

APPLICABILITY OF LIBS ON THE MOON: ELEMENTAL ANALYSIS OF LUNAR SIMULANTS IN VACUUM. J. Lasue^{1,2}, R.C. Wiens¹, S.M. Clegg³, D.T. Vaniman⁴, K.H. Joy², S. Humphries³ ¹ISR-1, D-466, LANL, Los Alamos, NM-87545 USA (lasue@lanl.gov), ²LPI, 3600 Bay Area Blvd, Houston, TX-77058, USA, ³C-PCS, MS J565, LANL, Los Alamos, NM-87545 USA, ⁴EES-14, D-462, LANL, Los Alamos, NM-87545 USA

Introduction: Laser-induced Breakdown Spectroscopy (LIBS) is an active analytical technique that makes use of a pulsed laser to ablate material of interest at a distance. The atoms constituting the high temperature plasma emit at specific wavelengths and the light can be analyzed to determine the composition of the target [1]. The technique has been validated for planetary exploration purposes under low pressure [2] and still gives good results under vacuum conditions [3]. The LIBS technique has been selected for the next Mars exploration mission (see the description of the ChemCam instrument on-board the Mars Science Laboratory [4]). In this work, we review the capability and advantages of the LIBS technique for lunar rock and regolith analysis up to 1.5 m distance from a lunar rover. This technique can ablate dust covering rocks.

LIBS challenges relevant to lunar applications: Because LIBS creates an expanding plasma, it is very sensitive to local pressure conditions. Under pressures greater than 1.5×10^4 Pa, the plasma is perturbed as it expands against the surrounding atmosphere and collisional deactivation reduces its intensity. Between 1.5×10^3 Pa and 1.5×10^4 Pa, the plasma is brightest as it is confined in the field of view by the surrounding atmosphere, but collisional deactivations occur much less frequently. However, as the environmental pressure is further reduced, the plasma is free to expand beyond the field of view, thus reducing the detected intensity.

LIBS experimental setup: We used the setup described in [5]. A Nd:YAG laser of 17 mJ at 1064 nm with 10 Hz pulse repetition rate and 10 ns pulse width is focused on powdered samples. The laser flux [$\text{W} \cdot \text{m}^{-2}$] on the surface ablates part of the material (typically a few ng) which then forms an expanding plasma. As the excited ions and atoms relax to the ground state, they emit light at characteristic wavelengths. The light emitted by the plasma is collected by a telescope (1.5 m away) and directed into Ocean Optics HR2000 dispersive spectrometers. There are three spectrometers used to detect emission in the 220-325 nm (UV), 380-470 nm (VIS), and 490-800 nm (VNIR) spectral regions. The experiments were conducted at pressures of 0.1 Pa or less. At these pressures the mean free path of the molecules is about 20 cm, one order of magnitude longer than the dimension of the emitting plasma, effectively duplicating much the rarefied lunar atmosphere. This is verified by the absence of pressure effects on the LIBS plasma within an order of magnitude of the pressure used in this experiment.

LIBS capabilities for elemental analysis on the Moon: As one of the most pristine bodies located in the vicinity of the Earth, geological studies of the

Moon give us a better understanding of the formation of the Solar System, of the Earth-Moon system and its impact history (see e.g. [6, 7]). Moreover, it is important to study potential resources and hazards for future lunar exploration missions.

Description of the samples. We used 12 terrestrial geostandards (basalts, andesite and the JSC-1 lunar regolith simulant). The samples have been ground to $<100 \mu\text{m}$ to be homogeneous at the scale of the LIBS beam ($<200 \mu\text{m}$ dia.). These powders were pressed into pellets for analysis. The elemental compositions of the standards and typical lunar sample compositions are shown in Table 1. Some ranges that are of interest for the lunar context are not covered, for example no high-Ti basalts compositions were used in the sample set. However, analysis of the spectra taken for these samples provides information on detection limits and accuracy of the elemental composition quantification under lunar conditions. All elements shown in Table 1 have been detected in the sample spectra.

Table 1: Sample compositions in oxide wt.% and ppm compared with typical lunar compositions along with LIBS measurement uncertainties in relative (REP) and root mean square (RMSEP) error predictions. The lunar composition ranges are from [6] and references therein.

sample names	SiO ₂	FeO	Al ₂ O ₃	MnO	MgO	CaO	Na ₂ O	TiO ₂	K(ppm)	Ni (ppm)
BHVO-2	49.90	11.18	13.50	0.17	7.23	11.40	2.22	2.73	4317	119
BIR-1	47.77	10.21	15.35	0.17	9.68	13.24	1.75	0.96	224	166
Grano Dike	48.08	14.15	12.93	0.25	6.21	6.93	4.51	3.58	7720	37
GUWBM	49.51	16.07	16.25	0.14	7.47	6.47	4.65	1.14	1660	57
JB2	53.20	12.94	14.67	0.20	4.66	9.89	2.03	1.19	3487	16.6
JSC-1	47.71	10.48	15.02	0.18	9.01	10.42	2.70	1.59	6807	137
KV0417	50.25	11.10	13.05	0.17	9.82	9.83	2.12	2.34	1934	260
KV0424	50.10	11.00	12.91	0.17	9.81	10.10	2.05	2.38	2050	256
MO12	49.87	9.51	16.74	0.14	7.38	8.73	3.85	1.61	9298	137
MO14	46.85	9.79	17.06	0.15	8.05	9.60	3.00	1.62	3819	111
Moppin	50.78	13.28	15.63	0.36	4.82	8.30	2.41	1.67	3238	87
NBS688	48.35	7.64	17.35	0.17	8.46	12.17	2.16	1.17	1577	150
Predictions error										
Med REP (%)	1.26	11.28	7.31	25.34	21.46	18.63	49.96	37.81	57.26	48.07
Med REPb (%)	1.70	16.56	7.43	22.06	18.04	15.48	54.52	25.37	68.03	44.74
RMSEP (wt%)	1.84	1.81	1.58	0.07	2.06	2.26	1.17	0.89	2977	83.45
RMSEPb (wt%)	1.72	2.33	1.70	0.07	1.85	2.04	1.18	0.89	3079	81.49
typical lunar composition range										
Maximum (wt%)	70	30	35	0.3	20	20	0.7	15	15000	2000
Bulk (wt%)	43.4	13	6	0.15	10	4.5	0.1	0.3	83	
Minimum (wt%)	30	0	1	0.05	6	4	0.1	0	0	0

Quantitative analysis. Given the known compositions of the geostandards, it is possible to apply multivariate regression analyses to the spectral data. One of the most used and most accurate techniques is the Partial Least Squares regression (PLS) [8, 9]. The multivariate regression technique is used to predict the elemental composition of unknown samples. The procedure used in our case is to leave one sample out of the model for each prediction. The composition predictions are then used to obtain the median relative error prediction (Med REP in Table 1) and the root mean

square error prediction (RMSEP), which are indications of the accuracy of the predictions. The RMSEP essentially gives the error standard deviation and the detection limit of the considered elements. The values obtained for the RMSEP are coherent with the ones obtained with a large set of geological samples using an instrumental set-up duplicating ChemCam [9]. Two lines of values are given corresponding to results of the calculations, one for the original spectra and “b” for the spectra corrected for the bremsstrahlung effect (background emission from the free electrons in the plasma). The two sets of values are marginally different, and depend on the coupling of the element with the laser energy (Fe couples better than other elements [9]).

Application to the geological analysis of lunar samples: In Table 1, the RMSEP obtained for oxides and elements such as TiO₂ (1 wt.%), Al₂O₃ (1.6 wt.%) or K (3000 ppm) allow reliable classification of most lunar mare basalts following the lunar mare basalt classification scheme shown in Table 2 [10]. Moreover, RMSEP for Al₂O₃ and FeO very easily allow the differentiation of lunar feldspathic highlands samples from lunar mare basalts. MgO can be used to help identify rocks derived from the Mg-Suite.

Table 2: Lunar mare basalt classification scheme adapted from [10]. Mare basalt suites and basaltic lunar meteorites are shown.

	TiO ₂	Al ₂ O ₃	K	Landing Site/Meteorite
0 wt.%			<2000 ppm	Low-K Apollo 17, Luna 24
VLT	<11wt.% Low-Al >11wt.% Low-Al	>2000 ppm	High-K	
		<2000 ppm	Low-K	
1 wt.%	<11wt.% Low-Al >11wt.% Low-Al	>2000 ppm	High-K	Apollo 12, Apollo 15, LAP02205, etc. NWA 032, NEA 003, Y-793169, A-881757
		<2000 ppm	Low-K	
Low-Ti	<11wt.% Low-Al >11wt.% Low-Al	>2000 ppm	High-K	Dhofar 287
		<2000 ppm	Low-K	Apollo 14, Luna 16
6 wt.%	<11wt.% Low-Al >11wt.% Low-Al	>2000 ppm	High-K	Apollo 11
		<2000 ppm	Low-K	Apollo 11, Apollo 17
High-Ti	<11wt.% Low-Al >11wt.% Low-Al	>2000 ppm	High-K	Apollo 11
		<2000 ppm	Low-K	
		>2000 ppm	High-K	
		<2000 ppm	Low-K	

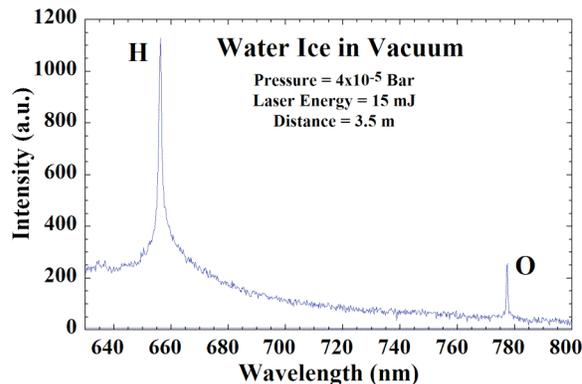
Mare basalt compositional classification scheme adapted from Neal and Taylor (1992)
Apollo and Luna basalt suites and examples of lunar meteorites basalt types are listed.

The errors calculated for K and Na mean that these elements can also be used to identify samples that are rich in K (>0.24wt.%), rare-Earth elements and phosphorus (termed KREEP). Most minor elements are difficult to probe with LIBS on geological samples at abundances near detection limits and where coupling and matrix effects from major rock components interfere. In our case, the major P emission lines at 529.4 nm and 255.3 nm are not sensitive enough to allow the reliable detection of P. Finally, analysis based on Ni (detected by emission at 459 nm) in bulk regolith samples or in actual individual fragments of meteorites found in the lunar regolith (e.g. [11]) will be an important indicator of the amount and type of extra-terrestrial material delivered to the lunar surface.

The LIBS technique is advantageous for the detection of light elements that are difficult to characterize with other measurement methods. During these experiments at low pressure, the lunar stimulant JSC-1

was mixed with water ice in various proportions and the LIBS instrument was able to detect H emission lines in each case. These results are of interest for locating and eventually exploiting water resources at the lunar poles. Figure 1 shows an example spectrum of water ice, taken at 3.5 m.

Figure 1: Detection of H and O lines from water ice mixed with lunar simulant JSC-1.



Conclusions and future work: This work shows the potential of LIBS analysis for rapid and accurate elemental analysis of lunar materials and characterization of potential resources for future exploration. More study is required to assess fully the possibilities of LIBS for detection of trace elements (e.g. Sr, Ba) in lunar materials.

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