fiber to both deliver the laser pulse to the target surface and collect the plasma emissions. An optical fiber might have interesting utility during a space mission (maybe to explore a cavity or hole found on the surface), though the fiber was originally selected as an engineering choice. As a consequence of our passively Q-switched laser, a 10 m long optical fiber (F1) is used to deliver the beam; whereas the pulses from an actively Q-switched laser could be timed in parallel with the ICCD gating using

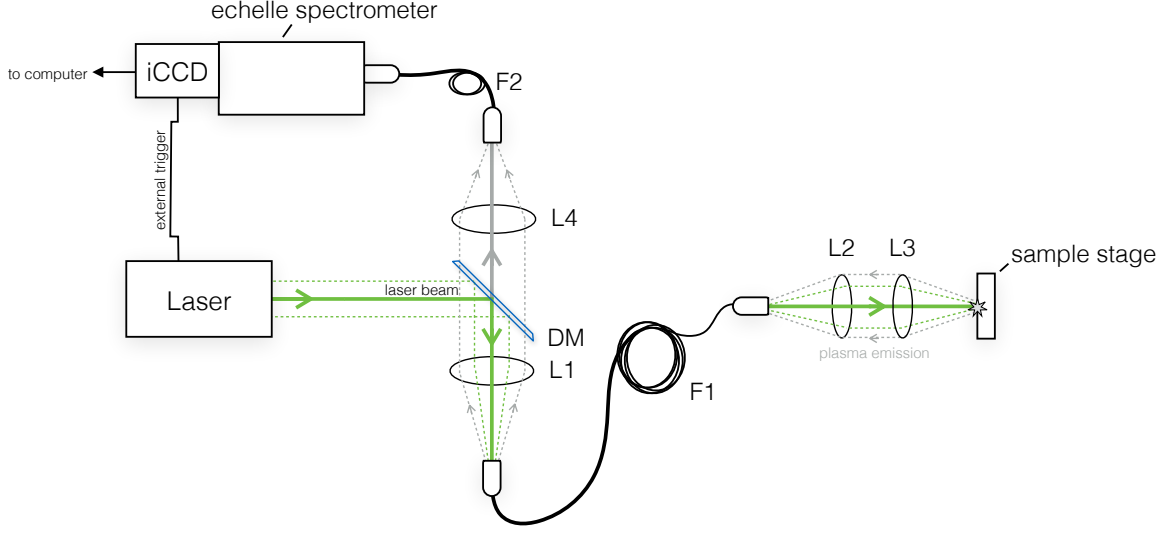


Figure 11: Simplified schematic of the μ LIBS instrument design (in Configuration 1).

a function generator, our ICCD gate must be triggered using a photodetector which introduces a 30 ns trigger insertion delay. The 10 m fiber delays the light long enough to make up the 30 ns before the gate could be opened. This instrument was intended to be integrated into an environmental chamber. Using a fiber delivery system would also make this process extremely simple. Following the light in Figure 11, the 532 nm beam is emitted from the laser. A trigger signal is sent to the ICCD from the laser to synchronize the two systems. The light from the laser is reflected off of a 532 nm dichroic mirror (DM) onto a lens (L1, $f = 20$ mm, $R = 12.7$ mm) that focuses the light into a 100 μ m fiber (F1). The DM reflects light only at 532 nm. Once the light exits the fiber, lens L2 ($f = 35$ mm, $R = 25.4$ mm) collimates and lens L3 (Thorlabs AL2520M aspheric lens, $f = 20$ mm, $R = 25.4$ mm) focuses the beam onto the sample surface. Once the plasma is initiated, light is collected through the same delivery optics (L3 and L2, and back through F1) passing through the DM on the other side. The beam is focused into the second fiber F2 (50 μ m) by the lens L4 ($f = 20$ mm, $R = 12.7$ mm). F2 delivers the light to the spectrograph.

The optical design of the μ LIBS instrument was originally completed using first approximation paraxial ray tracing equations and matrix mechanics, where one considers the limiting case where angles between rays and the optical axis approach zero. Given some starting parameters (e.g. the laser diameter and divergence) the properties of the beam (diameter, divergence, focal spot) through

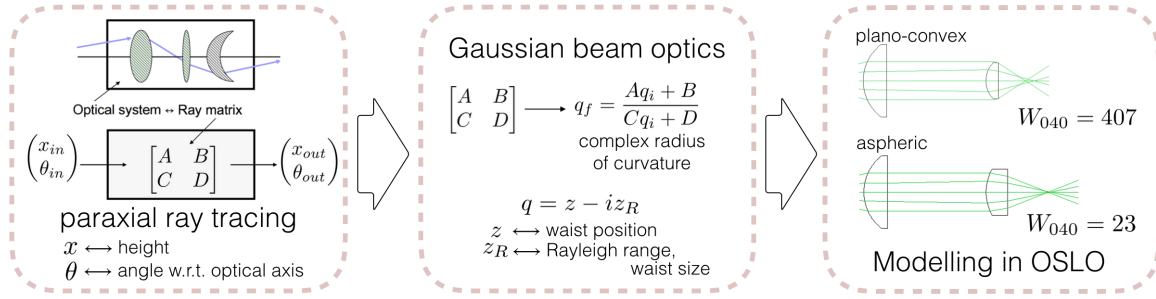


Figure 12: Flowchart of the optical design process.

the entire system can be determined using only the transport and refraction equations (taking $n_{air}=1$ and $n_{lens} = 1$). Although this is useful as a starting point for designing an optical layout, it was advantageous to use Gaussian beam optics and further modelling of certain components in OSLO (Optics Software for Layout and Optimization, Lambda Research Corporation) to ensure the required beam focusing (and therefore the required peak intensity) was achieved. Prior to this, though, proper characterization of our laser (and spectrograph) was performed to ensure the advanced models are given accurate inputs of initial beam waist, divergence, and laser beam quality (M^2 factor).

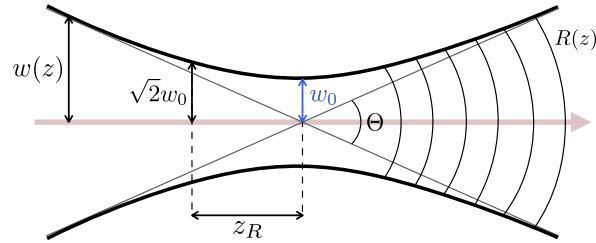


Figure 13: Propagation of a Gaussian beam in air. The radius of the beam $w(z)$ is at the smallest value at the *beam waist* w_0 and expands outwards based on the full angle divergence Θ and the radius of curvature R .

The most relevant laser parameter for μ LIBS systems (and LIBS systems in general) is the spot size at the target. In order to surpass the threshold intensity needed for laser-induced breakdown, the laser must be carefully focused to a known spot size at the target. To do this properly the beam must be fully characterized by determination of the waist diameter d_0 (or waist radius w_0), the beam divergence angle Θ , and the M^2 factor. A Gaussian beam is one whose transverse electromagnetic waves have Gaussian profiles, implying the intensity distribution follows a Gaussian profile as well.

Most lasers are Gaussian, following what's called a TEM₀₀ profile. Figure 13 shows the propagation of a Gaussian beam in air, showing how the waist radius of the beam $w(z)$ changes depending on the distance along the beam. The smallest waist radius occurs at the beam waist radius w_0 . Many laboratory methods have been identified to perform these measurements for Gaussian beams, such as the slit method or knife-edge method. In both, the slit or the edge is translated across the beam at the waist while the power is measured. After plotting the transmitted power as a function of

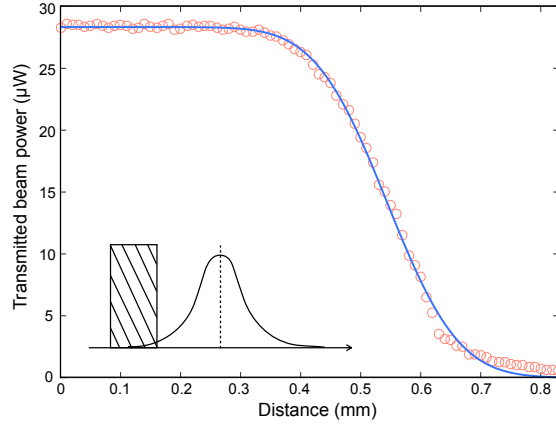


Figure 14: Power of Gaussian beam transmitted past an edge as it is translated across, perpendicular to the optical axis.

the distance translated by the edge across the beam and fitting an equation, w_0 can be determined (Figure 14). Experimental data can be fit with

$$P = P_0 + \frac{P_{max}}{2} \left[1 - \operatorname{erf} \left(\frac{\sqrt{2}(x - x_0)}{w_0} \right) \right], \quad (14)$$

and w_0 solved numerically. This is the most basic beam profile measurement. For a more accurate analysis of beam parameters the Gentec-EO Beamage beam profiling camera is used instead. This is a triggered USB 2.2MPixel CCD detector that includes specialized beam diagnostic software.

The initial beam waist is the easiest to measure, by simply placing the camera at the specified distance from the exit plane of the laser head and taking a measurement with Beamage. To measure the divergence, an aberration-free lens is placed between the Beamage and the laser in the far-field, and place the Beamage at the focal point of the lens. The focal length of the lens used and the wavelength of the light is entered into the software and the relevant calculations are performed

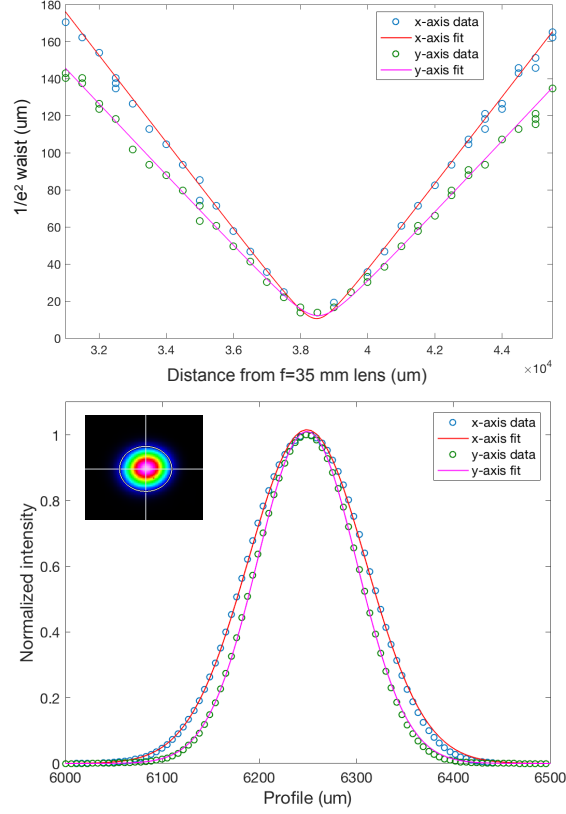


Figure 15: Characterization of laser performance. Top: measurement of beam waist size and laser quality (M^2). Bottom: measurement of spot size formed using a $f = 35$ mm lens.

within the software itself. The measurement is based on the proposition that the beam diameter is equal to the focal length of the lens multiplied by the incident beam divergence. Here our $f = 35$ mm plano-convex lens (Thorlabs, LA4052) is assumed to be aberration free, meaning it does not introduce significant errors to the wavefront. The M^2 factor can be measured using the same lens, with the addition of a moveable stage to record the beam diameter at various points from the lens along the optical axis. The beam profile was measured at 0.5 mm increments from the lens and the $1/e^2$ radius was plotted with distance from the lens. The $1/e^2$ width is equal to the distance between the two points on the intensity distribution that are $1/e^2 = 0.135$ times the maximum value. Figure 15 shows the measurements of $1/e^2$ radius along the optical axis (top), and the beam profile at the focal point of the lens (bottom). Assuming a Gaussian beam, the behaviour of the laser at a waist is well-described using the concept of Rayleigh range. Along the optical axis the radius of the beam $w(z)$ is described by

Table 4: Validation of system parameters for the 532 nm μ LIBS system.

Laser parameters	Expected	Measured
pulse energy (μ J)	41.8	39.11
pulse width (ps)	300	349
peak power (kW)	139	112
beam divergence (mrad)	$\Theta_x = 5 \pm 1$	$\Theta_x = 5.8$
	$\Theta_y = 4 \pm 1$	$\Theta_y = 4.8$
M^2	1.3	$M_x^2=1.4615$
		$M_y^2=1.3807$
Spectrograph parameters	Expected	Measured
resolving power	4000	3750 (average)
spectral resolution (nm)	0.07-0.19 nm	0.15-0.36 nm (50 μ m fiber input) 0.09-0.17 nm (25 $\times$ 50 μ m slit)

$$w(z) = \sqrt{w_0^2 + \frac{M^4 \lambda^2 (z - z_0)^2}{\pi^2 w_0^2}} \quad (15)$$

$$= w_0 \sqrt{1 + \frac{(z - z_0)^2}{z_R^2}}, \quad (16)$$

where w_0 is the beam waist radius, z is the position along the optical axis, and

$$z_R = \frac{M^2 \lambda}{\pi w_0^2}, \quad (17)$$

is called the Rayleigh range. Experimental data are fit using the above equation to determine the Rayleigh range, and therefore the beam quality factor in both axes. The fit to experimental data is shown in Figure 15). Using this method, it was found that $M_x^2=1.4615$ and $M_y^2=1.3807$. From beam diameter measured at the precise focal length of the lens, the divergence was calculated to be $\Theta_x=4.8$ mrad and $\Theta_y=5.8$ mrad, for beam profiles measured along the x and y axis, respectively. Other instrument parameters were characterized, including laser pulse energy, width, and peak power, along with the resolving power of the spectrometer. The results are shown in Table 4. Although some values differ slightly from specifications, these parameters are still within an acceptable range.

3.1.1 Paraxial ray tracing

Once these major components were selected, the optical design was created using first approximation paraxial equations and matrix mechanics [3]. A *paraxial* analysis is where one considers the limiting case where angles between rays and the optical axis approach zero. The ray-tracing equations in the paraxial limit reduce to a linear relationship in both angle and distance from the axis, hence the term *first-order*. It is this linearity that allows matrix representations and ray tracing matrix mechanics to be used [3]. At the same time, the ideal thin lens approximation is used where lenses are assumed to have a sufficiently small thickness such that the thickness of the lens does not contribute to its focal length. In this case, the change in the beam path while going through a lens is considered to occur instantaneously at the midplane of the lens [3]. The system was calculated considering the real thickness of the lenses but this did not change our results significantly. Properties of the beam throughout the system are determined using only the transport and refraction equations (taking $n_{air}=1$ and $n_{lens} = 1$) [3]. The transport equation is

$$y' = y + d\theta, \quad (18)$$

where the height of the paraxial ray in the plane of the optical axis with ray angle θ changes from height y to y' over a distance d . Along with an equation describing refraction at a surface,

$$\theta' = \theta - \frac{y}{f}, \quad (19)$$

where θ' is the refracted ray angle and f is the focal length of the lens. The diameter and divergence of the beam after exiting the first optical fiber (labelled F1) and the requirements on spot size at the target are known, allowing the focal lengths of the two lenses needed to collimate then focus light onto the target to be determined from a set of three equations. The first describes the light exiting the fiber, travelling to the collimating lens (L2), then the region between the two lenses, and finally the region from the focusing lens (L3) to the target surface. This can also be done using

matrix mechanics, where linear algebra is used to make system layouts easier. The goal is to solve

$$\begin{pmatrix} y_f \\ \theta_f \end{pmatrix} = \begin{bmatrix} A & B \\ C & D \end{bmatrix} \begin{pmatrix} y_i \\ \theta_i \end{pmatrix}, \quad (20)$$

where A , B , C , and D (making up the ‘ABCD matrix’) describe how the light travels through optical components. As a system of equations, y_f and θ_f are determined completely using the initial beam parameters,

$$y_f = Ay_i + B\theta_i, \text{ and}, \quad (21)$$

$$\theta_f = Cy_i + D\theta_i. \quad (22)$$

There are standard matrices representing propagation, reflection, and refraction. These matrices can be multiplied (in reverse order in which they’re encountered) to arrive at a matrix representation of the system. Only two types of ray matrices are relevant. The transport matrix,

$$\begin{bmatrix} 1 & \frac{d}{n} \\ 0 & 1 \end{bmatrix}, \quad (23)$$

where again d is the distance travelled, and n is the index of refraction through which the distance was travelled. The other relevant matrix is the thin lens matrix,

$$\begin{bmatrix} 1 & 0 \\ -\frac{1}{f} & 1 \end{bmatrix}, \quad (24)$$

where f is the focal length of the lens. If it is assumed that the fiber is filled such that the light exiting the fiber exits with y_1 equal to the fiber radius, and θ_1 equal to half the numerical aperture (NA) of the fiber, then the spot size at the target can be determined using

$$\begin{bmatrix} A & B \\ C & D \end{bmatrix} = \begin{bmatrix} 1 & d_3 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 \\ -\frac{1}{f_2} & 1 \end{bmatrix} \begin{bmatrix} 1 & d_2 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 \\ -\frac{1}{f_1} & 1 \end{bmatrix} \begin{bmatrix} 1 & d_1 \\ 0 & 1 \end{bmatrix}, \quad (25)$$

$$= \begin{bmatrix} \left(1 - \frac{d_3}{f_2}\right) & d_3 \\ -\frac{1}{f_2} & 1 \end{bmatrix} \begin{bmatrix} 1 & d_2 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & d_1 \\ -\frac{1}{f_1} & \left(-\frac{d_1}{f_1} + 1\right) \end{bmatrix}, \quad (26)$$

$$= \begin{bmatrix} \left(1 - \frac{d_3}{f_2}\right) & d_2 \left(1 - \frac{d_3}{f_2}\right) + d_3 \\ -\frac{1}{f_2} & \left(-\frac{d_2}{f_2} + 1\right) \end{bmatrix} \begin{bmatrix} 1 & d_1 \\ -\frac{1}{f_1} & \left(-\frac{d_1}{f_1} + 1\right) \end{bmatrix}, \quad (27)$$

$$= \begin{bmatrix} 1 - \frac{d_3}{f_2} - \frac{1}{f_1} \left[d_2 \left(1 - \frac{d_3}{f_2}\right) + d_3 \right] & d_1 \left(1 - \frac{d_3}{f_2}\right) + \left(-\frac{d_1}{f_1} + 1\right) \left[d_2 \left(1 - \frac{d_3}{f_2}\right) + d_3 \right] \\ -\frac{1}{f_2} - \frac{1}{f_1} \left(-\frac{d_2}{f_2} + 1\right) & \frac{d_1}{f_2} + \left(-\frac{d_2}{f_2} + 1\right) \left(-\frac{d_1}{f_1} + 1\right) \end{bmatrix}, \quad (28)$$

implying,

$$A = 1 - \frac{d_2}{f_1} - d_3 \left(\frac{1}{f_2} + \frac{1}{f_1} - \frac{d_2}{f_1 f_2} \right), \quad (29)$$

$$B = d_1 + d_3 - d_1 d_3 \left(\frac{1}{f_1} + \frac{1}{f_2} \right) + d_2 \left(1 - \frac{d_3}{f_2} - \frac{d_1}{f_1} + \frac{d_1 d_3}{f_1 f_2} \right), \quad (30)$$

$$C = -\frac{1}{f_1} - \frac{1}{f_2} + \frac{d_2}{f_1 f_2}, \text{ and}, \quad (31)$$

$$D = 1 - \frac{d_2}{f_2} - d_1 \left(\frac{1}{f_1} + \frac{1}{f_2} - \frac{d_2}{f_1 f_2} \right). \quad (32)$$

where d_1 , d_2 , and d_3 are distances between optical components, and f_1 and f_2 are focal lengths of the lenses. All parameters are referenced in Figure 16. These were solved symbolically in MATLAB. Using these paraxial methods the laser spot size radius at the target was calculated as 28.6 μm . Using the relationship depicted in Figure 8, the intensity at the target should be $\sim 6 \text{ GW}/\text{cm}^2$ (this number accounts for the power losses due to fiber coupling and surface reflections, which is about 30%).

3.1.2 Using gaussian beam optics

Although most of the components and their layout were chosen using paraxial matrix methods, Gaussian beam matrix methods were used to more accurately determine the spot size at the sample surface. This included optimization of the most important components, those delivering the light from the fiber output to the target surface. For Gaussian beams the matrix methods are much like those for paraxial methods. Instead of solving for the image height (y_f) and the ray angle (θ_f), however, a complex quantity called the ‘q-parameter’ is used instead to determine the waist

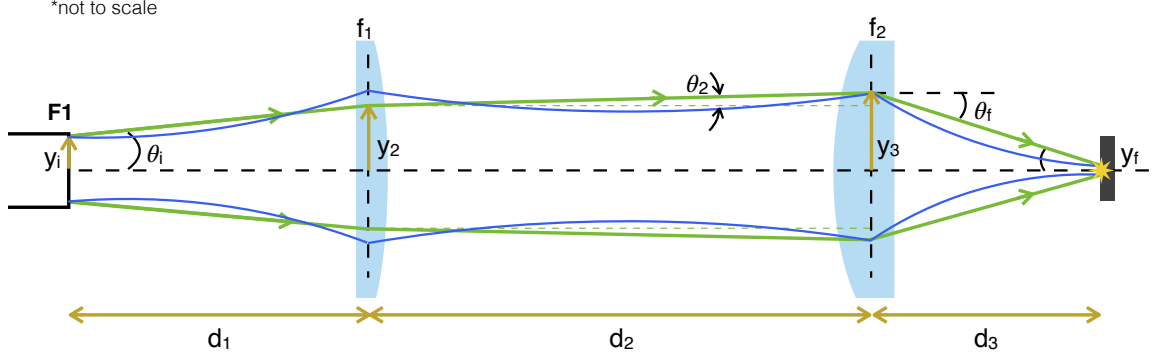


Figure 16: Schematic of the optical system used to collimate and focus the beam from the fiber (F1) to the sample surface (far right). The first lens is spherical with $f_1 = 35$ mm, and the second lens is aspheric with $f_2 = 20$ mm. The green rays depict a paraxial ray, whereas the blue represent a Gaussian beam.

position and the Rayleigh range (and therefore the waist size). Gaussian beams have a complex radius of curvature defined by

$$\frac{1}{q(z)} = \frac{1}{R(z)} - i \frac{\lambda}{\pi w^2(z)}, \quad (33)$$

where R is the radius of curvature and recall, $w(z)$ is the spot size radius. In free space this parameter obeys the propagation law $q(z) = q_0 + z = z + iz_R$, where again, z_R is the Rayleigh range (Equation 17). The radius of curvature R can be related to coefficients from the ABCD matrix by using $\theta = y/R$ (using the small angle approximation) and Equations 21 and 22,

$$R_f = \frac{AR_i + B}{CR_i + D}, \quad (34)$$

and after generalizing this to spherical Gaussian beams using the complex radius of curvature [54],

$$q_f = \frac{Aq_i + B}{Cq_i + D}. \quad (35)$$

By equating the real and imaginary components of the above equation, z_f and z_{Rf} (and therefore the waist radius) can be determined, respectively. At the beam waist $R \rightarrow \infty \implies q = i\pi w_0^2/\lambda M^2$

(from Equation 33), and

$$\frac{i\pi w_{0,f}^2}{\lambda M^2} = \left[A \frac{i\pi w_{0,i}^2}{\lambda M^2} + B \right] \left[C \frac{i\pi w_{0,i}^2}{\lambda M^2} + D \right]^{-1}. \quad (36)$$

Equating the real parts gives information about the beam waist position,

$$0 = BD + AC \left(\frac{\pi w_{0,i}^2}{\lambda M} \right), \quad (37)$$

and the imaginary parts give the waist size,

$$\frac{\pi w_{0,2}^2}{\lambda M^2} = \left[\frac{\pi w_{0,1}^2}{\lambda M^2} (AD - BC) \right] \left[C^2 \left(\frac{\pi w_{0,1}^2}{\lambda M^2} \right)^2 + D^2 \right]^{-1}. \quad (38)$$

We can use the same ABCD matrix, and therefore the same coefficients (Equations 29 to 32). Again, MATLAB is used to solve everything symbolically, arriving at a waist size of 28.3 μm . This is in agreement with our paraxial analysis.

3.1.3 Modelling in optical design software

The OSLO optical design software was used to validate our calculations. Originally, all lenses used were simple plano-convex lenses, but while playing with the collimating and focusing optics it was found that using only these lenses did not result in spot size radius matching those calculated in the previous sections. This is most likely due to the presence of various aberrations that the previous methods cannot account for. Obtaining a $\sim 30 \mu\text{m}$ beam waist radius was possible, however, if an aspheric lens was used for focusing. This is because an aspheric lens works to eliminate any wavefront errors acquired from the increased refraction of rays striking near the edges of lenses (via any spherical surfaces the rays encounter). This is called spherical aberration. For this reason the last focusing lens (f_2 in Figure 16) was changed to an aspheric lens.

3.2 Verification of performance

Figure 17 shows the $1/e^2$ waist radius along the optical axis measured using the Beamage camera. At the focus the laser spot size, $w = 30.1 \mu\text{m}$ agrees with both theoretical values. According to the

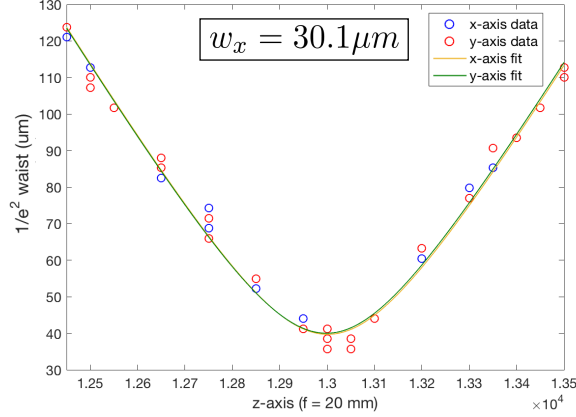


Figure 17: Beam waist radius at the target in Configuration 1.

measured peak power, the power density at the target surface, including 30% losses due to coupling efficiency and surface losses is $\sim 5.4 \text{ GW/cm}^2$, five times over the ablation and plasma formation threshold found in the literature.

The system was assembled and aligned for both laser delivery and plasma light collection (Figure 18). Performance was briefly tested using aluminium before testing the ability of a $50 \text{ }\mu\text{m}$ fiber to transmit light to the sample surface. This was originally intended to reduce the spot size and increase the laser power density at the target by a factor of 2 (Figure 8) but there were issues with power losses (and burning the fibers, see Appendix C).

The $100 \text{ }\mu\text{m}$ fiber was replaced, and some measurements were taken on aluminium (Figure 19). The major aluminium peaks are visible in the spectrum, specifically 309.2 nm and 396.1 nm (both Al I), including others as labelled. Most notably, there is also a AlO signature in the range $460\text{--}540 \text{ nm}$. Some work has been done to inform the use of LIBS for discerning organic compounds by looking at molecular signatures in LIBS spectra (see [46] for a Mars-specific example). Graphite and ilmenite (Ti ore) were also tested and found to produce spectra with identifiable peaks but low signal to noise ratios (SNR).

The system was upgraded to include a moveable mirror to switch from one configuration to another. If the mirror is in its nominal position, the beam follows the path according to the previous schematic (Figure 11). This is Configuration 1 (C1). If the mirror is moved to a position where it intercepts the beam from the laser, the light is reflected at 90° through a beam expander and an aspheric focusing lens ($f = 20 \text{ mm}$). This setup is called Configuration 2 (or the “high-

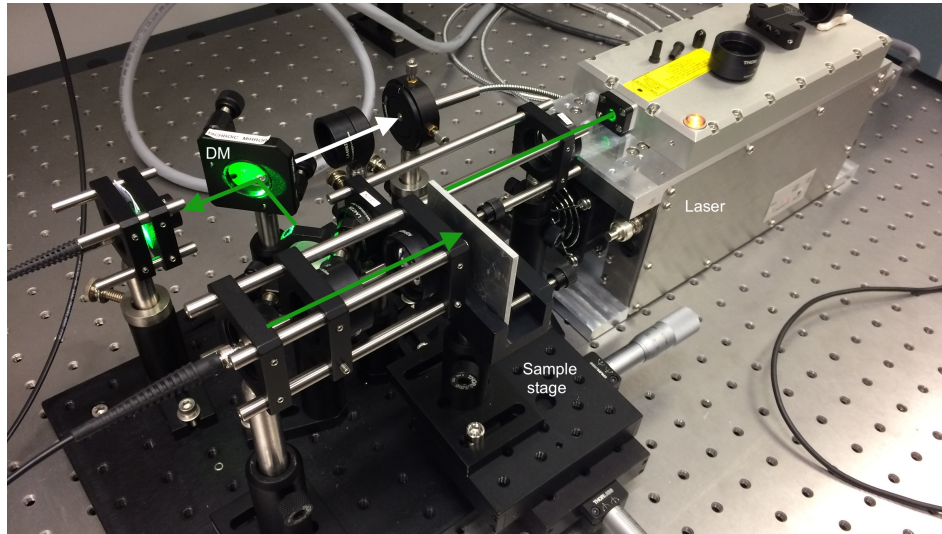


Figure 18: The μ LIBS system in configuration 1. The green arrow represents the laser beam. In this configuration the beam enters a beam expander that corrects for large divergence and is coupled into a 100 μ m fiber using two mirrors (one being a dichroic labeled DM) and a $f=20$ mm lens. The 10 m, 100 μ m fiber brings the light to the sample stage (foreground) where a lens system is used to focus the beam to ~ 30 μ m.

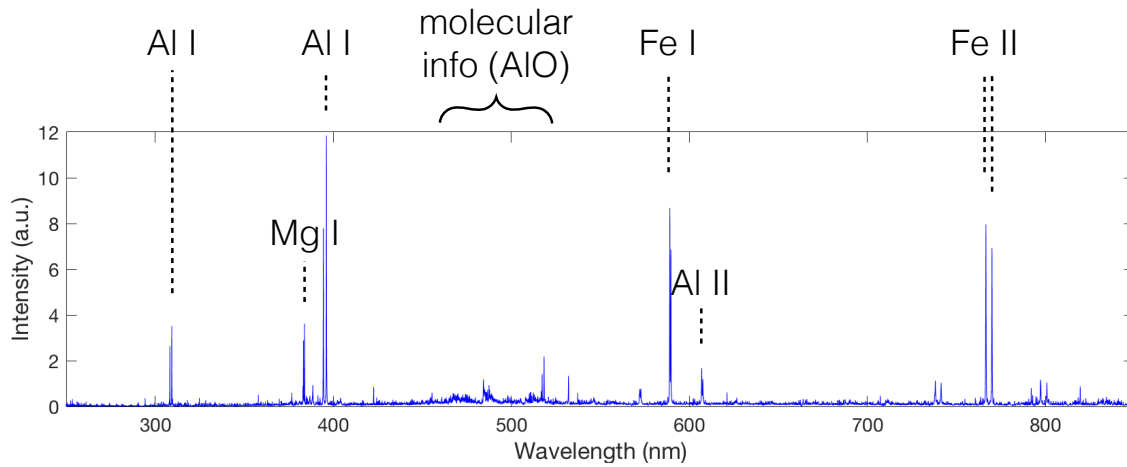


Figure 19: An example of a LIBS spectra of aluminium using the 532 nm μ LIBS instrument.

power” configuration) because it loses much less power before it reaches the sample target; the beam only encounters six surfaces (compared to 12), and there is no loss from fiber coupling. The total loss through this configuration is only 4%, meaning the power delivered to the target is ~ 108 kW. The 10 m fiber is instead using on a off-axis collection system, which guides the emitted light from the plasma to the spectrograph with a proper delay. The laser spot size at the target was measured with the Beamage camera at $10.1\text{ }\mu\text{m}$, which is three times smaller than that of the nominal configuration. This is possible because the beam is expanded to fill the aspheric focusing lens. The peak intensity at the the target is 67 GW/cm^2 , significantly higher than the threshold intensity found in the literature. This configuration has yet to be tested, but would be useful to investigate the threshold intensity needed for samples that did not work in the first configuration, which has one-tenth the peak intensity.

4 The LIBS/Raman Sensor (LIRS)

Together with MacDonald, Dettwiler and Associates (MDA) and Institut national d’optique/National Optics Institute (INO), York is part of a Canadian Space Agency (CSA) contract to design the LIBS/Raman Sensor (LIRS) instrument which combines μ LIBS with Raman and laser-induced fluorescence (LIF) spectroscopy. Since the three techniques utilize similar equipment, such as a laser, spectrograph, and a detector, the combination of LIBS and Raman/LIF spectroscopy into one unit is attractive for planetary exploration missions where mass, volume, and power are greatly restricted. Although some LIBS/Raman combined systems exist (see SuperCam and others [11, 26, 42, 48, 55]), the best concept for combining Raman and LIBS technologies in a way that maximizes flight potential is uncertain. York is involved in the characterization phase of the instrument, which will determine its capabilities for detection different elements, minerals, and organics in Mars-relevant samples, and will clarify system requirements. The characterization of the LIRS instrument proceeded in two parts (herein Phase 1 and Phase 2). All descriptions of the LIRS breadboard (layout, lasers, beam parameters, etc.) pertain to the current state of the instrument and correspond to Phase 2 of characterization. Section 6 briefly overviews the results of the Phase 1 and the changes made to the breadboard for Phase 2.

4.1 LIRS Concept

Table 5 gives an overview of the LIRS breadboard requirements and Figure 20 is a schematic of the instrument. Two laser sources are used on the breadboard to provide different excitation wavelengths for LIBS and Raman/LIF: 1064 nm and 266 nm. The two beams are overlapped at a motorized beam expander that is controlled by a computer and is used to focus at different sensing distances (over 0.2–0.5 m). The beams hit two mirrors, one of which has motorized tip/tilt control for alignment (labeled M). From here, the beams are focused by an off-axis parabolic mirror to the target. Of course, only one mode is operated at a time, thus only one laser is on at a time. Light from the sample (whether from a LIBS plasma, Raman scattering, or fluorescence) is collected by an $f/2.3$ telescope and coupled into a 50 μ m diameter, 1 m long fiber (labelled F). The NA of the fiber is 0.22, which ensures the $f/\#$ of the telescope and the fiber are matched (via $f/\# = 0.5/\text{NA}$). The telescope has a motorized secondary mirror to adjust the focus of the collection optics according to

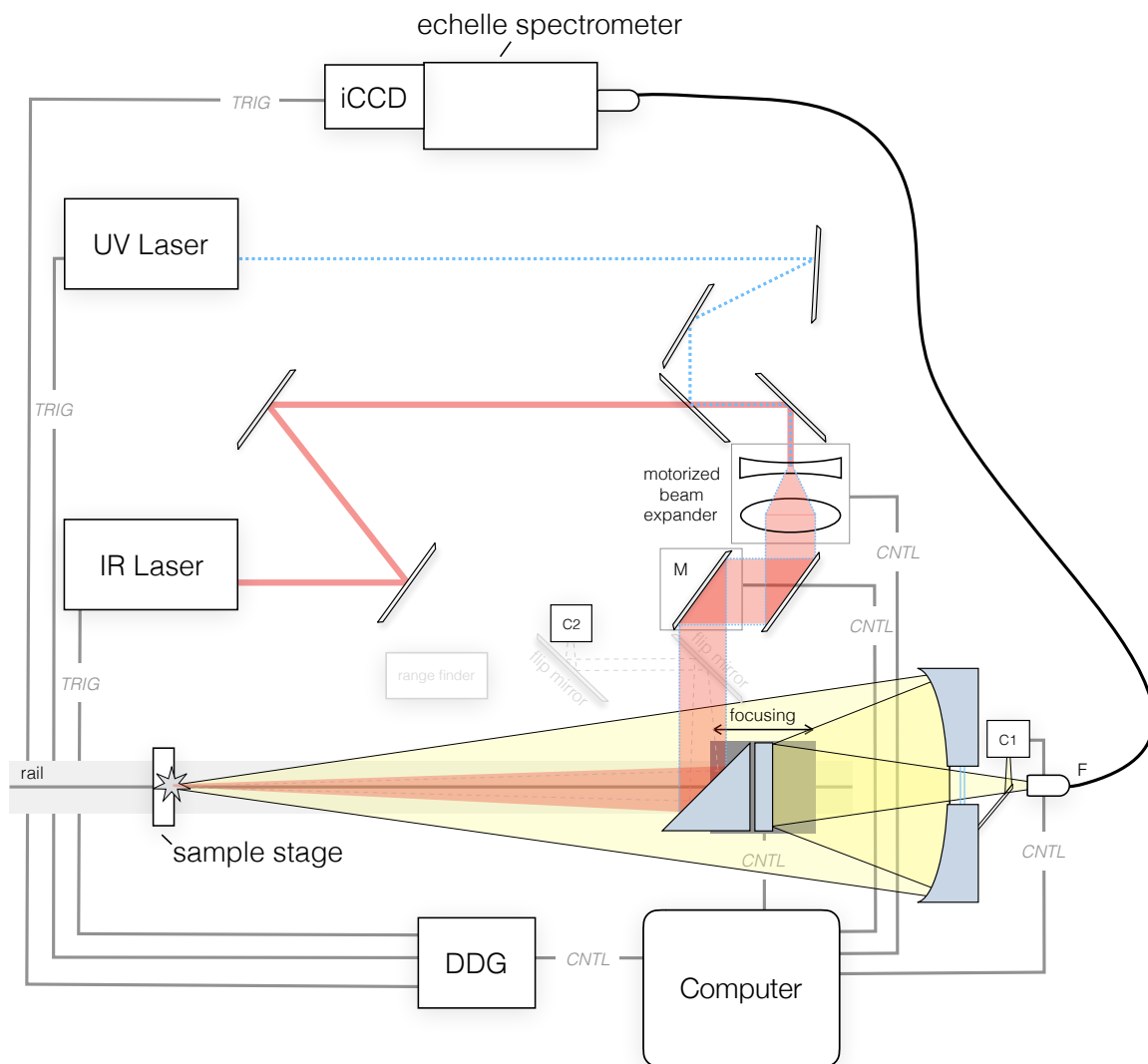


Figure 20: Schematic overview of the LIRS concept instrument. The blue and red lines represent the paths of the UV and IR lasers, respectively, and the yellow represents the collected light from the sample (either characteristic emissions from a plasma, Raman scattered photons, or a fluorescence signature).

Table 5: LIRS instrument requirements.

LIBS		Raman	LIF
Target range		0.2–0.5 m	
Spatial resolution	30–60 μm	< 1 mm	
Detection limits	0.03 wt%	100 ppm for organics	
Laser wavelength	1064 nm	266 nm	
Spectral range	270–850 nm	267–300 nm 100–4000 cm ^{−1}	300–800 nm
Resolution	0.04–0.16 nm (UV-NIR)	20 cm ^{−1} (0.14 nm)	0.2–0.5 nm
Pulse energy	>100 μJ*	Few 10s μJ	
Repetition rate	Up to 10 kHz	Few kHz	
Pulse duration	0.2–1 ns*	<1 ns	
Spectrograph	Echelle spectrograph		
Detector	ICCD		
Time-resolved detection	Yes, 1 ns resolution		
Mounting	Arm, deck		

*These are updated requirements that were changed from Phase 1 to 2.

the target distance. Both the beam expander and the focusing stage are calibrated to any sensing distance for the IR and UV beams separately. The fiber transports the light to a combined echelle spectrograph and ICCD system. Here the Andor Mechelle spectrograph and the Andor iStar ICCD are used. Together they allow for a wide spectral range (200–850 nm) and a high resolution (0.04–0.16 nm with a $25 \times 50 \mu\text{m}$ slit). I should note here that the Andor Mechelle spectrometer is an $f/7$, meaning the telescope and the spectrometer are *not* ideally matched for the highest throughput. The telescope was originally designed for a $f/3$ spectrometer, but this instrument did not meet our science requirement for spectral resolution. The impact of this $f/\#$ mismatch on our results is currently unknown. The ICCD is connected to a computer where data read off the detector is received and converted to a spectrum. A digital delay generator (DDG) controls the timing of all processes (e.g. laser on/off, camera on/off).

Included on the breadboard are a range finder, alignment camera (C1), and a context camera (C2). The range finder is used to determine the distance to the target sample. A flip mirror is

used to direct the beam from the range finder to the target surface, and the measured distance is inputted into the program which directs the motorized beam expander and secondary mirror to move accordingly. The alignment camera is then used to ensure the collection optics are aligned with the laser beams by using an 532 nm alignment laser injected into the telescope. Changes to the laser alignment can be performed using the motorized kinematic mirror. The context camera can be used to take images of the samples on the target stage. This camera is extremely important for obtaining the geological context of any measurements. Figure 27 shows examples of images taken with the context camera.

Figure 21 gives an overview of the data products produced by LIRS. Elemental information is given by LIBS spectra, molecular bonding information is given by Raman spectra (which is more-often-than-not used for mineral identification), and LIF spectra can be used to identify certain organic compounds. The latter is especially true when looking at how the LIF spectrum evolves over time, called time-resolved LIF or TR-LIF.

4.2 LIBS mode

The LIBS technique was extensively discussed in Section 2. Currently, LIRS uses an active Q-switched 1064 nm laser (Bright Solutions Wedge HF) with 293 kW peak power and 560 ps pulse width at a 10 kHz repetition rate. The $1/e^2$ diameter of the beam was measured with a Spiricon SP620 camera and found to vary from 21 to 47 μm over the whole sensing range. The peak intensity is calculated at the target to vary from 40.9 to 8.3 GW/cm^2 over the same sensing distance. The highest peak intensity occurs at the shortest target distance, but the lowest peak intensity encountered is still eight times the plasma formation threshold given in the literature (1 GW/cm^2).

4.3 Raman mode

Raman scattering occurs when a molecule is excited by some excitation source (in this case a laser), which causes vibration, rotation, or stretching of molecular bonds. These movements result in scattered photons that are shifted in energy (and hence wavelength via $E = hc/\lambda$) depending on if the photons gained or lost energy. Here the photons scattered at longer wavelengths compared to incident photons are measured. This is called Stokes scattering. Raman spectra have peaks at

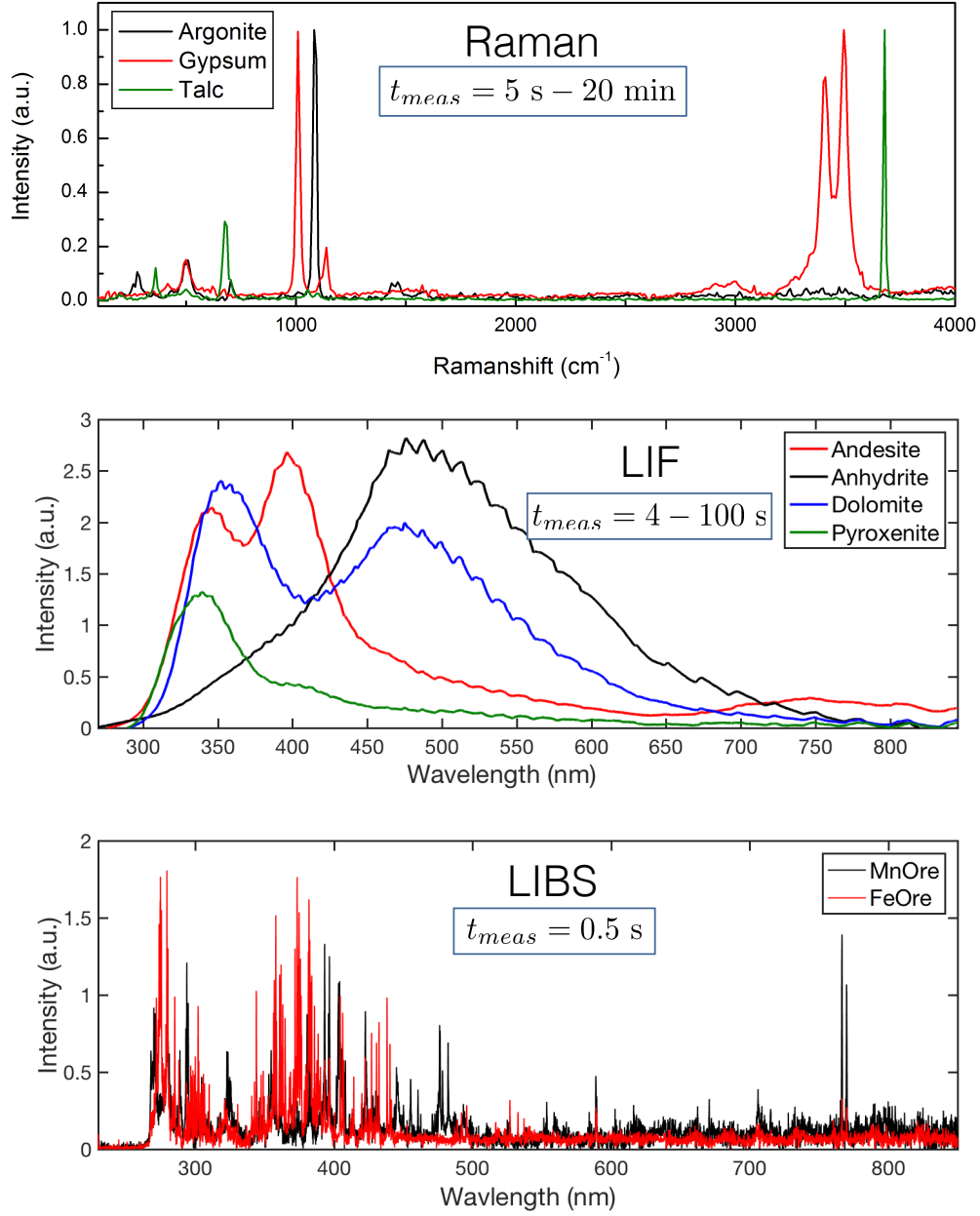


Figure 21: Overview of the data products available from the LIRS instrument. Elemental and molecular bond information is given by LIBS and Raman techniques, respectively, and organic identification is possible via LIF. Not shown here is an example of a time-resolved LIF measurement. All spectra are normalized.

different wavenumbers (cm^{-1}), each corresponding to a different shift in energy of photons (see Figure 21). Each peak, therefore, denotes a different vibrational frequency of a molecule, and can together be used to identify a material.

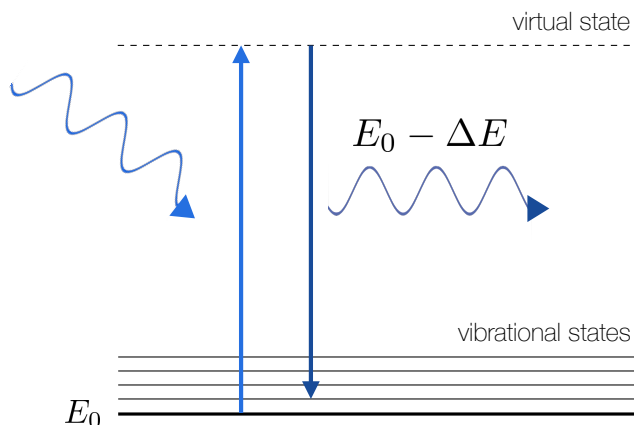


Figure 22: Molecular energy level diagram depicting Stokes Raman scattering, where emitted photons have lower energy (and therefore, longer wavelength) than the incoming radiation.

Figure 22 gives a visual representation of the process occurring during Stokes Raman scattering. Here, the energy level diagram depicts molecular orbitals (which can be thought of as the result of overlapping atomic orbitals). Superimposed onto the electronic energy level of each molecular orbital is a series of closely spaced vibrational states. This can be represented on an energy level diagram using the addition of a harmonic oscillator potential, but since these diagrams can get a bit confusing, and since Raman spectroscopy is not the focus of this thesis, a simplified version is presented. Stokes Raman scattering occurs when a molecule is excited to some virtual state, and after a short period of time (10^{-15} to 10^{-14} s [56]) the molecule returns from the virtual state to the first excited vibrational level of the ground state (E_0). The energy of the emitted photon will be less by a quantized amount corresponding to the difference in energy between the ground state and the first vibrational level, ΔE .

Raman spectroscopy is very similar to LIBS in terms of instrumental requirements. At the most basic level, both require a laser, camera, and spectrometer. Currently, LIRS utilizes an active Q-switched 266 nm laser (currently Bright Solutions Wedge HF) for both Raman and LIF modes (LIBS uses a separate 1064 nm laser). Although complicated by absorption, the intensity of

Raman peaks is directly proportional to ν^4 lending LIRS a major advantage over 532 nm systems, but UV photobleaching effects must be considered (i.e., effects of the UV radiation on the materials themselves). The spot size of the UV laser over the whole sensing range is $\sim 10\text{ }\mu\text{m}$, allowing for spatially high-resolution measurements.

4.4 Laser-induced fluorescence (LIF) mode

Fluorescence is a familiar process to most people (at least those who have seen anything glow-in-the-dark²). Stated simply, fluorescence is the re-emission of absorbed electromagnetic energy. Figure 23 presents a visual representation of this process. Excitation of a molecule to any one of the higher vibrational states of a higher energy level (E_1) occurs via absorption of photons [56]. The excited molecule will transfer through non-radiative processes to the ground vibrational state of the first excited state (E_1), then release a photon, de-exciting the molecule to some vibrational level of the ground state energy level (E_0). The fluorescence signature is broad since the de-excited electron can return to any ground state vibrational level. In the case of a laser instrument like LIRS, this method is called *laser-induced* fluorescence (LIF) because a laser is used as an excitation source. In the literature this is also called laser-induced natural fluorescence. This technique is not to be confused with a similar technique where the wavelength of the laser is specifically tuned to fluoresce a certain molecular species (also called LIF).

Measurement of the duration of a fluorescence signature, called the *fluorescence lifetime*, permits the identification of or discrimination between many organic species [19,32]. For this reason, LIF is an important addition to an instrument whose purpose is to determine future or past habitability on another planet.

The LIF mode and Raman mode share the same excitation source (266 nm Bright Solutions Wedge HF laser) and optics. All three modes share the same focusing mechanisms, collection optics, and spectrograph.

²Although, technically, anything that re-emits radiation for a long time after exposure to radiation is typically called phosphorescent. Fluorescence and phosphorescence are both types of *photoluminescence*.

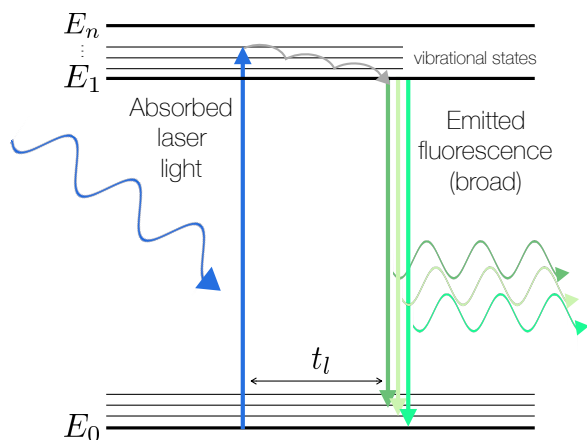


Figure 23: Molecular energy level diagram depicting laser-induced fluorescence. The de-excitations through vibrational states are non-radiative transitions.

4.5 Science Team at York University

Characterization of the LIRS instrument was performed by Emmanuel Lalla and I. Emmanuel's focus was the Raman and fluorescence modes, and all data collection for those techniques was performed by him. He also had a large part in sample preparation and development of those methods, making >90% of the pellets used in this study. Specifically, in addition to performing all data acquisition in LIF and Raman modes, Emmanuel performed the acquisition parameter determination for both Raman and LIF (Section 7.3.1 and the beginning of Section 7.5), and found the main sources for discussion of our Raman results ([8, 20, 58], Section 7.3.3). He also compiled a list of bands we were able to see in our Raman data, leading to Figure 35 and the following discussion. Considering this, the Raman mode and LIF mode are left in much less detail than that of the report presented to the CSA, and are presented only to give context for the instrument's performance collectively.

Although I was heavily involved with the instrument as a whole, my main focus was the μ LIBS mode which is why the μ LIBS characterization is presented in complete detail here. Everything presented in Section 7.4 was performed by me, with the exception of coding for multivariate analysis. Menelaos Konstantinidis wrote the code for μ LIBS (and Raman) multivariate analysis under our guidance, following [62]. While μ LIBS was my priority, I conducted testing and diagnosis of the instrument on a regular basis (including instrument calibration and alignment) and performed

analyses and interpretation of results in all modes. Major contributions to Raman and LIF modes are the organic LOD and multivariate analysis (Sections 7.3.4, 7.3.5), time-resolved fluorescence data analysis and discussion (Section 7.5.2), passive reflectance measurements (Section 7.6), and the combined characterization discussion (Section 7.7).

The characterization plan – presented in the next section – was prepared by me with input from Emmanuel for the LIF and Raman methods.

5 LIRS Performance Characterization Strategy

What follows is an overview of a report delivered to the CSA detailing our performance characterization strategy for the LIRS instrument.

The main characterization and testing approach for the LIRS breadboard instrument uses geologic standards relevant to Mars with known concentrations. The standards represent compositional and mineralogical varieties that correlate with geological processes on Mars such as volcanic eruptions, submarine-subaerial processes, and secondary mineralization processes, among others. The sample suite includes basalts, sedimentary minerals, and clays, where a variety of primary and secondary mineralization can be observed (e.g. silicates, sulfates, Fe- or Ti-oxides, carbonates). Additional samples will be manufactured to supplement the measurements derived from geological standards. The objective of the characterization phase is to determine the capabilities of individual techniques (LIBS, Raman, and LIF) and to work towards a refined concept for a future flight. This includes the identification of typical operational parameters, such as the measurement time, standoff distance, ICCD acquisition parameters, etc. for each analysis mode. This includes determination of LODs, along with the precision and accuracy of the instrument. A secondary goal is to identify typical operational parameters of the combined system, where measurement protocols are determined for a real-world scenario.

The plan is divided in the following parts: LIBS, Raman, and fluorescence objectives (Section 5.1), sample list and sample preparation (Section 5.2), methods of characterization in LIBS, Raman, and fluorescence (Sections 5.3, 5.4, and 5.5), and combined methods (Section 5.6).

5.1 LIBS, Raman, and fluorescence objectives

Raman Objectives

- Identification of the minerals present in standards from Raman spectra.
- Determine basic acquisition parameters the Raman mode.
- Determine the limits of detection (LODs) for organic compounds.
- Ensure preservation of target integrity.

LIBS Objectives

- Establishing basic acquisition and measurement protocols for the LIBS mode.
- Establishing spectral pre-treatment requirements, such as background correction, denoising, and normalization.
- Quantitative determination of the major element concentration in oxide wt% of standards using predictive model.
- Determine the LODs for Si, Ca, Ti, Fe, Al, Mg, Mn, Na, K, H, N, and O.
- Creation of an atomic spectra database from measured LIBS spectra for interpretation of laboratory results and future gathered in-situ results.

LIF Objectives

- Establishing basic acquisition parameters for the LIF mode.
- Determination of fluorescence signature (organic or inorganic) and sample identification by the decay life-time.
- Ensure preservation of target integrity.
- Creation of a LIF database from organics measurements for interpretation of fluorescence results.

5.2 Samples and sample preparation

The main LIRS breadboard characterization objectives will be met using a subset of geologically relevant standards from the Brammer Standard Company that have been utilized previously in Koujelev et al. [31]. Table 6 lists the identification number or name, type, and major element concentrations in oxide wt% for each selected standard. These certified materials have been pressed into 2–3 mm thick pellets 13 mm in diameter. Composition of the standards encompasses the required elements for LIBS detection Si, Ca, Ti, Fe, Al, Mg, Mn, Na, K, and O over a wide range of concentrations, along with P and B (represented visually by Figure 24). These standards do not contain any appreciable amounts of both H and N. In both cases, manufactured samples can be created to calculate LODs for these ‘missing’ elements (KOH and analine $C_6H_5NH_2$ in ethanol on silica, for H and N, respectively). Characterizing the performance of LIRS using geological samples with likeness to potential real world targets is valuable. Calculating, for example, the LOD for each element using test targets that have near-ideal range of concentrations and use similar

substrates may be more simple, though these types of targets are not akin to those the instrument would encounter during a mission, making the measured LODs impractical. Prediction of rock concentrations (both elemental and mineral) using a partial least squares (PLS) model requires the target to be as similar as possible to samples used during the characterization stage, making geological (or even better, Mars analogue) samples desirable. For a similar reason, standards covering many matrix types were chosen. The mineral composition of each geologic sample (Table 6) can be confirmed with x-ray diffraction techniques for comparison with LIRS breadboard measurements.

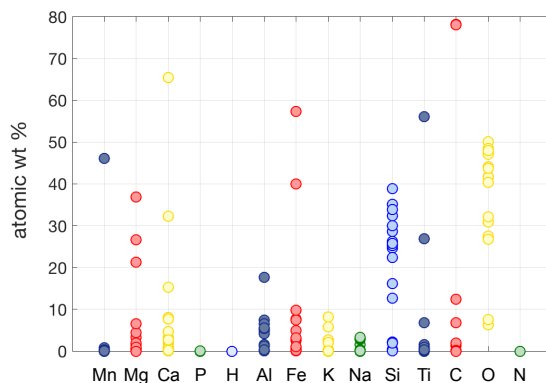


Figure 24: Overview of the elemental composition range (in wt%) for the sample set used to test the performance of LIRS. In total there are 20 geologic standards from the Brammer Standard Company.

These geologic standards alone are not enough for fully characterizing the LIRS breadboard (especially to determine instrument performance for organic detection). Manufactured organic samples will be created to supplement measurements from the standards listed in Table 6. The organics used in this study are listed in Table 7. Organic compounds include fatty acids (stearic acid and tetracosanoic acid), amino acids (alanine, cystine, lysine, and serine), and others. The aromatic amino acids (phenylalanine, tryptophan, and tyrosine) are particularly interesting for LIRS because they exhibit strong UV fluorescence. Preparation of the samples follows previous methods developed during the Raman Sensor for Identification of Carbon study [12,16]. Organics will be doped on a silica substrate at varying concentrations. Since the field of view of the laser is on the 10s of microns scale, it is important to ensure the dopant is homogeneously combined with the substrate. To establish accurate dopant/substrate ratios, substance losses during the mixing process must be accounted for. The procedure used to generate varying concentration mixtures of

Table 6: Certified major element compositions (in oxide wt%) for selected geological standards. Table 10 has more information on these standards, among others.

Type	Ref. Number	Certified major element compositions (wt% oxide)												
		SiO ₂	CaO	TiO ₂	TFe ₂ O ₃	Al ₂ O ₃	MgO	MnO	Na ₂ O	K ₂ O	P ₂ O ₅	CO ₂	S	Cr
Andesite	JA-1	63.97	5.7	0.85	7.07	15.22	1.57	0.157	3.84	0.77	0.165	0.099	0	0
Anorthosite	MO-6	51.77	10.06	1.87	10.92	22.78	2.1	0.076	4.04	0.76	0.14	1.32	0.069	0
Basalt	JB-2	53.25	9.82	1.19	14.25	14.64	4.62	0.218	2.04	0.42	0.101	0.103	0	0
Coulsonite	DC19003a	3.96	1.05	12.96	75.43	4.44	3.17	0.364	-	-	0.005	-	0.609	0
Flint Clay	SRM97b	42.4	0.035	2.4	1.18	39.24	0.18	0.006	0.066	0.62	0.05	-	0	0.0227
Granite	JG-2	76.83	0.7	0.044	0.97	12.47	0.037	0.016	3.54	4.71	0.002	0.013	0	0
Ilmenite	SARM59	0.75	0.05	48.8	50.3	0.61	0.56	1.05	-	-	-	-	0	0
Mn Ore	DC47005	22.24	3.6	0.1	3.203	3	1.44	57.789	0.048	0.46	0.186	-	0.012	0
Pyroxenite	SARM5	51.1	2.66	0.2	12.7	4.18	25.33	0.022	0.37	0.09	0.02	1.07	0	0
Syenite	SARM2	63.63	0.68	0.044	1.4	17.34	0.46	0.0103	0.43	15.35	0.12	9.00	0	0.0012
Wollastonite	DC60124	50.5	40.39	0.022	0.38	0.39	0.95	0.096	0.052	0.14	0.05	-	0.01	0

Table 7: Organic compounds for Raman/LIF analysis

Name	Comments/targeted bonds
Octacosane	C-C, C-H
Stearic acid	C-C, C-H, C-O, C=O
Tetracosanoic acid	
β -alanine	C-C, C-H, C-N, C-O, C=O
Cystine	C-C, C-H, C-N, C-O, C=O, S-S
Lysine	C-C, C-H, C-N, C-O, C=O
Serine	
Thymine	
β -carotene	biosignature
Phenylalanine	Exhibit strong deep UV fluorescence; essential amino acids for animals
Tryptophan	
Tyrosine	

compounds on a single mineral substrate is as follows:

- The mineral substrate (silica sand) is measured and heated to 600°C to remove any organic contamination.
- Some quantity of the desired compound is dissolved thoroughly into an appropriate solvent (ethanol for elemental compounds and dichloromethane or distilled water for organics).
- The compound and solvent mixture is added to the baked mineral substrate. The solvent is evaporated in a rotary evaporator, resulting in an even distribution of the compound across the substrate.
- Once the doped mixture is removed from the rotary evaporator, additional solvent should be used to clean off any leftover compounds that might have adhered to glass walls. This resulting solvent is used to determine the amount of chemical compound lost during the mixing process.

Since development of a calibration model (and instrument characterization) is the ultimate aim of this study, the concentrations of each compound are important and should be standardized. The detection goals of the LIRS breadboard for elements is 0.03 wt% and for organics is 100 ppm. Considering this, mixtures containing 1, 0.5, 0.1, 0.05, 0.01, and 0.001wt% of each will be

created. Once the mixtures have been successfully evaporated, powders are pressed into pellets approximately 2 mm thick with a 13 mm diameter. Additional samples could be manufactured, if needed, to either corroborate or extend LIBS/Raman/LIF results.

5.3 LIBS characterization methods

All samples should be analyzed under the same experimental conditions and instrument parameters. To accurately represent the compositions of the geological standards and reduce the effect of sample inhomogeneity, LIBS spectra acquisitions should be performed multiple times across each sample. This is very common for LIBS instrument sensitivity assessment (see [33, 52, 62]). Measuring multiple spectra at each location then averaging to produce one spectrum at each site will act to reduce noise [52]. The five spectra from each sample are averaged to produce a single, representative spectrum. Suggested acquisition parameters include a total measurement time of less than 5 minutes taken over a variable sensing distance of 0.2–0.5 m.

For each element (Si, Ca, Ti, Fe, Al, Mg, Mn, Na, K, O, N, and H) a spectral line catalogue has been created from the NIST Spectral Line Database which includes characteristic emission wavelengths for each element, along with the Einstein coefficient (transition probability), energy levels and their degeneracies [30]. Once the emission peaks of relevant elements are identified within measured spectra, a representative peak (at a specific wavelength) must be chosen for each element. Selection of appropriate lines for the LIRS instrument response should be done based on the following factors:

- Strong line in the spectral range (267³-850 nm).
- Minimum overlapping with other characteristic emissions.
- Usually, ground state and lower energy transition lines will experience more self-absorption characteristics [12]. Self-absorption occurs when an emitted photon from a species is re-absorbed by an atom of the same species. Self-absorption will alter spectral line profiles and thus hinder qualitative determination of major elements, so higher energy level transitions are preferred [31]. Note that lines that are self-absorbed at atmospheric pressure are not necessarily self-absorbed in Martian conditions.

³Note that the spectral range of the spectrometer (Mechelle and iStar system) is 200-850 nm but here a 267 nm edge filter is used to remove the UV laser signature in Raman/LIF spectra

For quantitative analysis a calibration curve of instrument response (peak signal intensity versus concentration) of the element to be detected must be prepared [12]. An example of a calibration curve is shown in Figure 25, where each point is the line intensity from a different sample containing the element of interest. The main performance figure of merit that is given for LIBS instruments is the LOD, which describes the minimum amount of analyte that can be present and can be found to be present within a sample. The slope of the calibration curve is used to determine the LOD at some confidence level, along with the standard deviation of the measurements. The measured LODs can be compared with ChemCam and other portable LIBS systems (see [34,50,62]). Quantitative

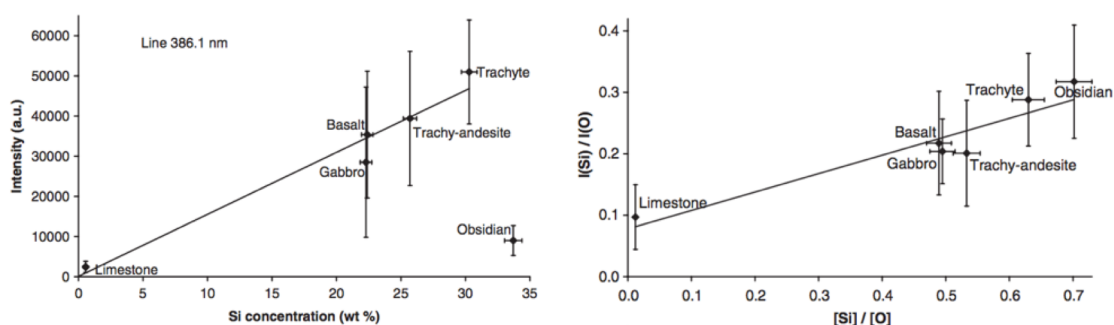


Figure 25: Comparison of calibration curves for Si with a) non-normalized spectra and b) internally normalized spectra. In the left it is clear from the Obsidian and Limestone data points that matrix effects were occurring in these species. Multiple spectra from each sample were averaged. The error bars represent one standard deviation. Adapted from [52].

LIBS analyses of complex matrices, like geological samples, are hampered by matrix effects that can result from shot-to-shot variations in the vaporized mass and/or in the excitation temperature of the plasma resulting from fluctuations in laser intensity, coupling efficiency of the laser with the target material, and other instrumental variations [12]. Because of this, a linear regression on the calibration curves (used to then calculate the LODs) may not have a good fit, and some processing is needed to correct for the effects. Using an internal standard for normalization of peak intensities⁴ is a common approach for correction of matrix effects in LIBS studies [12,13,23,31,37,52]. In this scheme, calibration curves are created using intensity ratios where the normalization intensity is usually the major element of the matrix, and preferably an element that occurs in all samples. In the case of geologic materials, the preferred normalization element is either Si, Fe, or O [31]. Before

⁴Generally when calculating the intensity of emission peaks, it is more accurate to use peak integration (finding total area underneath the peak) than using a maximum value [8].

internal normalization with emission peaks, the spectra can also be normalized to a total intensity of 1 and filtered (using moving average or Fourier transform filters), removing some variability in instrument response [9].

5.4 Raman characterization methods

The Raman mode of the LIRS breadboard uses a 266 nm laser pulse up to 50 kHz. The frequency at which the laser pulses can be optimized, and the maximum permissible intensity should be determined. For both Raman and LIF, the laser spot size and the detection field of view (FOV) should be matched to reduce the effect of interfering ambient light, though the FOV is limited by the spectrograph entrance (50 μm). The spot size is such that a single Raman spectra could encompass several mineral species with micron grain sizes, and become monomineralic with larger grains up to several mm. It will be necessary to take several acquisitions or/and accumulations at different locations to accurately represent the minerals present in each standard. Suggested acquisition parameters for Raman mode are the same as those in LIBS mode (measurement time of less than 5 min, taken at five different spots across one sample, and over a variable sensing distance of 0.2–0.5 m).

Both the geologic standards and manufactured organic standards should be measured in Raman mode. LODs in Raman spectroscopy are sometimes taken to be the lowest measurement at which the Raman peak intensity is 2–3 times greater than the noise within the spectrum. Instead, the same strategy as that of LIBS analysis is used, i.e., the slope of the calibration curve created for an organic is used to determine the LOD of that organic.

5.5 Fluorescence characterization methods

LIF mode will mainly be used for detection of organics. This is achieved via time-resolved fluorescence measurements. Organic compounds have fluorescence lifetimes on the order of 10 ns or less, while un-organic compounds decay much slower. A time-resolved fluorescence measurement, taken using kinetic mode on the Andor iStar ICCD, will identify organics by the quick decay of a spectral response. The time taken for the fluorescence signal to increase, reach a maximum, and decay is called the fluorescence lifetime. Calculation of fluorescence lifetimes are possible with fast-gated ICCDs (like the one used in LIRS), and can be used to fingerprint the particular organic present,

or distinguish between families of organic materials [19].

5.6 Combined methods

Another way to characterize the performance of the LIRS instrument is in measurement repeatability or precision; a measure of the agreement of a set of results among themselves. There is an inherent variability between laser shots and consecutive spectra because of the short-lived nature of a LIBS event and because the minerals covered by each laser shot could vary [12]. The relative standard deviation (RSD) can be used to describe measurement repeatability. The RSD can be calculated using peak intensity measurements for each element or the main mineral peak intensity using spectra from all samples.

Quantitative elemental and organic abundances along with compound LODs can be calculated using a MVA model [16]. The prediction capability of the model depends on the samples used for calibration. The uncertainty of any new sample lying in the compositional range covered by the calibration standard and the expected error in future tests can be estimated using the root mean square error of prediction (RMSEP) in the units of prediction quantity. RMSEP values will correspond to the absolute error made in the major element and mineral content predictions and are somewhat equivalent to the limit of quantification [12, 33]. While the RSD is a measure of precision, the RMSEP can quantify the accuracy.

5.7 Performance and sensitivity test summary

A summary of the proposed characterization and calibration activities for each LIRS mode is listed below.

LIBS characterization

- Manufacture samples for H and N analysis.
- Determine LODs for Si, Ca, Ti, Fe, Al, Mg, Mn, Na, K, O, N, and H at 0.2 and 0.5 m working distance.
- [For each sample] Acquire spectra on five points across sample. Sampling spots should be separated by 0.06 mm to test mapping resolution.

- [At each spot] Acquire an individual spectrum. Determine the required integration time for each spectrum and ICCD parameters (gate width, gain, etc.).
- Take the average of the five spectra.
- Determine the required measurement time of the 5-point map.
- Determine the spectral pre-processing requirements. At the minimum, the background should be removed. Background should be measured in close time proximity to the measurement. 30 spectra using the same spectrometer settings but without the laser light are taken as the background. The average of these spectra is subtracted from each “active” spectrum (there should be 65 total spectra from 13 samples total).
- Both L0 (not pre-processed) and L1 (pre-processed) spectra are saved into a database.
- Identify the spectral lines in each spectrum using the NIST spectral lines database. The Andor Solis software labels each line with its wavelength, but elemental identification must be performed.
- Choose representative lines for each element following the selection criteria presented in Section IV.I.
- Create calibration curves for each required major element. The LODs for each element (along with RMSEP values) are determined from this analysis.
- Inspect the resulting ablation crater at 0.2 and 0.5 m working distances (cross-sectional area and depth) using optical microscope.

Raman/LIF characterization

- Manufacture organic doped silica samples with varying concentrations.
- Determine the minerals present in each sample using x-ray diffraction (Royal Ontario Museum).
- Determination of the LOD of organics at 0.2 m and 0.5 m working distance.
- [For each sample] Acquire spectra on five points across sample. Sampling spots should be separated by 0.06 mm or less in order to test mapping resolution.
- [At each spot] Acquire Raman spectra on accumulation mode. Some minerals need more time to become measurable. A standard accumulation time should be determined, though this time can be adjusted if looking for tricky compounds.

- [At each spot] Acquire LIF spectra on accumulation mode.
- [At each spot] Acquire a time-resolved fluorescence spectra.
- Create calibration curves for each organic compound.
- Identify minerals present at each spot via the vibrations present in the spectra.
- Determine the time needed for the 5-point map.
- Determine the spectral pre-processing requirements. At the minimum, the background should be removed (this can be done with a non-Raman active sample such as zinc).
- Both L0 (not pre-processed) and L1 (pre-processed) Raman and fluorescence spectra are saved into a database. This is especially important for fluorescence.
- Ensure the Raman mode is nondestructive using optical microscope.

Combined characterization and practical demonstration

Since the characterization of the LIRS breadboard will be performed using geologically relevant samples, the practical demonstration can serve to confirm LIRS capabilities further, on a whole rock sample (instead of a powdered, pressed sample). The main portion of the characterization involves testing of individual modes of the LIRS breadboard (LIBS/Raman/LIF) and calibrating these individual systems, while this phase focuses on the combined methods and synergy of the instrument. To identify the combined capabilities:

- Determine the complete sample mineralization and its geological/environmental context.
- Characterization of the organics/inorganics material by the Raman (structural characterization and identification), LIBS (elemental composition and quantification) and LIF (organic distribution/quantification on the samples).
- Identify an interesting sample region using the context imager.
- Create a 2.5×2.5 mm square mapping area (this corresponds to 1600 points).
 - [At each point] A “flight” protocol will be tested. The working distance determined such that the Raman beam matches the LIBS crater should be used.
 - Perform a Raman acquisition utilizing measurement parameters determined in the individual mode.
 - Perform a LIF accumulation.
 - Perform a LIBS measurement.

- Perform a Raman acquisition.
- Ensure the resolution of the mapping is the same to the point-to-point resolution measured in individual modes.
- Determine minerals, elements, and if possible, organics present.
- Selecting representative Raman peaks for creating heat maps (maps are generated plotting the point of maximum intensity of a single characteristic peak in each compound).
- Select representative elemental peaks for creating heat maps.
- Select representative LIF peaks for creating heat maps.
- Create a 2D map of the 2.5×2.5 mm area.
- Determine the time required for a mapping of this size.

6 LIRS Characterization Results: Phase 1

The following chapter gives a very brief overview of LIRS performance during Phase 1 of the characterization performed at York. The upgrades to the breadboard are summarized at the end of the section, and Phase 2 of characterization is detailed thoroughly thereafter.

6.1 Raman mode Results

Characterization of the Raman mode on the LIRS instrument, at the most basic level, included determining which of our selected samples (Table 6) produced a Raman scattering signal using a UV laser excitation source, and which of those showed no Raman scattering signal. Although a thorough plan for each mode was established (see Section 5.7), the entire proposal was not completed. Camera acquisition parameters and instrument timing were optimized for each sample individually, yet there were still some samples that did not produce any usable spectra. Table 8 gives an overview of the samples that worked (i.e., those that LIRS could acquire a Raman spectrum from and from which constituent minerals could be identified) and those that did not work (i.e., those that LIRS could not acquire a Raman spectrum from).

Table 8 contains organics, the original geologic standards chosen for characterization (see Section 5.2), and some extra geologic standards used to extend the original sample set. These were added because most of the original samples did not work in Raman mode (they were originally chosen to optimize LIBS analysis in that they contain a large range in concentrations of all elements). Some samples are listed as NM in Table 8, meaning they were not measured. Most samples (except for tetracosanoic acid and thymine) were attempted at 35 cm and measurements at other sensing distances were performed time permitting.

There were some issues with the UV laser originally chosen for the LIRS breadboard (266 nm ALPHALAS laser with a passive Q-switch) including a very low pulse energy, a less than ideal beam profile, and a high beam divergence. After travelling through the fore optics and focused on the sample, the beam profile was elliptical at best and blotchy at the worst (i.e., the beam did not have a distinct circular/elliptical shape). In this sense, it was hard to optimize the collection optics to get a maximum throughput. It was speculated that some of the samples did not produce successful Raman spectra because of the low average energy of the ALPHALAS laser. Raman scattering is a

Table 8: Summary of Phase 1 Raman measurement results. Green/M = Raman measurement was successful, Red/CM = Raman measurement was unsuccessful, NM = no measurement was attempted.

Standard	20 cm	35 cm	45 cm
Alanine	NM	M	NM
β -Carotene	NM	M	NM
Cystine	NM	M	NM
Lysine	NM	CM	NM
Octacosane	NM	M	NM
Phenylalanine	NM	CM	NM
Serine	NM	CM	NM
Stearic acid	NM	CM	NM
Tetracosanoic acid	NM	NM	NM
Thymine	NM	NM	NM
Tyrosine	NM	M	NM
Tryptophan	NM	M	NM
Andesite	CM	CM	CM
Anorthosite	CM	CM	CM
Basalt	CM	CM	CM
Coulsonite	NM	CM	NM
Flint Clay	NM	M	NM
Granite	NM	M	NM
Mn Ore	CM	CM	CM
Pyroxenite	CM	CM	CM
Syenite	NM	M	M
Ti Ore (Ilmenite)	CM	CM	CM
Wollastonite	M	M	M
Aragonite	M	M	M
Anhydrite	M	M	M
Dolomite	NM	M	M
Feldspar	NM	M	M
Gypsum	M	M	M
Olivine	NM	M	M
Talc	NM	M	M
Quartz	NM	M	M

linear process, so the number of photons incident on the sample is directly related to the number of photons scattered back. Both the spot profile and the average power were used as a rationale for upgrading the UV laser to one with better parameters. The new 266 nm Bright Solutions Wedge HF laser has a better beam profile and a higher average energy (variable from 22–215 mW, up from 15 mW with the ALPHALAS). Characterization performed with this new laser is detailed in Section 7.

Table 9: Summary of Phase 1 LIBS measurement results. M = measurement was successful, CM = measurement was unsuccessful, NM = no measurement was attempted, Green = plasma is formed, Red = no plasma is formed.

Standard	20 cm	35 cm	45 cm
Andesite	NM	CM	NM
Anorthosite	NM	CM	NM
Basalt	NM	CM	NM
Coulsonite	M	M	M
Flint Clay	NM	CM	NM
Granite	NM	CM	NM
Mn Ore	M	M	M
Pyroxenite	CM	CM	NM
Syenite	CM	CM	NM
Ti Ore (Ilmenite)	M	M	M
Wollastonite	NM	CM	NM
Aragonite	NM	NM	NM
Anhydrite	NM	CM	NM
Dolomite	NM	CM	NM
Feldspar	NM	NM	NM
Gypsum	NM	CM	NM
Olivine	NM	NM	NM
Talc	NM	NM	NM
Quartz	NM	NM	NM
Graphite	M	M	M
Aluminium	M	M	M

6.2 μ LIBS mode Results

During Phase 1 characterization it was immediately noticed that the μ LIBS mode was not working for some samples using the 1064 nm INO MOPAW laser with 480 μ J pulse energy, 10 ns pulse width, and 10 kHz repetition rate. The peak intensity of this laser at 35 cm is right at the LIBS threshold, ~ 1 GW/cm². Theoretically, LIBS has no limitations for target type, but only three of the original 11 geological standards (Table 6) produced successful LIBS spectra, plus graphite and aluminium. Table 9 gives an overview of μ LIBS functionality for the original samples and an extended set. For some samples like andesite and basalt, a visible plasma was formed on the surface of these samples but a successful LIBS spectrum could not be acquired. These spectra had no identifiable atomic emission lines and were not repeatable. In the second phase, the INO MOPAW laser was switched out for the Bright Solutions Wedge HF laser with a much larger peak intensity, up to 20 GW/cm² at the shortest sensing distance.

6.3 LIF mode Results

In the first phase, the performance of the LIF mode was briefly investigated, and no conspicuous issues arose. For those samples that were able to be measured in this brief period, all of them produced a LIF spectra in which features could be identified. These samples include organics (alanine, β -carotene, tyrosine, and tryptophan) and geologic standards (flint clay and granite).

6.4 Breadboard upgrades

Limitations on laser power clearly affected the performance in both LIBS and Raman modes. As mentioned in the previous sections, both the UV and IR lasers were be upgraded to higher power models. The upgraded UV laser has the added benefit that the beam profile is circular (TEM₀₀), and the residual green light after conversion to 266 nm is eliminated. Also, the new lasers are actively Q-switched lasers (the ALPHALAS and MOPAW lasers are passively Q-switched), allowing ease of control and improving our ability to synchronize instruments. With the breadboard upgrades the performance of the LIRS breadboard was re-characterized.

7 LIRS Characterization Results: Phase 2

What follows is an overview of a 188 page report delivered to the CSA detailing the performance of the LIRS breadboard.

7.1 Samples and Sample Preparation

The main LIRS breadboard characterization objectives were attempted using a subset of geologically relevant standards from the Brammer Standard Company (listed in Table 6) that have been utilized previously in Koujelev et al. [31]. These samples (Table 15) were found to be insufficient for full characterization in each mode so the sample suite was extended in different ways for both Raman/LIF and LIBS analyses. Manufactured organic samples were created to supplement measurements from the geologic standards especially for LIF and Raman measurements. Preparation of the samples loosely follows previous methods developed during the Raman Sensor for Identification of Carbon study [16], with minor modifications.

To determine organic LODs samples were manufactured using gypsum as a substrate, instead of silica sand as originally planned (see Section 5.2). The gypsum powder (reference number DC60112) is a standard material from the Brammer Standard Company. Organic doped sand samples were tested following the plan, but these samples show little to no Raman effect (even at higher concentrations), certainly not enough to perform any quantitative analysis with. The strategy for organic LOD analysis was modified to use a gypsum substrate and more analysis points across each sample (20 points instead of the baseline 5 points). The silica sand itself does not produce a strong Raman effect. This would seem like an advantage for using this particular compound, but using something that has strong and well known Raman peaks (like gypsum) was thought to be more useful for detecting the small changes imparted in the spectrum by the organic dopants. The strong substrate peaks could also then be used as internal normalization for quantitative analysis.

Doped samples were created at 50%, 25%, 10%, and 2.5% samples for alanine, octacosane, stearic acid, and serine. There were other organic compounds that produced successful Raman spectra, but when doped on gypsum with distilled water, there was a reaction that made these samples unusable. Future work could include determining the proper way to create doped gyp-

sum samples for lysine and tyrosine to extend this analysis to those organics (among others). A press from Pike Technologies (Figure 26, right) was used to press all samples into small, 13 mm diameter, 3 mm thick pellets. No binder was used. The pellets were glued to microscope slides (see Figure 27). All samples (including standard geologic powders) are pressed not only for easy handling and mounting into the sample stage, but also for LIBS analysis; although LIBS analysis with powders are possible, the impact pressure of the LIBS laser would spread powder around and make measurements difficult.

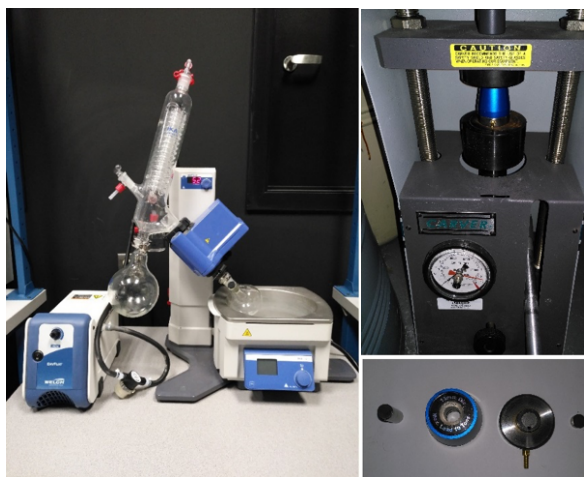


Figure 26: Equipment for sample preparation. Left: rotary evaporation system, right: pellet press and 13 mm pellet press die used to press manufactured samples and geologic standard powders.

A more advanced sample preparation method for doped standards at varying concentration was developed and is summarized by the following:

- Gypsum powder is heated to 600°C to remove organic contamination (alternately SiO₂ powder can be used, though particle size should be larger than 45 μm).
- A measured quantity of the organic compound is dissolved in distilled water. The amino acids have high solubility in water, and it is also generally easier to use.
- The mixture is evaporated in a rotary evaporator (Figure 26, left), resulting in an even distribution of the organic compound across the substrate.
- Before compressing the powders they are rehydrated with 1 ml of distilled water. These humidified samples were left to dry by evaporation at room temperature. This helped formation of stable pellets that won't break apart.

- The obtained pellet is glued to a microscope slide for easy handling.

With the breadboard upgrade the performance of the Raman mode on all original geologic standards (Table 6) was tested. UV Raman was again found not to work for some samples and therefore the sample set was extended to include anhydrite, aragonite, dolomite, gypsum, feldspar, olivine, and quartz. These additional minerals are similar to those used in Abbey et al. [1], where sulfates and carbonates were used as substrates for detecting organics by means of deep UV Raman spectroscopy. Characterizing these classes of minerals is advantageous because they are an important part of organic habitability. Certain sulfates and carbonates are necessary for the preservation of life, because their decomposition under varying environmental conditions can produce carbon dioxide and oxygen [1]. Additional samples (mainly Fe ore, ferrous rock, ultrabasic rock, and Cu-Mo ore) were added after testing plasma formation on original samples in μ LIBS mode. All samples used throughout the characterization are listed in Table 10. Reference materials for these samples can be found in catalogs from Brammer Standards [6], NIST [40], the National Research Council of Canada [44], and the United States Geological Survey [61].

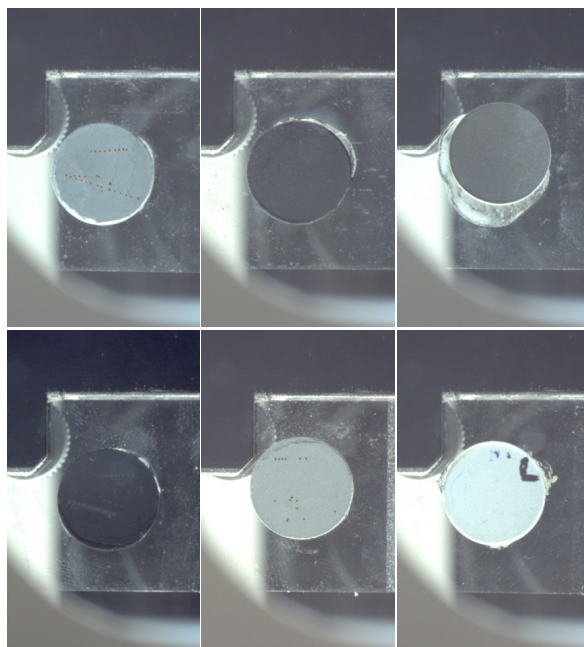


Figure 27: Context camera images. From left to right, top: andesite, coulsonite, flint clay, bottom: ilmenite, pyroxenite, wollastonite.

Table 10: Certified concentrations of all geological standards used in LIRS characterization.

Type	Name	Certified major element compositions (wt% oxide)							
		SiO ₂	CaO	TiO ₂	TFe ₂ O ₃	Al ₂ O ₃	MgO	MnO	Na ₂ O
Aluminosilicate	CRM 3486-86	70.54	0.52	0.62	5.24	11.29	0.48	0.11	1.67
Andesite	AGV-2	59.3	5.20	1.05	6.69	16.91	1.79	0.077	4.19
Andesite	DC73302	60.62	5.20	0.309	4.90	16.17	1.72	0.06	3.86
Andesite	JA-1	63.97	5.70	0.85	7.07	15.22	1.57	0.157	3.84
Andesite	JA-3	62.27	6.24	0.70	6.6	15.56	3.72	0.104	3.19
Anhydrite	DDR-AN	0.22	40.7	0.003	0.014	0.023	0.34	0.002	0.032
Anorthosite	MO-6	51.77	10.06	1.87	6.26	22.78	2.10	0.076	4.04
Anorthosite	MO-11	53.46	10.95	0.18	1.74	27.42	0.49	0.037	4.39
Aragonite	UNS-AK	0.64	54.9	(0.002)	0.13	0.11	0.11	0.003	0.047
Basalt	BHVO2	49.9	11.4	2.73	12.3	13.5	7.23	0.129	2.22
Basalt	JB-2	53.25	9.82	1.19	14.25	14.64	4.62	0.218	2.04
Coulsonite	DC19003a	3.96	1.05	12.9	75.43	4.40	3.17	0.364	
CuMo Ore	USZ 3-85	67.02	0.29	0.47	3.95	16.35	0.71	0.02	1.59
Dolomite	DC71306	0.62	30.02	0.015	0.21	0.10	21.8	0.01	(0.03)
Feldspar	DC61102	66.26	0.76	0.048	0.19	18.63	0.054		3.69
Fe Ore	DC11013	48.27	0.99	0.043	48.68	0.74	2.86	0.093	0.065
Ferrous Rock	FeR-2	49.21	2.17	0.18	39.21	5.16	2.10	0.12	0.51
Flint Clay	SRM97b	42.38	0.034	2.39	1.188	39.23	0.187	0.006	0.066
Gabbro	DC71304	35.69	9.86	7.69	24.75	14.14	5.25	0.193	2.11
Granite	JG-2	76.83	0.7	0.044	0.97	12.47	0.037	0.016	3.54
Granodiorite	GSP-2	66.6	2.10	0.66	4.90	14.9	0.96	0.04	2.78
Granodiorite	JG-1a	72.30	2.13	0.25	2	14.30	0.69	0.057	3.39
Grey Soil	CRM 2504-83	52.65	11.47	0.64	4.60	11.48	2.99	0.089	1.64
Gypsum	DC60112	1.68	39.24	0.016	0.16	0.34	1.74		0.065
Hornblende	JH-1	48.18	15.02	0.67	10.27	5.66	16.73	0.18	0.71
Ilmenite	SARM59	0.75	0.05	48.8	50.3	0.61	0.56	1.05	
Mn Ore	DC47005	22.24	3.6	0.1	3.203	3	1.44	57.76	0.048
Obsidian	NIST SRM278	73.05	0.983	0.245	2.04	14.15	(0.23)	0.052	4.84
Olivine	SX49-12	41.6	0.081	0.002	7.25	0.432	49.18	0.096	
Pyroxenite	SARM5	51.10	2.66	0.2	12.70	4.18	25.33	0.22	0.37
Quartz	SARM49								
Red Clay	CRM 5372-90	48.80	3.03	0.98	9.23	15.97	3.17	1.77	3.50
Red Soil	CRM 2501-83	59.18	0.17	1.56	7.86	17.01	0.92	0.051	0.15
Serpentine	SARM47	36.30	(0.1)	(0.01)	4.14	1.09	42.09	0.06	(0.05)
Syenite	SARM2	63.63	0.68	0.044	1.40	17.34	0.46	0.01	0.43
Talc	BCS-RM 203a	59.7	0.25	(0.01)	0.22	0.30	32.08		0.02
Ultrabasic Rock	DC72302	34.34	0.1	0.008	6.90	0.67	41.03	0.068	0.008
Wollastonite	DC60124	50.50	40.39	0.022	0.41	0.39	0.95	0.096	0.052

Table 10: Continued.

Certified compositions										Total*	Reference/source
K ₂ O	P ₂ O ₅	CO ₂	H ₂ O+	Ba	Cu	Cr	S	V			
2.21	0.28			0.039	0.025	0.008	0.43	0.006		98.91	Brammer
2.88	0.48			0.114	0.005	0.002		0.012		98.7	USGS
1.89	0.103	3.47	(1.5)	0.102	0.006	0.003	0.02	0.009		99.94	Brammer
0.77	0.165	(0.027)	0.72	0.031	0.004		0.002	0.011		100.11	Brammer
1.41	0.116	(0.014)	0.2	0.032	0.004	0.007	0.021	0.017		100.21	Brammer
0.013		0.65	0.5				23.07			95.56	Brammer
0.76	0.14	0.36	0.40	0.051	0.003	0.004	0.069	0.013		101.12	Brammer
0.65	0.041	0.0	0.33	0.032	0.003	0.001	0.01	0.002		99.74	Brammer
0.037	0.029	43	(0.324)	(0.003)			0.046			99.38	Brammer
0.52	0.27			0.013	0.013	0.028		0.032		100.27	USGS
0.42	0.101	(0.022)	0.25	0.022	0.023	0.003	0.002	0.058		99.07	Brammer/GSJ
	0.005				0.014		0.609	0.313		102.22	Brammer/NCS
3.68				0.089	0.817	0.0021	2.09			97.08	Brammer/CGL
0.038	0.006	46.77	(0.34)	0.004	0.003		0.011			99.98	Brammer/NCS
9.60										100.09	Brammer/NCS
0.165	0.124				0.0031		0.118			102.15	Brammer/NCS
1.33	0.27	0.07	0.98	0.024	0.005	0.005	0.17	(0.004)		101.52	NRCCRM
0.618	(0.046)			(0.018)		0.0227				86.19	NBS/NIST
0.15	0.028	0.12	1.09	0.009	0.003	0.001	0.37	0.077		101.53	Brammer
4.71	0.002	(0.004)	0.33	0.008						99.66	Brammer/NCS
5.38	0.29			0.134	0.004	0.002		0.005		98.76	USGS
3.96	0.083	(0.108)	0.59	0.047	0.0002	0.002		0.002		99.91	Brammer
2.09	0.17			0.05	0.003	0.008	0.04	0.009		99.73	Brammer
0.094		(4.02)	0.39				20.79			103.08	Brammer
0.53	0.099	0.60	1.82	0.011	0.008	0.062	0.057	0.023		100.63	Brammer/GSJ
						0.068		0.14		102.33	Brammer/MINTEK
0.46	0.186			0.42	0.014		0.012			92.48	Brammer/NCS
4.16	0.036	(0.01)		(0.114)	0.0006	(0.001)				99.91	NBS/NIST
0.014		0.046	1.25			0.26	(0.013)			100.22	Brammer
0.09	0.02	(0.08)		(0.005)	0.002	2.39		0.023		99.77	Brammer/MINTEK
											Brammer/MINTEK
2.79	0.72	1.00		0.11	0.032	0.009	0.15	0.015		100.58	Brammer
0.98	0.10			0.027	0.005	0.018	0.04	0.018		99.95	Brammer
(0.02)	(0.02)			(0.008)		0.20	(0.02)	(0.002)		84.11	Brammer/MINTEK
15.35	0.12	0.09	0.22	0.24	0.002	0.001		0.001		100.02	Brammer/MINTEK
0.005	0.13									99.50	BCS-RM
0.01	0.004	0.58	14.17	0.0006	0.0005	1.07	0.051	0.004		99.01	Brammer/NCS
0.14	0.052						(0.01)			99.94	Brammer/NCS

*includes L.O.I

7.2 Instrument Calibration

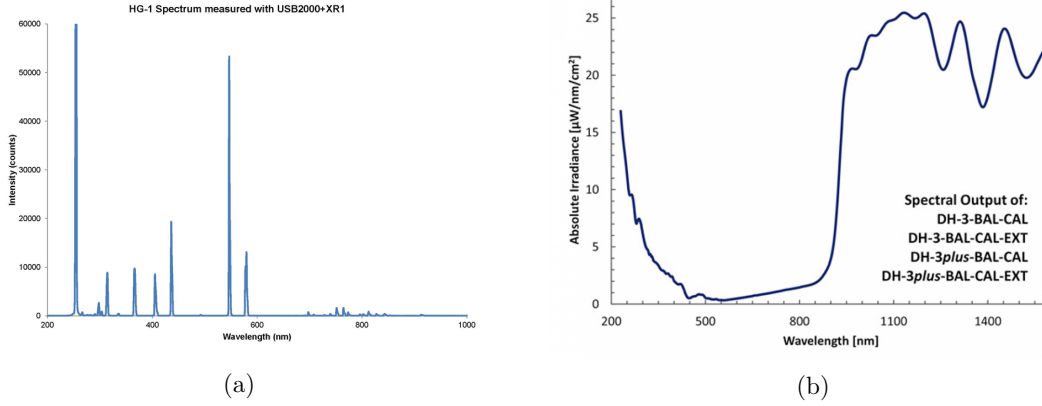


Figure 28: Spectra of required calibration sources: (a) HG-1 mercury-argon lamp, (b) DH-3p-BAL-CAL tungsten-halogen-deuterium lamp (230-1100 nm). Source: Ocean Optics.

Before performing any measurements the spectrometer must be properly calibrated. Calibration is necessary in order to ensure measurement accuracy and reproducibility and to carry out proper quantitative analysis. This process consists of a wavelength calibration followed by a relative intensity calibration (called the relative efficiency correction (REC) process). The latter is especially important to correct the instrument response between orders and the intra-order vignetting from this specific echelle spectrometer. On each order of the echelle, the light collection efficiency should theoretically drop by a factor of two, though in practice a larger discrepancy is seen. The REC correction is supposed to remove the effects of this efficiency difference. The wavelength calibration is performed using an Ocean Optics HG-1 Mercury-Argon lamp (Figure 28a). The calibration depends on the position of the HG-1 emission lines on the ICCD image. The procedure is straightforward, carried out using the Andor Solis software. The REC correction can also be performed using the Solis software, though for data presented here, the REC correction is done in MATLAB. Figure 29 gives an overview of the REC process.

First, the background of the measured spectra from the DH-3plus-BAL-CAL (Figure 28b) from Ocean Optics is subtracted and the result divided by the spectral response provided by the supplier. DH-3plus-BAL-CAL, a NIST certified calibration source, combines deuterium and tungsten-halogen lamps, providing balanced correction over 230-850 nm. The inverse of this is the correction factor (CF) which can be multiplied by any spectrum to correct for relative intensity.

Acquisition parameters for this correction usually include high exposure times (considering the weakness of the lamp in the UV) with low MCP gain.

Figure 29 shows both the raw and corrected spectra of the DH-3plus-BAL-CAL lamp. The corrected spectrum matches the shape of the true spectral response. An HG-1 spectra is corrected with the CF to ensure a good correction. For example, if the peaks are not located at the same wavelength before and after the correction, then the REC process should be repeated. This does not happen often, however, but it is valuable to double check the process. Three examples of the effect of REC correction of raw spectra are shown in Figures 30b, 30a, and 30c, for a Raman spectrum of gypsum, a LIBS spectrum of ilmenite, and a LIF spectrum of alanine, respectively.

Figure 30c shows the extent of the REC correction for spectra that are not the correction lamp spectrum. Although the correction works perfectly for the lamp used to create the correction, the CF applied to other spectra (taken with sometimes vastly different camera parameters) will not work as well.

The REC and wavelength calibration procedures were performed daily, and re-performed if the fiber was detached from the Mechelle at any point or if there was a large change in ambient air temperature.

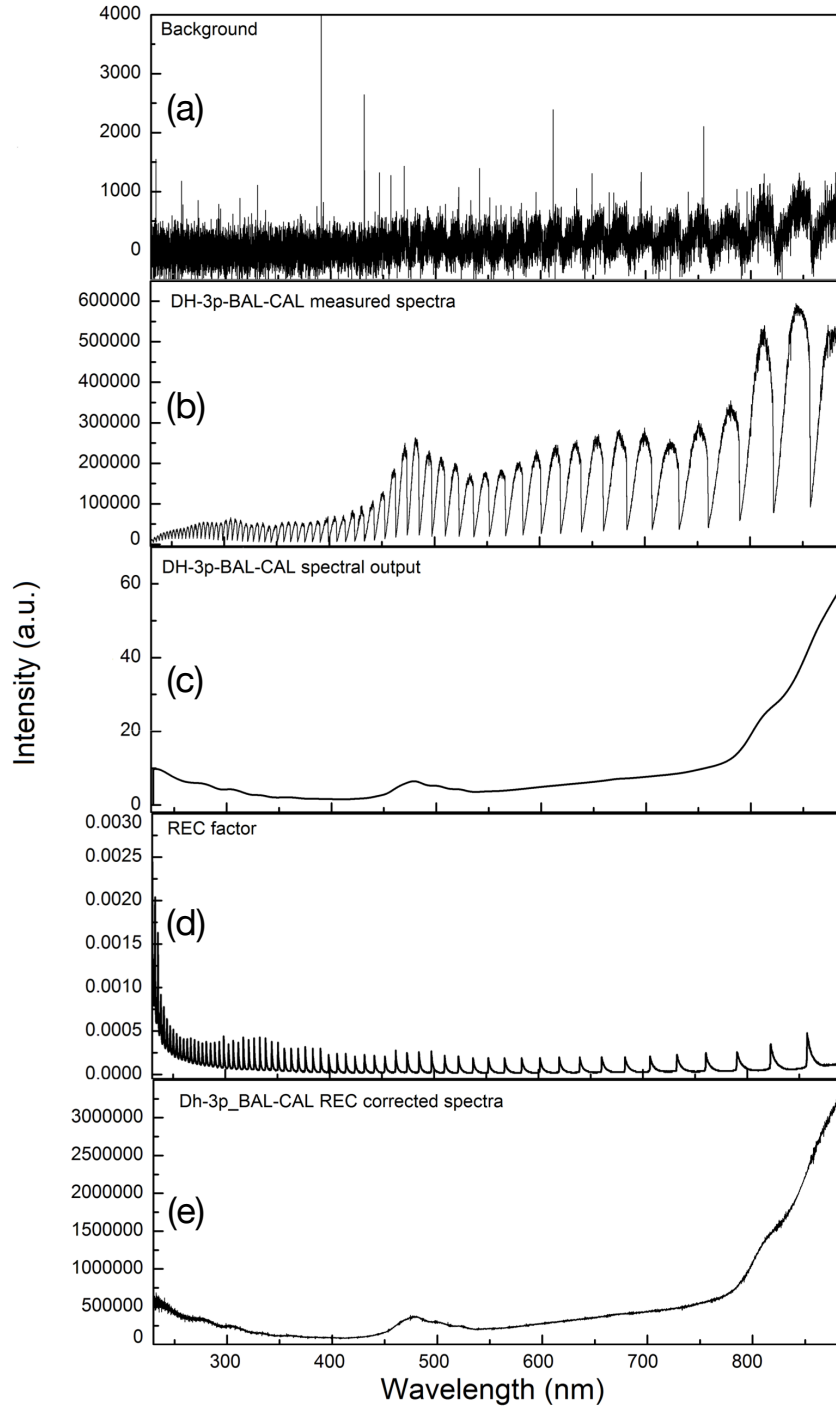
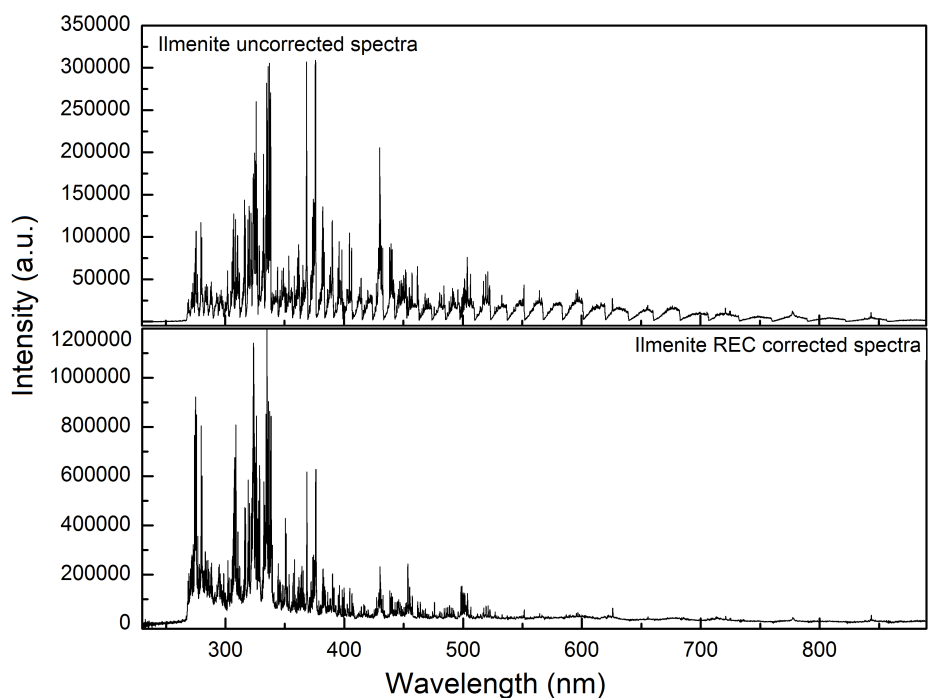
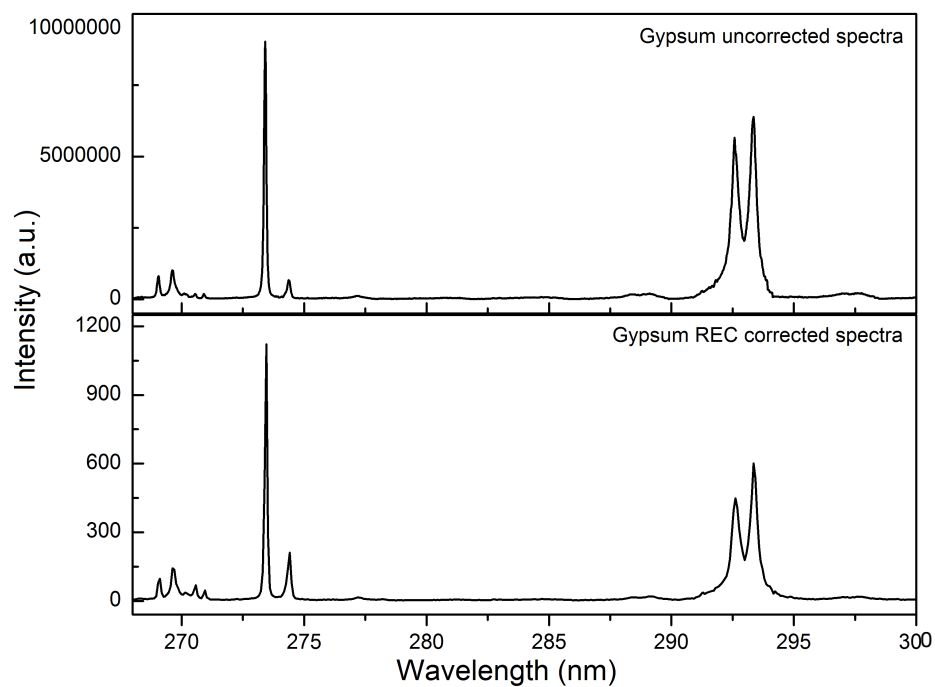


Figure 29: Overview of the relative efficiency correction (REC) process: (a) lamp background, (b) the measured spectra from the lamp, (c) the spectra provided by the supplier in our wavelength range, (d) the correction factor (CF) that is multiplied by all spectra to correct for intensity, and (e) the corrected lamp spectra showing the agreement with the theoretical spectrum after correction.

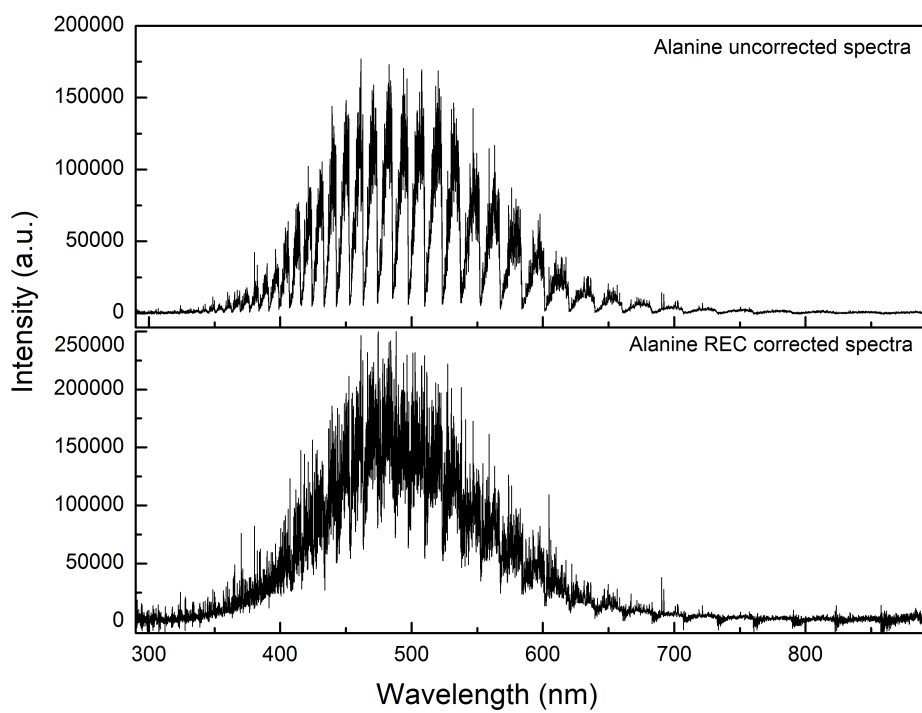


(a) LIBS spectrum of ilmenite.



(b) Raman spectrum of gypsum.

Figure 30: Examples of uncorrected and corrected spectra (REC correction) for (a) LIBS, (b) Raman, and (c) LIF on ilmenite, gypsum, and alanine, respectively.



(c) LIF spectrum of alanine.

Figure 30: Continued.

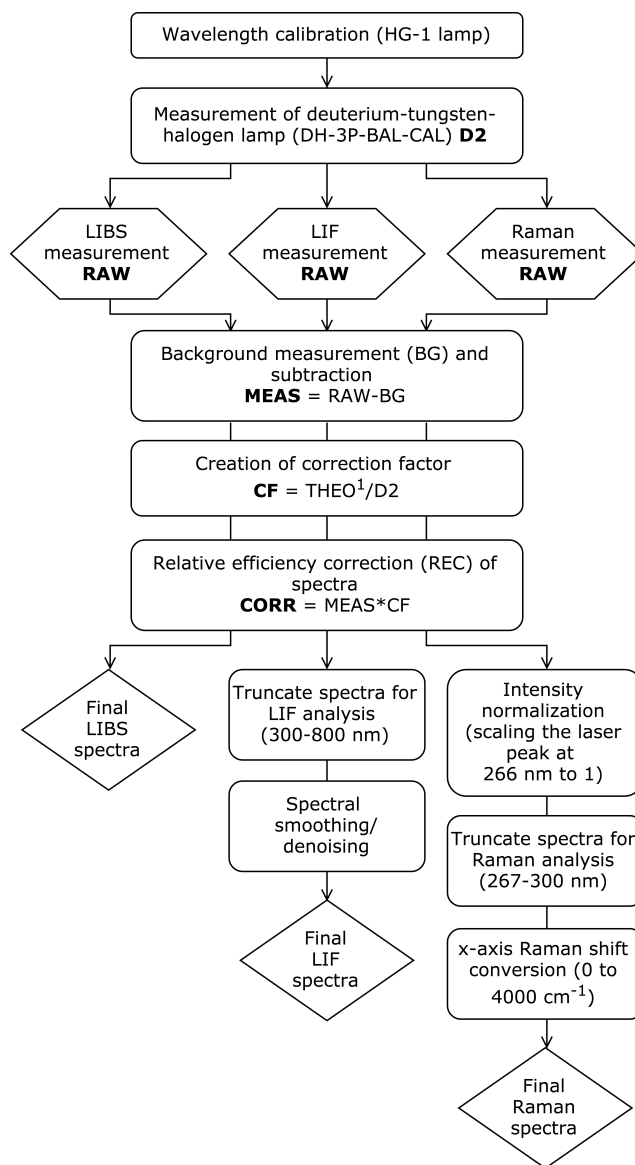


Figure 31: Calibration and brief overview of basic data processing for each measurement mode.

7.3 Raman Characterization

7.3.1 Comparison to previous breadboard

In Phase 1 the signal to noise ratio (SNR) was calculated for some Raman peaks in gypsum, quartz, and olivine spectra taken at 35 cm. SNR can be used as a figure of merit to compare the previous breadboard to the upgraded version. It is common in Raman spectroscopic analysis to define SNR as $(I_{peak} - I_{baseline})/\sqrt{I_{baseline}}$ where I_{peak} is the intensity of the peak and $I_{baseline}$ is the intensity at the bottom of the peak [4]. This is the definition used in throughout the Raman characterization section. Calculations of SNR using spectra acquired with the new breadboard at 35 cm were greatly improved. SNRs increased by a factor as low as 3 and as high as 50 for those peaks that can be identified.

Table 11: Typical acquisition parameters for Raman measurements. Each spectrum in this report was acquired using parameters following these guidelines.

Typical acquisition parameters				
Measurement time		5 s–35 min		
Sensing distance		0.25–0.43 m		
Laser frequency		10–20 kHz		
Laser power		100%		
Exposure time		varies		
		25 cm	35 cm	43 cm
ICCD gate delay	10 kHz	10.2 ns	11.8 ns	12.2 ns
	20 kHz	12.6 ns	12.8 ns	13.3 ns
	30 kHz	15.3 ns	16.0 ns	16.4 ns
	50 kHz	19 ns	20 ns	20.5 ns
ICCD gate width		4–5.5 ns		
ICCD MCP gain		4000		
# of acquisition spots per sample		5		
# of Raman spectra obtained per spot		1		
Total # of spectra per sample		5		

7.3.2 Optimal acquisition parameters

Table 11 details typical acquisition parameters (intensifier gate delays, gate widths, the MCP gain, and exposure times) for Raman measurements. Optimal gate delay was determined using kinetic mode. In kinetic mode a series of spectra is acquired where each consecutive spectrum has been delayed by a specific amount, therefore, when viewing the kinetic series the Raman signal is clearly seen to appear, reach a maximum, and disappear. The optimal gate delay is the point at which the Raman signal first appeared, and the optimal width encompasses the entire duration of the signal. Because the Raman effect is an inelastic scattering of laser light, the Raman signal is obtained at the same delay for each sample. Anhydrite was used for all timing optimizations because it has a strong peak at 1017 cm^{-1} (a symmetric stretch vibration of SO_4). Figure 32 shows the integrated peak intensity of the 1017 cm^{-1} band for each laser frequency at 35 cm. Changes in the optimal intensifier gate delay come when the sensing distance or the laser frequency changes, but over the 0.2–0.43 m dynamic range⁵ the optimal gate delay does not change with distance significantly. For the laser frequency however, the timing does change significantly, as evident from Figure 32. The optimal gate delays for each distance and at each laser frequency are summarized in Table 11.

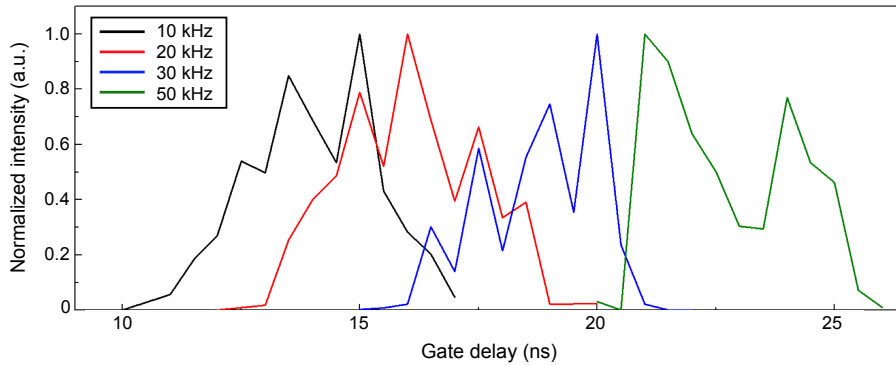


Figure 32: Timing and duration of the 1017 cm^{-1} band of anhydrite at four different laser frequencies. Each point on the curve is an integrated peak intensity at a different gate delay. Credit: E. Lalla.

It is clear that the laser repetition frequency has a large impact on timing when measuring in Raman mode. For this reason, laser frequency must be optimized for the best Raman spectra (high SNR) and for ensuring the method is non-destructive (for example, at 10 kHz the laser has 65 times

⁵The nominal sensing range is 0.2–0.5 m but the UV laser was only calibrated to 43 cm.

higher peak power than when the laser is pulsed at 50 kHz, or 10 times the average power). The latter is especially important when considering sensitivity of some of our samples to UV radiation. Frequency was optimized by tracking the Raman band SNR in four samples while varying the laser repetition rate. These are anhydrite, dolomite, alanine, and octacosane. For the organics both the C-H and C-C bonds were tracked. In most cases it was found that using the laser at 10 kHz results in the highest SNR, though there were certain cases where 20 kHz (with a lower laser intensity) give similar results. The SNR of Raman peaks using 30 kHz or 50 kHz was significantly lower.

The effect of high peak power UV radiation on organic compounds was briefly investigated and found to pose a problem for measurements that required a measurement time over 10 minutes. Further investigation into the mechanisms behind the damage (photobleaching versus photodissociation) for many different organics is needed for both the LIRS instrument and the SHERLOC instrument, which uses deep UV excitation [4].

7.3.3 Results at 35 cm

Typical LIRS Raman spectra are shown in Figure 33 and Figure 34 for geologic standards and organics, respectively. These spectra are an average of five spectra taken at different points along each sample, with the target stationed at 35 cm. Principal Raman peaks have been identified in each spectrum. For each target type the exposure time is optimized to the point where the noise floor is less than 1% of the total intensity (up to a maximum exposure time of 35 minutes). All Raman data presented here have been processed via a background subtraction and intensity calibration (as detailed in Section 7.2). All spectra are also normalized to their maximum value for clarity.

Some of our results can be compared to Abbey et al. [1]. They use a simple peak to noise ratio for the most prominent peak in the spectrum as a figure of merit. Correcting the noise level to 1, they then measure only the peak value (and not the integrated intensity), e.g. 241:1 would indicate that the most prominent peak is 241 times bigger than the background level on the corrected spectrum. Their deep UV Raman system acquired spectra with 30:1 peak ratio for dolomite, 705:1 for calcite, and 1720:1 for gypsum. Following this definition, our peak to noise ratios are 97067:1 in gypsum and 83867:1 in dolomite using optimal measurements. Note that these values are calculated using raw data, while the spectra presented in Figures 33 and 34 are normalized. Although here

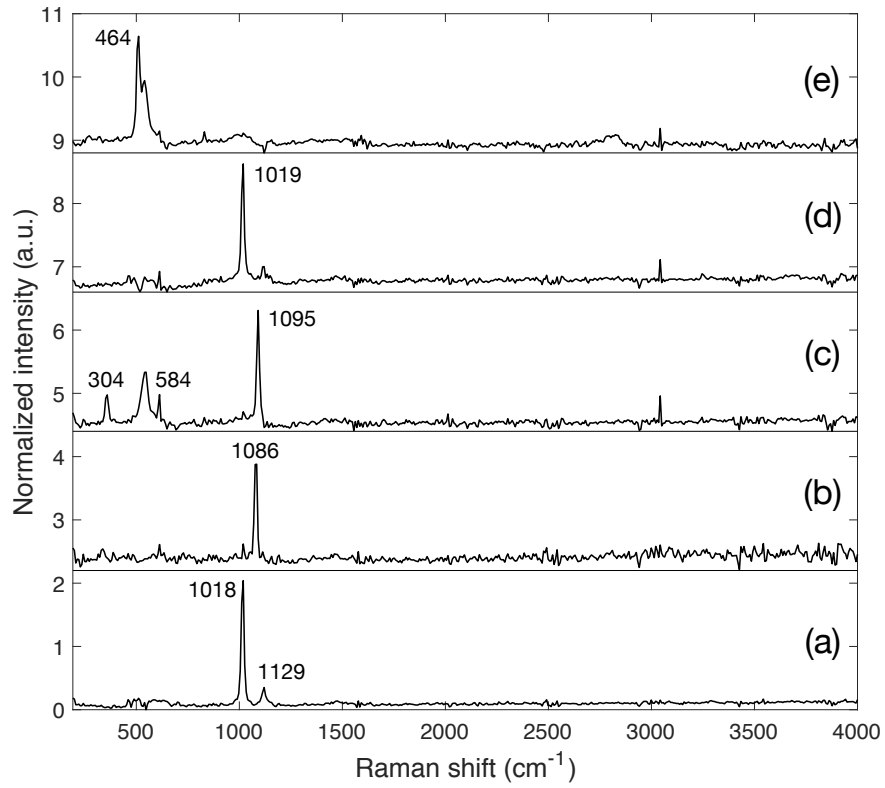


Figure 33: Raman spectra of (a) anhydrite, (b) aragonite, (c) dolomite, (d) gypsum, and (e) quartz taken with their optimal parameters. Spectra are vertically offset for clarity.

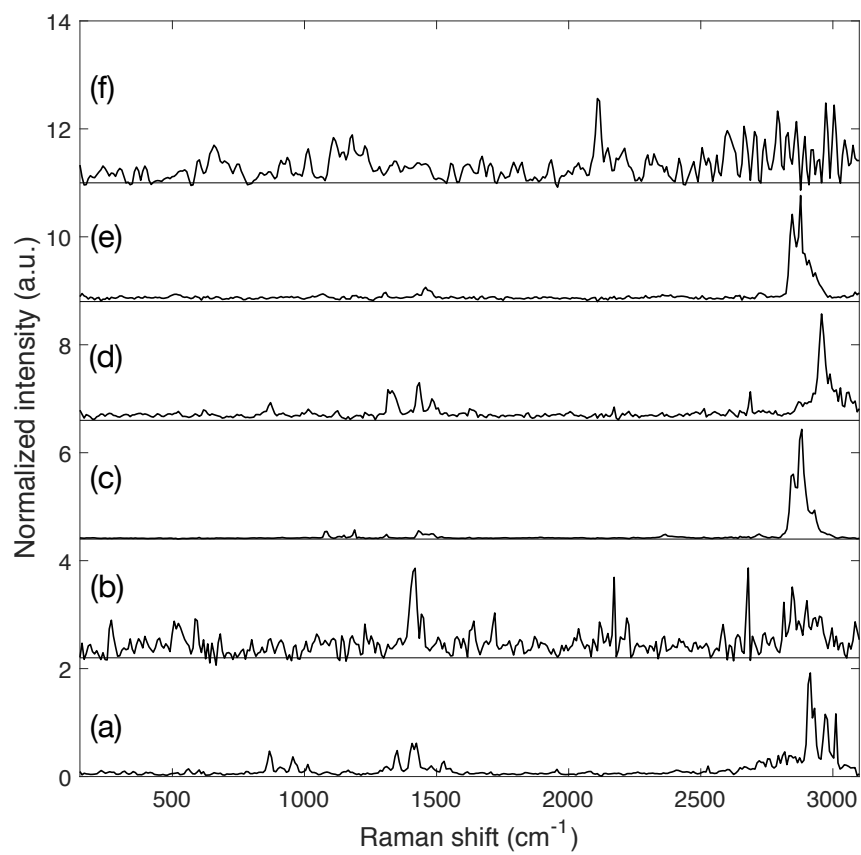


Figure 34: Raman spectra of pure organics, (a) alanine, (b) lysine, (c) octacosane, (d) serine, (e) stearic acid, and (f) tyrosine taken with their optimal parameters. Spectra are vertically offset for clarity.

Table 12: Summary of Phase 2 Raman measurement results for (a) geologic standards and (b) organic samples. Green/M = Raman measurement was successful, Red/CM = Raman measurement was unsuccessful, NM = no measurement was attempted.

(a)	
Standard	35 cm
Andesite	CM
Anorthosite	CM
Basalt	CM
Coulsonite	CM
Flint Clay	CM
Granite	CM
Mn Ore	CM
Pyroxenite	CM
Syenite	CM
Ti Ore (Ilmenite)	CM
Wollastonite	M
Aragonite	M
Anhydrite	M
Dolomite	M
Feldspar	CM
Gypsum	M
Olivine	CM
Quartz	M

(b)	
Standard	35 cm
Alanine	M
β -Carotene	CM
Cystine	CM
Lysine	M
Octacosane	M
Phenylalanine	CM
Serine	M
Stearic acid	M
Tetracosanoic acid	CM
Thymine	CM
Tryptophan	CM
Tyrosine	M

geologic standards of “gypsum” and “dolomite” are used, these standards aren’t actually mono-mineralic. In fact, none of the chosen geologic-standards are made up of only one mineral; these standards are created from whole rock samples which are ground into powder. Abbey et al. uses instead samples which only contain one mineral [1]. Abbey et al. have also measured some of the same organic samples in deep UV. For serine they list a SNR of 1690:1 (for 1320 cm^{-1}) and for tyrosine, 45:1 (at 1202 cm^{-1}) [1]. LIRS has 14834:1 and 3:1 for serine and tyrosine, respectively, at the same wavenumbers.

A summary of LIRS Raman performance is given in Table 12. Similar to the first phase (Table 12), UV Raman did not work for many geologic standards, but this time LIRS could also not obtain a successful Raman spectrum from feldspar or olivine. Both the very small UV laser spot

size ($<10\text{ }\mu\text{m}$ at 35 cm) and the Raman scattering efficiency of certain materials could be major issues. Stopar et al. [58] carried out several 532 nm , long distance Raman studies of natural rocks, finding similar results to ours. They calculated the Raman scattering efficiency, the ratio of Raman radiant exitance to incident laser irradiance for all their target materials. The sulfates (gypsum, anhydrite) and carbonates (aragonite, dolomite) showed a mean relative efficiency around 25–30 times larger than that of dacite (olivine) and 200 times to that of biotite granite (felsic). Similarly, our sulfate and carbonate spectra are high-quality, whereas feldspar and olivine are unsuccessful. The higher Raman scattering efficiency of sulfates and carbonates is shown via the time required to obtain relatively good spectra. For those two groups the average minimum exposure time, which provides a peak intensity to baseline level of 3, is $\sim 115\text{ s}$, while it is $>600\text{ s}$ for other geologic samples.

The quality of Raman spectra are also highly affected by the combinations of small laser spot size and the multi-mineral grains (and their sizes) within the sample. Chio et al. [8] showed that the Raman efficiency decreases with decreasing grain size. This is because with small grains come multiple reflections of incoming light and increased absorption of incident energy. Foucher et al. [20] confirmed this experimentally, where samples measured in bulk mode had 7 times higher peak intensities than those measured of powders with grains $<45\text{ }\mu\text{m}$. Of course, exact results are system dependent. One of our standards (olivine) was sifted using a sieve-shaker and the following distribution of grain sizes were found: 1.85% $>150\text{ }\mu\text{m}$, 8.49% between 90 and $150\text{ }\mu\text{m}$, 56.9% between 45 and $90\text{ }\mu\text{m}$, 30.8% between 25 to $45\text{ }\mu\text{m}$, 1.96% and $<25\text{ }\mu\text{m}$. This is taken as representative of our geologic standards on the whole.

It should also be considered that our samples are not mono-mineralic. Although LIBS instruments are often tested with geologic standards, Raman instruments are more often than not tested with samples which only comprise one mineral, thus not investigating possible interferences between different minerals. The same samples were chosen for characterization of LIBS so that, ideally, data sets could be integrated (though this might be the wrong choice for future testing of baseline performance of the Raman mode).

Figure 35 shows an overview of the vibrations that were successfully observed and identified in our Raman spectra. Compared to the previous version, most of the Raman bands vibrations have been observed on the new upgraded breadboard system, but the $\nu(\text{Si-O})$ vibration ($800\text{--}900$

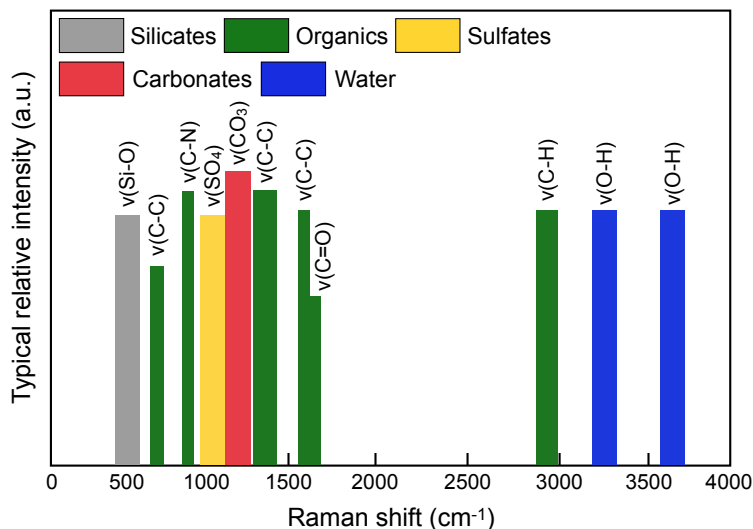


Figure 35: Observable and identifiable molecular vibrations in LIRS Raman results.

cm^{-1}) was not detected. This vibration is found in olivines. There are some vibrations that are unable to be observed and identify in both Phase 1 and Phase 2. Titanium and iron oxide vibrations (e.g. from anatase, rutile, and hematite) would be found in the $150\text{--}400\text{ cm}^{-1}$ region. A measurement of rutile was attempted, but it did not produce a successful UV Raman spectrum. There are many iron oxide minerals that could be used to identify signs of aqueous alteration on Mars (e.g. goethite is the aqueous version of magnetite). There are phosphate vibrations (e.g. from apatite) in the $900\text{--}1000\text{ cm}^{-1}$ region, but nothing was measured which contains these species. It would be advantageous to test phosphate minerals with LIRS in the future because these species will commonly undergo alteration by bio-organisms. There are nitrate vibrations in the $1800\text{--}2200\text{ cm}^{-1}$, but these are not natural and would not be found on Mars.

7.3.4 Organic Limits of Detection (LODs)

Figure 36 shows Raman spectra of alanine, octacosane, serine, and stearic acid at varying concentrations. The total exposure time used for these was 120 s (20 s exposure, 6 accumulations) to ensure both the organic and gypsum peaks were optimally acquired. The major organic peaks can be integrated and plotted versus the sample's known concentration to create calibration curves for each organic. For all organics the C-H band (near 3000 cm^{-1}) was integrated and normalized by

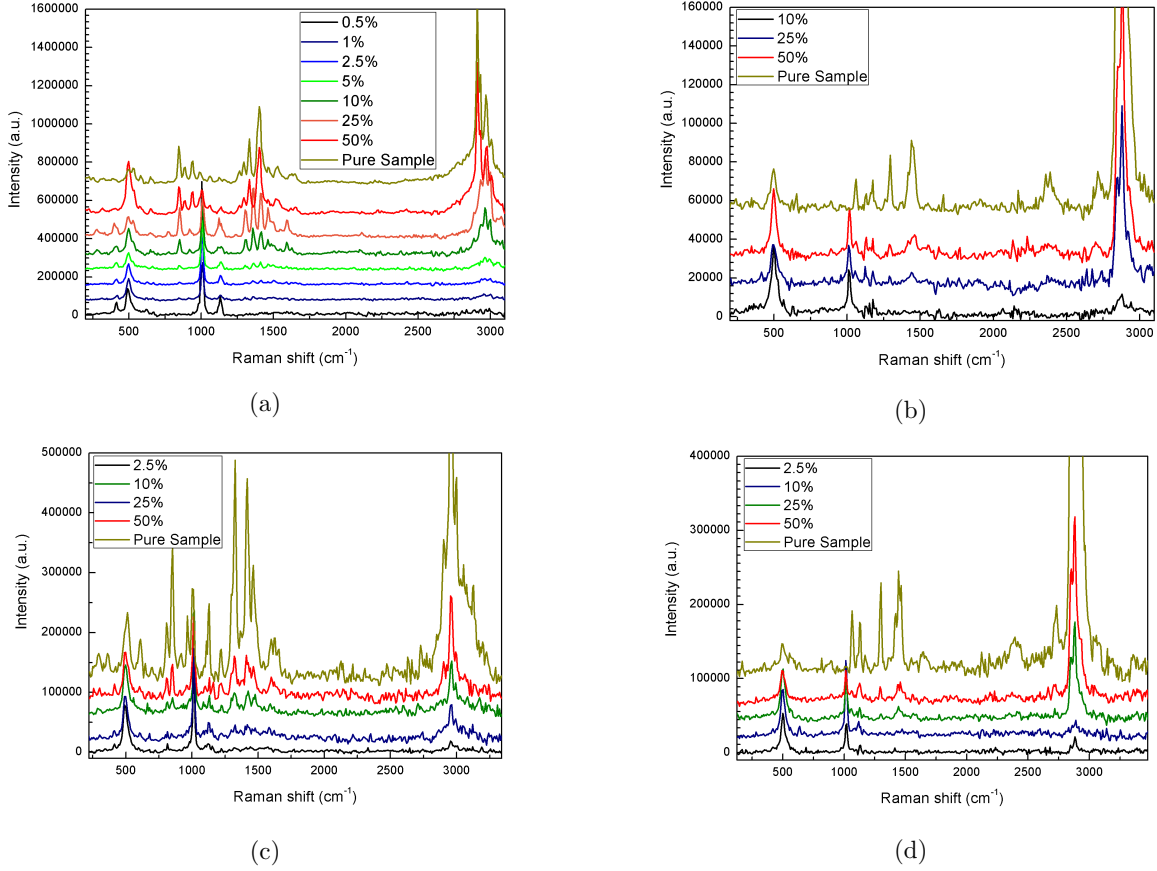


Figure 36: Raman spectra of organic doped gypsum at different concentrations: (a) alanine, (b) octacosane, (c) serine, and (d) stearic acid. Major gypsum peaks are at 500 cm^{-1} and 1000 cm^{-1} . Credit: E. Lalla.

the 1000 cm^{-1} gypsum peak. Calibration curves for each organic are shown in Figure 37.

Once the calibration curves are created, LOD can be calculated using

$$LOD = \frac{k\sigma}{m}, \quad (39)$$

where k is a confidence factor that determines the probability of reporting false positives, σ is the standard deviation of measurements made at the lowest concentration, and m is the slope of the regression line. Here a k -factor of 2 is chosen, which represents a 2-sigma case (a confidence interval of 95%). This is similar to analysis performed in [13, 21, 62]. A k -factor of 2 implies that there is a 2.5% chance that a peak that measures greater than the LOD is from a random fluctuation in the noise level of the instrument. A confidence interval of 95% was chosen following Wiens et al.

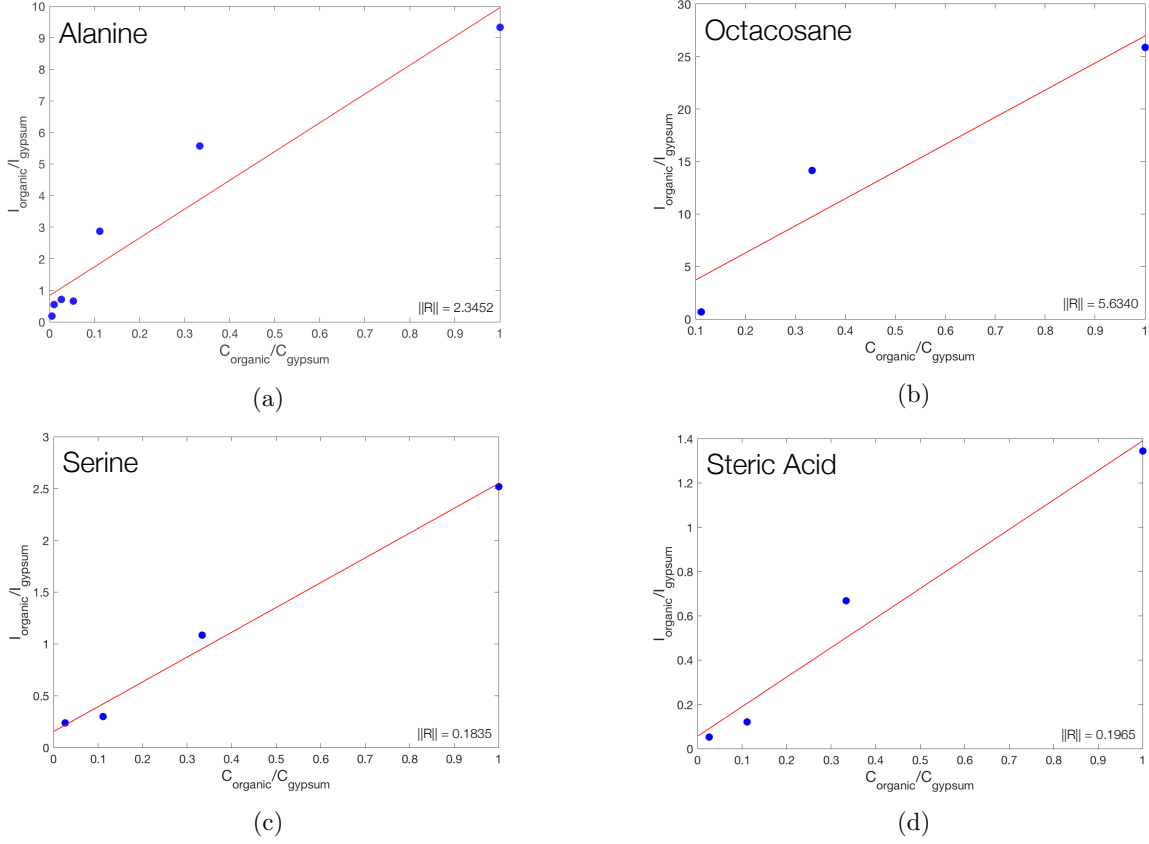


Figure 37: Calibration curves for amino acids created from the ratios of integrated peak intensities of the organic to the integrated peak intensity of gypsum: (a) alanine, (b) octacosane, (c) serine, and (d) steric acid.

[62], so that a consistent method for LIBS analysis could be used, enabling direct comparisons of our LODs with those of the ChemCam instrument. This is consistent with the IUPAC definition of LOD, which says that the LOD, *is derived from the smallest measure x_L that can be detected with reasonable certainty for a given analytical procedure* [39]. Specifically, $x_L = \overline{x_B} + k\sigma$, where $\overline{x_B}$ is the mean background signal, and σ is the standard deviation of the background. The LOD is a function of x_L ,

$$LOD = \frac{(x_L - \overline{x_B})}{m}, \quad (40)$$

$$= \frac{(\overline{x_B} + k\sigma - \overline{x_B})}{m}, \quad (41)$$

$$\Rightarrow LOD = \frac{k\sigma}{m}, \quad (42)$$

where m is the analytical sensitivity. The LOD (a measure of concentration) is found by relating $k\sigma$ to a concentration value, and this is accomplished by dividing by the slope of the calibration curve line obtained by linear regression analysis (Figure 38) [36,39]. The obtained value is a true reflection of the LOD when the slope of the linear regression is well-defined and the intercept is near zero [36]. Here we're using a slight modification where σ is defined as the standard deviation of measurements made at the lowest concentration (a function of the noise of the instrument), following Wiens et al. [62]. The calculated LODs for these four organics are 0.3893 wt% (3893 ppm) for alanine, 0.1641 wt% (1641 ppm) for octacosane, 0.0313 wt% (300 ppm) for serine, and 2.0313 wt% (20313 ppm) for stearic acid. Only the LOD of serine is close to the proposed LIRS detection capabilities (100 ppm), similar to the target LODs for SHERLOC (from 100–10000 ppm for specific organic compounds) [4].

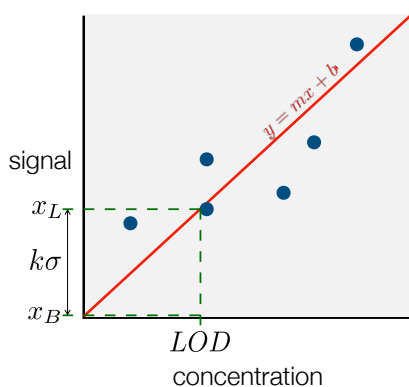


Figure 38: Signal versus concentration calibration curve emphasizing the relationship between $k\sigma$ to the LOD. Adapted from [36].

LODs could be improved if the number of points of analysis were increased on each sample (instead of only five). This would decrease the standard deviation of peak intensities at the lowest concentration. It should also be considered that there exists a major throughput issue with the telescope-spectrometer f/# mismatch. This directly impacts the our LODs in all modes. It is critical that the instrument is reassessed with a matching collection optics system (see Section 10).

A sample was created of 7.5% alanine doped gypsum to test our detection capabilities. Using the alanine calibration curve as a primitive model, the concentration of this sample can be predicted as long as the same peak that was used to make the curve is integrated (and is divided by the integrated intensity of the gypsum peak). This $I_{\text{alanine}}/I_{\text{gypsum}}$ value is 4.32. Using the linear fit parameters,

the predicted value of concentration of alanine to the concentration of gypsum is $C_{\text{alanine}}/C_{\text{gypsum}} = 0.141$. This can be converted to C_{alanine} if it is assumed that the concentration of gypsum is 100% - C_{alanine} [%]. Making this assumption, the concentration of alanine in this sample is predicted at 12.4% (making the percent error around 65%). In a real scenario, the percent concentration of gypsum could not be assumed, and instead a gypsum calibration curve (or other predictive model) is used to decouple the predicted concentration of alanine from the predicted $C_{\text{alanine}}/C_{\text{gypsum}}$ value. A gypsum calibration curve was created using the integrated peak intensities of the 1000 cm^{-1} gypsum peak in the alanine series of measurements. Using $I_{\text{gypsum}} = 38198$ in this particular spectrum, $C_{\text{gypsum}} = 90.9\%$, meaning our prediction of alanine using this method is $C_{\text{alanine}} = 12.82 \text{ wt\%}$, similar to the previous prediction.

7.3.5 Multivariate analysis

The use of multivariate analysis techniques was explored to predict the concentration of organic compounds more accurately. This could be especially useful if a model was created using many different organics, and it could predict both the type and concentration of the organic seen within a spectrum. Of course, minerals would eventually have to be integrated into the model as well, so that the model could distinguish between organic material and non-organic material by their Raman spectra (instead of only relying on time-resolved fluorescence measurements).

The model is similar to an advanced model created in Wiens et al. [62]. Instead of a regular partial least squares (PLS) model, the standards that are the least similar to the unknown sample are successively removed, the PLS model is re-calculated, and the prediction accuracy is optimized. The workflow is shown in Figure 39. First, the spectra that is being predicted is taken out of the dataset (called the target spectra). The Euclidean distance from the target spectra is calculated in a reduced 10-dimensional space created with independent component analysis (ICA). This means only 10 components/latent variables/factors that describe most of the variation in the dataset are kept. The norm between the target spectra and all the others is computed and the spectra with the largest norm is removed. A PLS analysis is performed and RMSEP is calculated. *RMSEP* is defined as

$$RMSEP = \sqrt{\frac{1}{n} \sum_{i=1}^n (c_{\text{known}} - c_{\text{predicted}})^2}, \quad (43)$$

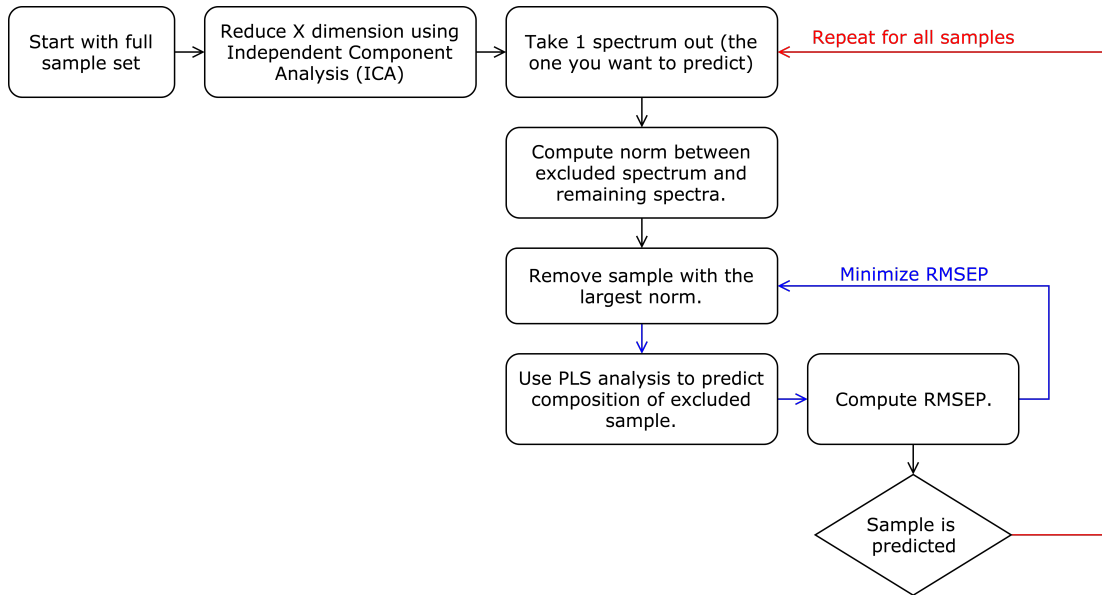


Figure 39: Workflow for the advanced algorithm similar to that found in Wiens et al. [62].

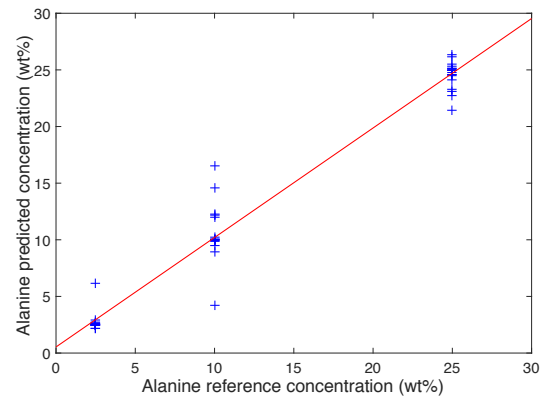


Figure 40: Predicted versus reference plot for alanine using spectra taken of the 2.5%, 10%, and 25% alanine doped gypsum samples.

where c_{known} is the known concentration, $c_{predicted}$ is the predicted concentration, and n is the number of spectra (or samples, depending on if the spectra acquired for a single sample is averaged or not). This cycle continues until $RMSEP$ is optimized. Both ICA and PLS algorithms are summarized in Appendix A.

The performance of the prediction model can be determined using a predicted versus reference plot, where the predicted concentration is plotted versus the known concentration for each element. Each point on these plots corresponds to a different sample (or spectrum). Figure 40 gives the predicted versus reference plot for alanine. If a fit to the predicted versus reference plot is linear, has a slope close to 1, and an intercept near zero, the model should be able to accurately predict the target species.

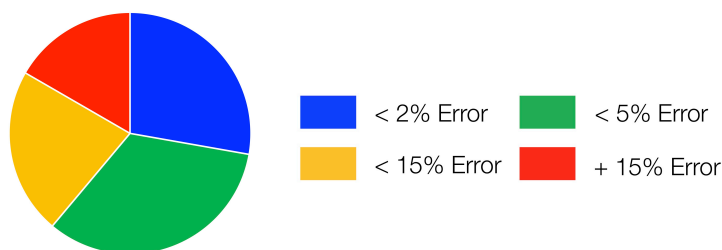


Figure 41: Percent error of prediction of alanine using multivariate analysis techniques.

As a simple test, spectra from 2.5%, 5%, and 10% alanine concentration samples were used as a training set (60 spectra in total, average spectra weren't used) to predict twenty 7.5% alanine spectra. Figure 41 shows the results of the prediction. Most spectra were predicted to within 2–5% error of the actual value. The average of all the prediction outcomes of the 7.5% alanine concentration sample is $7.586 \pm 1.15\%$. For all the samples (2.5%, 5%, 7.5%, and 10%) the $RMSEP$ is 1.49%. The model can be further improved by performing an outlier analysis, i.e., removing predictions that lie a certain distance from the others, but this was not explored here.

7.3.6 Comparison at other sensing distances

Raman spectra of alanine and anhydrite were taken at 25, 35, and 43 cm. The spectra produced at 25 cm have both a higher peak intensity and peak SNR, but the results at 35 were very similar. As expected the spectra taken at 43 cm have the lowest SNR, but band identifications could still be performed.

7.3.7 Other measurements: size of focus

The performance of the instrument was tested in a defocused mode, where the beam size on the target was expanded while the telescope focus was kept at the optimal position. Measurements of the laser beam reflection off of sample at 35 cm using the alignment camera showed that the defocused beam size was about double that of the focused beam size, about 23 μm . The 1%, 5%, and 10% alanine doped gypsum samples were measured with this larger spot size so they could be compared with spectra taken for LOD analysis (Figure 36a). Signal intensities are much higher when the spot size was doubled, but the SNR of both the organic bands (C-C and C-H) are comparable to spectra taken with the nominal spot size.

This defocusing method would be useful for a first pass on a target to narrow down the location of any organic compounds to be further investigated. Since this method covers a much larger area, this method could be used as a first pass to restrict the region of interest, then use LIF with the correct spot size in the smaller region to again narrow down the interesting locations with organic signatures, and then finally change to Raman for spectra with optimal acquisition parameters. SHERLOC has a similar survey method for scanning. The laser will raster a 7×7 mm area with 0.2 mm spacing, generating 1225 spectra arranged in a 35×35 grid [4]. A combined Raman and fluorescence spectrum is acquired in 1 s at each point, meaning the total time for mapping the 49 mm^2 area is 1225 s. In this defocused mode, an area of $34\text{ }\mu\text{m}\times 3\text{ mm}$ can be measured in a similar amount of time (with a much smaller spacing).

7.4 μLIBS Characterization

7.4.1 Comparison to previous breadboard

To compare the previous breadboard to the upgraded version the relative standard deviation (RSD) of specific peaks was calculated, which is used as a measurement of repeatability. RSD will be a combination of (1) the instrumental noise, (2) the uncertainties intrinsic to the LIBS measurements, (3) the variations of peak intensities induced by the small differences in concentrations at different sample sites and (4) small morphological differences. The RSD is defined as the standard deviation

Table 13: Summary of RSD and average intensity values from both Phase 1 and Phase 2 of the characterization plan for four different lines in ilmenite and manganese ore.

		Ti II 375.9 nm (Ilmenite)	Ti II 323.5 nm (Ilmenite)	Mn I 294.9 nm (Mn Ore)	Fe I 427.17 nm (Ilmenite)
Relative Standard Deviation (RSD)					
20 cm	Phase 1	1.40%	—	—	—
	Phase 2	7.39%	—	—	—
35 cm	Phase 1	6.83%	14.69%	41.94%	13.92%
	Phase 2	11.75%	3.84%	8.07%	12.19%
45 cm	Phase 1	41.4%	—	—	—
	Phase 2	23.04%	—	—	—
I_{peak} (from average spectra)					
45 cm	Phase 1	0.5883	0.4838	0.68	0.5034
	Phase 2	0.5085	0.9953	0.7409	0.1648

divided by the mean (and is usually represented as a percentage):

$$\text{RSD} = \frac{\sigma}{\mu}. \quad (44)$$

The lower the RSD value the more precise measurements are. RSD values were calculated from peak intensities measured from five points across ilmenite and manganese ore at three different distances in both phases (Table 13). It is difficult to make conclusions about the superiority of the Phase 2 breadboard from the RSD alone, but this is the only quantitative information available. For most lines the RSD value in Phase 2 is the same or better than that measured in Phase 1. The only exceptions are the 375.9 nm line (at 20 and 35 cm). What is certain is that a different temperature plasma is created on the sample surface as evidenced by the change in relative intensities of the selected lines. A Boltzmann plot could be created to determine the temperature of the plasma on the surface, but this would change for each sample type.

Table 14: Typical acquisition parameters for LIBS measurements. Each spectrum in this report was acquired using parameters following these guidelines.

Typical acquisition parameters	
Measurement time	<5 min
Sensing distance	0.25–0.43 m
Laser frequency	10 kHz
Laser power	100%
Exposure time	0.5 s
ICCD gate delay	224–226 ns
ICCD gate width	1000 ns
ICCD MCP gain	3000
# of acquisition spots per sample	5
# of LIBS spectra obtained per spot	5000
	(accumulated on chip)
Total # of spectra per sample	5

7.4.2 Optimal acquisition parameters

Light was collected from different total number of laser pulses to determine the optimal number of pulses for a high-quality, high SNR μ LIBS spectra. To determine the optimum number of laser shots to obtain a high-quality spectrum the DDG was set to output a specific number of pulses and subsequently recorded the emission for 1 (0.0001 s), 10 (0.001 s), 100 (0.01 s), 1000 (0.1 s), 3000 (0.3 s), 5000 (0.5 s), 8000 (0.8 s), and 10000 (1 s) laser pulses. This was performed at 35 cm using both ilmenite and coulsonite. Peaks in each spectrum were chosen and their SNR calculated. Unlike in Raman analysis, SNR here refers to the standard signal-to-noise definition,

$$SNR = \frac{I_{int}}{\sigma_{noise}}, \quad (45)$$

where I_{int} is the integrated peak intensity, and σ_{noise} is the standard deviation of the noise. Because the noise is expected to change with the level of the signal present, noise is taken as the segments known to have no emission peaks.

The results are shown in Figure 42, where SNR is plotted versus the number of laser pulses. Spectra taken with 5000 laser shots, or 0.5 s exposure time, had the highest SNR and therefore

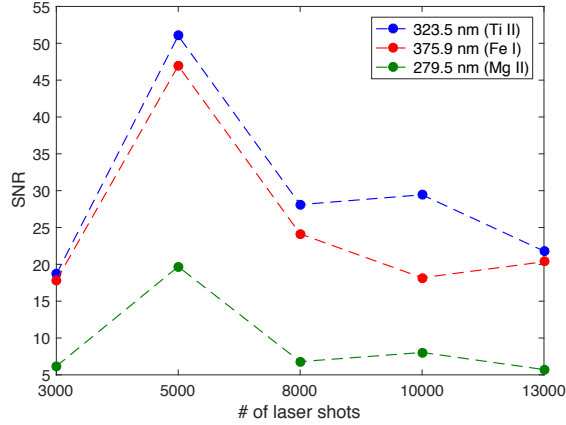


Figure 42: SNR with number of total laser shots for three lines in ilmenite.

was used for all measurements presented here. Emission from these 5000 shots is integrated onto the ICCD and read out all at once.

The acquisition parameters similar to all measurements (unless otherwise noted) are shown in Table 14. A μ LIBS measurement was acquired at five points on each sample to reduce the effect of sample inhomogeneity. Since the 5000 laser pulses are integrated onto the ICCD at each spot we're left with a total of 5 spectra from each sample. A laser repetition rate of 10 kHz was consistently used because it allows the highest peak power (293 kW). Similar to Raman characterization, the ICCD gate delay for each sensing distance was optimized using kinetic mode. The LIBS plasma will die out if the same spot is continually irradiated, but the LIBS plasma can be maintained on a sample if the sample is continuously moved around. Moving the sample during a measurement to sustain plasma formation is a common strategy for LIBS analysis of metals (see Cristoforetti et al. [13], Lopez-Moreno et al. [37], and Freedman et al. [21], for example). The gate width was then optimized as usual and the one with the highest SNR was chosen (when tested with ilmenite). Optimal values of gate delay and width were used for all samples that are capable of creating strong emissions in the μ J regime.

7.4.3 Spectral pre-treatment

Spectra in this report were relative intensity calibrated (as described in Section 7.2), background subtracted, and normalized to their maximum value. Spectra were also baseline corrected in OPUS

(Opus Spectroscopic Software BRUKER OPTIK GMBH). Figure 43 gives an example of this baseline correction with an ilmenite spectrum at 35 cm. The baseline correction works to lower the baseline and remove the leftover instrument response (the jagged behaviour seen in the region >600 nm). Because a gated detector is used here, there is no need for a continuum emission removal.

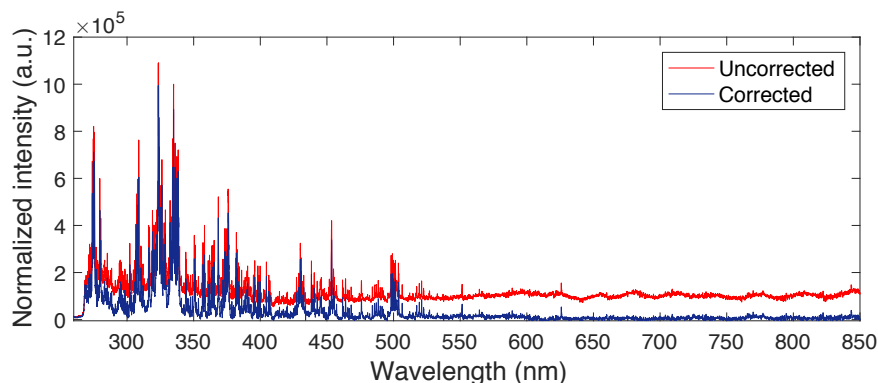


Figure 43: Example of baseline correction for LIBS spectra. The baseline correction both corrects the baseline height and the leftover instrument response.

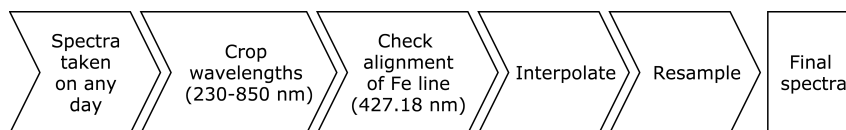


Figure 44: Result of the algorithm that aligns and resamples LIBS spectra taken on different days (with slightly different wavelength calibrations).

Wavelength calibrations performed on different days will change the wavelength binning and values of each spectrum. A simple algorithm was created that is able to align spectra taken on different days so that they have the same number of points and are sampled at the same wavelengths. Figure 44 gives an overview. For any spectrum, the wavelength values are cropped to fall within 230–850 nm. The algorithm will search for the Fe 427.17 nm peak (which is relatively isolated from other strong peaks) and either ensure it is at 427.18 nm within a tolerance of 0.05 nm, or shift the spectrum by the difference. After this, spectra are interpolated by a factor of ten, and then resampled at specific wavelength intervals. This was especially useful for inserting spectra into our multivariate analysis models (see Section 7.4.6).

7.4.4 Results at 35 cm

μ LIBS results at 35 cm are summarized in Figures 45–47. The original sample suite was tested initially (using the optimized measurement parameters). Some of them were found not to work, i.e., some samples did not produce successful spectra from which elemental emissions could be identified. The sample suite was extended to include CuMo ore (USZ 3-85), Fe ore (DC11013), ferrous rock (FeR-2), and ultrabasic rock (DC72302). See Table 10. These were not chosen for any specific reason, but rather, were the only other samples other than coulsonite, ilmenite, and manganese ore, from which successful LIBS spectra could be obtained out of a larger available sample suite of around 38 standard powders. Figure 45 shows LIBS spectra of the geologic samples for which μ LIBS was found to work. Figure 46 shows spectra for those samples which did not work. Samples that did not work in a single-spot measurement produced a successful μ LIBS spectrum if moved around during the 0.5 s measurement. This way the plasma on the sample was sustained. This was discovered while moving the samples around to optimize ICCD gate delay. Figure 47 shows the spectra produced when moving the samples around over the course of one measurement. A total of 28 standard powders produced successful μ LIBS spectra if they were moved around during a measurement.

The spectra in Figure 46, except wollastonite, have the same pattern. This increase towards the red could be a fingerprint of thermal heating. As the laser is incident on granite, for example, a plasma is only visible for a brief moment (if any, it seems plasma formation is spot dependent) but then the sample is quickly heated and orange light is visible. These geologic standards are no problem for typical LIBS instruments that use tens of mJ pulse energies (like the studies in Koujelev et al. [31] or the LIRA instrument [34]).

An overview of μ LIBS functionality at 35 cm is presented in Table 15. Out of the 11 original characterization standards, only three concluded in successful, single-spot μ LIBS spectra. Some samples (highlighted in green) formed a plasma on the surface at some point in the measurement, but did not result in a successful measurement. Samples were included in this category if a visible plasma was formed at some point, although for some the plasma was intermittent and short-lived or irregular (as was the case with andesite). The spectra of these samples did not show any strong characteristic emissions and any small lines were not repeatable. Others did not form any

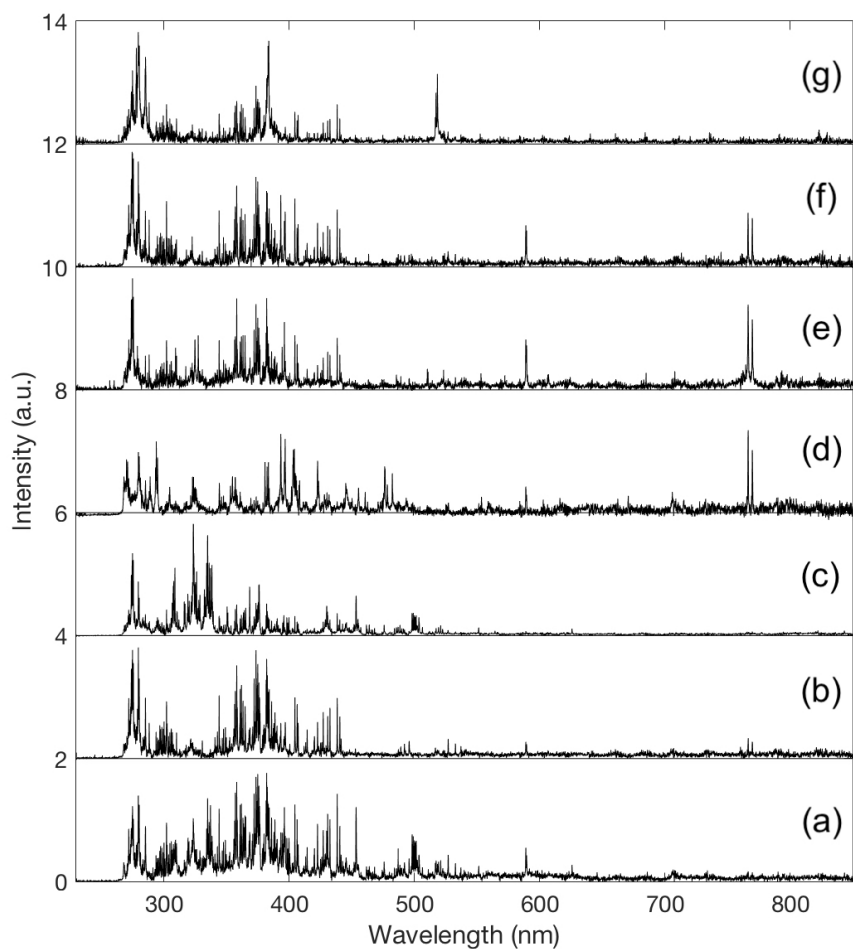


Figure 45: Overview of LIBS spectra for samples which LIBS in the μJ regime works well: (a) coulsonite, (b) Fe ore, (c) ilmenite, (d) manganese ore, (e) copper-molybdenum ore, (f) ferrous rock, and (g) ultrabasic rocks. One of the major features of LIBS spectra is the absence of spectral lines below 266 nm (due to the UV filter).

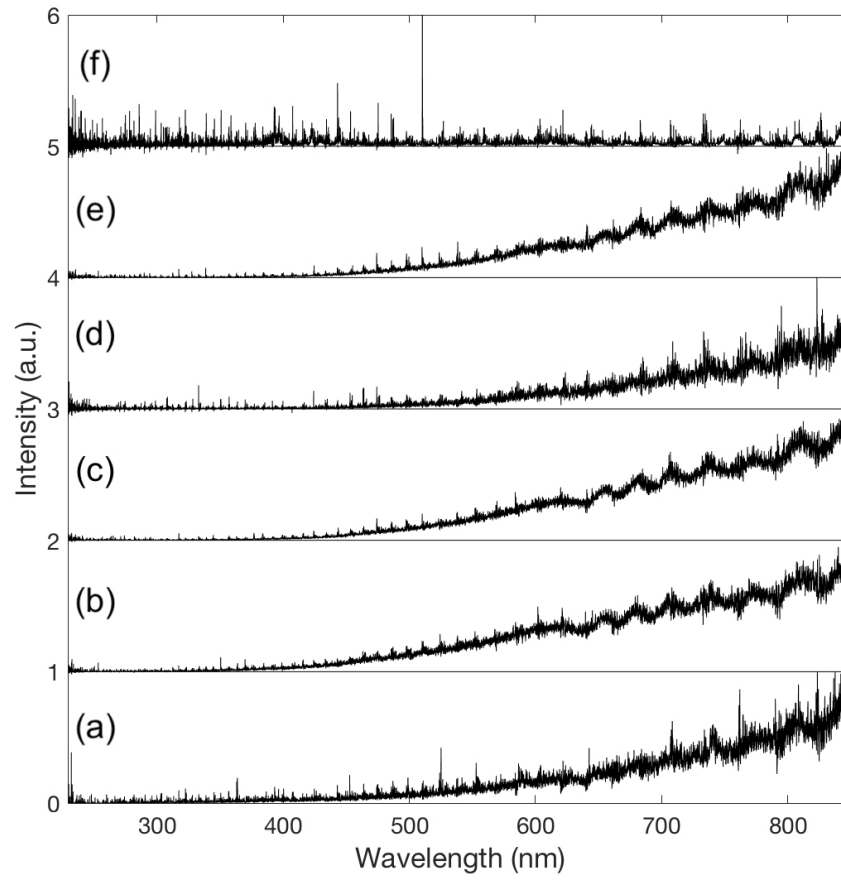


Figure 46: Overview of LIBS spectra for samples that do not work in the μJ regime: (a) andesite, (b) anorthosite, (c) basalt, (d) granite, (e) pyroxenite, and (f) wollastonite.

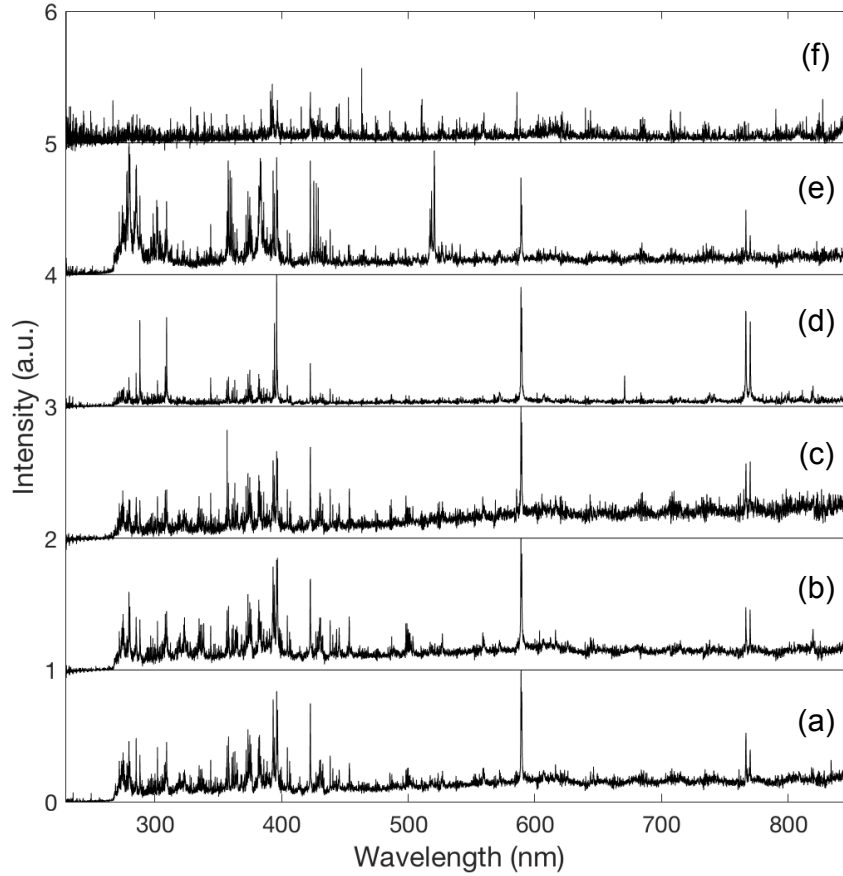


Figure 47: Standards which do not produce a good μ LIBS spectrum under typical, single spot conditions do produce a successful μ LIBS spectrum when the target is continuously sampled during the measurement, i.e., when the sample is kept in motion over the 0.5 s measurement ((a) andesite, (b) anorthosite, (c) basalt, (d) granite, (e) pyroxenite, and (f) wollastonite). These spectra were not baseline corrected.

visible plasma (in red), and instead either showed thermal heating or nothing at all, except for wollastonite, which exhibited green fluorescence in some spots. If the surface of the wollastonite sample was marked with a black sharpie, a plasma was formed. This is a quick test to indicate that reflectance plays a big part in the laser-matter interaction.

A detailed view of all the working spectra are presented in Figure 48 to Figure 54, where elemental lines are identified. For example, Figure 48 shows LIBS spectra for manganese ore, ilmenite, ultrabasic rocks, copper-molybdenum pore, ferrous rock, iron ore, and coulsonite over the region 268–315 nm. Major lines are identified with gray bands, and other peaks are identified directly. Figure 48 to Figure 54 demonstrate that LIRS spectra are dominated by lines in the region <500 nm. Any sample with any appreciable amounts of iron are flooded with iron lines at various ionization levels. No oxygen, carbon, or phosphorous lines were identified in the spectra at 35 cm.

Other, whole-rock samples were investigated as an aside, and their results are shown in Ap-

Table 15: Summary of Phase 2 LIBS measurement results. M = measurement was successful, CM = measurement was unsuccessful, NM = no measurement was attempted, Green = plasma is formed, Red = no plasma is formed.

Standard	25 cm	35 cm
Andesite	CM	CM
Anorthosite	CM	CM
Basalt	CM	CM
Coulsonite	M	M
Flint Clay	CM	CM
Granite	CM	CM ⁶
Mn Ore	M	M
Pyroxenite	CM	CM
Syenite	CM	CM
Ti Ore (Ilmenite)	M	M
Wollastonite	CM	CM
CuMo Ore	M	M
Fe Ore	M	M
Ferrous Rock	M	M
Ultrabasic Rock	M	M
Graphite	M	M
Aluminium	M	M

pendix B. These measurements are significant because LIRS was able to measure hematite. Recall from Section 2.5.2 that the only previous studies of μ LIBS on similar samples was that of Dreyer et al. [17], who used μ LIBS on hematite, and Lefebvre et al. [35], who used μ LIBS on ilmenite. LIRS can measure these samples, but there are clearly samples for which this technique does not work.

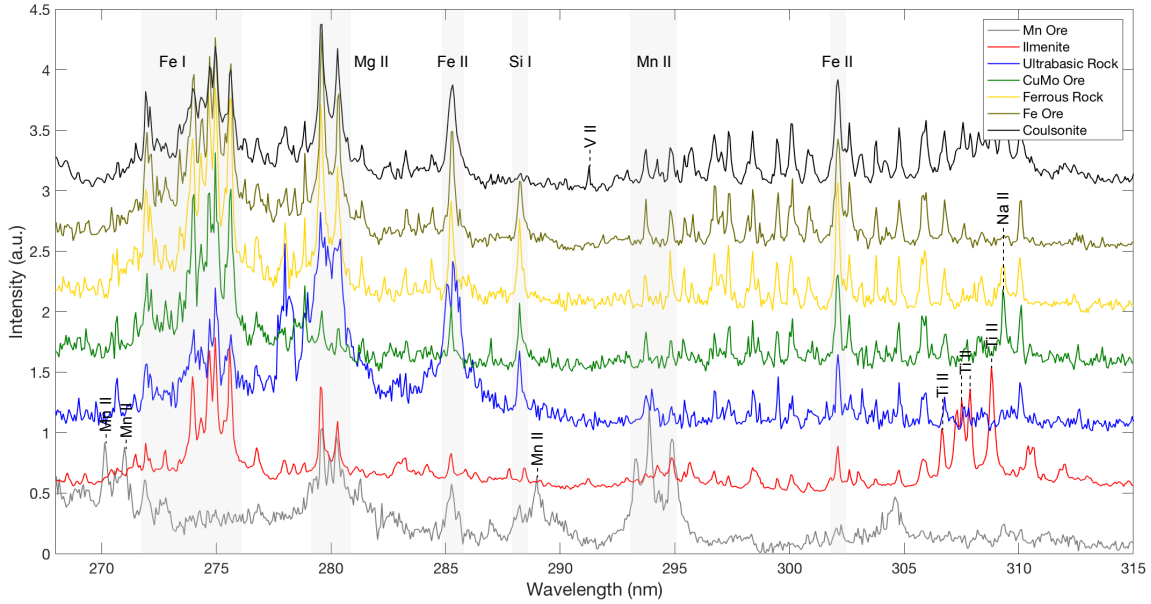


Figure 48: Overview of LIBS spectra with major peaks identified (268-315 nm).

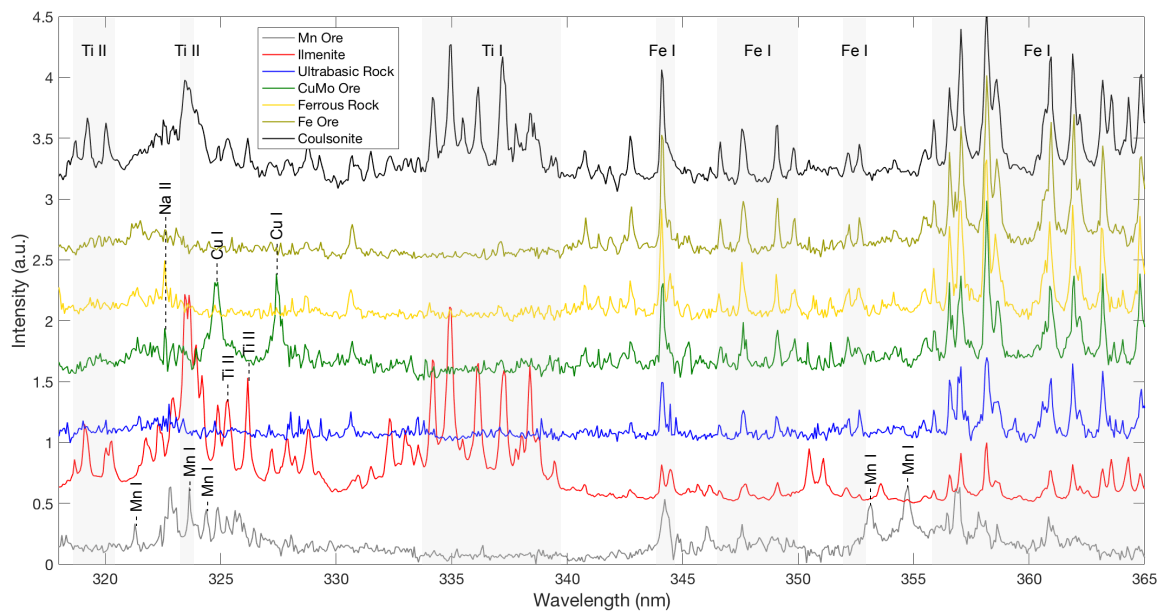


Figure 49: Overview of LIBS spectra with major peaks identified (318-365 nm).

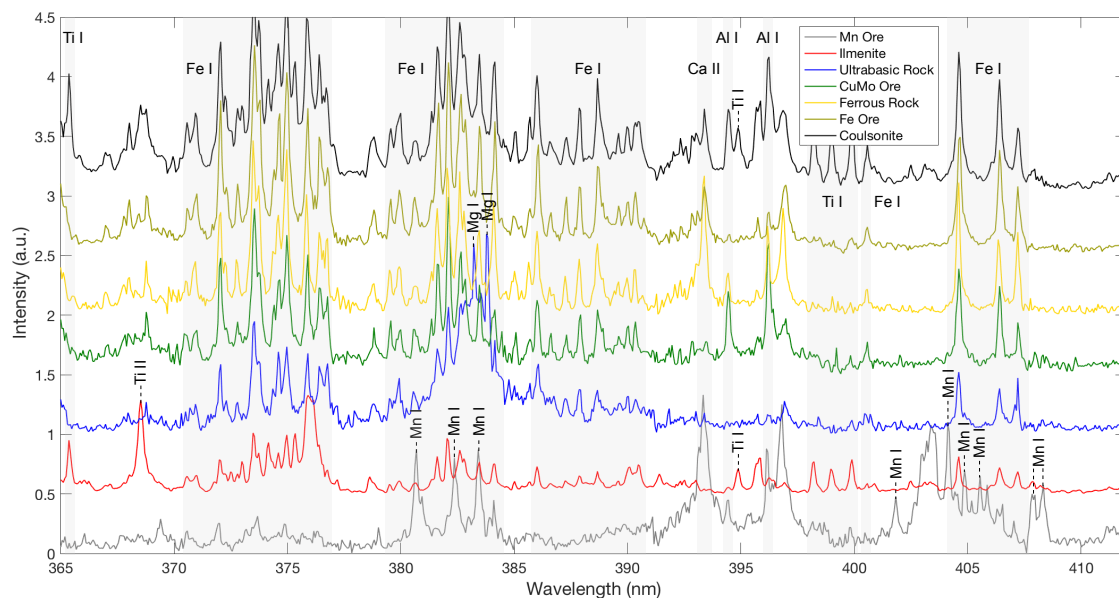


Figure 50: Overview of LIBS spectra with major peaks identified (365-412 nm).

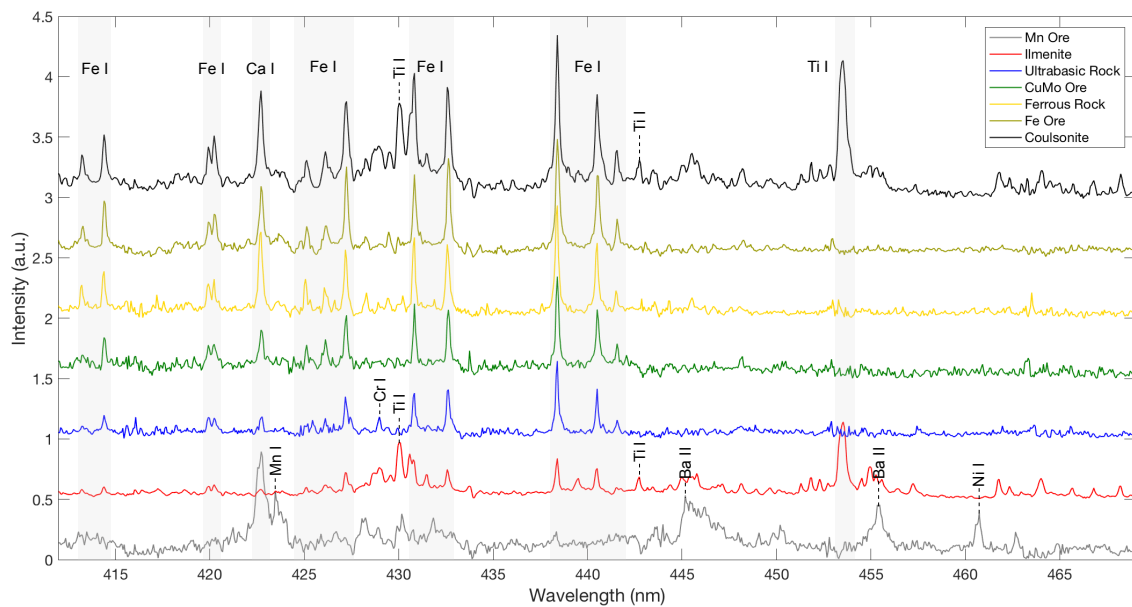


Figure 51: Overview of LIBS spectra with major peaks identified (412-468 nm).

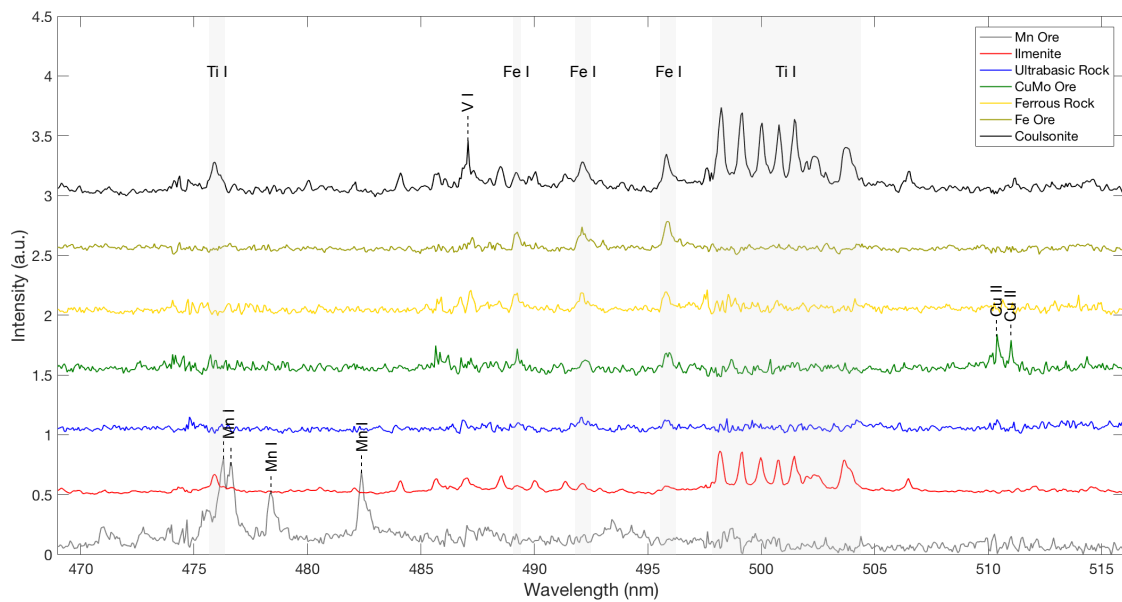


Figure 52: Overview of LIBS spectra with major peaks identified (469-516 nm).

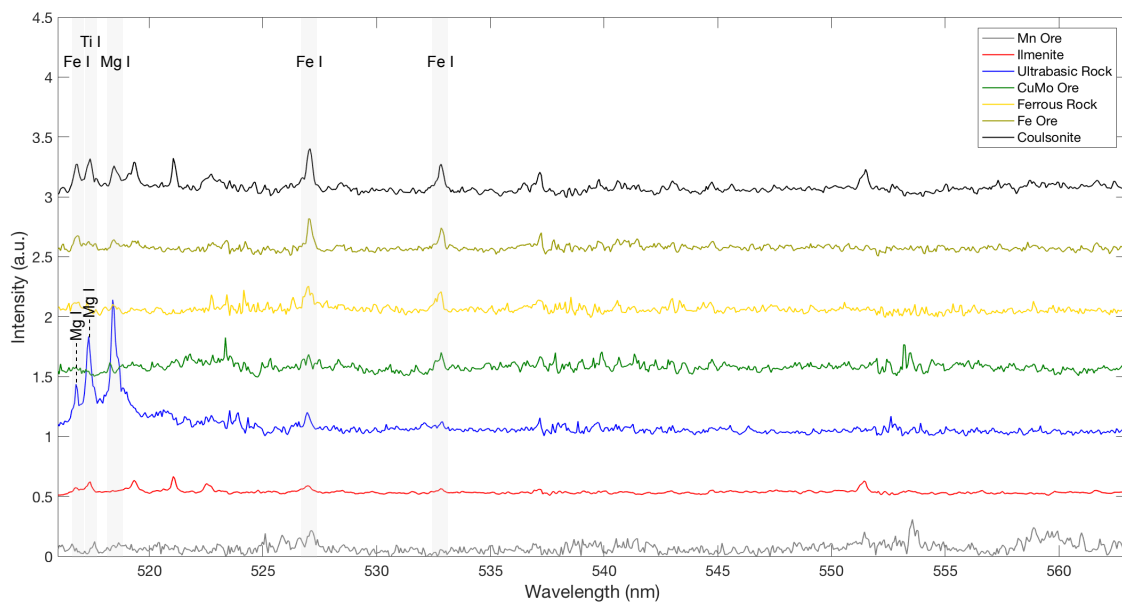


Figure 53: Overview of LIBS spectra with major peaks identified (516-563 nm).

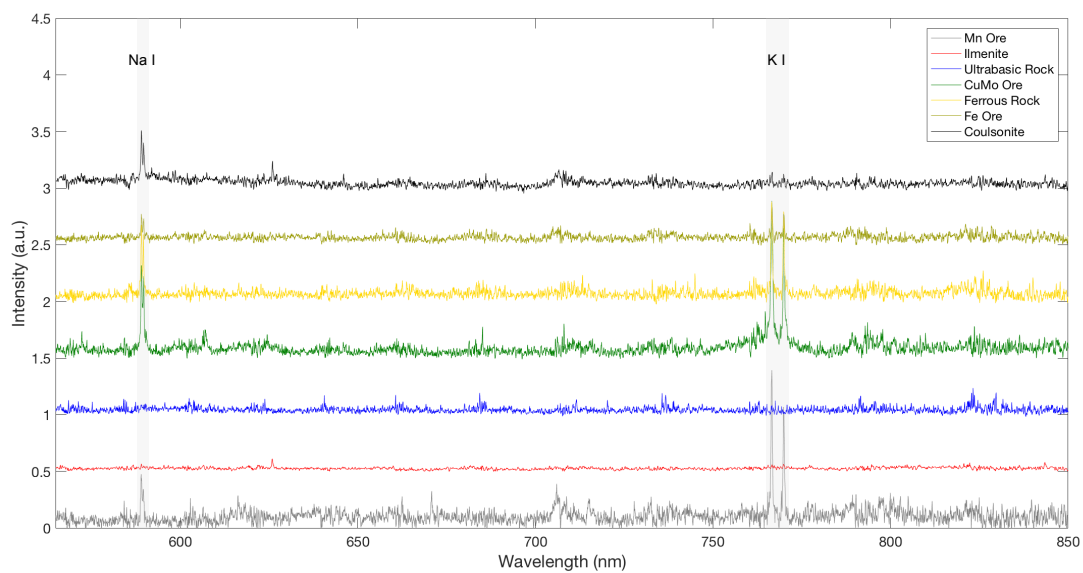


Figure 54: Overview of LIBS spectra with major peaks identified (563-850 nm). Note the lack of lines in this region.

7.4.5 Elemental Limits of Detection (LODs)

Once the emission peaks in all working spectra (the seven spectra which produced μ LIBS spectra with a one-spot measurement) were identified, representative peaks at specific wavelengths must be chosen for each element to create calibration curves. Table 16 lists the lines chosen for each element. Representative lines were selected that were both strong and had minimum overlapping with other characteristic emissions (although the latter was impossible for some lines). Once representative lines were chosen, the integrated intensities of each were measured using Lorentzian curve fitting in OPUS (Figure 55). This method was especially helpful for determining the integrated intensities for peaks which were surrounded by other strong peaks.

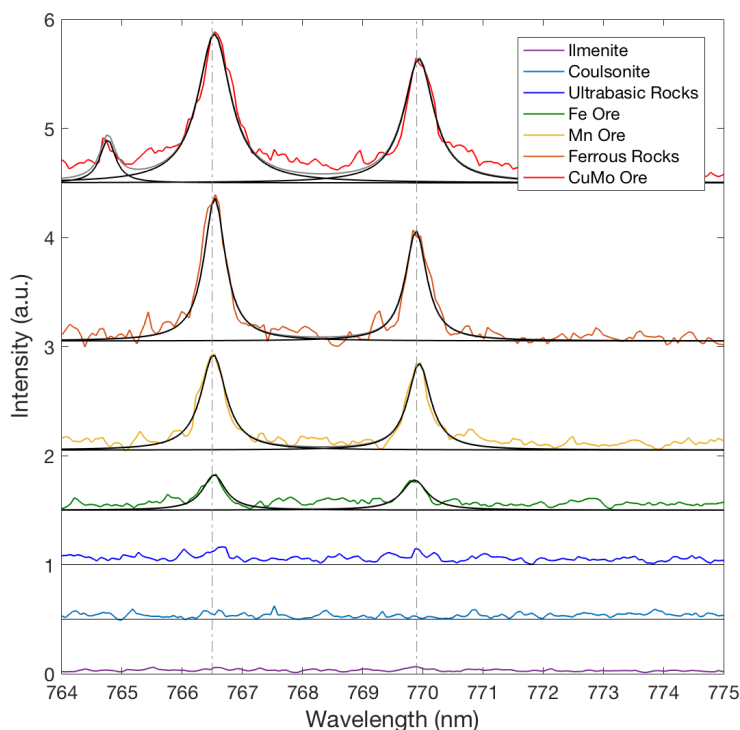


Figure 55: Example of line fitting for potassium peaks in various geologic standards (K I at 766.5 nm and 769.9 nm). Spectra are plotted from the least amount of potassium (ilmenite and coulsonite at the bottom) to the most (Cu-Mo ore at the top). Lorentzian fitting was especially useful to obtain accurate intensity values when there were nearby peaks.

To create calibration curves, integrated peak intensities for each element, from each sample are plotted versus the certified sample concentration. Only intensities for which a peak could be distinguished are plotted. For example, in Figure 55, the area under the curve in the region of the

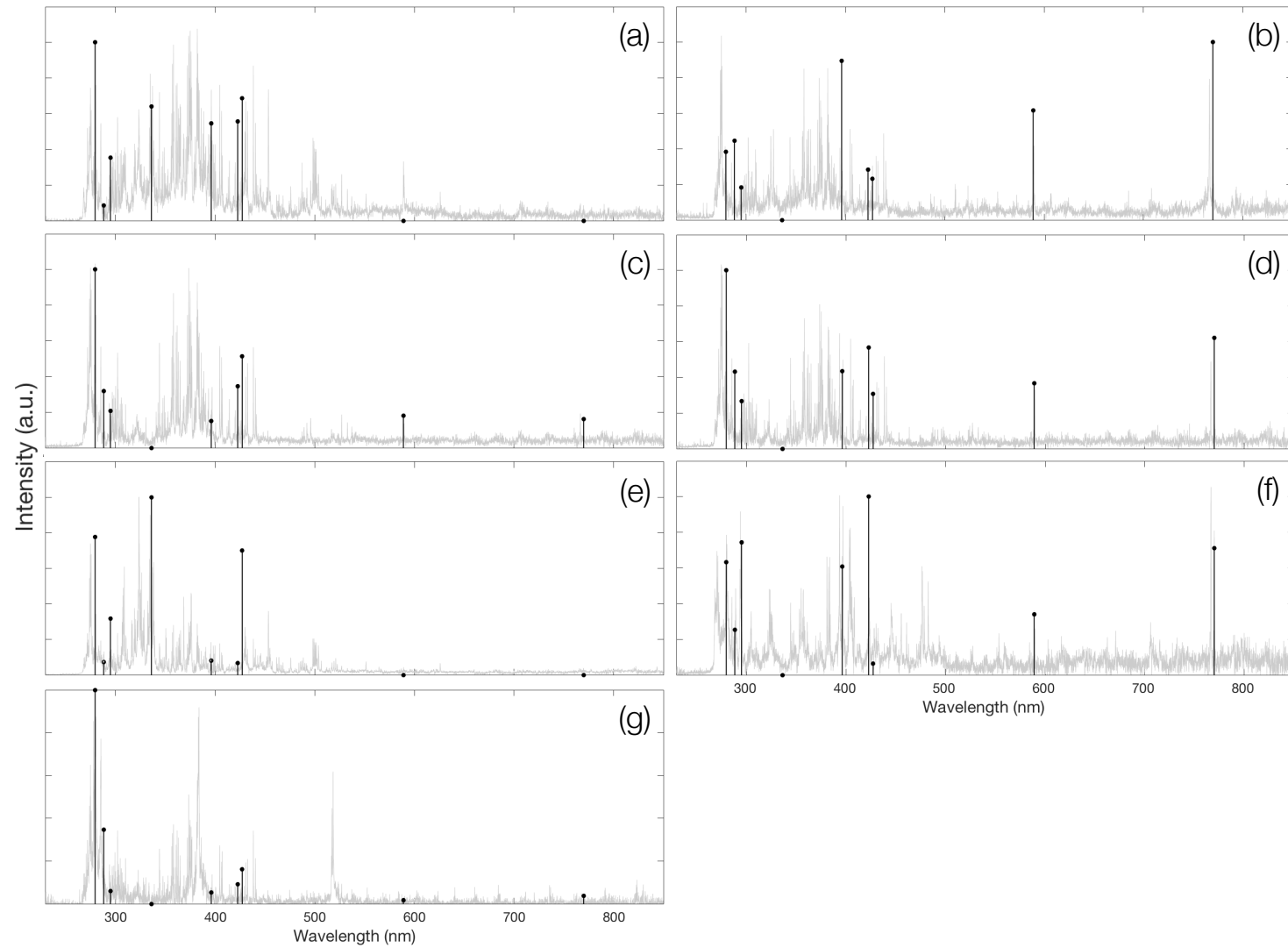


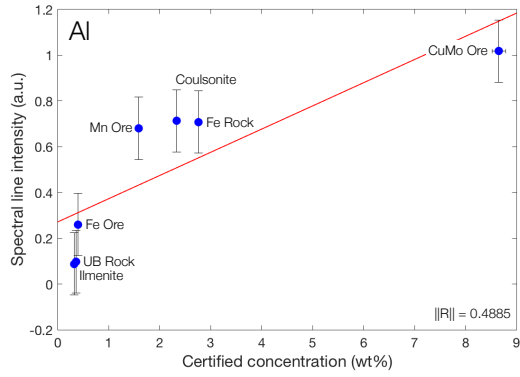
Figure 56: Visual representation of the reduced data set used in calibration curve analysis for (a) coulsonite, (b) CuMo ore, (c) Fe ore, (d) ferrous rocks, (e) ilmenite, (f) Mn ore, (g) ultrabasic rocks. Peak intensities of selected lines (Table 16) are in black overtop raw spectra in grey.

Table 16: Line parameters for those lines selected for calibration curve analysis. A_{mn} is the Einstein coefficient and g_m and E_m are the degeneracy and energy of the upper energy level, respectively.

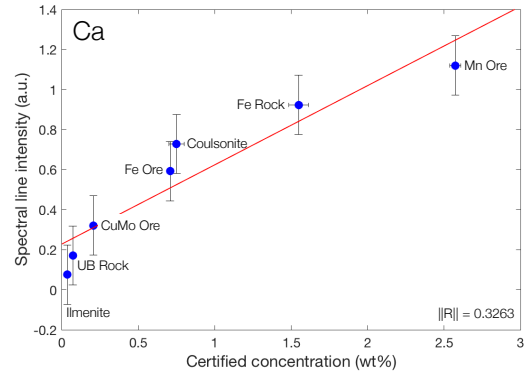
Element	λ (nm)	A_{mn} (s^{-1})	g_m	E_m (cm^{-1})
Al I	396.15	9.85e+07	2	25 347.756
Ca I	422.67	2.18e+08	3	23 652.304
Fe I	427.18	2.28e+07	11	35 379.208
K I	769.90	3.75e+07	2	12 985.185
Mg II	279.55	2.60e+08	4	35 760.88
Mn II	294.92	1.96e+08	7	43 370.537
Na I	588.99	6.16e+07	4	16 973.366
Si I	288.16	2.17e+08	3	40 991.884
Ti II	336.12	1.58e+08	10	29 968.330

K peaks in the ultrabasic rock spectrum (blue) could be summed to some number, but there is really no distinguishable peak, so this was not done. Only those peaks which could be fit with a Lorentzian profile were used. This process reduces the data set significantly. By selecting individual lines for each element, each sample is represented by only nine numbers, in this case (because there were nine elements identified that were relevant to characterization goals). Figure 56 is a visual representation of how the nine selected lines in each spectrum describe the sample, and the amount of information that is missing from the analysis. A calibration curve for each identified element is created, where the peak integrated intensity is plotted versus known concentration. Figure 57 shows the calibration curves for Al, Ca, Fe, K, Mg, Mn, Na, Si, and Ti. The norm of residuals for each fit ($\|R\|$) is given for each calibration curve, and the R^2 values have been calculated from these values (Table 17). The error bars in intensity are the standard error in peak intensity across all samples (standard deviation divided by the square root of the number of samples). The horizontal error bars are the uncertainties in concentration given by the standards' supplier. Most of these errors are too small to show up on the Figure. The calibration curves for Mg and Mn are not ideal because both have mostly samples with a low concentration and then one sample with a large concentration. Most of the other calibration curves are nearly linear.

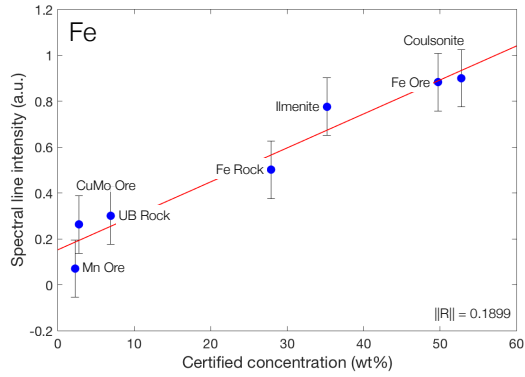
The LOD for each element using the above calibration curves were calculated in the same way as for the organics in Section 7.3.5. Using the slope of the calibration curve and the standard deviation



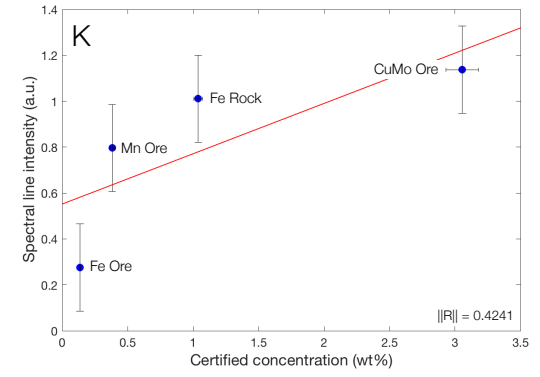
(a)



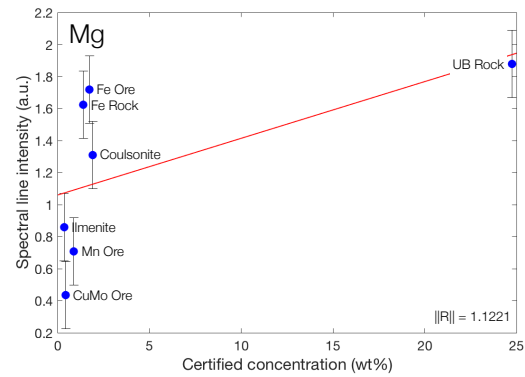
(b)



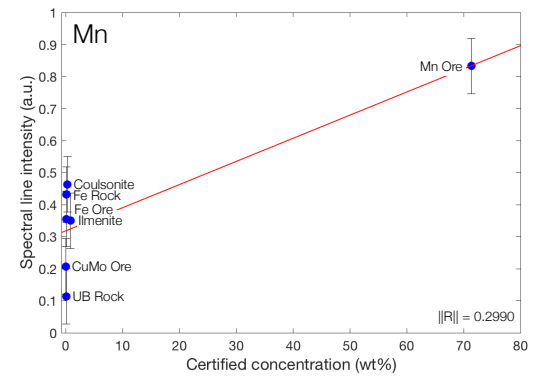
(c)



(d)

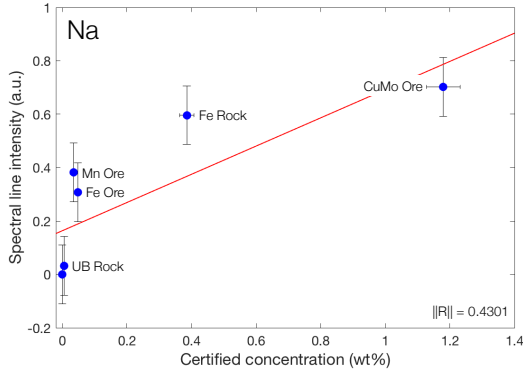


(e)

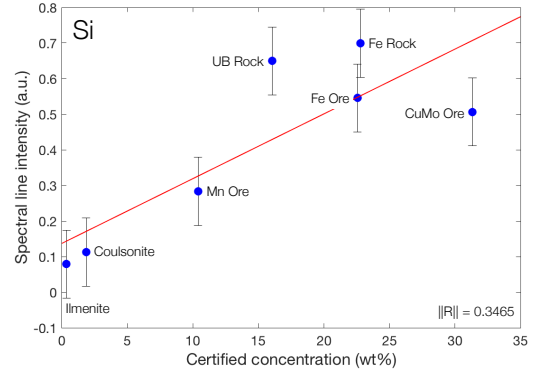


(f)

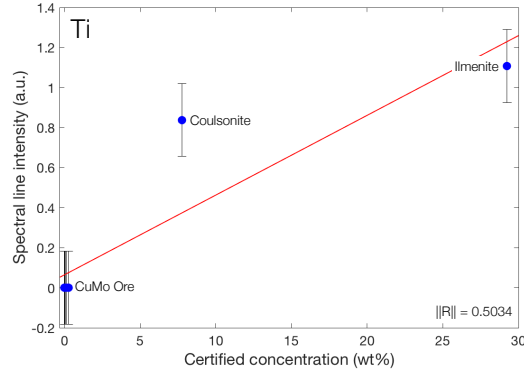
Figure 57: Primitive calibration curves. $||R||$ is the norm of the residuals. In (g) coulsonite and ilmenite are overlapping at (0,0) and not labeled.



(g)



(h)



(i)

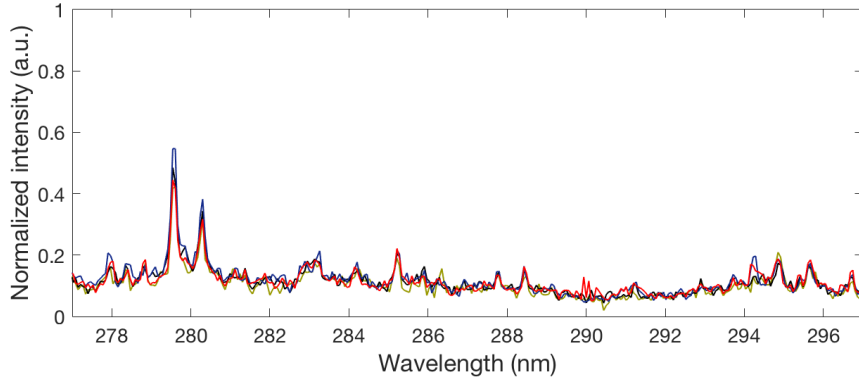
Figure 57: Continued.

of measurements at the lowest concentration (for which a distinguishable peak was present), LOD can be calculated from $\text{LOD} = k\sigma/m$, with $k = 2$ for a 95% confidence level (Equation 42). This is the same strategy for calibration curves used in Wiens et al. [62]. The resultant LODs are listed in Table 17. Both Mn and Ti have LODs that are greater than 30%. For titanium, this can be attributed to the fact that only two samples with large Ti concentrations show any Ti lines. This is not enough to make a reasonable prediction about the behaviour of spectra at low Ti concentrations. The sample set should be extended to include more samples with lower concentrations of titanium. In the case of manganese, error is introduced by neighbouring iron emission lines. The relative standard deviations (RSD) of these values are also listed. These are calculated from the standard deviation used in the calculation of the LOD, i.e., RSD is standard deviation of the integrated

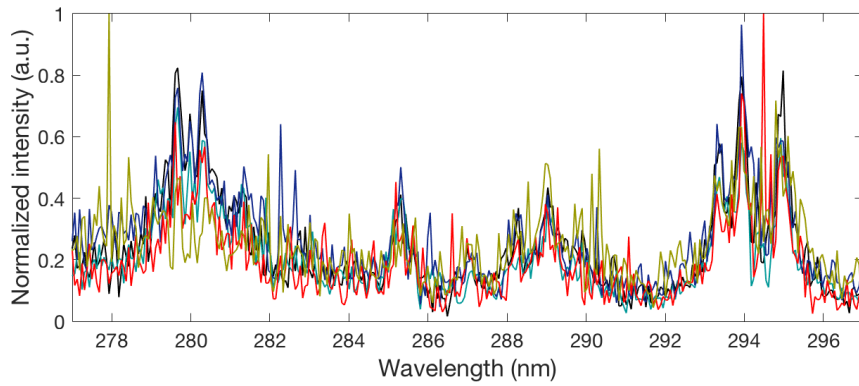
Table 17: Limits of detection (LODs) for major elements determined using primitive calibration curves.

Element	λ (nm)	R^2	LOD _{CC} (wt%)	LOD _{CC} (ppm)	RSD
Al	396.15	0.4108	1.78	17800	28%
Ca	422.67	0.8385	0.217	2170	18%
Fe	427.18	0.5826	1.42	14200	11%
K	769.90	0.5841	0.773	7730	14%
Mg	279.55	0.5615	6.83	68300	11.3%
Mn	294.92	0.9842	36.8	368000	36%
Na	588.99	0.8643	1.56	15600	26%
Si	288.16	0.3787	12.2	122000	25%
Ti	336.12	1.000	34.8	348000	23%

line intensities at the lowest concentration divided by the mean of the same values (times 100%). Again, RSD gives an estimate of the preciseness of measured data, and is often included along with LOD in the literature. ChemCam aims for <10% RSD in their major elements and <20% in minor trace elements [52]. For all others the LODs are greatly increased by the standard deviation factor, and the LODs are higher for elements in which their lowest concentrations are found in samples with lower repeatability. For example, LODs for sodium and iron are calculated with the standard deviation of the 588.99 nm and 427.18 nm lines, respectively, in manganese ore, as this sample has the lowest concentration of both sodium and iron. Figure 58b shows the variation in manganese ore spectra taken at five different points. Although the major features are represented in each spectrum, there is still a large variability present that works to increase the standard deviation used in the LOD calculation. Figure 58a is the same figure, but for ilmenite. There is much less variation in this data, so elements which are in their lowest concentration in this sample (Ca, Na) will have less error from repeatability. As a contrast to this, Figure 59 shows 4 spectra from four different spots along two geologic standards taken with the ChemCam instrument. MHC1356 is a jarosite (52.66 wt% SiO₂, 40.28 wt% TFe₂O₃, and others with <1 wt% oxide) and UNSZK is a feldspar (74.38 wt% SiO₂, 14.19 wt% TFe₂O₃, 4.5 wt% Na₂O, 4 wt% K₂O, and others with <2 wt% oxide). Although not the same standards as ours, this is a great representation of the high repeatability of the ChemCam instrument.



(a) Five μ LIBS spectra of ilmenite.



(b) Five μ LIBS spectra of manganese ore.

Figure 58: Visual representation of (a) small, and (b) large variation within a set of spectra for five LIBS spectra of ilmenite and mn ore, respectively. Spectra are normalized to the maximum intensity found within the spectrum.

The composition of a sample that was not used in the creation of the calibration curve model was predicted in order to determine the suitability of calibration curves as a predictor for sample composition. Figure 47 (d) shows the spectrum of granite that was acquired when the sample was rotated during a measurement. Major peaks in this spectrum are Si I (288.1 nm), Na I and II (588.9 nm and 314.9 nm), Al I (396.15 nm), and two K I lines (766.9 and 769.9 nm). Note that peaks in the 350–400 nm region seem to be oxygen lines (the only other possibilities are iron or titanium, of which there is none in this sample). Relevant peaks were integrated and the calibration curves (Figure 57) were used to predict the concentration of various elements within this sample. The results are shown in Table 18.

Only those elements for which a calibration curve was created are able to be predicted (i.e.,

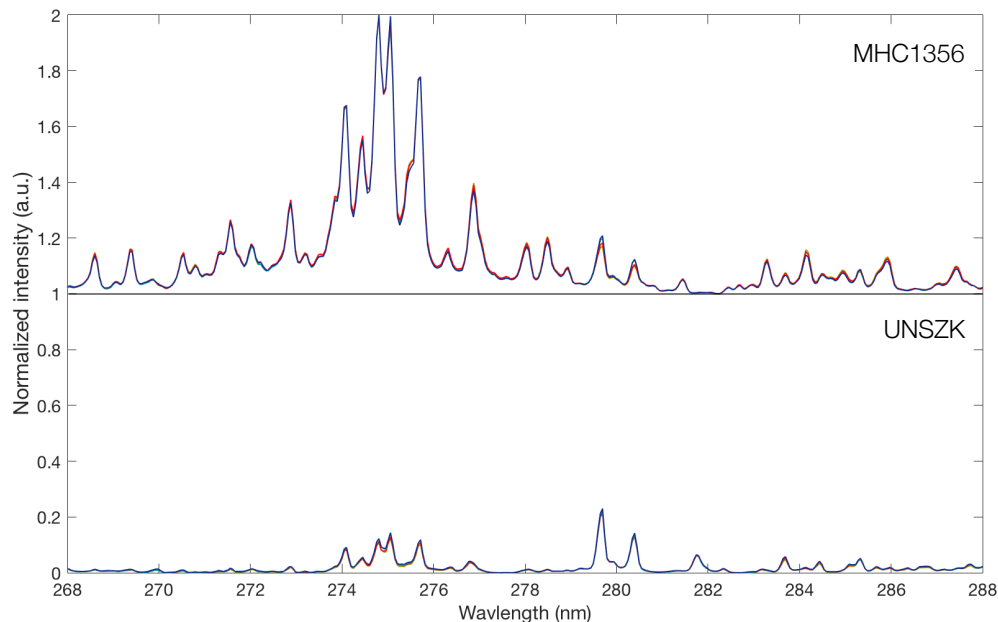


Figure 59: Example spectra (jarosite/MHC1356 and feldspar/UNSZK) from the ChemCam instrument demonstrating the small variations between spectra from the same sample (taken from CITE PDS). Spectra (there are four in total for each sample) overlap almost completely. LIRS spectra looks highly variable in comparison (Figures 58a, 58b).

only Al, Ca, Fe, K, Mg, Mn, Na, Si, and Ti). In this spectrum, a Mn peak at 294.92 nm, and a Ti peak at 336.12 nm were not identified so concentrations of these elements are not predicted. In all three cases this is because the certified concentration of these elements are below the LOD for that element (significantly below for Mn and Ti). A line for Mg was found and integrated, but the concentration was unable to be predicted because it did not follow the previous pattern in intensity with concentration as shown in Figure 57, i.e., the integrated intensity gave a negative concentration. Concentrations of Al, Ca, Fe, K, Na, and Si were predicted for this sample and error percentages were calculated based on its certified concentration (Table 18). Although the error is high, the relationship between elemental concentrations is preserved in the predicted set. Using the predicted concentrations, and the fact that—from our results—the concentrations of Mn and Ti should be small, some conclusions can be made about the type of rock being analyzed. For example, rocks with high silica content are either felsic or mafic (igneous) rocks. The low iron and magnesium content however, and the relatively higher sodium and potassium content points towards a felsic rock. These are igneous rocks that are rich in feldspar and silica. Looking to a

turnery diagram for igneous rocks (Figure 60), an idea of the type of rock can be obtained. Since the predicted concentration had appreciable amounts of potassium and sodium, the lower half of the triangle is relevant, and because of the amount of potassium (compared to calcium), the prediction leans towards the alkali feldspar (A) corner. This analysis gives us an idea of the type of rock, but corroboration with Raman analysis would give a more accurate rock identification. A similar analysis is performed with quartz in the combined characterization section (Section 7.7).

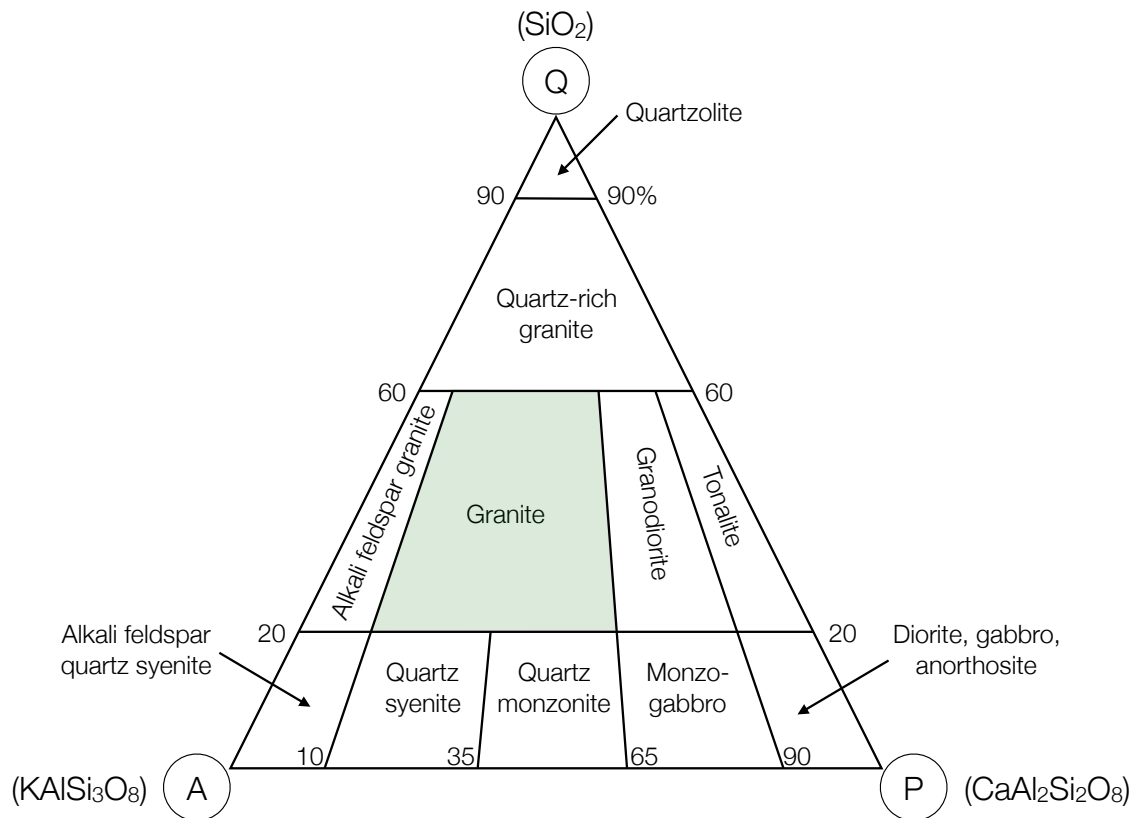
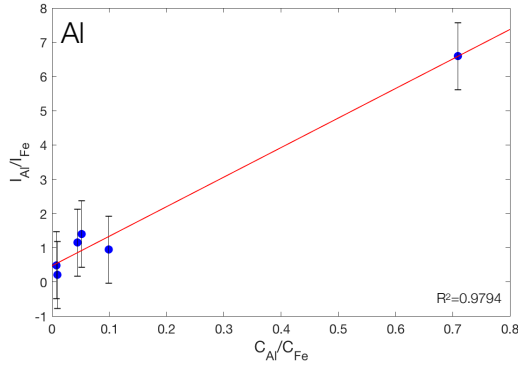


Figure 60: QAP turnery diagram for the identification of igneous rocks (adapted from R.W. Le Maitre 2002. *Igneous Rocks: A Classification and Glossary of Terms*).

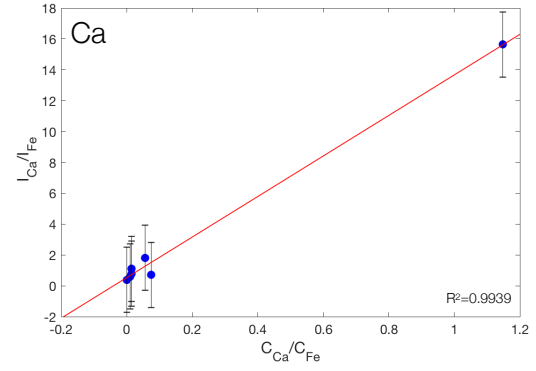
Table 18: Prediction of elemental concentrations of granite including errors in prediction.

Element	I_{int}	Predicted concentration (wt%)	Certified concentration (wt%)	% Error
Al	1.053	7.705	6.599	16.76%
Ca	0.267	0.677	0.5003	17.67%
Fe	0.104	0.376	0.679	80.59%
K	1.208	2.99	3.91	30.77%
Mg	0.196	-	0.022	-
Mn	-	-	0.012	-
Na	1.331	5.25	2.62	50.09%
Si	0.381	58.04	35.92	38.11%
Ti	-	-	0.03	-

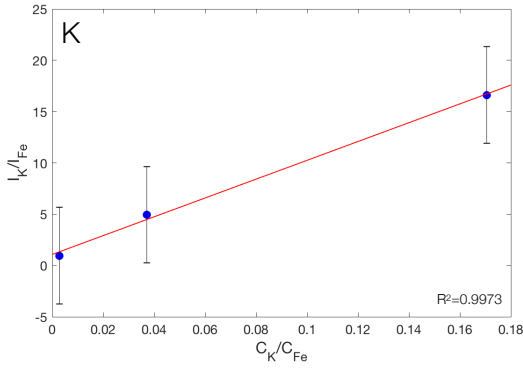
Spectral line intensity should have a linear relationship with concentration, however, quantitative LIBS analyses of complex matrices (like geological samples) are hampered by matrix effects that can result from shot-to-shot variations in the vaporized mass and/or in the excitation temperature of the plasma resulting from fluctuations in laser intensity, coupling efficiency of the laser with the target material, and other instrumental variations [12]. Primitive calibration curves (like those in Figure 57) can be skewed by chemical properties of the material that influence the ratio of a given emission line to the abundance of the element producing that line [52]. Using an internal standard for normalization of peak intensities is a common approach for correction of matrix effects in LIBS. Instead of the peak intensities, intensity ratios are used where the normalization intensity is that of a major element in the matrices of all samples. Iron is used as a normalization species, as it is a common element among all samples. Normalized calibration curves are presented in Figure 61. Here the strategy found in Cristoforetti et al. [13] is followed, where only the linear portion is taken (since intensity should follow a linear relationship with concentration). In most cases this removes the highest concentration member. The most intense lines (and therefore the highest concentrations) show saturation effects via self-absorption, meaning characteristic emissions are emitted and absorbed by the same species. This works to reduce the intensity of lines, especially at high concentrations. This was done for Al, K, Mg, Na, and Si. For the most part this produced more linear fits, except for sodium (comparing Table 17 and Table 19). LODs for each element are calculated



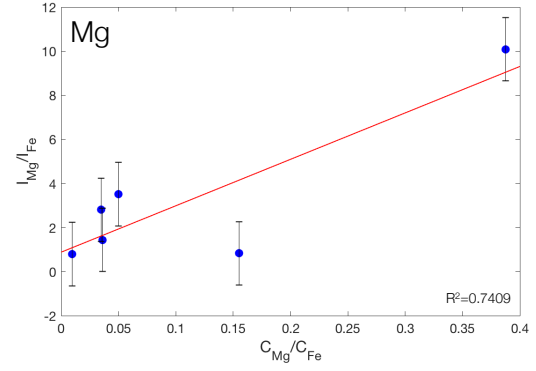
(a)



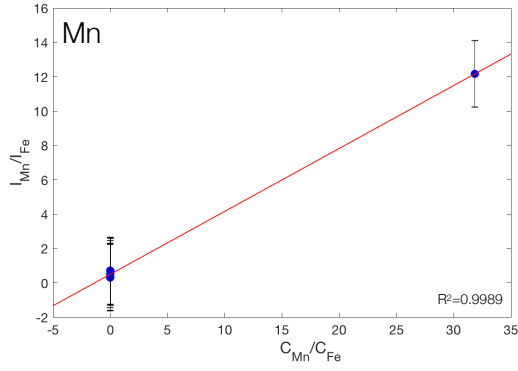
(b)



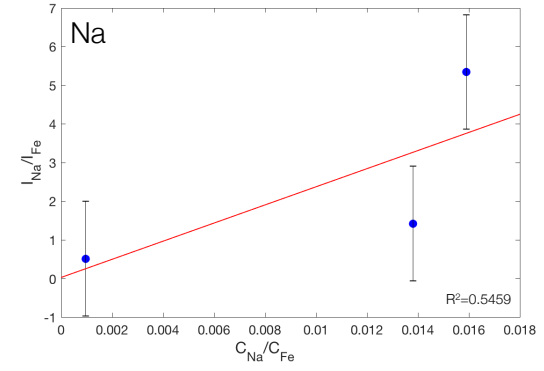
(c)



(d)



(e)



(f)

Figure 61: Calibration curves obtained from Fe normalized peak intensities of (a) Al, (b) Ca, (c) K, (d) Mg, (e) Mn, (f) Na, (g) Si, and (h) Ti. Each point represents an integrated peak in the average sample spectra that is normalized by the integrated intensity of the Fe 427.18 nm line.

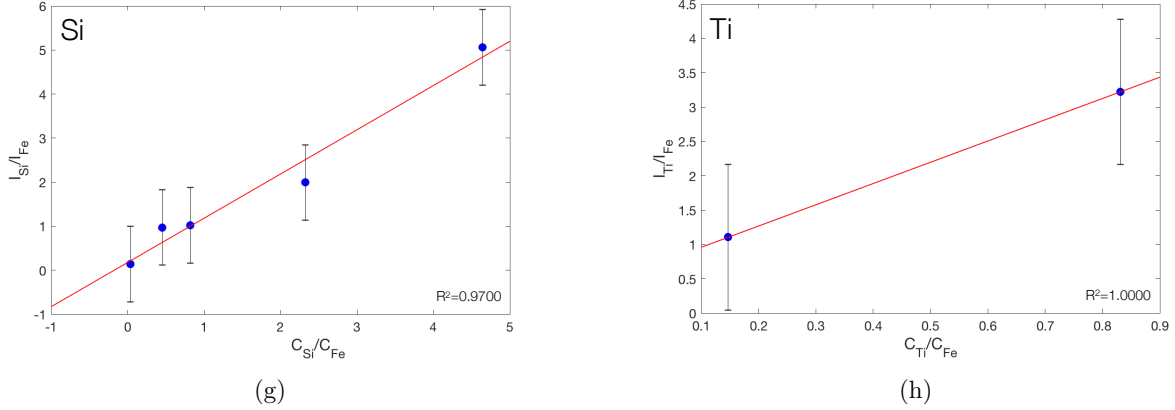


Figure 61: Continued.

in the same way as before, except now the standard deviation of *ratioed* peak intensities is used. Resulting LODs are listed in Table 19. The LODs calculated using internal normalization are much smaller than those the LODs from the most basic calibration curves. Most elements meet the LOD goal of 300 ppm, although there are still some issues. The highest LOD is manganese but this is to be expected considering the very high deviation in concentration. Iron is missing from the above table because a regular calibration curve (i.e., that found in Figure 57) is used. A different Fe line could be used to ratio the selected Fe line but this is not done. The LOD for iron, then, remains at 14200 ppm. The relative standard deviations (RSD) of these values are also listed. These are calculated from the standard deviation used in the calculation of the LOD, i.e., RSD is standard deviation of the integrated line intensity ratios (I_-/I_{Fe}) at the lowest concentration divided by the mean of the same values (times 100%). The high RSD values here are directly related to the earlier conversation about repeatability (e.g. Figure 58a and Figure 58b).

7.4.6 Multivariate analysis

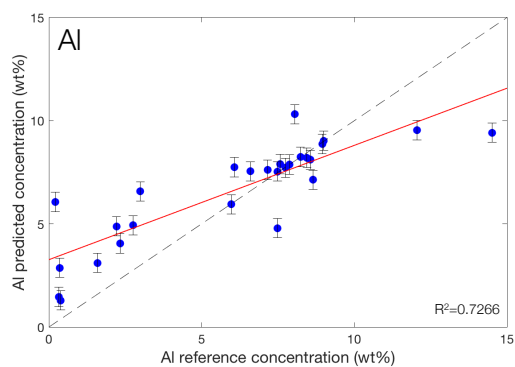
PLS analysis has been used in many LIBS studies (e.g. [9, 62]). A basic model with only seven working samples could be optimized, but instead a more advanced algorithm with all 28 samples from successful μ LIBS spectra could be obtained (whether the spectrum was acquired while the sample was moving or not), was optimized. Seven samples with very different compositions in most elements was not enough to create a robust predictive model. The same algorithm that was detailed in Section 7.3.5 is used here. Instead of a regular partial least squares (PLS) model, the standards

Table 19: Limits of detection (LODs) for major elements calculated from calibration curves created using internal normalization. Al, Ca, K, and Na meet the LOD goal of 300 ppm for major elements.

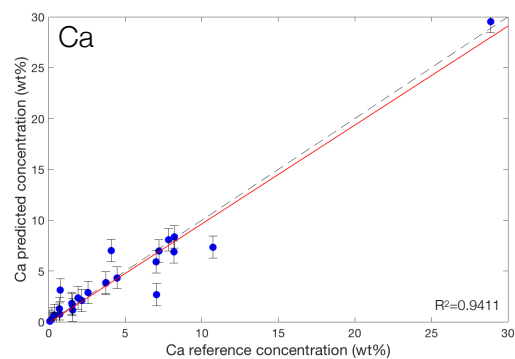
Element	λ (nm)	R^2	LOD _{CC,norm} (wt%)	LOD _{CC,norm} (ppm)	RSD
Al	396.15	0.9794	0.0097	97	25%
Ca	422.67	0.9939	0.0039	39	16%
K	769.90	0.9973	0.0028	28	12%
Mg	279.55	0.7409	0.0492	492	11%
Mn	294.92	0.9989	2.4134	24134	36%
Na	588.99	0.5459	0.03	300	22%
Si	288.16	0.9700	0.4466	4466	21%
Ti	336.12	1.000	0.3218	3218	19%

that are the least similar to the unknown sample are successively removed, the PLS model is recalculated, and the prediction accuracy is optimized. Here PLS1 is used, where each element is optimized separately (instead of the PLS2 algorithm where all elements are optimized together). PLS1 usually gives better results because each element is optimized separately, and each element's model uses a different number of factors. Across all elements, the average number of factors used is 7. The results of this advanced predictive model are shown in Figure 62. Each element has its own predicted versus known curve. Ideally, these predictions should be linear with a slope of one (shown on each plot via the dashed line). This would signify that the model predicted the correct concentrations throughout the available range. R^2 values are listed on each plot. Most elements show a very linear trend (signified by high R^2 value), have slopes close to one, and have very small intercept values. The model should therefore predict the concentration of Al, Ca, Fe, K, Mg, Mn, Na, Si, and Ti with good precision.

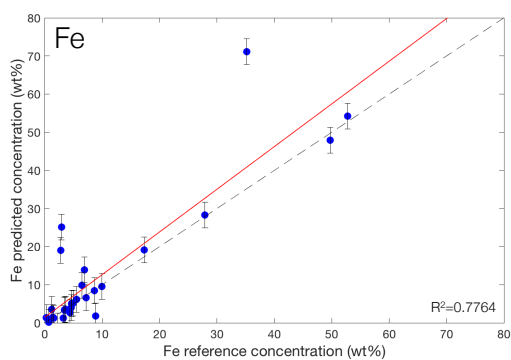
To obtain LODs from a PLS model, the standard deviation of the residuals of the validation set from the linear fitting divided this by the slope of the fit (in red) is calculated, then multiplied by our confidence factor, k . This is the same procedure as outlined in Freedman et al. [21]. Again, it should be mentioned that there does not seem to be a consistent or accepted method to determine LODs from multivariate analysis techniques. A comparison of our LODs with other similar LIBS instruments is presented in Table 20. SuperCam has not yet published any specific LODs, ChemCam only lists specific LODs for trace elements but have listed their sensitivity as



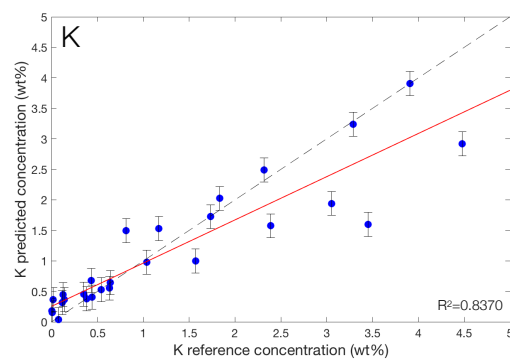
(a)



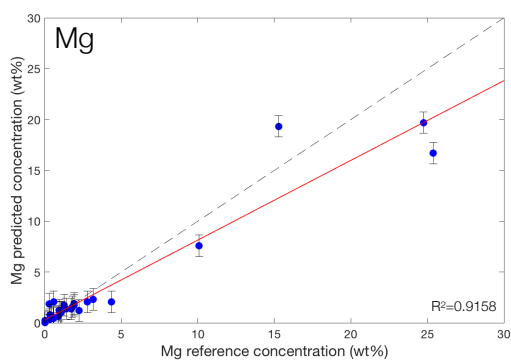
(b)



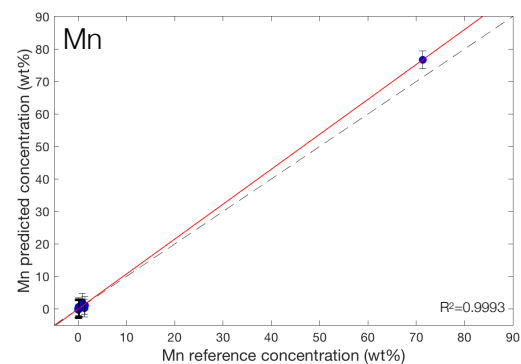
(c)



(d)

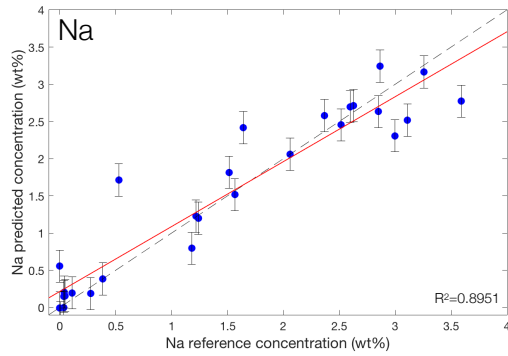


(e)

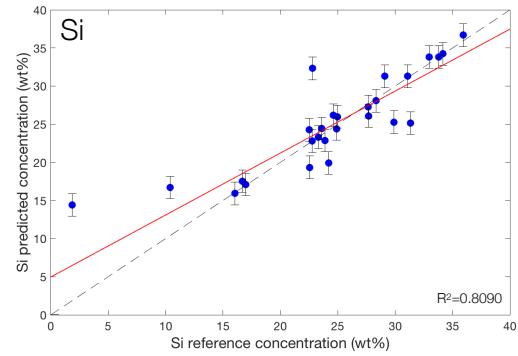


(f)

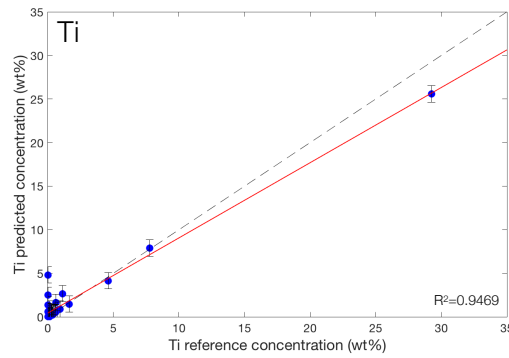
Figure 62: Predicted vs known plots for the elements (a) Al, (b) Ca, (c) Fe, (d) K, (e) Mg, (f) Mn, (g) Na, (h) Si, and (i) Ti created using the advanced PLS prediction algorithm. Dashed lines represent the ideal linear fit for a predictive model (with slope=1, and intercept=0), while the red line is the linear fit to the data.



(g)



(h)



(i)

Figure 62: Continued.

1 wt% for major elements generally [62]. There are other combined LIBS/Raman instruments, but these publications do not necessarily focus on LIBS LODs. With our internal standardization analysis ($\text{LOD}_{\text{CC,norm}}$) we're competitive with similar instruments. Because determining LODs from PLS analysis is less standardized than that of the usual calibration curve method, and since most LIBS literature used LODs determined from the calibration curve method, $\text{LOD}_{\text{CC,norm}}$ is used as our instrument sensitivity figure of merit until more work can be done with multivariate analysis methods.

What the advanced PLS model does do for us—as evident in Figure 62—is predict concentrations of samples very well. In order to determine how precise our model is over all possible sample predictions, the RMSEP is calculated for each element, which takes into account the model's prediction for each of the 28 samples' concentrations. RMSEP, here measured in wt%, is a major figure of merit for LIBS analysis, because predicting the concentrations of samples using spectra

Table 20: Comparison of LODs from LIRS with similar instruments. ChemCam doesn’t explicitly give LODs for most major elements, but cites their LOD as 1 wt% (10000 ppm).

Element	LIRS (this work)			ChemCam	LIRA	Other portable
	LOD _{CC}	LOD _{CC,norm}	LOD _{PLS}	[62]	[34]	LIBS [50]
	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
Al	17800	97	-	-	1820	190
Ca	2170	39	28100	-	150	160
Fe	14200	14200	168600	-	-	490
K	7730	28	8400	12	60	550
Mg	68300	492	32500	-	-	20
Mn	368000	24134	26600	63	-	50
Na	15600	300	7400	-	30	10
Si	122000	4466	68600	-	-	160
Ti	348000	3218	23000	-	-	30

is the ultimate goal of an analytical instrument like this one. Table 21 summarizes these results alongside those from ChemCam. Out of nine elements our model can predict the concentration better or at the same level as ChemCam for just over half of those elements. This model can be added to continuously so that additional elements can be predicted, as long as they are actually present within our spectra. This would involve choosing additional samples with a satisfactory range in target element concentrations. It should also be noted that these results are competitive even though the LIRS collection efficiency is hindered by the telescope-spectrograph $f/\#$ mismatch.

To summarize, when it comes to both LODs and prediction precision, LIRS is competitive with current single-mode, portable LIBS instruments.

Wiens et al. investigates the prediction capabilities of their advanced PLS model with decreasing resolution [62]. In their study, they degrade the resolution of their spectra using Gaussian peaks with FWHM up to ten points, and create a new PLS model with previously unpredicted samples. Ten points corresponds to ~ 1 nm, on average throughout the entire spectral range. In our case, all 28 spectra are convolved with varying Lorentzian profile widths and the concentration re-predicted. Figure 63 shows an example of iron ore spectra, where both the original spectra and degraded spectra with about 1 nm line widths is included (the average linewidth of our original spectra is about 0.1 nm). The advanced model was used to predict the concentrations of each sample and

Table 21: Comparison of prediction capabilities between LIRS and ChemCam using advanced PLS algorithm.

Element	LIRS	ChemCam [62]
	RMSEP (wt%)	RMSEP (wt%)
Al	2.14	2.35
Ca	1.41	2.84
Fe	8.85	4.03
K	0.57	0.66
Mg	2.21	1.83
Mn	1.08	0.10
Na	0.40	0.72
Si	3.77	3.61
Ti	1.37	0.47

the RMSEP was calculated for each element, for each type of spectra. Figure 116 shows how the RMSEP varies for each element with decreasing spectral resolution. Although some elements behave as expected, i.e., the RMSEP increased with decreasing spectral resolution, like Ca and Mn, some elements show no overall change (Al, Mg, Ti), and some have decreasing RMSEP, like Fe. RMSEP is expected to increase with decreasing resolution because there could be overlapping spectral lines that would make it hard to find patterns within the spectra for specific elements. This is the case with Ca and Mn. With Fe, however, since there are so many Fe spectral lines within LIRS spectra, the resolution probably doesn't change any major patterns in where Fe lines appear with decreasing spectral resolution. The purpose of this exercise was to determine the impact of different spectral resolutions on the predictive capabilities of the model. Although the prediction of the model is relatively unaffected by the change in resolution, LODs would most likely decrease due to decreasing signal to noise.

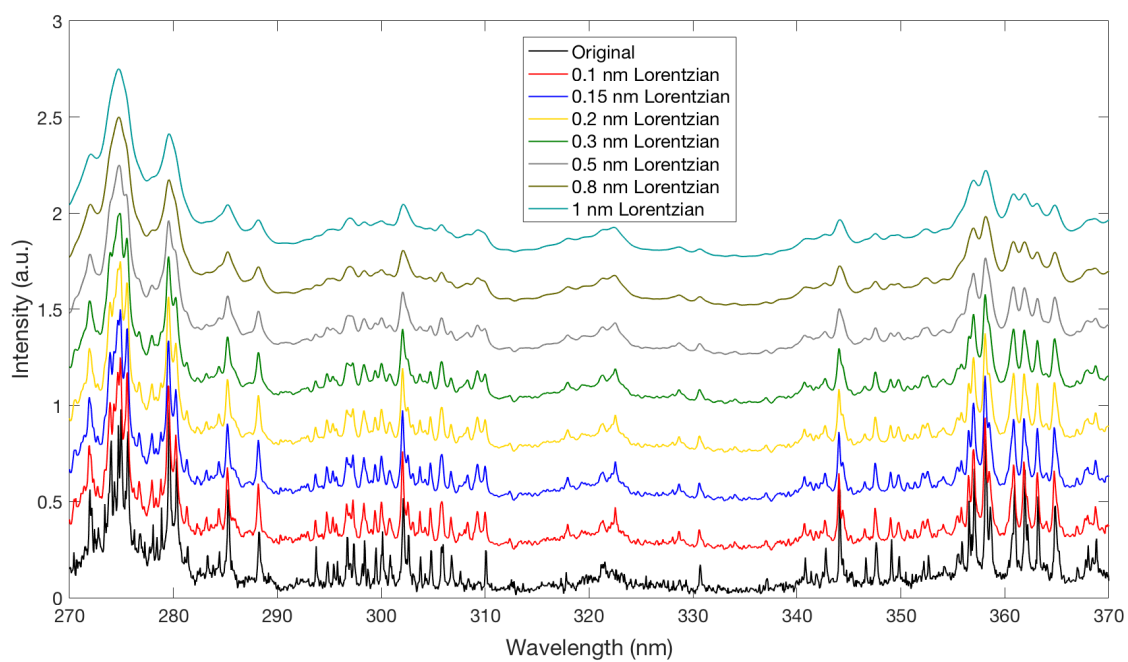
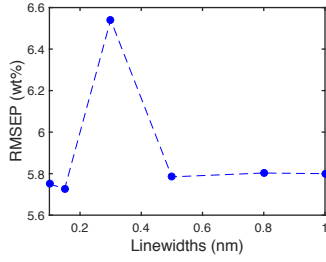
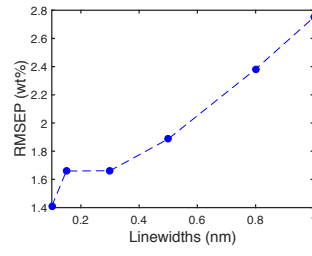


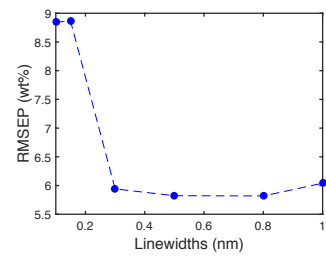
Figure 63: Various LIBS spectra of iron ore with degraded resolution used to test prediction capabilities at varying resolutions.



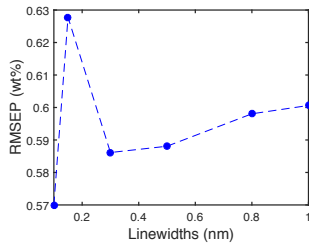
(a)



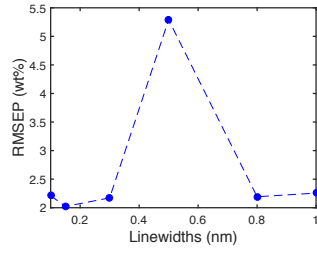
(b)



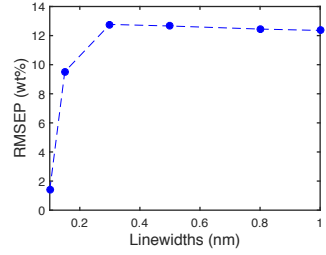
(c)



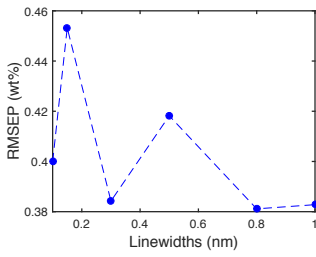
(d)



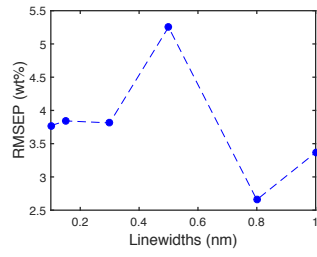
(e)



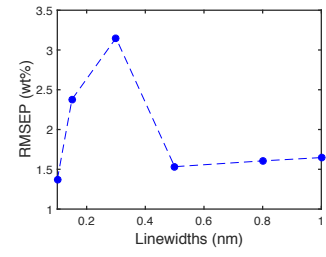
(f)



(g)



(h)



(i)

Figure 64: RMSEP (wt%) versus Lorentzian profile line widths for (a) Al, (b) Ca, (c) Fe, (d) K, (e) Mg, (f) Mn, (g) Na, (h) Si, (i) Ti. There is no trend across all elements (unlike [62]).

7.4.7 Comparison at other sensing distances

A full characterization was only completed at 35 cm. Although the full range in sensing distance should be explored in the future, the restriction to one sensing distance is realistic considering variable distance instruments such as ChemCam choose to keep their sensing distance constant, for simplicity. In spite of this, Figure 65 and Figure 66 show LIBS spectra of aluminium and ilmenite, respectively, at 25, 35, and 43 cm. Although the IR laser could be focused to distances much greater than 43 cm, sensing distances were kept the same across all modes. Figure 65 shows that there is not much difference between the three spectra. The intensity is the highest at 25 cm, but the noise floor is also raised. In contrast, for ilmenite (Figure 66), the intensity at 35 cm is the highest, though the spectrum at 45 cm is very similar (this is the same for aluminium as well). Although the intensity of major lines is the lowest at 25 cm, the noise floor is the lowest. The standard deviation of the noise (σ_{noise}) was calculated in a region with no spectral lines (700-780 nm) for each ilmenite spectra. For 25 cm $\sigma_{noise} = 0.0106$, for 35 cm $\sigma_{noise} = 0.0589$, and for 45 cm $\sigma_{noise} = 0.0884$. Using the 375.9 nm line, a representative SNR was calculated for each spectrum. They are 58.4 at 25 cm, 47 at 35 cm, and 18.1 at 45 cm. The spectrum taken at 25 cm is therefore the highest quality spectrum (although, it should be considered that only one line is used for this analysis).

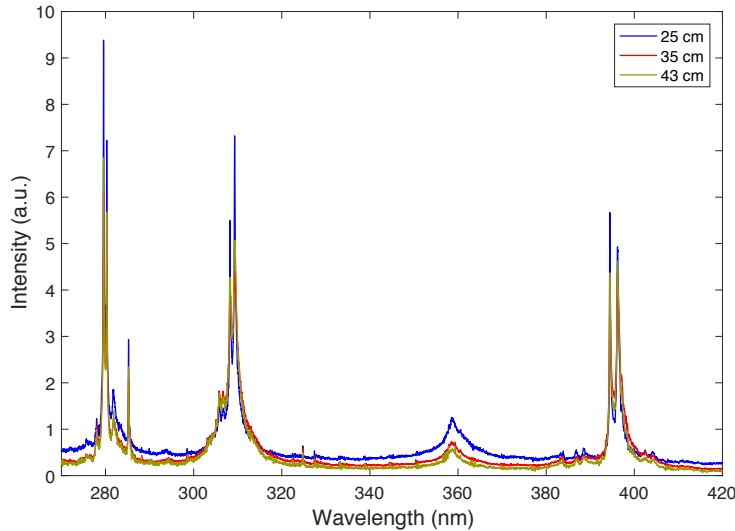


Figure 65: Comparison of LIBS spectra of aluminum at different sensing distances. Measurement conditions: 5000 laser pulses, 1000 MCP Gain, 224-226 ns gate delay, 1000 ns gate width.

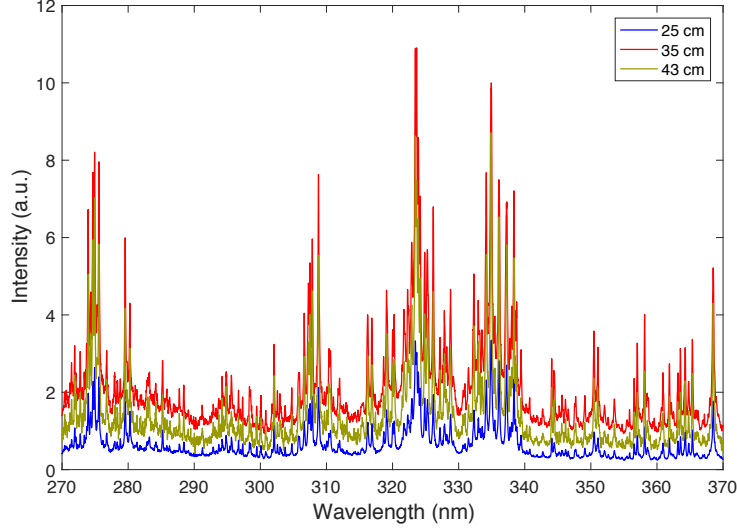


Figure 66: Comparison of LIBS spectra of ilmenite at different sensing distances (taken with optimal parameters listed in Table 14).

7.4.8 Other Measurements

One of the major advantages of using μ LIBS is the small spot size. At 35 cm the laser spot size is around $50\text{ }\mu\text{m}$ in diameter, which is small compared to ChemCam (around 1 cm). This would allow for higher resolution spatial mapping and the ability to identify in-situ conditions and processes that would have aided preservation and/or degradation of physical structures on a smaller scale than ever before. Of course, the amount of material sampled by laser-ablation and the laser spot sizes are two different things. Figure 67 shows optical microscope images of μ LIBS craters on all of the original characterization samples as well as the extended set (including Fe ore, ferrous rock, CuMo ore, and ultrabasic rock). The size of the craters r_c should scale with material properties and the laser beam waist, i.e., $r_c \propto w_0 + \delta_h$, where δ_h is the heat penetration depth [12, 45]. The heat penetration depth $\delta_h \sim \sqrt{\kappa \Delta t_{pulse}}$ depends on thermal properties of the material (specifically the thermal conductivity) and the laser pulse width. The craters should then scale with both the beam waist and the pulse duration, of which μ LIBS uses particularly small values.

The average size of the ablation craters range from $49.38\text{ }\mu\text{m}$ (syenite) to $254\text{ }\mu\text{m}$ (basalt). The average crater size amongst all samples is $112\text{ }\mu\text{m}$. Maurice et al. [38] lists LIBS ablation craters for the ChemCam instrument on anodized aluminium. They measured $180\text{--}290\text{ }\mu\text{m}$ radius (0.36–0.58

mm diameter) depending on the distance to the target. Looking only at one distance (2.5 m), the LIBS crater is around twice the size of the laser spot size, and has a diameter of 400 μm . Our spot size and resulting LIBS craters will be a major improvement over current instruments for enabling high-spatial resolution mapping, even though the craters don't follow the 60 μm spot size.

It is also important to note that there is a general trend towards LIBS craters being larger for samples that do not produce successful LIBS spectra. Figure 67 separates the samples for which LIBS works (bottom section) and those that were unsuccessful (top section). Since the laser-matter interaction is the most important for forming a plasma on the surface, it is worthwhile to examine any morphological differences in LIBS craters between the successful and unsuccessful samples. Generally, the samples that don't work seem to fall into two categories: either there is not enough mass ablated (syenite, flint clay, and wollastonite), or there is a left over 'pool' of material (mainly anorthosite, basalt, and pyroxenite). For those that fall into the latter category, it is posited that these materials might not be able to dissipate much of the thermal energy imparted into the sample by the beam. Because some of these do form a visible plasma at the surface (see Table 15), there might be a certain number of pulses for which LIRS *could* be able to get information from the sample but because of our collection optics inefficiencies, spectral lines are not able to be distinguished from the noise. Section 8 introduces some of the preliminary experiments performed in moving towards the determination of why μLIBS does not work for some geologic samples.

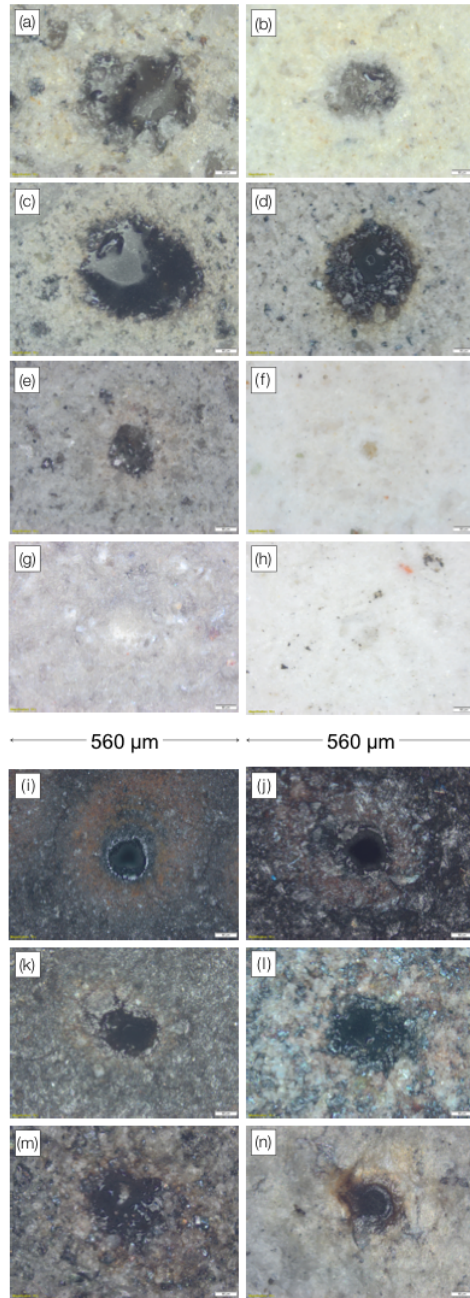


Figure 67: Craters left over after LIBS measurement with 5000 laser pulses at 10 kHz: (a) anorthosite, (b) granite, (c) basalt, (d) pyroxenite, (e) andesite, (f) syenite, (g) flint clay, (h) wollastonite, (i) ilmenite, (j) coulsonite, (k) manganese ore, (l) iron ore, (m) iron rock, and (n) ultrabasic rock. Samples (a-h) do not present good LIBS spectra, while samples (i-n) do. The average spot sizes from five measurements across each samples are listed in Table 37.

Table 22: Mean LIBS crater sizes on each standard from 5 pulses.

Standard	Mean diameter (μm)	Standard deviation (μm)
Andesite	110	5.03
Anorthosite	163.59	22.31
Basalt	254.5	25.90
Coulsonite	110.31	2.53
Flint clay	73.75	5.15
Granite	141.56	11.83
Mn ore	128.13	8.02
Pyroxenite	103.75	7.94
Syenite	49.38	-
Ilmenite (Ti ore)	100	3.75
Wollastonite	98.13	-
CuMo ore	-	-
Fe ore	89.53	8.51
Ferrous rocks	96.72	12.50
Ultrabasic rocks	84.06	3.63
Aluminium	89.53	4.93

7.5 LIF Characterization

Table 23 details typical acquisition parameters (intensifier gate delays, gate widths, the MCP gain, and exposure times) for LIF measurements. LIF measurements are performed with similar acquisition parameters as with Raman, only switching the gate delay and width to optimize fluorescence signal in the 300–800 nm range. Like the other modes, optimal gate delay was determined with anhydrite using kinetic mode. The main goal was the optimization of the fluorescence signal after the Raman effect. The duration depends on the sample type, but typical fluorescence lifetimes are upwards of 40 ns for some compounds. The fluorescence signal should be seen at the same time regardless of the sample type. The optimal gate delays for each distance and at each laser frequency are summarized in Table 23.

7.5.1 Results at 35 cm

LIF spectra are shown in Figure 68 and Figure 69 for geologic standards and organics, respectively. These spectra are an average of five spectra taken at different points along each sample, with the

target stationed at 35 cm. For each target type the exposure time is optimized to the point where the LIF response becomes 12–15 times bigger than the background (up to a maximum exposure time of 20 minutes). For geologic standards, the minimum exposure times vary from as short as 10 s to about 7 minutes (depending on the standard), making this technique much quicker than Raman spectroscopy in most cases. Organics are initially detected quickly, but optimal times are of the same magnitude as the geologic standards.

Most samples produce fluorescence, except those that have high UV absorption (e.g. coulsonite, manganese ore, ilmenite, and basalt). Table 24 gives a summary of LIF functionality. Samples which do not present good Raman effect in the UV may still provide a good fluorescence signal as the fluorescence signal intensity is typically much larger than any Raman signal. It is important to note that certain minerals like carbonates, sulfates, and silicate members that are easily detected by LIF will not necessarily be detected in Raman spectroscopy. Section 7.3.3 clarifies the cause of inadequacies of UV Raman for certain polymineralic samples. The fluorescence effect, however,

Table 23: Typical acquisition parameters for LIF measurements. Each spectrum in this report was acquired using parameters following these guidelines.

Typical acquisition parameters				
Measurement time		1–400 s		
Sensing distance		0.25–0.43 m		
Laser frequency		10–20 kHz		
Laser power		100%		
Exposure time		varies		
		25 cm	35 cm	43 cm
ICCD gate delay	10 kHz	15.8 ns	17.5 ns	18 ns
	20 kHz	18 ns	18.5 ns	19 ns
	30 kHz	21 ns	21.5 ns	22 ns
	50 kHz	24.5 ns	25.5 ns	26 ns
ICCD gate width		150–200 ns		
ICCD MCP gain		4000		
# of acquisition spots per sample		5		
# of Raman spectra obtained per spot		1		
Total # of spectra per sample		5		

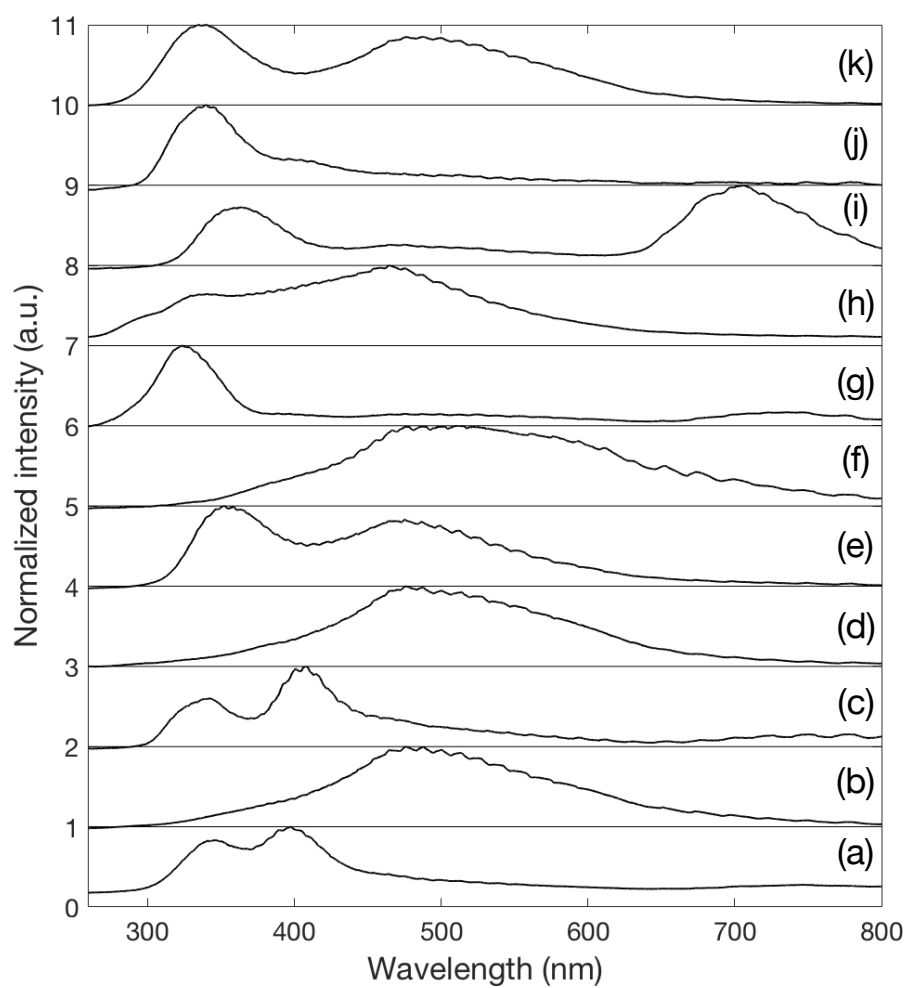


Figure 68: Raman spectra of (a) andesite, (b) anhydrite, (c) anorthosite, (d) aragonite, (e) dolomite, (f) flint clay, (g) granite, (h) quartz, (i) syenite, (j) pyroxenite, and (k) wollastonite, taken with optimal parameters.

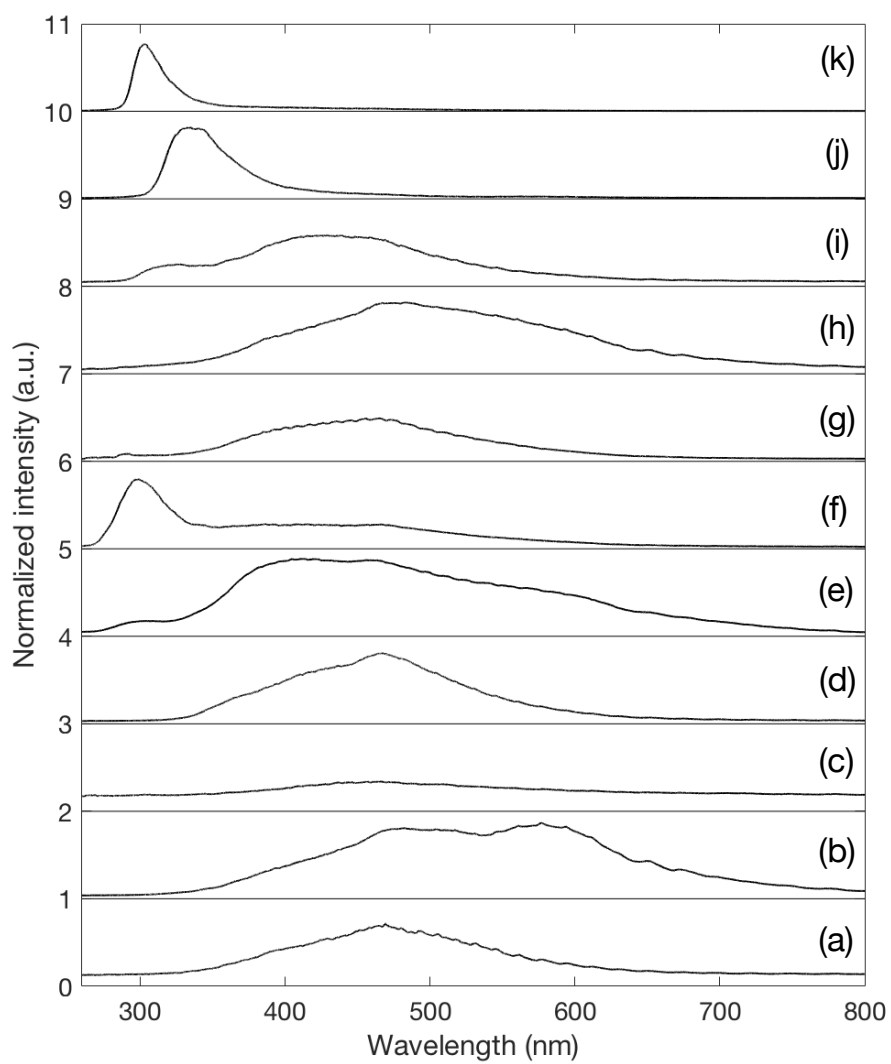


Figure 69: LIF spectra of pure organics: (a) alanine, (b) β -carotene, (c) cystine, (d) lysine, (e) octacosane, (f) phenylalanine, (g) serine, (h) stearic acid, (i) thymine, (j) tryptophan, and (k) tyrosine, taken with their optimal parameters.

Table 24: Summary of Phase 2 LIF measurement results for (a) geologic standards and (b) organic samples. Green/M = Raman measurement was successful, Red/CM = Raman measurement was unsuccessful, NM = no measurement was attempted.

(a)		(b)	
Standard	35 cm	Standard	35 cm
Andesite	M	Alanine	M
Anorthosite	M	β -Carotene	M
Basalt	CM	Cystine	M
Coulsonite	CM	Lysine	M
Flint Clay	M	Octacosane	M
Granite	CM	Phenylalanine	M
Mn Ore	CM	Serine	M
Pyroxenite	M	Stearic acid	M
Syenite	CM	Tetracosanoic acid	M
Ti Ore (Ilmenite)	CM	Thymine	M
Wollastonite	M	Tryptophan	M
Aragonite	M	Tyrosine	M
Anhydrite	M		
Dolomite	M		
Gypsum	M		
Quartz	M		

is an absorption process rather than a scattering process. Raman scattering is a process that will happen only when photons are close to the transition energy needed between the two energy states [56]. In contrast, LIF will involve several processes during a non-selective excitation (such as non-radiative transitions, quenching, excitation, and energy transfer between the powder particles, etc.). Fluorescence spectra are therefore observed as broad bands, with the most intense band being governed by the minerals within the sample that present fluorescence behaviour.

In rocks, a UV fluorescence response is activated by impurities (or activators) within a target, each of which have a specific band region and shape. In the spectra of geologic standards were able to identify Ca^{2+} , SO_4 , and O_2 activators, for example. LIF spectra of organics give information about the organic structure, and LIF spectra can be used to distinguish organics into their respective classes (e.g. aromatic amino acids like tyrosine verses hydrocarbons like β -carotene). Interpretation of LIF spectra was completed by E. Lalla, and is not detailed here.

7.5.2 Time-resolved fluorescence

Time-resolved fluorescence (TR-LIF) has been shown to be a valuable technique for detecting and discriminating organic material and may be useful for locating regions of interest for subsequent Raman and LIBS analysis [19]. With the limited measurement opportunities inherent on a rover platform, time-resolved capabilities can assist in identifying the locations on a sample most likely to contain organic material. Time-resolved measurements of targets are taken with the same parameters as samples usual LIF spectra, with some modifications. Instead of taking one exposure to capture the entire fluorescence signature, a very small gate width (2–5 ns) is used and the gate itself is stepped forward in incremental amounts (~ 1 ns). Figure 70 demonstrates the results of a TR-LIF measurement. A LIF spectrum is taken with 2–5 ns exposure, starting at some nominal gate delay (which depends on the sensing distance and laser frequency). The gate is stepped forward by ~ 1 ns and another short LIF spectrum is taken, the gate is stepped forward again, and so on. This results in a series of short LIF spectra that are taken ~ 1 ns apart, showing the evolution of the fluorescence signature for each target.

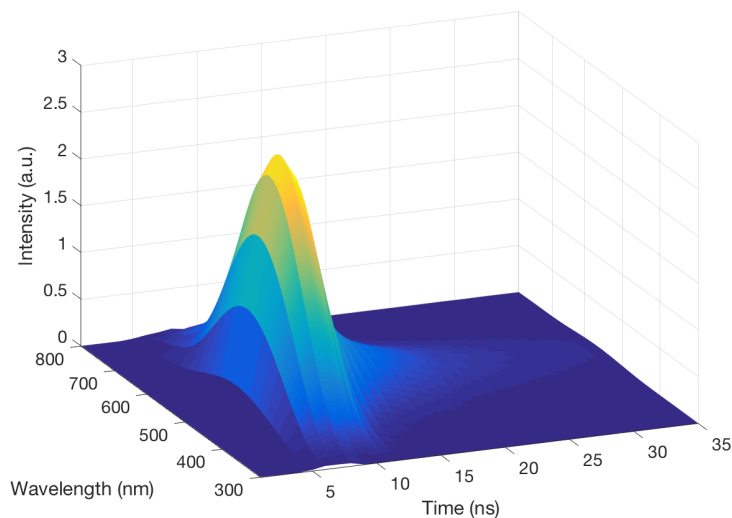


Figure 70: Time resolved measurement of lysine. Each time slice corresponds to a measured spectrum at a different time delay.

Figure 71 shows examples of TR-LIF spectra for three samples which are representative of the

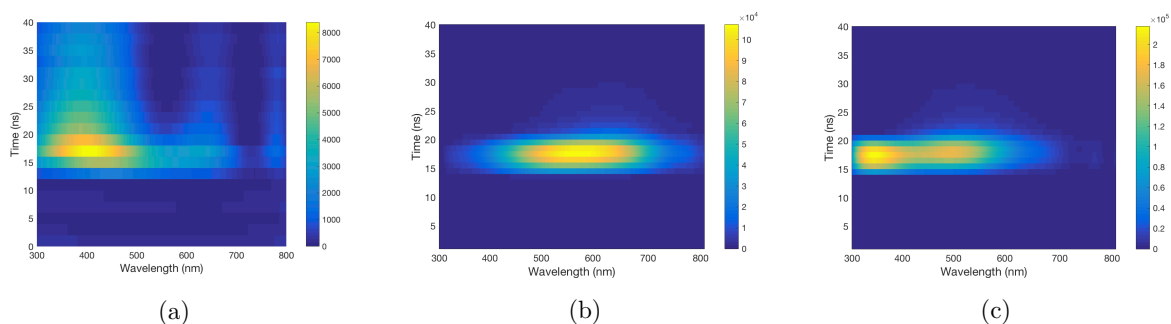


Figure 71: Examples of time-resolved fluorescence for (a) dolomite, (b) β -carotene, and (c) thymine. Organic compounds usually exhibit fluorescence with shorter lifetimes.

larger sample set. Generally, organic fluorescence signatures decay within 10 ns, while most mineral fluorescence signatures will take much longer to degrade [19, 32]. This is evident in Figure 71, where the dolomite geologic standard (Figure 71a) still has a detectable LIF signature at the end of the measurement (around 40 ns), while the two organic compounds (Figures 71b and 71c) fluoresce for only a short period. Because of this, TR-LIF can be used as an organic detection method. Further, not only can the *presence* of an organic material be identified, the *type* of organic can be identified by its fluorescence decay time. This has been studied extensively in [19]. Obviously TR-LIF is valuable for a planetary science mission in which assessing the past and future habitability is a goal. The SuperCam instrument will also use a gated camera in which could perform similar measurements, but it is not a *fast* gated camera. Whereas our ICCD has a minimum gating resolution of ~ 1 ns, the SuperCam detector will have ~ 100 ns resolution, making TR-LIF measurements in which the type of organic can be identified impossible.

7.6 Passive reflectance measurements

Passive reflectance measurements—where utilization of solar radiation essentially gives ‘free’ data—is a good attribute for a flight instrument. Passive reflectance spectroscopy is, as it sounds, the study of light reflected from a target as a function of wavelength. In resulting spectra, absorption bands indicate which photons were absorbed by a material via electronic or vibrational processes. The location of absorption bands (troughs in a reflectance spectrum) will give us some information about the composition of the sample. Although LIRS is not designed to perform this type of spectroscopy specifically, the capabilities of the breadboard in this mode using a white LED lamp to mimic the

sun were tested. It is shone onto each target at 35 cm, and the light is collected via the telescope into the spectrometer over the 300–850 nm range.

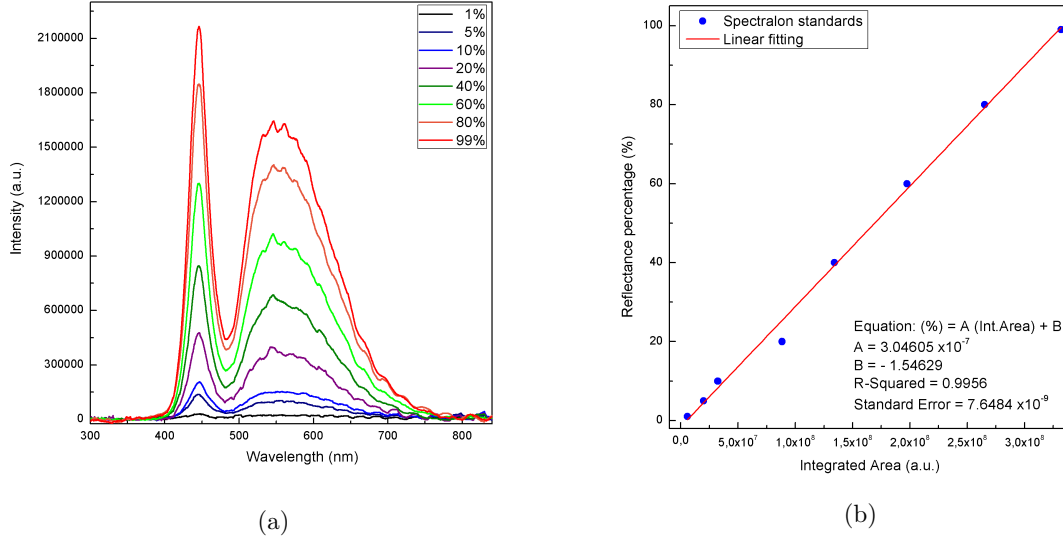


Figure 72: Passive reflectance: (a) measurements of spectralon standards and (b) reflectance calibration curve. Credit: E. Lalla.

Figure 72 shows measurements of reflectance standards (Labsphere Spectralon diffuse reflectance standards) illuminated with a white LED lamp. The area under the curve in the whole range (300–850 nm) is integrated and plotted versus the known reflectance percentage to create a reflectance calibration curve (Figure 72b). The reflectance spectra of geologic targets was integrated over the same range and the calibration curve was used to determine a raw % reflectance. These are, for andesite 11.1%, anorthosite 40.8%, flint clay 16.8%, ilmenite 2%, basalt 23.3%, Mn ore 10%, syenite 73%, pyroxenite 35%, wollastonite 15%, and granite 46%. For each sample spectrum, the 99% spectralon spectrum was normalized and subtracted from the sample spectra, removing the spectral shape of the LED lamp. The remaining spectra should therefore show characteristic absorptions across the spectral range for each sample.

Figure 73 shows the passive reflectance spectra of ten geologic samples (from Table 6). These measurements possess similar features to those found in the literature, mainly Cloutis et al. [10] and Rencz et al. [51]. Cloutis et al. covers similar minerals in UV, and Rencz et al. has a broad overview of passive remote sensing as it applies to Earth observation. The spectral shape of ilmenite and manganese ore are similar to those acquired under UV reflectance from Cloutis et

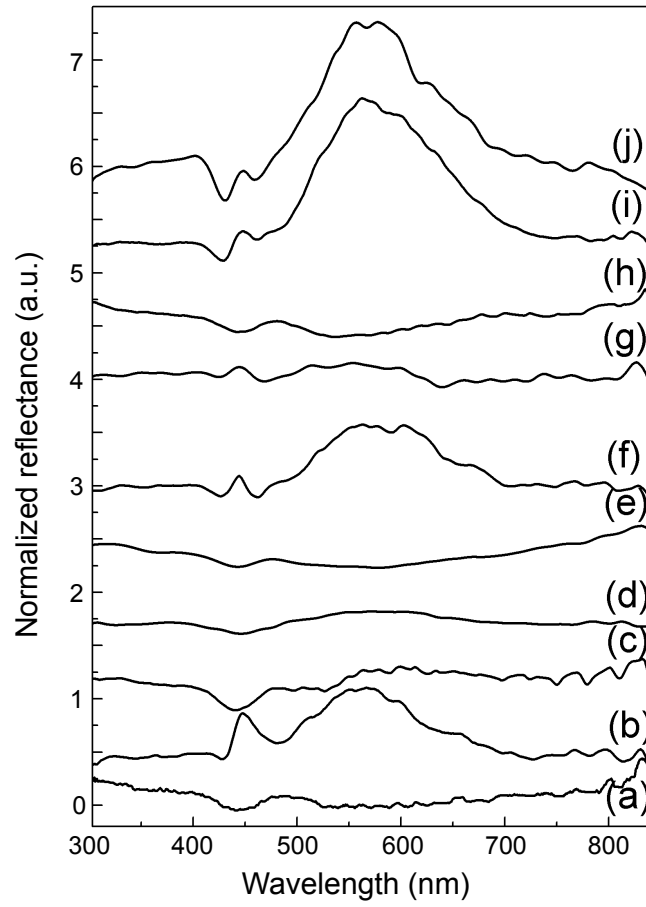


Figure 73: Passive reflectance spectra of various samples: (a) andesite, (b) anorthosite, (c) flint clay, (d) wollastonite, (e) ilmenite, (f) pyroxenite, (g) basalt, (h) manganese ore, (i) granite, and (j) syenite. Credit: E. Lalla.

al. up to 400 nm [10]. A similar broad feature is seen between 550–600 nm in both ores. This has been related to Ti^{3+} and $\text{Fe}^{2+,3+}$ [51]. A plagioclase feature in the region between 450–650 nm can be observed in granite and syenite [51]. There is a similar feature (although on a smaller scale) in anorthosite and pyroxenite. These minerals tend to have less absorption in the 450–650 nm region [51]. There are other important features in the literature, but these are outside of the spectral range (>1000 nm).

If the passive reflectance mode was used during flight, a more thorough analysis including measurement of more samples and different types of minerals within the same family is needed. Johnson et al. [29] covers VIS-IR reflectance (400–1000 nm) as it relates to Mars, specifically those obtained with the ChemCam instrument. They perform a similar analysis.

7.7 Combined characterization

Prediction of an unknown sample was performed using information obtained from all three modes (plus TR-LIF). Figure 74 shows LIF, Raman, and LIBS spectra of quartz latite, and Figure 75 shows the TR-LIF spectrum.

From the μLIBS spectrum, Table 25 gives the predicted elemental concentration of this sample using the advanced PLS model, with standard percent error.

The Raman spectrum has a peak that matches the quartz spectrum (Figure 57), but the sample is clearly not only silicate (SiO_2) because of the LIBS composition results and the peaks present within the LIBS spectra. With the predicted concentrations of Na, K, Ca, and Al it could be a feldspar, but since Na, K, and Ca are in almost equal proportion, these concentrations fall into the miscibility gap of the feldspar ternary diagram, thus this sample is most likely not simply a feldspar. It is especially unlikely having found a large amount of aluminum. It could be, however a rock type that includes some feldspar and quartz, something like granite or a basalt. In a real world situation the instrument would include a micro imager which allows investigation of grain sizes, giving more clues to the rock-type. The incorrect prediction of magnesium would throw off this analysis (though only slightly), and the prediction would lean towards a dacite or granodiorite rather than a latite.

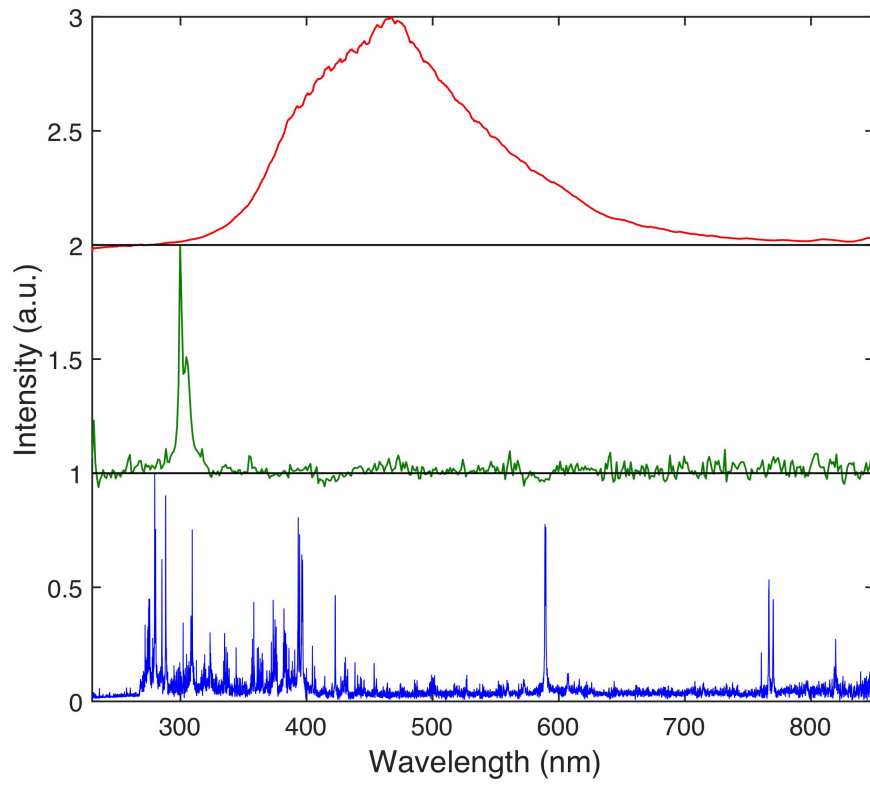


Figure 74: LIF (top), Raman (middle), and LIBS (bottom) measurements of quartz latite. The Raman range is 0–4000 cm^{-1} .

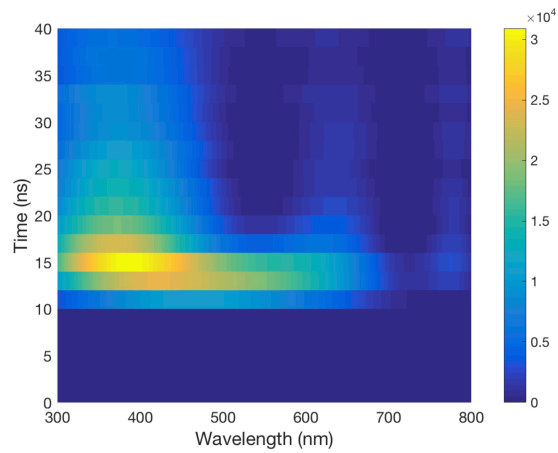


Figure 75: Time-resolved LIF spectrum of quartz latite standard.

Table 25: Prediction of elemental concentrations of quartz latite including errors in prediction using advanced PLS model.

Element	Predicted concentration (wt%)	Certified concentration (wt%)	% Error
Al	7.3776	8.57	16.16%
Ca	1.8785	2.27	20.8%
Fe	6.4889	3.04	53.15%
K	2.8637	2.99	4.4%
Mg	2.9439	0.6030	79.52%
Mn	0.2657	-	-
Na	2.5576	3.12	21.99%
Si	30.3436	30.66	1.04%
Ti	0.3623	0.37	2.13%

7.8 Implications for LIRS flight concept

This section lists some of the lessons learned from the characterization of the LIRS breadboard and the implications of the results of this study for a future combined LIBS/Raman sensor. Given that there are a number of samples which do not produce useful Raman spectra with excitation at 266 nm, there is a need for another Raman wavelength to make LIRS as flexible as possible (532 nm is recommended). The UV excitation for Raman (and LIF) is still very valuable for certain minerals as well as organic material. Additionally, some organic materials are damaged after a short (<10 minute) exposure with UV excitation. A laser with a lower peak power is recommended. Lastly, having a defocusing mechanism to check for organic materials would be useful to then zoom in and

Table 26: Comparison of laser parameters for this study and for ChemCam and SuperCam.

	Peak intensity (GW/cm ²)	Peak fluence (J/cm ²)	Pulse duration (ns)	Pulse energy (mJ)	Spot radius (μm)
LIRS Phase 1	1	10	10	0.5	59*
LIRS Phase 2	18	10	0.5–0.6	0.106	25*
SuperCam [48]	>1	>5	5	>12 (typ. 20)	-
ChemCam [62]	1–4	5–25	4.7	10	360–540

*measured at 35 cm.

examine with a smaller spot size. Without a defocusing mechanism, a maximum laser spot size of 50 μm is recommended to stay competitive as a microanalysis instrument.

For the LIBS mode it is recommended that a laser is used that more highly resembles a “typical” LIBS instrument. When comparing the lasers used in Phase 1 with those used in Phase 2, along with the lasers in the ChemCam and SuperCam instruments, it is clear that the only factor which is different between LIRS values and their values is the pulse energy (Table 26). It is therefore recommended that the LIRS flight concept uses a laser with mJ pulse energies. The small laser spot size presents a major improvement over other available instruments for spatial mapping. It is recommended that the LIRS flight concept uses a spot size similar to that of the current system, if not smaller. With the current setup, the image of the fiber on the target at 35 cm is 160 μm , thus it is a bit small to collect all the light from the plasma formed on some samples with our current spot size (evident by the LIBS crater sizes).

Finally, having time resolved fluorescence capabilities integrated within the instrument will help distinguish organic material from inorganic material. A detector with a minimum gate width of 100 ns (like SuperCam) would most likely be able to detect the presence of organics, but only with the fast gating capabilities used here could specific organics be fingerprinted. A defocusing mechanism and fast scanning mirror would be useful for fast detection of organics using LIF mode.

7.9 LIRS flight concept

The characterization of the LIRS breadboard was instrumental in determining the feasibility of a highly combined instrument for small-scale compositional analysis. Testing the breadboard with commercial components is the first step to narrow down requirements for a future flight instrument. Because of our analysis, and our recommendations, the LIRS flight instrument would have the following key changes:

- Single IR laser at 1064 nm with active Q-switch and ~ 10 mJ pulse energy. Built-in frequency generation would create the 532 nm and 266 nm wavelengths at lower peak power.
- Mapping mechanism by translating optical fiber.
- Improved echelle spectrograph (more compact, higher throughput).

- Improved telescope optics (delivering the beams and collecting emissions through the same telescope). Defocusing can be performed by the telescope mechanics.
- Custom intensified camera with fast gating capabilities.
- Single context/alignment camera.

Currently, the LIRS flight instrument is designed to have a sensor head (that would be mounted on an arm) and a flight box stowed away on the rover body. The instrument would be around 40 cm x 30 cm x 12.5 cm with a volume of 15 L.

8 μ LIBS Experiments

During measurement of geologic standards it was found that LIBS in the μ J regime does not produce successful single-spot LIBS spectra for most of the eleven original samples chosen for LIRS characterization. In fact, out of a larger sample suite of 38 standards, only 7 of them were successful. Table 15 gives an overview of the results for the eleven original samples chosen in the LIRS characterization study. Some of them (including andesite and basalt) were able to form a plasma at the surface but still resulted in an unsuccessful μ LIBS spectrum, while some (including syenite and wollastonite) did not form a plasma on the surface at all. A similar trend was found with the 532 nm μ LIBS system, though this instrument was only used to confirm the functionality of μ LIBS on certain samples. The same samples that did not produce successful μ LIBS spectra on the LIRS instrument also did not work on the 532 nm system. Although for most samples a bulk μ LIBS spectra could be acquired for LOD analysis by performing a measurement while the sample was in motion, a single-spot measurement is ideal. One of the major benefits of μ LIBS in the first place is its high spatial resolution. Determining why successful μ LIBS spectra were not possible in a single spot for most samples is therefore high priority for this technique to ever be considered for a future flight.

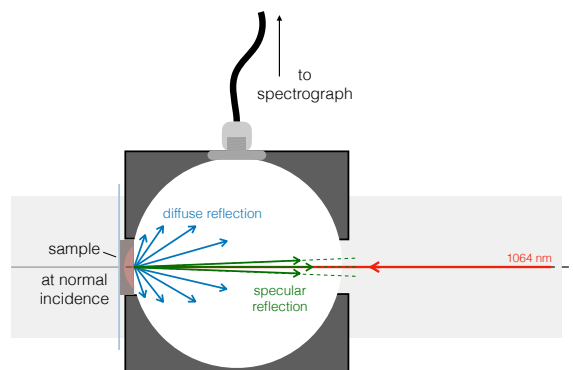


Figure 76: Reflectance experiment geometry.

For all samples which do not work, there seems to be a problem with the amount of energy absorbed by the sample to either create or sustain the plasma. For those samples which do not form a plasma at the surface, there most likely isn't enough energy transferred from the beam to the sample over the pulse width. For those that do form a plasma, but are still not successful, recall that

the μ LIBS regime uses μ J pulses energies and very rapid repetition rates. LIRS specifically uses a 10 kHz repetition rate. It is possible that, at some low number of laser pulses, characteristic emissions *could* be detected (if either instrument could pick up this this low signal), but with increasing numbers of pulses, the sample will melt and solidify in between laser pulses. This creates a shiny, specular surface, which reflects most of the incoming beam. Figure 67 shows the craters left over after a μ LIBS measurement. The horizontal line separates those which were successful (bottom) and those which were unsuccessful (top). On the top, for those that do form a crater, there does appear to be a pooling of material that has melted and solidified. At some point, then, there is essentially no laser-material coupling. Because of this, the reflectance at 1064 nm of each standard before and after a LIBS measurement was taken using an integrating sphere (Thorlabs IS236A-4) to determine if there was a major difference between samples which worked and those that did not.

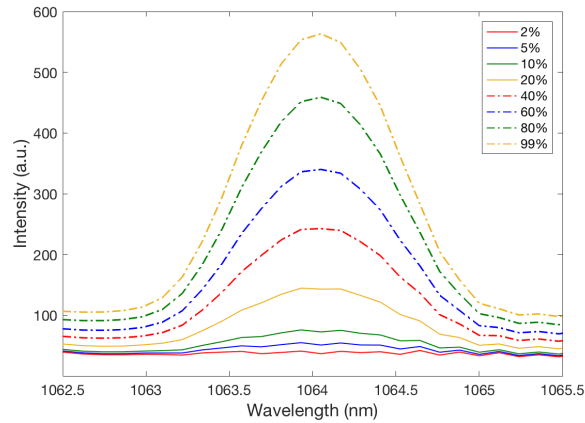


Figure 77: Spectral response from standard reflectance materials using the laser at 50%, and measured with the IS.

Figure 76 is a schematic of the experiment design. The measurement was restricted to normal incidence to ensure the reflectance was measured on the same spot before and after a μ LIBS measurement. It was important to mimic the process occurring during a μ LIBS measurement, meaning that it was essential that the sample was kept at normal incidence to the ablating laser beam. 1064 nm reflectance of each sample was measured before the sample was ablated, and after. The 1064 nm laser was used at 50% power for these measurements. Standard reflectance materials (LabSphere Spectralon pucks) were inserted into the back of the integrating sphere (IS) and measured to obtain

Table 27: 1064 nm reflectance before and after a LIBS measurement for geologic standards and aluminum. $\Delta\%R$ is the change in reflectance. Bolded entries are those samples which produce a successful single-shot μ LIBS spectrum.

Sample	Ref. Number	1064 nm % Reflectance		$\Delta\%R$
		Before LIBS	After LIBS	
Andesite	JA-1	42.0	26.3	15.7
Anorthosite	MO-6	62.8	34.8	28
Basalt	JB-2	31.9	22.1	9.8
Coulsonite	DC19003a	20.7	20.5	0.2
Flint Clay	SRM97b	45.4	37.9	7.5
Granite	JG-2	97.4	86.0	11.4
Ilmenite	SARM49	20.1	21.8	-1.7
Mn Ore	DC47005	23.4	23.4	0
Pyroxenite	SARM5	64.7	32.3	32.4
Syenite	SARM2	91.8	85.2	6.6
Wollastonite	DC60124	100	100	0
Aluminium	-	75.5	74.5	1

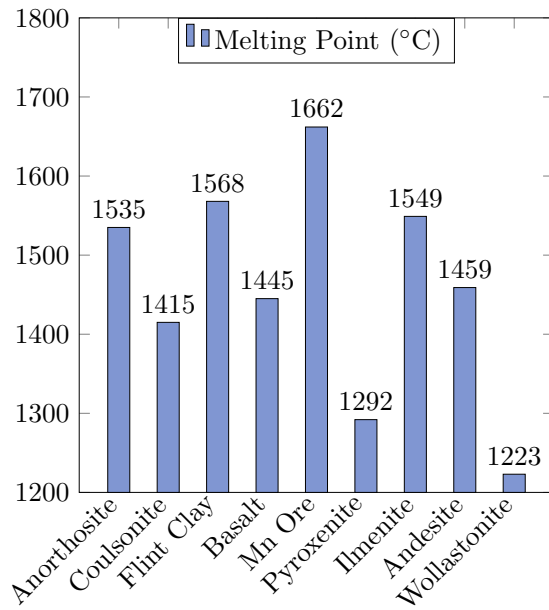
a reference. The resulting spectra are shown in Figure 77.

The spectral response was integrated between 1063–1065 nm and a calibration curve created (similar to that of Figure 71). The calibration curve was used to relate the integrated spectral response of the samples to a raw percent reflectance. These results are summarized in Table 27, where samples which produced successful, single-spot μ LIBS spectra are bolded. The standard error in the fit is lower than the significant digits presented in the table. Notice that the bolded entries all have a change in reflectance ($\%R$) close to 0, meaning that the reflectance is essentially the same before and after a μ LIBS measurement. For those that did not produce successful μ LIBS spectra, the change in reflectance is much higher, meaning the reflectance before is higher than the reflectance after. Because of the geometry of our experiment, our results imply that there is a larger specular component after the μ LIBS measurement that is not collected. This directly leads to the hypothesis that some samples have a large change in sample surface parameters that work to reflect the laser beam, hindering the ability to sustain a plasma at some point during the 5000 pulses. This is a good starting point, but further studies should look at the change in

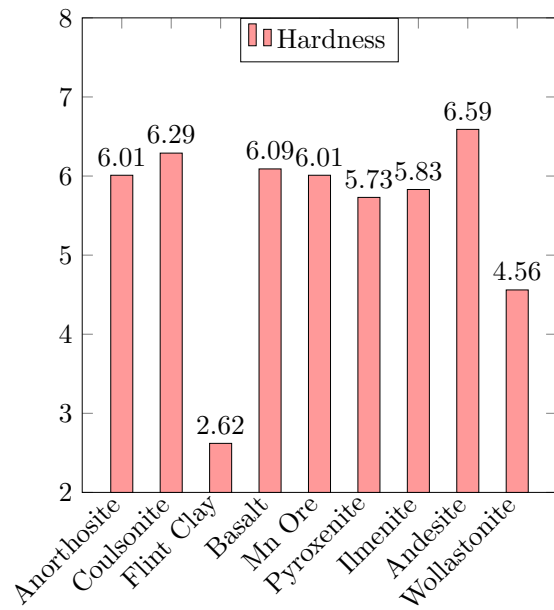
reflectance after some small number of pulses to determine how the surface changes with number of pulses.

Figure 78 overviews various material properties of nine of our original samples taken mostly from WebMineral.com. The thermal conductivities were found in [27]. Because these samples are made up of many minerals, a weighted average of mineral properties based on composition to determine bulk standard properties was used. Some minerals were missing both thermal conductivity and melting point information, so samples were given one of three confidence levels. High confidence implies >90% of the sample is determined, medium implies >50% is available, and low implies <50% of the information is available. Pertaining to thermal conductivity, samples which are high confidence are basalt, pyroxenite, andesite, and wollastonite, those that are medium confidence samples are anorthosite and ilmenite, and those which have low confidence are coulsonite, flint clay, and manganese ore. For melting point, there is even less confidence, which is why hardness was added to the group of material properties. The hardness is measured on the MoHs scale. For melting point, high confidence samples are basalt and ilmenite, medium confidence are anorthosite, flint clay, and andesite, and low confidence samples are coulsonite, manganese ore, pyroxenite, and wollastonite. The hardness, density, electron density and photoelectric effect (or work function) are all high confidence.

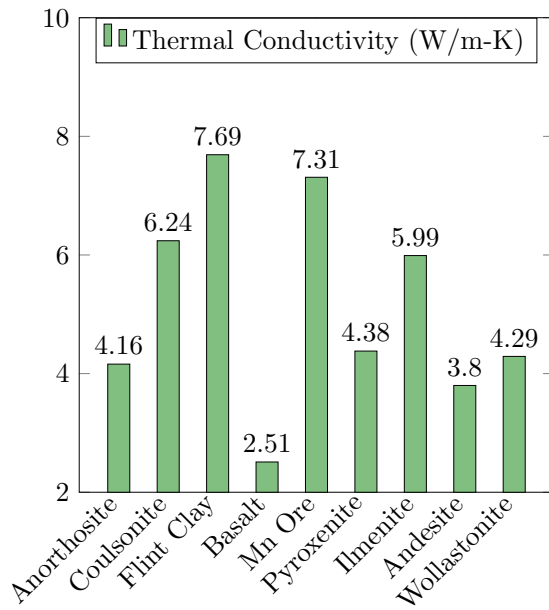
Out of these nine samples, the three that produced successful μ LIBS spectra are coulsonite, manganese ore, and ilmenite. While the melting point, hardness, and thermal conductivity do not show a clear pattern, the density and electron density hint at some correlation and the photoelectric effect shows a definite pattern. The photoelectric effect (PE) is the ability of an electron to leave a material, and is proportional to $Z^{3.6}$, where Z is the atomic weight of an atom. The total PE for a mineral is calculated from the chemical formula. The samples which produce successful μ LIBS spectra are those that have a high potential for releasing an electron. Ilmenite and coulsonite have high compositions of Fe ($Z = 26$) and Ti ($Z = 22$), and manganese ore is full of Mn ($Z = 25$). Iron and titanium covers >87% and >98% in coulsonite and ilmenite, respectively, and manganese ore has >57% manganese. The other samples, however, have much higher amounts of silicon ($Z = 14$) usually making up over half of the bulk composition (42–76%). The μ LIBS plasma seems to have enough energy to ionize electrons from these high PE materials, and characteristic emissions from the elements within these samples are seen clearly once electrons recombine and relax. As for



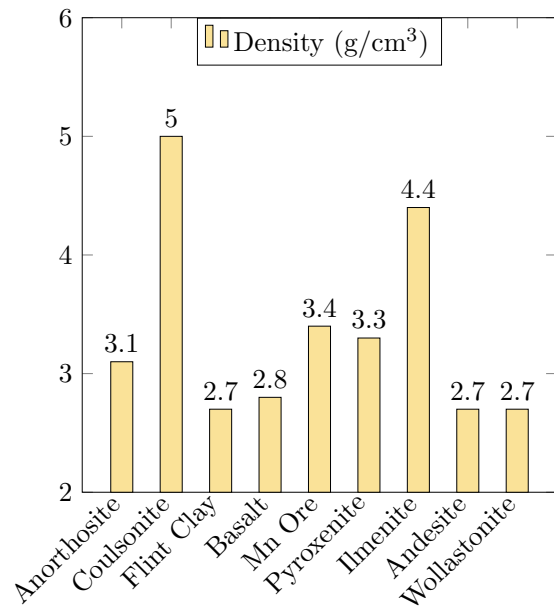
(a)



(b)



(c)



(d)

Figure 78: Comparing (a) melting point, (b) hardness, (c) thermal conductivity, (d) density, (e) electron density, and (f) photoelectric effect (or work function) for all most original samples. Data is taken from the WebMineral online database (webmineral.com). Some samples had missing information about thermal conductivity and melting point (see Page 8).

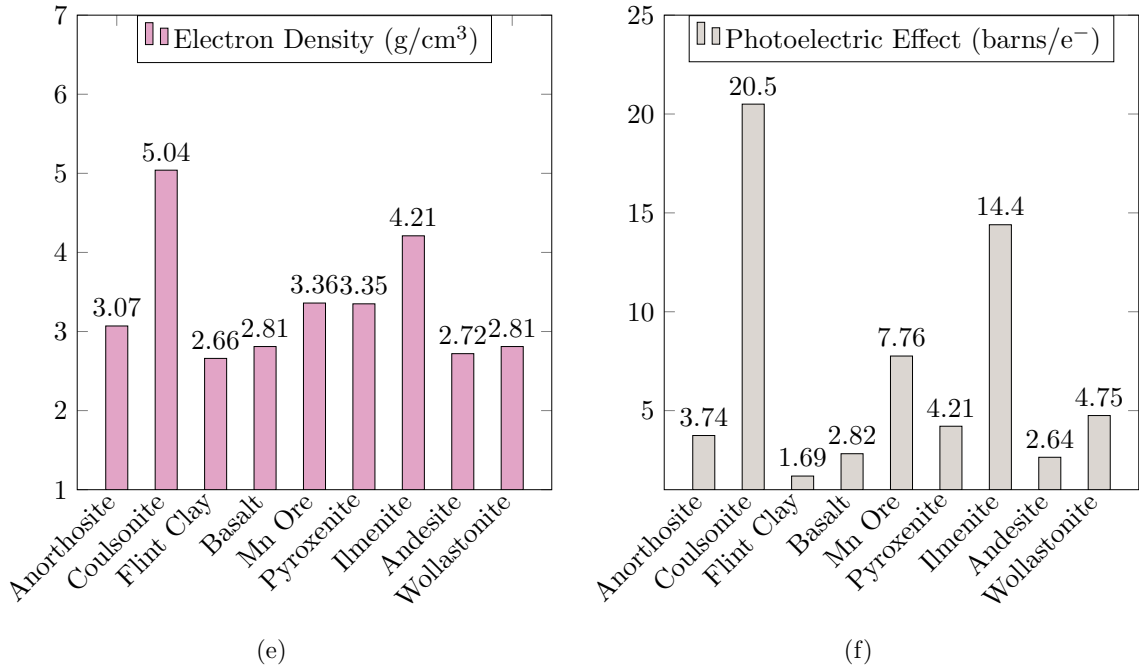


Figure 78: Continued.

the other samples, there many not be enough energy transferred to the plasma to excite *enough* of the elements which have lower PE scores (as characteristic emissions are not seen in a single-spot measurement).

The fact that most samples work while moving them around during a measurement is most likely a combination of overcoming both the melting problem and the low energy problem. While moving around the targets, the laser is able to sample more material and transfers less heat on one spot. At the same time, more electrons can be excited, recombined, and emit characteristic emissions.

Lastly, another system was designed to monitor the evolution of the plasma created on the sample surface. Using this system, differences in both the timing and size of the plasma for those geologic samples that do produce a successful μLIBS spectrum and those that don't, can be detected if present. This was accomplished using a simple tube lens and another Andor iStar ICCD, mounted 90° to the optical axis. This allows us to monitor the plasma evolution from the side. The field of view of each image was determined by taking an image of a microscope reference slide. The time delay from the laser pulse arrival was set by the ICCD gate delay. Figure 79 and 80 show

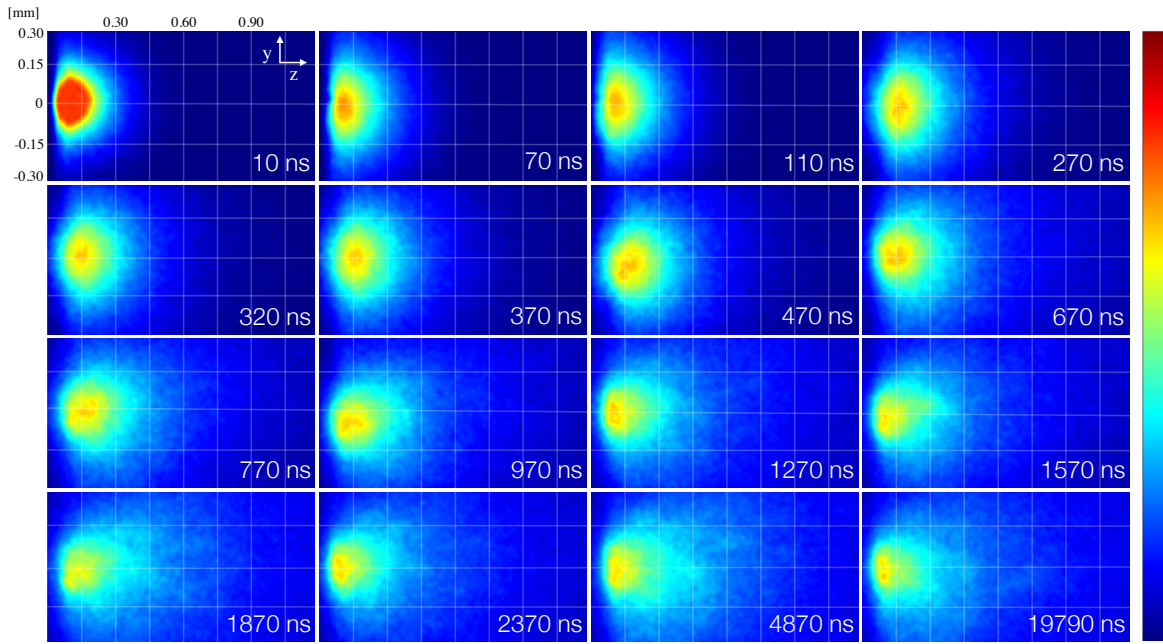


Figure 79: Evolution of the μ LIBS plasma on aluminium from 10 ns after the laser pulse arrival, to $\sim 20 \mu$ s. Note the scale on the upper left hand corner. The plasma emits less light very quickly, but doesn't expand much.

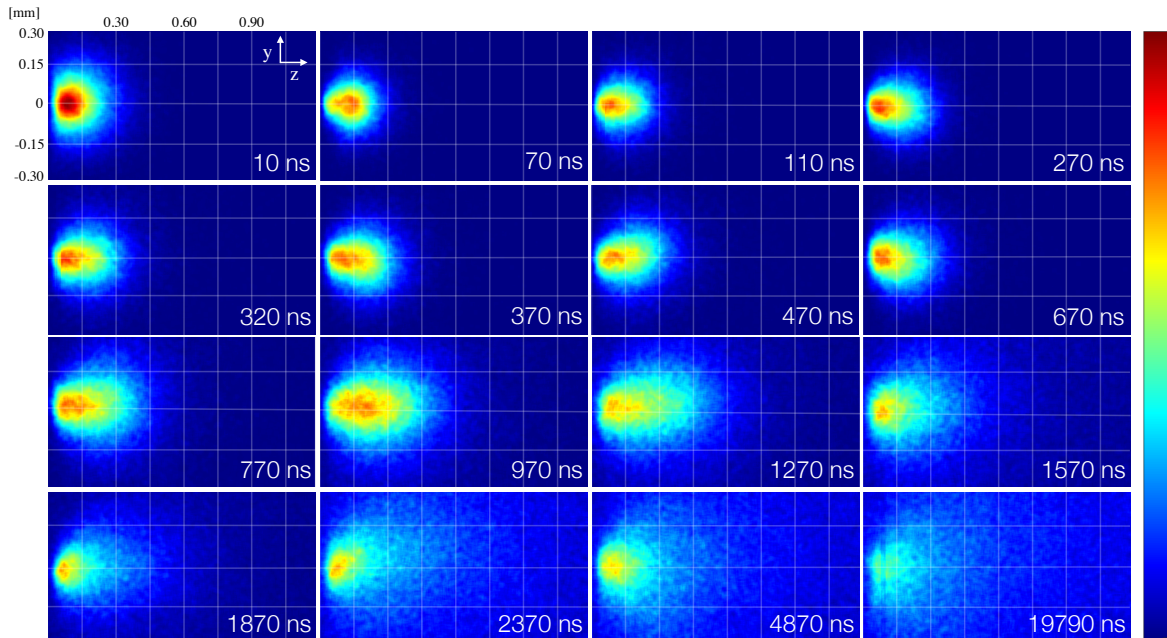


Figure 80: Evolution of the μ LIBS plasma on manganese ore from 10 ns after the laser pulse arrival, to $\sim 20 \mu$ s. Note the scale on the upper left hand corner. This plasma clearly expands over time.

the measured plasma evolution for aluminium and manganese ore, respectively. Figure 81 shows the same series of images for a sample which produces a visible plasma at the surface, but does not produce a spectrum with characteristic emissions. The bottom right hand lists a running total time after the laser pulse arrived at the target surface. The colorbar scale, representing intensity, is normalized to some arbitrary maximum value and is the same for Figures 79, 80, and 81. These both have similar features, though while the aluminium plasma plume does not expand, the plume formed of manganese ore clearly expands over time (which is more characteristic of a “typical” LIBS response) [12]. The brightest feature is the continuum emission that dominates the spectrum at early times. All images are normalized to the highest intensity of all three image series (the intensity scale is in arbitrary units and therefore is left unlabelled).

The fact that there is no continuum emission signature in the andesite series (i.e., no high-intensity emission in at least the first image), indicates that there isn’t much excitation or ionization happening in the first place. Recall that continuum emission occurs via recombination and Bremsstrahlung. If there aren’t any (or not many) free electrons ionized off of atoms, there cannot be any (or much) recombination or Bremsstrahlung emission. Because they are not ionized, the orbitals of these atoms would be full, and they would not be able to capture electrons via recombination. At the same time, if there is no ionization, there are no free electrons to create Bremsstrahlung radiation. There must, then, be not enough energy to induce any type of avalanche ionization process.

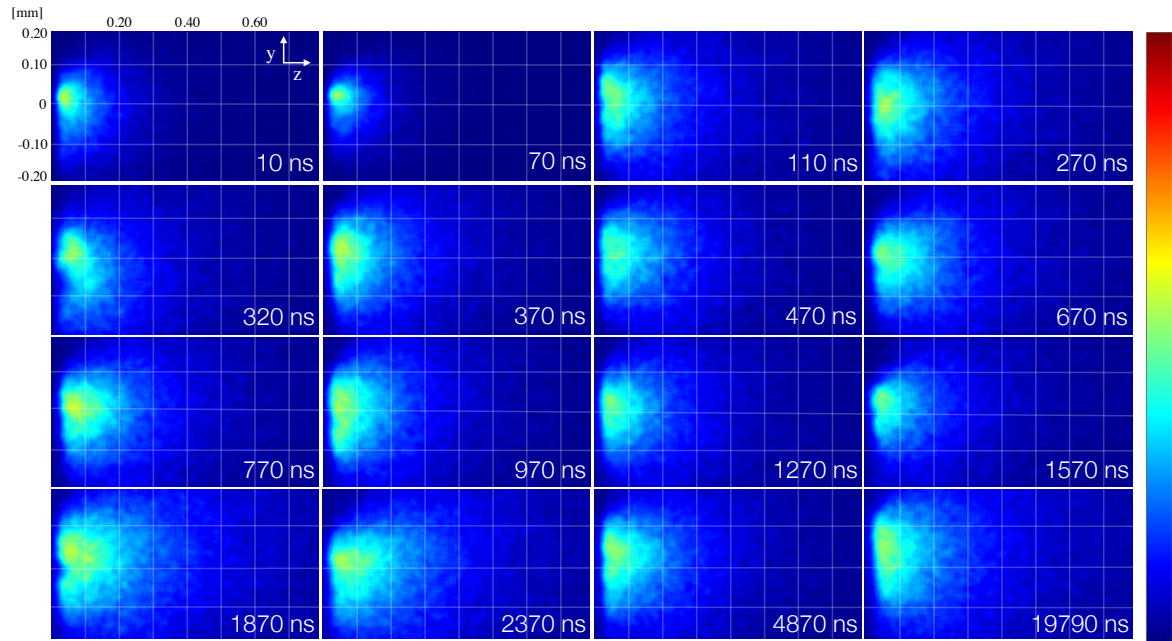


Figure 81: Evolution of the μ LIBS plasma on andesite from 10 ns after the laser pulse arrival, to $\sim 20 \mu\text{s}$. Note the scale on the upper left hand corner. Compared to the others (Figures 79 and 80), the most drastic feature is the lack of strong continuum emissions soon after the laser reaches the sample surface (in the first frame).

9 Conclusion

The ultimate aim of this research was to investigate the applicability of μ LIBS for geologic materials, both contributing to the LIRS project and extending LIBS techniques for space exploration applications. Specifically, a μ LIBS instrument was constructed, and a combined system containing μ LIBS functionality was characterized. The latter included performance and sensitivity testing for μ LIBS, Raman, and laser-induced fluorescence spectroscopy modes of the instrument. μ LIBS has previously been shown to result in low limits of detection (LODs) for major elements in metallic matrices, but is relatively unexplored for applications to geologic materials. There has only been two studies which use μ LIBS techniques on minerals, and only two minerals were studied (hematite and ilmenite).

In general, LIBS is particularly useful for space exploration because the technique requires relatively simple components. Although LIBS has already been flown (onboard the MSL/Curiosity rover), there is room to improve these methods for future missions to Mars and other planetary bodies. μ LIBS has two major advantages over “typical” LIBS systems. These are the ability to perform high-resolution spatial mapping and the relaxation of system cost and requirements via the low-energy laser and simple detector.

The LIRS instrument has the potential to leap-frog over current systems with its highly combined design. LIRS is a novel concept whose spatial, temporal, and spectral resolution is greater than that of similar combined systems. Characterization of the LIRS instrument showed similar results to other single mode instruments, including ChemCam, and others. Specifically, a model was created to predict the concentration of organic compounds and was verified with alanine. Additionally, a similar model was created to predict elemental concentrations for Al, Ca, Fe, K, Mg, Mn, Na, Si, and Ti, which was able to predict six out of nine elements at the same level or better than that of ChemCam (shown via root-mean-square errors in prediction of 28 geologic standards). Elemental limits of detection for most elements matched or exceeded the goal of 300 ppm, and are comparable to single-mode, portable instruments. Here μ LIBS has been tested on 38 total geologic standard materials. This work influenced a concept flight instrument that could become a major Canadian contribution to a planetary science mission.

Lastly, during characterization of the μ LIBS mode, there were certain samples for which a

single-spot μ LIBS measurement was not possible, i.e., no elemental lines could be identified from the measured spectra. A preliminary investigation was performed to determine the cause of inadequacies of μ LIBS for specific samples.

Although the μ LIBS technique is very promising for surface microanalysis of remote planetary bodies, more work is needed before μ LIBS can be used for flight.

10 Future Work

The μ LIBS instrument needs a few changes before it could be integrated into the environmental chamber (mostly involving the type of fiber), but the μ LIBS regime needs to be investigated generally for both the 532 nm μ LIBS instrument and the LIRS breadboard to be useful. LIRS, especially, has the potential to be a major Canadian contribution to a future mission, but further investigation into the μ LIBS technique is needed to shape a flight concept.

The current LIRS breadboard utilizes a 1064 nm laser which has ~ 160 μ J pulse energy and, at 10 kHz, a 563 ps pulse width for a calculated peak power of ~ 290 kW. At 35 cm, the sample will receive an intensity of 18 GW/cm². The typical intensity required for plasma formation with LIBS in the literature is 1 GW/cm². Despite our high peak intensity, a plasma was not formed on the surface of some samples in the μ J pulse energy regime, or a plasma was formed, but no characteristic emissions could be seen reliably. Typical LIBS studies use mJ pulse energies and longer pulse widths, usually on the order of 10 ns. For example, the ChemCam instrument described in Wiens et al. [62] uses a Nd:KGW laser at 1067 nm with 35 mJ pulse energies and 5 ns pulse width to acquire LIBS spectra of geologic standards. Many of the materials chosen for LIRS characterization are represented in [62], mainly andesite, basalt, clay, metallic ores, and syenite, among others. While LIBS spectra were obtained from all standards in [62], LIRS has trouble acquiring μ LIBS spectra from most samples chosen for study (Table 15). The reason for this is uncertain. While performing optimization of gate delay, it was found that a successful LIBS spectrum could be obtained if, over the 0.5 s exposure, most samples were moved continuously. This way, the laser is sampling fresh target material over the 0.5 s exposure. If the target was kept stationary, either no plasma was formed and only heating of the target material was visible, or a plasma was formed but quickly extinguished resulting in essentially no signal. It would be advantageous to study groupings of samples for which material properties (e.g. melting point, reflectance, grain size, thermal conductivity, work function, etc.) are similar.

Because a complete set of material properties for all original 11 samples was unavailable, a new sample should be chosen for which all relevant material properties are known. Using this new sample set the following should be completed:

- 1) Perform a PCA analysis to determine which properties of sample materials most greatly affect

the outcome of a μ LIBS spectra.

- 2) Comparison of μ LIBS and LIBS spectra using LIRS and a 1064 nm laser that has up to 100 mJ pulse energy, 1–20 Hz repetition rate, and ≤ 10 ns pulse width (Big Sky Lasers).
- 3) Comparison of μ LIBS and LIBS spectra using the 532 nm μ LIBS system and a 532 nm laser that has up to 55 mJ pulse energy, 1–20 Hz repetition rate, and ≤ 10 ns pulse width (Big Sky Lasers). This would definitively rule out possible variation with laser wavelength in the μ LIBS regime.
- 4) Comparison between plasma morphology for 1064 nm μ LIBS and LIBS using an imaging camera.
- 5) Use other plasma diagnostics, such as line widths, shapes, and shifts, along with Boltzmann plots in order to determine the electron density and temperature of μ LIBS plasma and compare this with a typical LIBS plasma. See Cvejić et al. [15] and Chapter 2 of [3].
- 6) Determine the cut-off intensity for plasma formation on geologic standards using the high power 1064 nm and 532 nm lasers by iterative reduction of laser intensity. If the intensities delivered by the LIRS instrument surpass the required intensities but still no plasma is formed, then further investigation is required.

If the μ LIBS technique is deemed useful, say, for some specific material upon further investigations, then it is recommended that the 532 nm μ LIBS instrument be integrated into the environmental chamber, and further tests conducted at Mars pressure.

The μ LIBS instrument could then also be investigated for a Europa-type environment with geologically relevant materials (minerals embedded in icy matrices and waterlogged rocks, for example). A previous study by Pavlov et al. [47] has explored the feasibility of this type of miniature LIBS system for Europa environment but waterlogged samples were not tested and inclusions in ice only included salts and a limited set of minerals. It would be advantageous to expand the study in these areas, especially since NASA and ESA have teamed up to land a life-searching spacecraft, part of the Joint Europa Mission (JEM), on the surface by 2025 [5].

If the μ LIBS technique is abandoned and the LIRS breadboard is upgraded to include a more typical laser, the impact of mismatching telescope and spectrometer $f/\#$'s on our results must be investigated. To do this, a special collimating accessory from Andor (CC52) has been ordered. This

system is optimized to ensure that light is collected at a high $f/2$ aperture and 'squeezed' into the Mechelle $f/7$ aperture. This collection system can be installed off-axis near the sample target.

In either case, the combined performance of the LIRS instrument using a flight protocol still has to be examined. This would include mapping a real, whole-rock sample with all three techniques and determining a standard procedure for efficiently determining the type of rock (see the combined characterization portion of the original characterization plan, Section 5.7).

References

- [1] William J. Abbey, Rohit Bhartia, Luther W. Beegle, Lauren DeFlores, Veronica Paez, Kripa Sijapati, Shakher Sijapati, Kenneth Williford, Michael Tuite, William Hug, and Ray Reid, *Deep UV Raman spectroscopy for planetary exploration: the search for in situ organics*, Icarus **290** (2017), 201–214.
- [2] Jose M. Andrade-Garda, *Basic chemometric techniques in atomic spectroscopy*, Royal Society of Chemistry, 2009.
- [3] Michael Bass (ed.), *OSA Handbook of Optics: Volume 1*, 3rd ed., McGraw-Hill, 2009.
- [4] Luther Beegle, Rohit Bhartia, Mary White, Lauren DeFlores, William Abbey, Yen-Hung Wu, Bruce Cameron, James Moore, Marc Fries, Aaron Burton, and 9 others, *SHERLOC: scanning habitable environments with raman & luminescence for organics & chemicals*, Aerospace Conference, 2015 IEEE, 2015, pp. 1–11.
- [5] Michel Blanc, Olga Prieto-Ballesteros, Nicolas André, Javier Gómez-Elvira, and the TJEM Team, *Joint Europa Mission (JEM). A Multiscale Study of Europa to Characterize its Habitability and Search for Extant Life.*, Lunar and Planetary Science Conf. **48** (2017).
- [6] Brammer Standards Company, *Brammer Standards Geological Materials Catalog [Online]*. Available: <http://www.brammerstandard.com/pdf/geological.pdf> [Thu Jul 19 2018].
- [7] F. Breech and L. Cross, *Optical microemission stimulated by a ruby maser.*, Appl. Spectrosc. **16** (1962).
- [8] Chi Hong Chio, Shiv K. Sharma, Paul G. Lucey, and David W. Muenow, *Effects of particle size and laser-induced heating on the Raman spectra of alpha quartz grains*, Applied spectroscopy **57** (2003), no. 7, 774–783.
- [9] Samuel M. Clegg, Elizabeth Sklute, M. Darby Dyar, James E. Barefield, and Roger C. Wiens, *Multivariate analysis of remote laser-induced breakdown spectroscopy spectra using partial least squares, principal component analysis, and related techniques.*, Spectrochim. Acta B **64** (2009), 79–88.

- [10] Edward A. Cloutis, Kaitlyn A. McCormack, James F. Bell III, Amanda R. Hendrix, Daniel T. Bailey, Michael A. Craig, Stanley A. Mertzman, Mark S. Robinson, and Miriam A. Riner, *Ultraviolet spectral reflectance properties of common planetary minerals*, Icarus **197** (2008), no. 1, 321–347.
- [11] Grégory B. Courrèges-Lacoste, Berit Ahlers, and Fernando Rull Pérez, *Combined Raman spectrometer/laser-induced breakdown spectrometer for the next ESA mission to Mars.*, Spectrochim. Acta A **68** (2007), 1023-1028.
- [12] David A. Cremers and Leon J. Radziemski, *Handbook of Laser-Induced Breakdown Spectroscopy*, 2nd ed., Wiley, 2013.
- [13] Gabriele Cristoforetti, Stefano Legnaioli, Vincenzo Palleschi, Azenio Salvetti, Elisabetta Tognoni, Pier Alberto Benedetti, Franco Brioschi, and Fabio Ferrario, *Quantitative analysis of aluminium alloys by low-energy, high-repetition rate laser-induced breakdown spectroscopy*, Journal of Analytical Atomic Spectrometry **21** (2006), no. 7, 697–702.
- [14] Gabriele Cristoforetti, Alessandro De Giacomo, M Dell’Aglio, Stefano Legnaioli, Elisabetta Tognoni, Vincenzo Palleschi, and Nicolo Omenetto, *Local thermodynamic equilibrium in laser-induced breakdown spectroscopy: beyond the McWhirter criterion*, Spectrochimica Acta Part B: Atomic Spectroscopy **65** (2010), no. 1, 86–95.
- [15] M Cvejić, *Diagnostics of laser-induced plasma by optical emission spectroscopy*, Journal of Physics: Conference Series, 2014, pp. 012014.
- [16] M. Daly et al., *Science Definition Study for an Ultraviolet Raman Spectrometer for the Identification of Organic Carbon on Mars* (2015).
- [17] Christopher Dreyer, Greg S. Mungas, Phihung Thanh, and Julie George Radziszewski, *Study of sub-mJ-excited laser-induced plasma combined with Raman spectroscopy under Mars atmosphere-simulated conditions.*, Spectrochim. Acta B **62** (2007), 1448-1459.
- [18] Jean Dubessy, Marie-Camille Caumon, and Fernando Rull, *Raman spectroscopy applied to earth sciences and cultural heritage*, Vol. 12, The Mineralogical Society of Great Britain and Ireland, 2012.

- [19] Evan Eshelman, *Stand-Off Detection of Organic Compounds on Mars Using Ultraviolet Raman Spectroscopy and Time-Resolved Laser-Induced Fluorescence*, York University, 2016. PhD thesis, <http://hdl.handle.net/10315/32346>.
- [20] Frédéric Foucher, G. Lopez-Reyes, Nicolas Bost, F. Rull-Perez, P. Rüßmann, and Francès Westall, *Effect of grain size distribution on Raman analyses and the consequences for in situ planetary missions*, Journal of Raman Spectroscopy **44** (2013), no. 6, 916–925.
- [21] Andrew Freedman, Frank J. Iannarilli Jr, and Joda C. Wormhoudt, *Aluminum alloy analysis using microchip-laser induced breakdown spectroscopy*, Spectrochimica Acta Part B: Atomic Spectroscopy **60** (2005), no. 7-8, 1076–1082.
- [22] Igor B. Gornushkin, K. Amponsah-Manager, Benjamin W. Smith, Nicoló Omenetto, and James D. Winefordner, *Microchip laser-induced breakdown spectroscopy: a preliminary feasibility investigation*, Applied spectroscopy **58** (2004), no. 7, 762–769.
- [23] Jean-François Y. Gravel, François R. Doucet, Paul Bouchard, and Mohamad Sabsabi, *Evaluation of a compact high power pulsed fiber laser source for laser-induced breakdown spectroscopy*, Journal of Analytical Atomic Spectrometry **26** (2011), no. 7, 1354–1361.
- [24] Victoria E. Hamilton et al., *MEPAG: Mars Science Goals, Objectives, Investigations, and Priorities: 2015 Version*. 74 p. white paper posted June, 2015 by the Mars Exploration Program Analysis Group (MEPAG) at <http://mepag.nasa.gov/reports.cfm>.
- [25] H.J. Häkkinen and J.E.I. Korppi-Tommola, *UV-laser plasma study of elemental distributions of paper coatings*, Applied spectroscopy **49** (1995), no. 12, 1721–1728.
- [26] Marek Hoehse, David Mory, Stefan Florek, Friederike Weritz, Igor B. Gornushkin, and Ulrich Panne, *A combined laser-induced breakdown and Raman spectroscopy Echelle system for elemental and molecular microanalysis*, Spectrochimica Acta Part B: Atomic Spectroscopy **64** (2009), no. 11-12, 1219–1227.
- [27] Ki-iti Horai, *Thermal conductivity of rock-forming minerals*, Journal of Geophysical Research **76** (1971), no. 5, 1278–1308.

- [28] A. Hyvärinen, J. Karhunen, and E. Oja, *Independent Component Analysis*, Adaptive and Learning Systems for Signal Processing, Communications and Control Series, Wiley, 2001.
- [29] Jeffrey R. Johnson, James F. Bell III, S. Bender, D. Blaney, Edward A. Cloutis, L. DeFlores, B. Ehlmann, O. Gasnault, B. Gondet, K. Kinch, M. Lemmon, S. Le Mouélic, S. Maurice, M. Rice, Roger C. Wiens, and MSL Science Team, *ChemCam passive reflectance spectroscopy of surface materials at the Curiosity landing site, Mars*, *Icarus* **249** (2015), 74–92.
- [30] Alexander Kramida, Yuri Ralchenko, Joseph Reader, and NIST ASD Team, *NIST Atomic Spectra Database (version 5.5.6)*, [Online]. Available: <https://physics.nist.gov/asd> [Tue May 15 2018], National Institute of Standards and Technology, Gaithersburg, MD (2018).
- [31] Alexander Koujelev, Vincent Motto-Ros, Daniel Gratton, and Alexander Dudelzak, *Laser-induced breakdown spectroscopy as a geological tool for field planetary analogue research*, *Canadian Aeronautics and Space Journal* **55** (2009), no. 2, 97–106.
- [32] Joseph R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Springer US, 2007.
- [33] Jeremie Lasue, Roger C. Wiens, Samuel M. Clegg, David T. Vaniman, Katherine H. Joy, S. Humphries, Alissa Mezzacappa, Nouredine Melikechi, R.E. McInroy, and S. Bender, *Remote laser-induced breakdown spectroscopy (LIBS) for lunar exploration*, *Journal of Geophysical Research: Planets* **117** (2012), no. E1.
- [34] Vincent Latendresse, Roman V. Kruzelecky, Piotr Murzionak, Jonathan Lavoie, Elad Wallach, Alireza Nakhaei, Ian Sinclair, Wes Jamroz, Edward Cloutis, Pierre Cottin, and Michel Doucet, *LIRA LIBS for Stand-Off Planetary and Asteroid Resource Prospecting*, *Earth and Space* **618** (2016).
- [35] Catherine Lefebvre, David Gay, Bruno Labranche, Francois Châteauneuf, and Alexander Koujelev, *Assessment of low energy, high-repetition rate fiber laser for LIBS experiment*. (2012).
- [36] Gary L. Long and James D. Winefordner, *Limit of detection. A closer look at the IUPAC definition*, *Analytical Chemistry* **55** (1983), no. 7, 712A–724A.

- [37] Cristina Lopez-Moreno, Benjamin W. Smith, Igor B. Gornushkin, Nicolás Omenetto, Santiago Palanco, Javier Laserna, and James D. Winefordner, *Quantitative analysis of low-alloy steel by microchip laser induced breakdown spectroscopy.*, Journal of Analytical Atomic Spectrometry **20** (2005), no. 6, 552–556.
- [38] Sylvestre Maurice, Roger C. Wiens, and 53 others, *The ChemCam instrument suite on the Mars Science Laboratory (MSL) rover: Science objectives and mast unit description.*, Space Sci. Rev. **170** (2012), 167–227.
- [39] Alan D. McNaught and A. Wilkinson, *Compendium of chemical terminology*, Available: <https://doi.org/10.1351/goldbook>. **1669** (1997).
- [40] Regina R. Montgomery, *SRM NIST Standard Reference Materials Catalog, NIST SP - 260-176 2018 ed [Online]*. Available: <https://www.nist.gov/publications/srm-nist-standard-reference-materials-catalog-january-2018> [Thu Jul 19 2018].
- [41] Vincent Morel, Bastien Pérès, Arnaud Bultel, Ammar Hideur, and Christian Grisolia, *Picosecond LIBS diagnostics for Tokamak in situ plasma facing materials chemical analysis.*, Phys. Scripta **T167** (2016).
- [42] Javier Moros, Mohamed ElFaham, and José Javier Laserna, *Dual-Spectroscopy Platform for the Surveillance of Mars Mineralogy using a Decisions Fusion Architecture on Simultaneous LIBS-Raman Data*, Analytical chemistry (2018).
- [43] Sergio Musazzi and Umberto Perini (eds.), *Laser-Induced Breakdown Spectroscopy: Theory and Applications*, Springer Series in Optical Sciences, Springer Berlin Heidelberg, 2014.
- [44] Measurement Science and Standards Research Team National Research Council of Canada, *NRC Certified Reference Materials Registry [Online]*. Available: <https://www.nrc-cnrc.gc.ca/eng/solutions/advisory/crm/list'product.html> [Thu Jul 19 2018].
- [45] Reinhard Noll, *Laser-Induced Breakdown Spectroscopy Fundamentals and Applications*, 2nd ed., Springer, 2012.
- [46] Ann M. Ollila, J.G. Blank, H.E. Newsom, P.L. King, and David A. Cremers, *Detection of Biosignatures in a Mars-Like Environment Using LIBS*, AGU Fall Meeting Abstracts, 2009.

- [47] Serguei G. Pavlov, Elmar K. Jessberger, Heinz Wilhelm Hübers, Susanne Schröder, I. Rauschenbach, Stefan Florek, J. Neumann, Hartmut Henkel, and Sabine Klinkner, *Miniaturized laser-induced plasma spectrometry for planetary in situ analysis - The case for Jupiter's moon Europa.*, Adv. Space Res. **48** (2011), 764-778.
- [48] René Perez, Laurent P. Parès, R. Newell, S. Robinson, P. Bernardi, J.-M. Réess, Ph. Caïs, K. McCabe, Sylvestre Maurice, and Roger C. Wiens, *The supercam instrument on the NASA Mars 2020 mission: optical design and performance.*, International Conference on Space Optics ICSO2016 (October 2016).
- [49] Awadhesh K. Rai, Hansheng Zhang, Fang Yu Yueh, Jagdish P. Singh, and Arel Weisberg, *Parametric study of a fiber-optic laser-induced breakdown spectroscopy probe for analysis of aluminum alloys.*, Spectrochim. Acta B **56** (2001), 2371-2383.
- [50] I Rauschenbach, Elmar K. Jessberger, Serguei G. Pavlov, and Heinz Wilhelm Hübers, *Miniaturized Laser-Induced Breakdown Spectroscopy for the in-situ analysis of the Martian surface: Calibration and quantification*, Spectrochimica Acta Part B: Atomic Spectroscopy **65** (2010), no. 8, 758–768.
- [51] Andrew N. Rencz and Robert A. Ryerson, *Manual of remote sensing, remote sensing for the earth sciences*, Vol. 3, John Wiley & Sons Incorporated, 1999.
- [52] Béatrice Sallé, Jean Luc Lacour, Patrick Mauchien, Pascal Fichet, Sylvestre Maurice, and Gérard Manhès, *Comparative study of different methodologies for quantitative rock analysis by laser-induced breakdown spectroscopy in a simulated Martian atmosphere*, Spectrochimica Acta Part B: Atomic Spectroscopy **61** (2006), no. 3, 301–313.
- [53] Giorgio S. Senesi, *Laser-Induced Breakdown Spectroscopy (LIBS) applied to terrestrial and extraterrestrial analogue geomaterials with emphasis to minerals and rocks.*, Earth-Science Revs. **139** (2014), 231-267.
- [54] A.E. Siegman, *Lasers*, University Science Books, 1986.

- [55] Shiv K. Sharma, Anupam K. Misra, Paul G. Lucey, and Rachel C.F. Lentz, *A combined remote Raman and LIBS instrument for characterizing minerals with 532 nm laser excitation*, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy **73** (2009), no. 3, 468–476.
- [56] Douglas A. Skoog and Donald M. West, *Principles of Instrumental Analysis*, 2nd ed., Saunders College/Holt, Rinehart and Winston, 1980.
- [57] Boris M Smirnov, *Physics of ionized gases*, John Wiley & Sons, 2008.
- [58] Julie D. Stopar, Paul G. Lucey, Shiv K. Sharma, Anupam K. Misra, G. Jeffrey Taylor, and Hugh W. Hubble, *Raman efficiencies of natural rocks and minerals: Performance of a remote Raman system for planetary exploration at a distance of 10 meters*, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy **61** (2005), no. 10, 2315–2323.
- [59] Michael T. Taschuk, Igor V. Cravetchi, Ying Yin Tsui, and Robert Fedosejevs, *Chapter 8: Micro-LIBS.*, in Laser-Induced Breakdown Spectroscopy, Jagdish P. Singh and Surya N. Thakur (eds.) (2007), 173–196.
- [60] THORLABS, *Guide to Connectorization and Polishing of Optical Fibers [Online]*. Available: <https://www.thorlabs.com/thorproduct.cfm?partnumber=FN96A> (2000).
- [61] United States Geological Survey (USGS), *USGS Geochemical Reference Materials and Certificates [Online]*. Available: <https://crustal.usgs.gov/geochemical/reference/standards/> [Thu Jul 19 2018].
- [62] Roger C. Wiens, Sylvestre Maurice, and 22 others, *Pre-flight calibration and initial data processing for the ChemCam laser-induced breakdown spectroscopy instrument on the Mars Science Laboratory rover.*, Spectrochim. Acta B **82** (2013), 1-27.
- [63] James D. Winefordner, Igor B. Gornushkin, Tiffany Correll, Emily Gibb, Benjamin W. Smith, and Nicolás Omenetto, *Comparing several atomic spectrometric methods to the superstars: special emphasis on laser induced breakdown spectrometry, LIBS, a future super star.*, J. Anal. At. Spectrom. **19** (2004), 1061-1083.

Appendices

A ICA and PLS algorithms

Many chemometric techniques used in atomic spectroscopy (including ICA and PLS) are overviewed in J.M. Andrade-Garda 2009 (specifically Chapter 4) and Hyvärinen, Karkunen, and Oja 2001 and are summarized here [2, 28]. ICA is a statistical technique that can be used to summarize large sets of multivariate data into a (relatively) small number of *factors* that represent underlying or hidden variables within the dataset. The smaller dataset is called a *representation*. The data is *multivariate*, because we’re using all of the available information—all values of intensities at each wavelength—rather than isolating one peak for each element. Multivariate analysis techniques rely on the fundamental assumption that the “directions with maximum variance” are directly related to hidden structure within the data [2].

Assume our dataset $x_i(t)$ consists of m variables (spectral responses at each wavelength), and T observations, where $i = 1, \dots, m$ and $t = 1, \dots, T$. The transformed data should be the factors that describe the essential structure of the data (and correspond to some physical cause that were involved in creating the data set, in this case, atomic emissions). Every factor, or *component*, $y_i(t)$ is expressed as a linear combination of the variables:

$$y_i(t) = \sum_j w_{ij} x_j(t), \quad \text{for } i = 1, \dots, n \text{ and } t = 1, \dots, m, \quad (46)$$

where w_{ij} are some coefficients [28]. We can write this as

$$\begin{bmatrix} y_1(t) \\ y_2(t) \\ \vdots \\ y_n(t) \end{bmatrix} = \begin{bmatrix} w_{11} & \dots & w_{1m} \\ w_{21} & & w_{2m} \\ \vdots & \ddots & \vdots \\ w_{n1} & \dots & w_{nm} \end{bmatrix} \begin{bmatrix} x_1(t) \\ x_2(t) \\ \vdots \\ x_n(t) \end{bmatrix}, \quad (47)$$

or

$$\mathbf{y} = \mathbf{W}\mathbf{x}. \quad (48)$$

This approach considers $x_i(t)$ as a “set of T realizations of m random variables” [28]. The

solutions to Equation 48 are such that the transformed dataset has statistically independent components. Statistical independence means that the value of any one of the components give no information on the values of the other components [28], but this can also be taken to mean independence from a linear algebra view. Here we're really finding a basis for some dataset that may have degenerate degrees of freedom.

Finding a good representation can also be approached from a different viewpoint, based off the blind source separation (BSS) problem. Hyvärinen, Karkunen, and Oja give a good example, where they relate finding $\mathbf{W}$ to the separation, or deconvolution, of recordings of two different people speaking made from two microphones located in different spots in the room. While each microphone would record a mixture of each person's audio, ICA works to estimate the two original speech signals using the mixed recorded signals [28]. This specific example is called the *cocktail-party problem*. In our case, the people emitting sound waves can be equated to individual elements emitting photons, and the different microphones as the different wavelengths (~ 22000 of them in the spectral range, each of which have a corresponding signal level). For simplicity, say there are two observed signals x_1 and x_2 (e.g. amplitudes of the recorded signals or spectral responses at each wavelength), and two original signals s_1 and s_2 (buried within our data), then

$$x_1(t) = a_{11}s_1(t) + a_{12}s_2(t), \text{ and} \quad (49)$$

$$x_2(t) = a_{21}s_1(t) + a_{22}s_2(t), \quad (50)$$

where a_{11} , a_{12} , a_{21} , and a_{22} are called mixing coefficients [28]. Both the mixing coefficients and the original signals are unknown, which is what makes the problem difficult. We want to determine the original signals $s_i(t)$ from the mixed signals $x_i(t)$. Assuming that the mixing coefficients are “nice enough” to ensure that the matrix $\mathbf{A} = a_{ij}$ is invertible (i.e., there are no dependent rows or columns, coming from the very definition of the inverse), then there exists a matrix $\mathbf{W} = \mathbf{A}^{-1}$ with coefficients w_{ij} such that the original signals are described by

$$s_1(t) = w_{11}x_1(t) + w_{12}x_2(t), \text{ and} \quad (51)$$

$$s_2(t) = w_{21}x_1(t) + w_{22}x_2(t). \quad (52)$$

$\mathbf{A}$ is called the *mixing* matrix, and $\mathbf{W}$ is appropriately called the *unmixing* matrix. $\mathbf{W}$ can be estimated using only the constraint that the signals must be independent [28], and the independent components are equal to the original signals.

In summary, the basic ICA model is

$$x_i = \sum_j a_{ij}s_j, \quad (53)$$

$$\mathbf{x} = \mathbf{A}\mathbf{s} = \mathbf{W}^{-1}\mathbf{s}, \quad (54)$$

where the t indices have been dropped, because it is assumed that each signal x_i is a random variable (instead of a proper time series) [28]. The independent components, or factors, $\mathbf{s}$ cannot be observed (and are therefore called *latent* variables), and the mixing coefficients $\mathbf{A}$ are unknown. Only the variables $\mathbf{x}$ are observed and, ICA estimates both the mixing coefficients and the independent components. ICA is analogous to PCA, except that ICA does not assume that the data has a gaussian distribution. ICA is used in this work to reduce the dimension of our dataset and perform a clustering analysis to remove outliers in a prediction algorithm. The built-in MATLAB function `rica` was used in this work.

PLS regression handles a set of spectral variables $\mathbf{X}$, and response variables $\mathbf{y}$ (in this case elemental compositions). The goal of the PLS algorithm is to determine the relationship between $\mathbf{X}$, a $n \times m$ matrix, and $\mathbf{y}$, a $1 \times n$ vector, where n is the number of samples and m is the number of wavelengths in the spectral range.

PLS regression is an extension of a basic multiple linear regression, which specifies the (linear) relationship between the response variables y_i and the predictor variables X_i such that $y = b_0 + b_1X_1 + \dots + b_nX_n$, where b_j are regression coefficients. The model can be described by

$$\mathbf{X} = \mathbf{t}\mathbf{p}^T, \text{ and} \quad (55)$$

$$\mathbf{Y} = \mathbf{u}\mathbf{q}^T, \quad (56)$$

where $\mathbf{t}$ and $\mathbf{u}$ are *scores* of $\mathbf{X}$ and $\mathbf{y}$, while $\mathbf{p}$ and $\mathbf{q}$ are their *loadings* [2]. Scores are projections of data points on to an axis which lies along the direction of maximum variance within the dataset

(these axes are called factors), while loadings are coefficients which define the factors themselves. In general, data = scores x loadings [2]. Both the scores and the loadings are estimated by constructing a linear regression between $\mathbf{X}$ and $\mathbf{y}$ as $\mathbf{y} = \mathbf{XB}$, i.e., the end product of PLS analysis is a regression coefficient matrix $\mathbf{B}$ that can be used to relate $\mathbf{X}$ (spectral response) to $\mathbf{y}$ (the elemental concentration).

The loadings of $\mathbf{X}$ are estimated from the relation of $\mathbf{X}$ and the $\mathbf{Y}$ -scores $\mathbf{u}_1 = \mathbf{y}$ using

$$\mathbf{w}_1^T = \frac{\mathbf{u}_1^T \mathbf{X}}{\mathbf{u}_1^T \mathbf{u}_1}, \quad (57)$$

where $\mathbf{w}$ are actually called the loading weights of $\mathbf{X}$, and the subscript 1 denotes the first factor [2]. The weights are converted to a unit vector so all weights lie in the range [0,1]. The $\mathbf{X}$ -scores are defined using

$$\mathbf{t}_1 = \mathbf{X}\mathbf{w}_1. \quad (58)$$

The $\mathbf{X}$ -scores ($\mathbf{t}$) are used to calculate the $\mathbf{X}$ - and $\mathbf{Y}$ -loadings using

$$\mathbf{p}_1^T = \frac{\mathbf{t}_1^T \mathbf{X}}{\mathbf{t}_1^T \mathbf{t}_1}, \text{ and} \quad (59)$$

$$\mathbf{q}_1^T = \frac{\mathbf{t}_1^T \mathbf{Y}}{\mathbf{t}_1^T \mathbf{t}_1}. \quad (60)$$

The $\mathbf{Y}$ -scores vector $\mathbf{u}$ can be recalculated using the $\mathbf{X}$ -scores given by Equation 59, and this process is repeated until some rounding error limit is achieved and calculation of the first factor is finished (with scores and loadings fully defined for both $\mathbf{X}$ and $\mathbf{Y}$). Factors are similar to principal components (PCs) found in PCA, but while in PCA, PCs explain the most variance in $\mathbf{X}$, factors in PLS take into account the variation of both the predictors and the response variables [2].

The regression coefficients used in a predictive model are determined using the relationship between the scores representing the concentrations to be predicted and the scores representing the spectral responses using $\hat{\mathbf{u}}_1 = b_1 \mathbf{t}_1$ so that

$$b = \frac{\mathbf{u}_1^T \mathbf{t}_1}{\mathbf{t}_1^T \mathbf{t}_1}, \quad (61)$$

where $\hat{}$ denotes a predicted value. After the first factor is defined, the second factor is extracted from

a new dataset of residual matrices in which the information related to the first factor is subtracted from $\mathbf{X}$ and $\mathbf{Y}$ [2]. The overall process is repeated for a user-specified amount of iterations (which corresponds to the chosen number of factors). The number of factors can be optimized by looking for the first minimum in a residual variance plot [2]. Matrices $\mathbf{P}$, $\mathbf{W}$, and $\mathbf{Q}$ made up of $\mathbf{p}$, $\mathbf{w}$, and $\mathbf{q}$ vectors that are obtained for each factor are compiled. A vector of regression coefficients can then be created that can be directly applied to $\mathbf{X}$,

$$\mathbf{b} = \mathbf{W}(\mathbf{P}^T \mathbf{W})^{-1} \mathbf{q} \text{ with,} \quad (62)$$

$$\mathbf{q} = (\mathbf{T}^T \mathbf{T})^{-1} \cdot \mathbf{y}. \quad (63)$$

From the vector of regression coefficients $\mathbf{b}$, the concentration of an element in a sample can be predicted as $\hat{y} = \mathbf{x}^T \mathbf{b}$. The PLS model was calculated in MATLAB using the built-in function `plsregress`.

B LIRS: μ LIBS whole rock spectra

The LIRS instrument was tested on various whole-rock samples such as pyrite, hematite, ilmenite, and limonite, to name a few (see Figure 82). Successful single-spot spectra were obtained from all of these samples (Figure 83). These are all dark coloured minerals. There were some samples in the collection which single-shot spectra were unsuccessful, and collection while moving the samples was not attempted. These include fluorite, microcline, calcite, apatite, and quartz, among others. These are all light coloured minerals.



Figure 82: In numerical order from 2-18, the samples are chalcocite, galena, sphalerite, chalcopyrite, pyrrhotite, stibnite, pyrite, arsenopyrite, molybdenite (on gypsum), smaltite, corundum, hematite, ilmenite, pyrolusite, limonite, magnetite, and chromite.

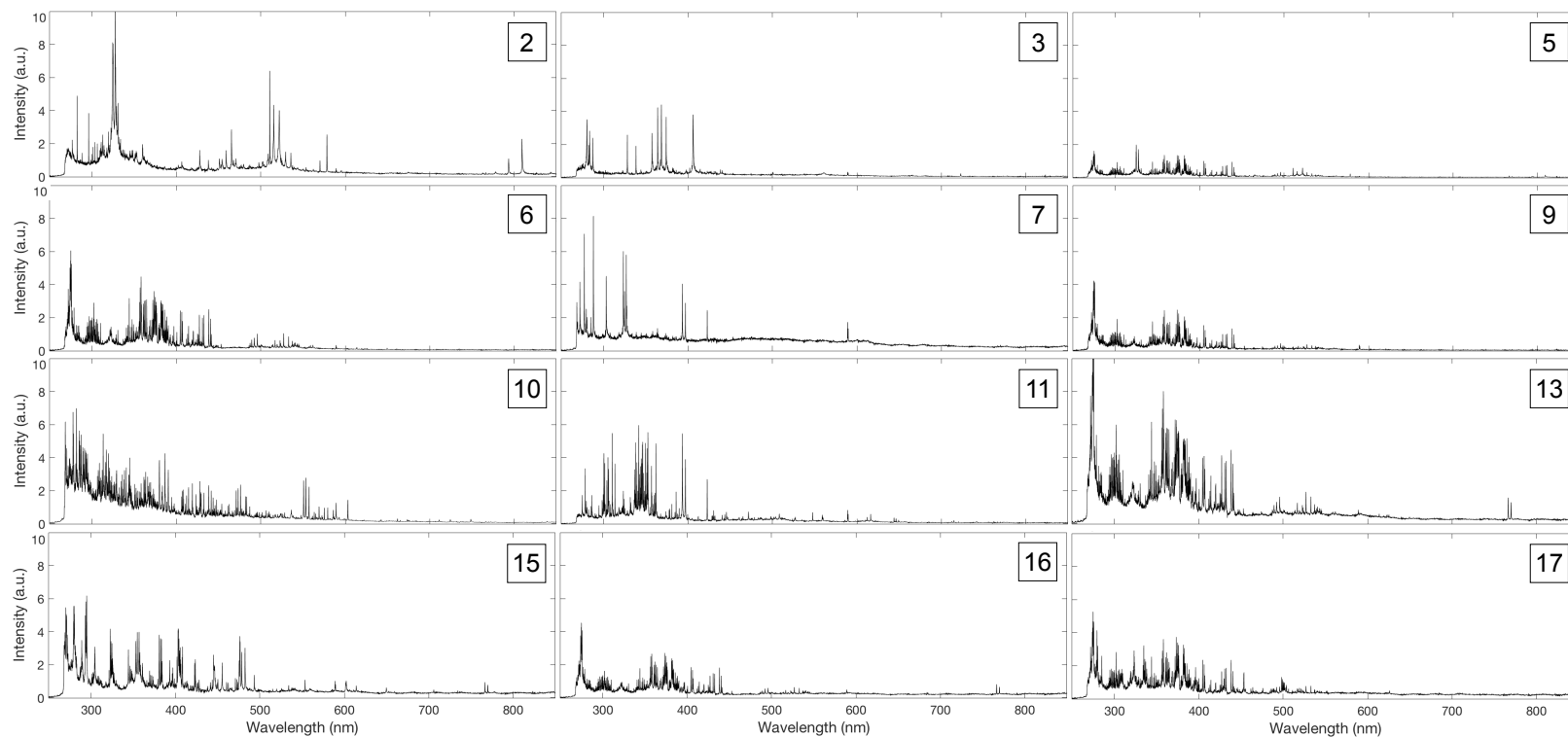


Figure 83: Single shot spectra of whole rock samples. In numerical order (matching their tags in Figure 82): chalcocite, galena, chalcopyrite, pyrrhotite, stibnite, arsenopyrite, molybdenite, smaltite, hematite, pyrolusite, limonite, and magnetite. All spectra shown here are on the same scale, and taken as an accumulation of 5000 laser shots, 3000 MCP gain, 225 ns gate delay, and 1000 ns gate width. Not all whole rock spectra are shown here.

C Polishing SMA-905 fiber connectors

Although there is a clear guide for polishing FC/PC and FC/APC fiber connectors (see [60]), the modifications needed to correctly polish SMA-905 connectors is left somewhat unclear. For this reason, this Appendix will go over the proper polishing procedure for SMA-905 connectors that has been tested and verified over the course of this work. Because the μ LIBS instrument uses a fiber delivery that requires a 150 kW peak power beam entering a 50–100 μ m fiber core, burning the connectors is a real possibility. Fibers should be checked relatively often using a fiber inspection scope (Thorlabs FS200) and the following procedure can be used to rescue burnt connectors, restoring them to their original performance.

If fibers become burnt from a high peak power laser, or if fibers become scratched they will need to be polished using the following items:

- D50-SMA polishing puck,
- FS200 fiber inspection microscope,
- FCC-7020 fiber end cleaner,
- LF5P silicon carbide lapping sheet (5 μ m grit),
- LF3P aluminium oxide lapping sheet (3 μ m grit),
- LF1P aluminium oxide lapping sheet (1 μ m grit),
- LF03P calcinated alumina lapping sheet (0.3 μ m grit),
- isopropyl alcohol (IPA),
- distilled water,
- lint free wipes,
- compressed air,
- and a hard, flat surface.

Lapping sheets are like sandpaper for fiber connectors. Some of these items can be found in the fiber polishing kit (TUK05) along with fiber polishing pucks for FC/PC and FC/APC connectors.

Step 1: Before polishing the surface of the connectors they should be cleaned with the connector cleaner tissue (FCC-7020). With the face of the fiber perpendicular to the tissue, move the fiber in a figure-8 motion across the tissue three times.

Step 2: Clean the bottom surface of the polishing disc (D50-SMA). The polishing disc is used to hold the fiber securely and at the correct angle while polishing the fiber, and results in a ferrule that is the correct length after polishing. Clean the bottom of the disc with IPA and a lint free wipe, and dry the disc with compressed air.

Step 3: Connect the fiber to the polishing puck.

Step 4: 5 μm polish. For stainless steel ferrules, all polishing should be done on a hard, flat surface. Place the 5 μm lapping sheet (green) with the shiny side down. Place five drops of distilled water at one side of the sheet (you'll be working your way across the sheet). Place the polishing puck on the lapping sheet onto the distilled water. Applying light to medium downward pressure on the connector, begin polishing the fiber in a figure-8 pattern, traversing the sheet, moving towards the dry end. Approximately 25 figure-8 patterns can be made across a sheet, and the figure-8's can overlap.

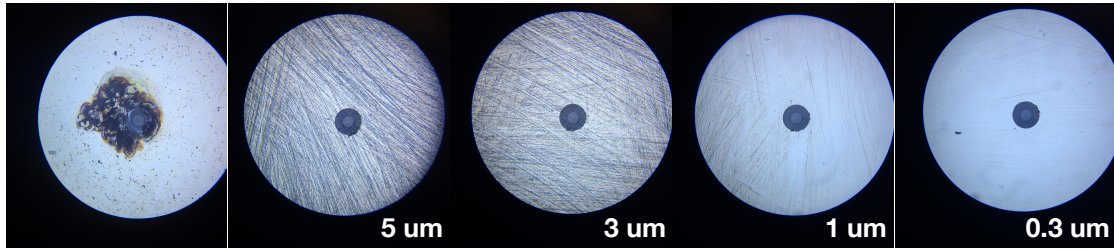
Step 5: Dry off the ferrule and inspect the face using the fiber microscope. The face should look something like the one labeled '5 μm ' in Figure 84a. If any deep scratches still appear, this process should be repeated. This is the largest grit lapping paper, so no further polishing (using other lapping sheets) would be able to remove any large imperfections. Between each polish the ferrule end should be cleaned with the connector cleaner tissue (FCC-7020), and the polishing disc should be cleaned with IPA and lint free wipes. The lapping paper can be wiped off with lint free wipes and reused up to six times [60].

Step 6: 3 μm polish. Repeat Step 4 with the 3 μm lapping paper (yellow). Repeat Step 5. The face should look like the one labeled '3 μm ' in Figure 84a.

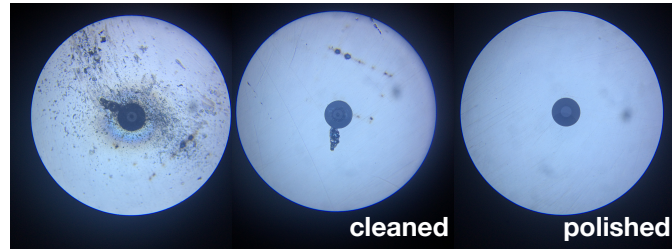
Step 7: 1 μm polish. Repeat Step 4 with the 1 μm lapping paper (pink). Repeat Step 5. The face should look like the one labeled '1 μm ' in Figure 84a.

Step 8: 0.3 μm final polish. Repeat Step 4 with the 0.3 μm lapping paper (blue). Repeat Step 5. The face should look like the one labeled '0.3 μm ' in Figure 84a. Clean the ferrule thoroughly with the connector cleaner tissue (FCC-7020). Perform a thorough inspection of the fiber face using the microscope, ensuring that there is no remaining damage to the fiber core.

Figure 84b gives an example of direct core damage where, because light was focused into a spot such that the damage threshold of silica glass (5 GW/cm²) was exceeded, the laser bore into the core. This is significant damage, and polishing using the largest grit (5 μm) was done 4–5 times



(a) Example of fiber polishing for superficial burning, where the metal facing and/or the cladding is damaged because of small miss-alignments. From left to right, each step shows the fiber end face after polishing with 5 μm , 3 μm , 1 μm , and 0.3 μm grit lapping paper.



(b) Example of fiber polishing for direct core damage. The middle image demonstrates the need for cleaning between each polish.

Figure 84: Examples of fiber polishing for (a) superficial burning and (b) direct core damage.

before inspection of the fiber face showed no remaining deep gouges (resembling Figure 84a, 5 μm), and the polishing process could continue.