

Elemental Mapping of Geological samples using Laser Induced Breakdown Spectroscopy (LIBS)

J.C. Jain ^{A,B}, J. Yoo^C, D.A. Hartzler ^{A,B}, A. Bolshakov ^C, D.L. McIntyre ^A,
^A National Energy Technology Laboratory, U.S. Department of Energy, Pittsburgh, PA 15236, USA .
^B AECOM, National Energy Technology Laboratory, Pittsburgh, PA 15236, USA.
^C Applied Spectra, Inc, Fremont, CA, USA

Research &
Innovation Center



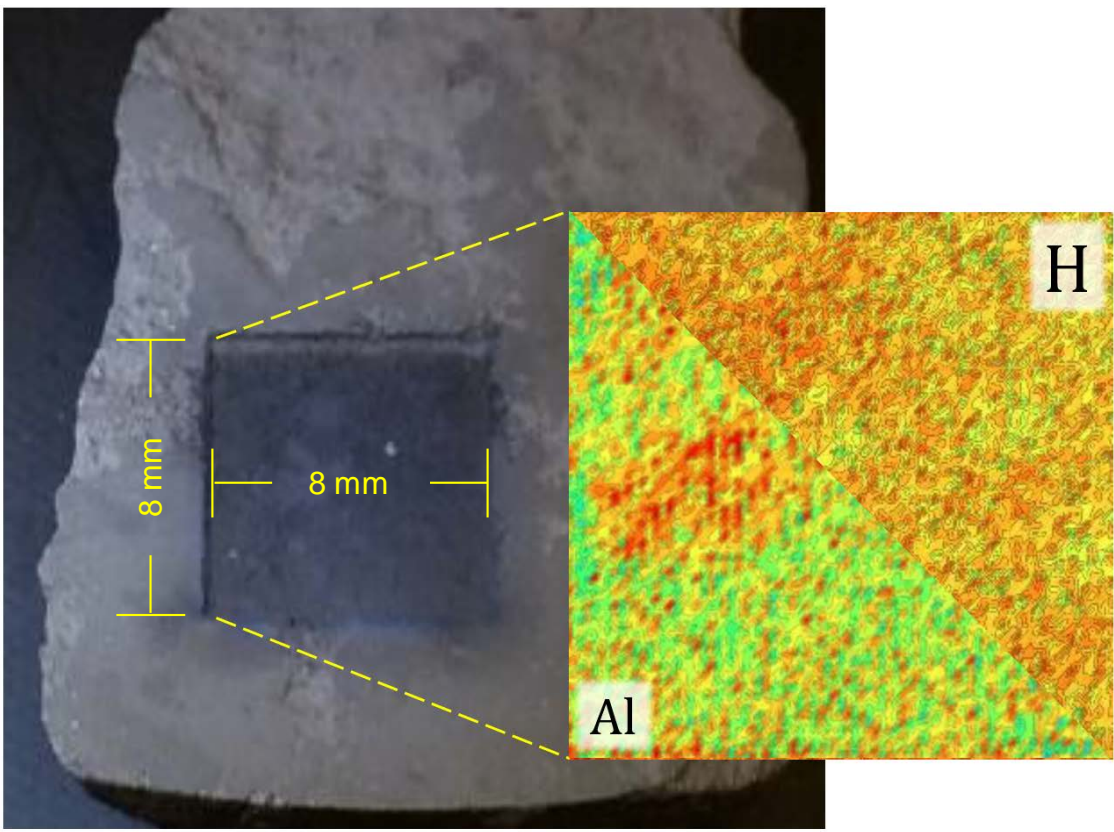
Abstract

Laser induced breakdown spectroscopy (LIBS) is an emerging spectroscopic technique for the elemental analysis and mapping of geological samples. While elemental composition is important to provide rock properties of a sample, the mapping for elemental distribution can be useful to determine mineral phases and chemical zonation within a mineral. In this study LIBS was used for the analysis and mapping of shale and rare earth element (REE) rocks obtained from various locations in the United States. LIBS is a fast and cost-effective analytical technique that can provide elemental information of every element in the Periodic Table (including C, H, N, O) of a given sample. Additionally, LIBS provides depth profiling and can be coupled with fiber optics to make it an attractive tool for *in-situ* analysis in extreme conditions and hard to reach places. The samples were analyzed using a 266 nm Nd:YAG nanosecond pulse duration laser (J200 LIBS instrument) and a grid pattern that covered 64-144 mm² area. The data collected from these experiments were used to construct 2D elemental maps and determine elemental concentration for each sample. The accuracy of analysis was assessed by analyzing the samples of known elemental concentrations. This study shows how the spatial elemental (including C and H) composition varies as a function of the sample location and illustrates the benefits of LIBS over existing analytical techniques.

Laser-Induced Breakdown Spectroscopy (LIBS)

- LIBS is an atomic emission spectroscopy-based analytical technique to obtain qualitative and quantitative elemental information of a sample's composition.
- A high energy laser pulse creates a micro plasma by ablating a very small sample volume.
- The ablated material dissociates into excited ionic and atomic species.
- The excited atoms/ions present in the plasma emit light at their characteristic wavelengths.
- Analysis of the emission spectrum from the plasma is used to infer the elemental composition of the sample.

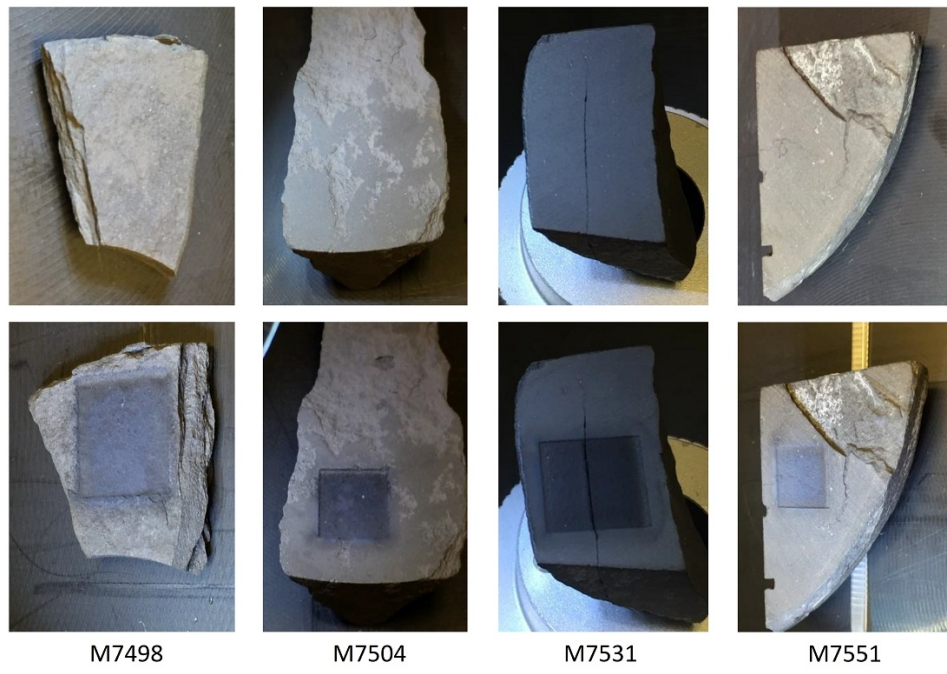
LIBS Mapping



- LIBS maps are produced by raster scanning (i.e. scanning point by point) across an area of interest.
- The spectrum at each point is analyzed to extract the elemental composition.
- Element concentrations are used to construct a map of the sample composition.

Samples

- Four gas producing Marcellus shale samples were retrieved from depths of 7498', 7504', 7531', and 7551' at the Marcellus Shale Energy and Environment Laboratory (MSEEL)².
 - M7498, M7504, M7531, M7551
- Marcellus shale outcrop samples were obtained from Petersburg, WV and Bedford, PA.



Analysis

- Samples were analyzed to assess LIBS in comparison with traditional techniques such as x-ray fluorescence (XRF) and CHN analysis.
- Calibration standards for the LIBS analysis were produced by characterizing the Marcellus shale outcrop samples
 - Inductively coupled plasma optical emission spectroscopy (ICP-OES)^{3,4} was used to determine their elemental composition while the total organic carbon (TOC) was measured by CHN analysis.
- LIBS analysis was performed using an automated mapping instrument (J200, Applied Spectra Inc).
- Both sample sets (calibration and gas shales) were mapped using LIBS.

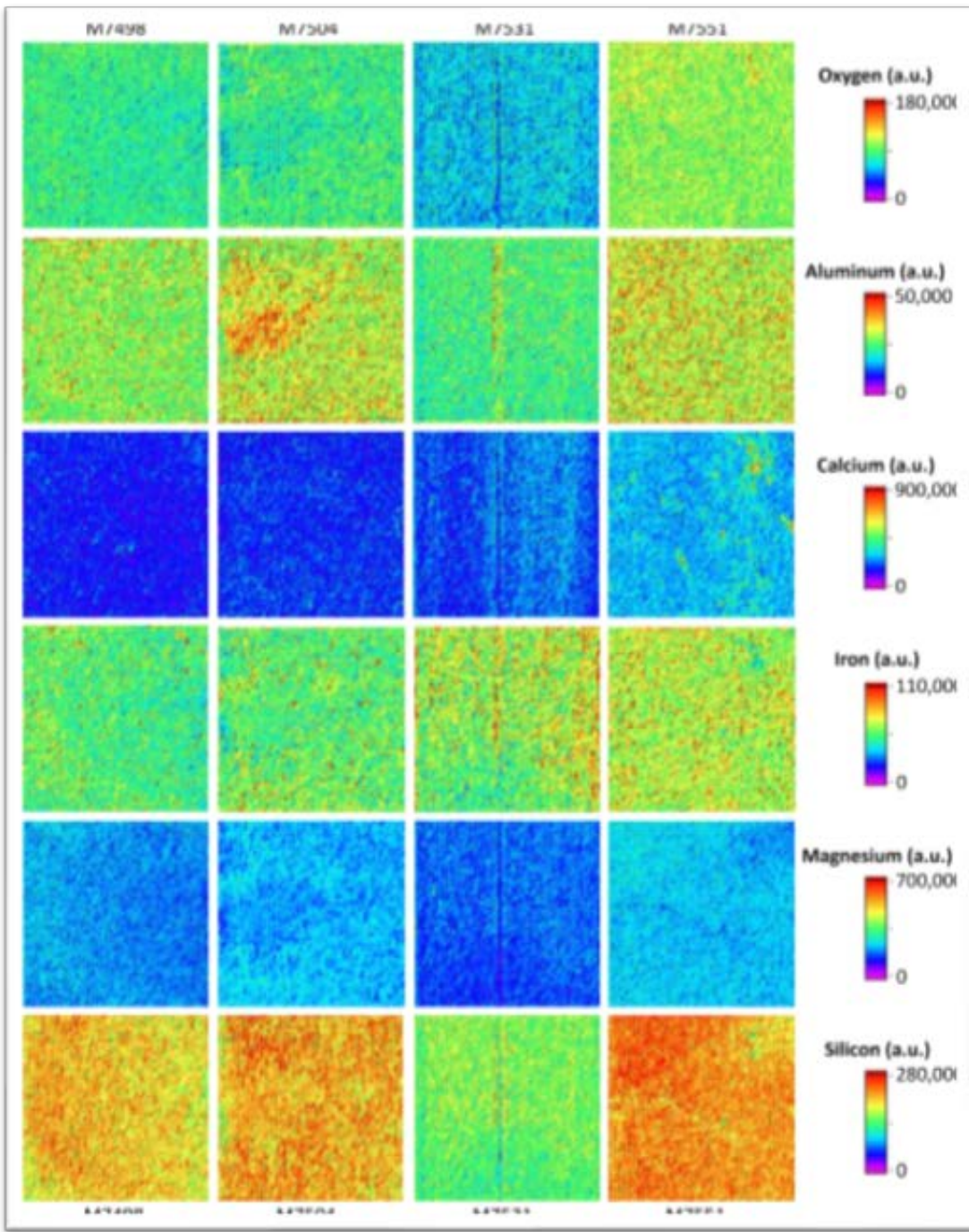


LIBS mapping instrument.

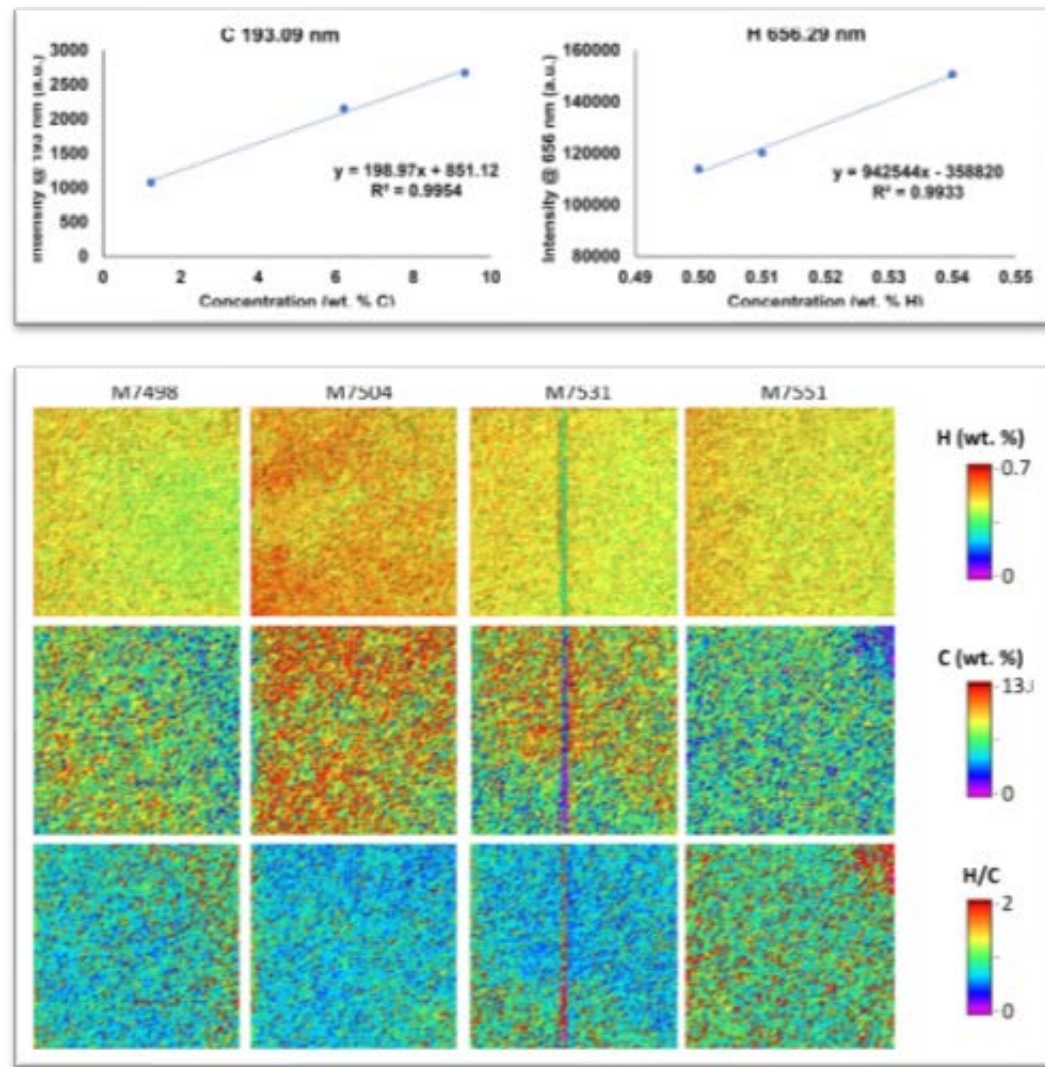
Table 1. LIBS conditions for the shale maps and calibration samples.

	Shale Maps	Calibration Samples
Laser spot size	50 µm	50 µm
Laser energy	6.75 mJ	6.75 mJ
Laser repetition rate	10 Hz	10 Hz
Gas environment	0.5 L/min He	0.5 L/min He
Spectrometer delay	0.25 µs	0.25 µs
Laser pulses	5 pulses per location	5 pulses per location
Analyzed area	8 mm x 8 mm (64 mm ²)	8 mm x 8 mm (64 mm ²)
Mapping method type	Grid points	Grid points
Mapping method size	81 x 81 (6561 data points)	5 x 5 (25 data points)
Time per sample	390 min	1 min 32 sec

Elemental Maps



- LIBS ability to measure light elements, specifically H and C, makes the technique well suited for analyzing hydrocarbon bearing rock.
- For analysis of H and C, their most intense and interference free lines, H 656.29 nm and C 193.09 nm, were used.
- Calibration curves for H and C were constructed using the outcrop samples (Right Top) which were then used to generate H and C concentration maps of the four gas producing shales (Right Bottom).



Method Comparison

X-ray Fluorescence

Table 2. Comparison between handheld XRF and LIBS concentrations for shale samples (Wt. % ± 1 SD). Note that the Mg XRF data was acquired using a different instrument than Al, Ca, Fe, and Si.

Sample		Al	Ca	Fe	Si	Mg
Average Concentration (Wt. % ± 1 SD)						
M7498	XRF	5.18 ± 0.13	1.60 ± 0.01	3.85 ± 0.03	21.27 ± 0.12	0.73
	LIBS	0.71 ± 0.52	1.22 ± 0.20	1.74 ± 0.11	21.70 ± 0.99	0.65 ± 0.04
M7504	XRF	3.39 ± 0.97	1.48 ± 0.01	2.75 ± 0.02	22.10 ± 0.11	0.72
	LIBS	1.63 ± 0.75	1.53 ± 0.19	1.82 ± 0.11	22.60 ± 1.06	0.68 ± 0.03
M7531	XRF	2.16 ± 0.11	0.84 ± 0.01	3.21 ± 0.03	15.44 ± 0.11	0.57
	LIBS	0.80 ± 0.29	2.12 ± 0.50	1.99 ± 0.19	17.30 ± 1.05	0.58 ± 0.04
M7551	XRF	2.13 ± 0.09	3.21 ± 0.02	3.55 ± 0.03	21.72 ± 0.12	N/A
	LIBS	1.67 ± 0.62	3.32 ± 0.48	2.06 ± 0.90	23.60 ± 1.05	0.70 ± 0.03

- The drill core from which the samples were obtained was analyzed using a handheld XRF instrument (Innov-X® Delta Standard M-6000).
- It's difficult to analyze light elements (i.e. below Si (Z = 14)) using a typical handheld XRF unit⁵ while LIBS is well suited to analyze most elements regardless of atomic number.
 - For instance the Mg concentrations in the shale samples were below the handheld XRF limit of detection (LOD) requiring further analysis using a laboratory scale XRF instrument (Thermo ARL Perform'X).
- Also note that the handheld XRF analysis was performed across the shale bedding planes while the LIBS analysis was performed along the bedding plane surface.

Carbon and Hydrogen Analysis

Table 3. C and H weight % measured by CHN analysis and LIBS.

Sample		C (Wt. %)	H (Wt. %)
M7504	CHN	9.33	0.51
	LIBS	9.26	0.53

Table 4. TC and TOC weight % measured by LIBS and pyrolysis.

Sample	TC (Wt. %)	TOC (Wt. %)	TOC/TC
M7498	7.13	4.78	0.67
M7504	9.26	5.92	0.64

- The H/C ratios can give an indication of the type of hydrocarbons present in the sample.
- Shale deposits rich in natural gas are expected to show the H/C ratio greater than 1.

- The total carbon (TC) and total organic carbon (TOC) for select samples were analyzed by CHN analysis (Leco TrueSpec) and pyrolysis respectively.
- Comparison of the TC obtained from CHN analysis and LIBS shows good agreement between the methods.
- The TOC/TC ratio suggest a possible predictive correlation.
 - More work is needed to establish a relationship.

Table 5. Average H/C ratio determined over the 8 x 8 mm area (n = 6,561 points) of each shale sample

Sample	H/C
M7498	0.85
M7504	0.76
M7531	0.84
M7551	1.05

Conclusions

- Spectral mapping by LIBS offers a valuable tool for distribution analysis and elemental composition of shale samples.
- The technique complements existing techniques used in the shale gas exploration.
- Shale gas is primarily composed of methane and H/C ratios can potentially predict the type of hydrocarbons and impurities in shale gas deposits.

References

- J.C. Jain, C.D. Quarles Jr, J. Moore, D.H. Hartzler, D.L. McIntyre, D. Crandall, Elemental mapping and geochemical characterization of gas producing shales by laser induced breakdown spectroscopy, Spectrochimica Acta Part B: Atomic Spectroscopy, 150 (2018) 1-8.
- T.R. Carr, T.H. Wilson, P. Kavousi, S. Amiri, S. Sharma, J. Hewitt, I. Costello, B. Carney, E. Jordan, M. Yates, Insights from the Marcellus Shale Energy and Environment Laboratory (MSEEL), in: Unconventional Resources Technology Conference (URTEC), 2017.
- H.K. Sanghavi, J. Jain, A. Bolshakov, C. Lopano, D. McIntyre, R. Russo, Determination of elemental composition of shale rocks by laser induced breakdown spectroscopy, Spectrochimica Acta Part B: Atomic Spectroscopy, 122 (2016) 9-14.
- C.W. Noack, J.C. Jain, J. Stegmeyer, J.A. Hakala, A.K. Karamalidis, Rare earth element geochemistry of outcrop and core samples from the Marcellus Shale, Geochemical transactions, 16 (2015) 6.
- A. Migliori, P. Bonanni, L. Carraresi, N. Grassi, P. Mando, A novel portable XRF spectrometer with range of detection extended to low-Z elements, X-Ray Spectrometry, 40 (2011) 107-112.