UNCONVENTIONAL RESOURCES TECHNOLOGY CONFERENCE
FUELED BY SPE • AAPG • SEG

Laser Induced Breakdown Spectroscopy (LIBS):

An Emerging Spectroscopic Technique for SHALE ROCKS Characterization

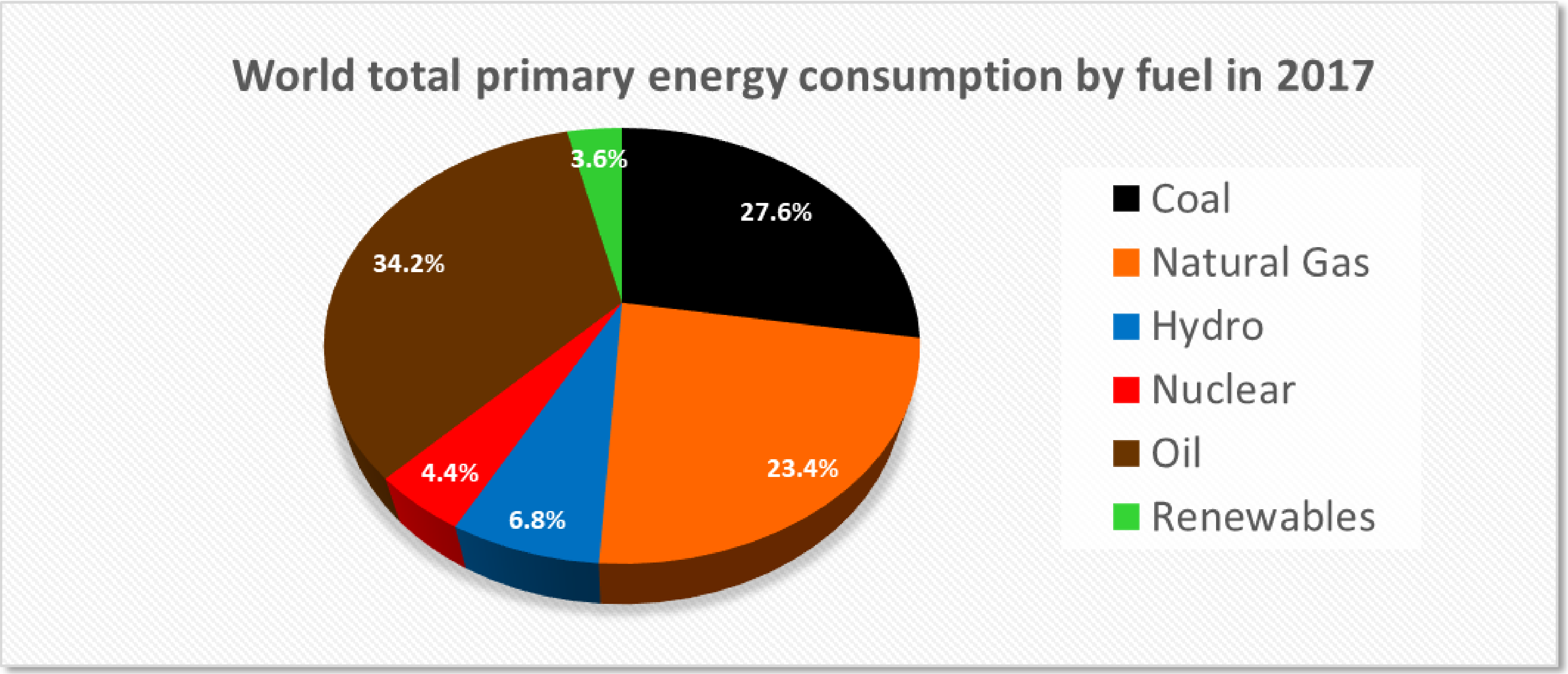
Jinesh Jain[1,2], Daniel Hartzler[1,2], Dustin McIntyre[1], Johnathan Moore[1,2], and Dustin Crandall[1]

[1]US-DOE National Energy Technology Laboratory,
[2]Leidos Research Support Team

U.S. DEPARTMENT OF ENERGY

NATIONAL ENERGY TECHNOLOGY LABORATORY

Energy Consumption



Source: BP Statistical Review of World Energy, 67th Edition, June 2018

Shale Oil and Gas Resources

NATIONAL ENERGY TECHNOLOGY LABORATORY

Resources	Oil (billion barrels)	Gas (trillion cubic feet)
Shale	345	7299
Non-shale	3012	15883
Total	3357	22882
% Shale	10	32

Source: U.S. Energy Information Administration, Independent Statistics and Analysis, June 2013

Projected Shale gas production

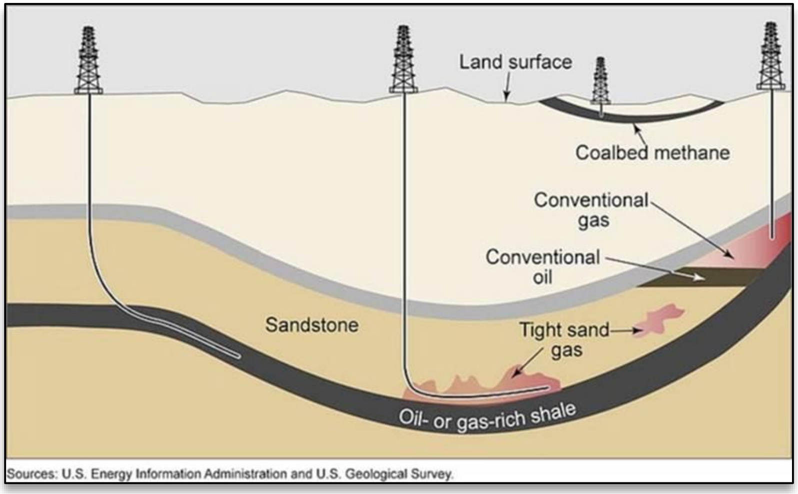
NATIONAL ENERGY TECHNOLOGY LABORATORY

Region	2015 (bcf/day)	2040 (bcf/day)
World	42	168
USA	37	79
Other countries: Canada, China, Mexico, Argentina, Algeria		

Source: U.S. Energy Information Administration, International Energy Outlook 2016 and Annual Energy Outlook 2016

Shale Characterization

- Shale formations have oil and gas trapped within the pore spaces and are considered largest natural gas deposits
- Elemental composition can provide clues to rock properties (porosity, permeability, minerals) that could effect oil and gas accumulation
- Higher amount of carbon and hydrogen (organic material) means high gas potential
- Knowledge of minerology helps in selection of drilling location, resolving drilling problems, and making engineering and production decisions.
- Environmental issues associated with shale retorting require substantial monitoring and control of waste product



Unconventional Shale

- **Fine grained sedimentary rocks**
  - < 2 microns
- **High clay content**
  - Generally > 50%
- **Low permeability**
  - Nano-Darcy
- **High organic content**
- **Hydrocarbon generation**
- **Susceptible to hydraulically induced fractures**
  - E.g. generally behaves in a brittle manner

Shale Core Logging

- XRF is a widely used technique for shale logging/mapping
- SEM-EDS for spectral mapping of shale
- Low atomic mass elements (i.e., C, H) are not measurable by XRF
- More than one technique is needed to obtain complete elemental information
- LIBS is capable of measuring these elements simultaneously.

Laser Induced Breakdown Spectroscopy

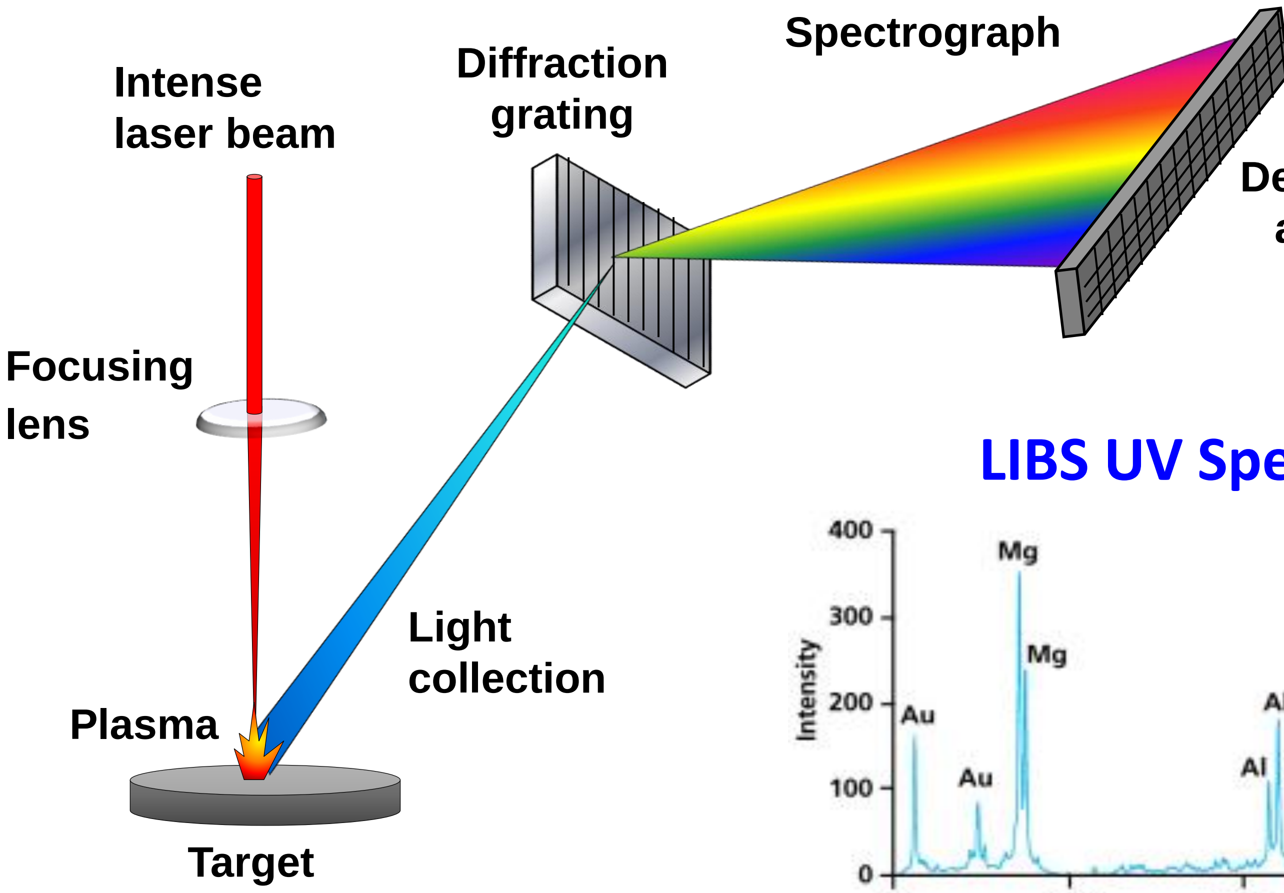
NATIONAL ENERGY TECHNOLOGY LABORATORY

- Laser is fired upon a given sample and laser energy focused to a small spot
- A hot luminous plasma vaporizes the material, and leads to atomization and excitation of elements
- As plasma cools, emission occurs and the emitted light can be collected
- Every element in the Periodic Table gives off light

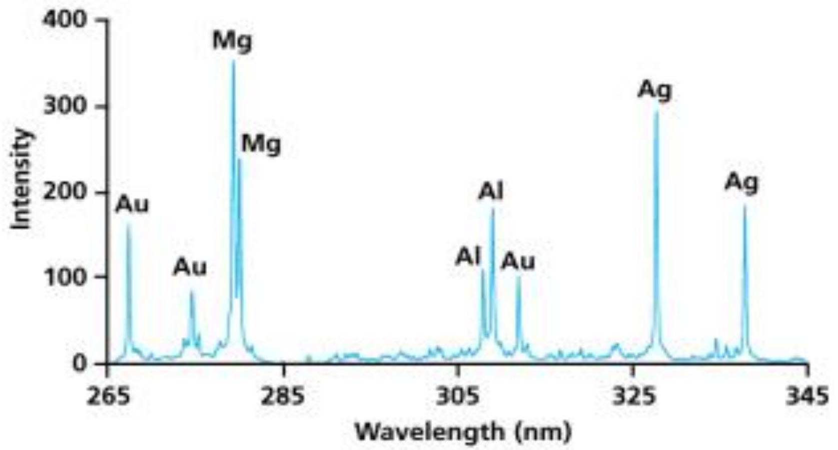
  at a distinct wavelength
- LIBS is capable of analyzing solid, liquid, and gaseous samples with minimum or no sample preparation
  - Matrix and/or major elements
  - Non-metals such as C, H, N, O and halogens (F)

- LIBS can perform both surface and depth analysis in both ambient and extreme conditions

Principle of LIBS



LIBS UV Spectrum



LIBS Instrument & Method Parameters

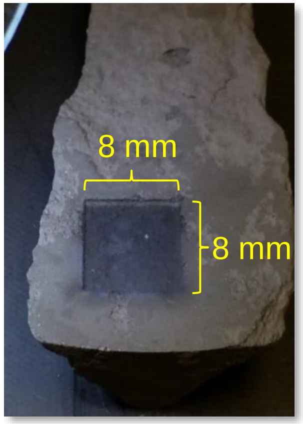
- **Experimental Conditions**
  - 266 nm Nd:YAG nanosecond laser
  - 50 um laser spot size
  - 81 x 81 grid pattern map
  - 8 X 8 mm (64 mm2)
  - 5 shots per location – Accumulated
  - 6561 data points per map
  - ~ 390 minutes per map
  - ASI's Axiom operation software

LIBS Instrument

Shale Samples Analyzed

Sample M7498

Sample M7504



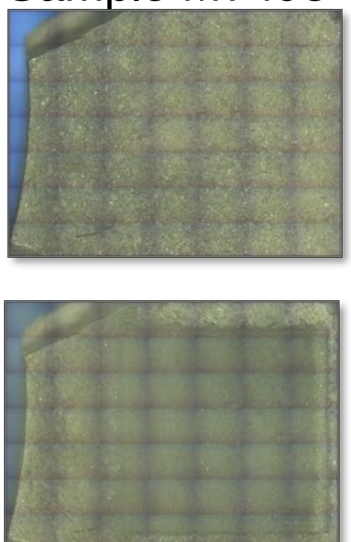
Sample M7531

Sample M7551

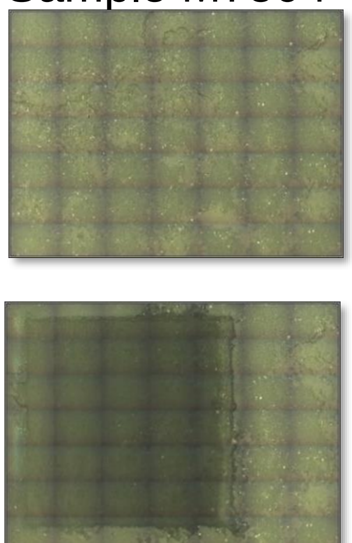
Sample B9655

Shale Samples Analyzed

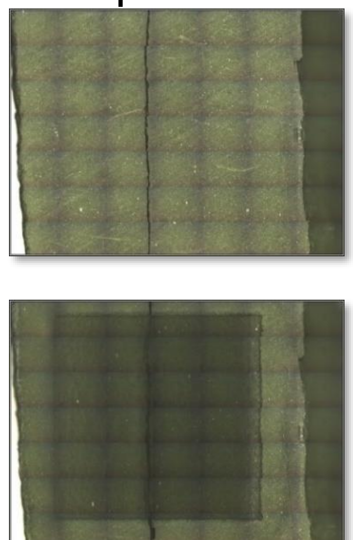
Sample M7498



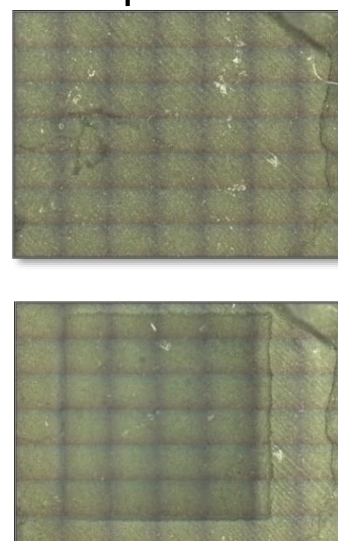
Sample M7504



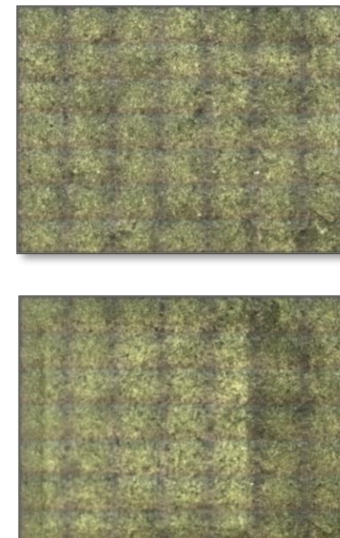
Sample M7531



Sample M7551

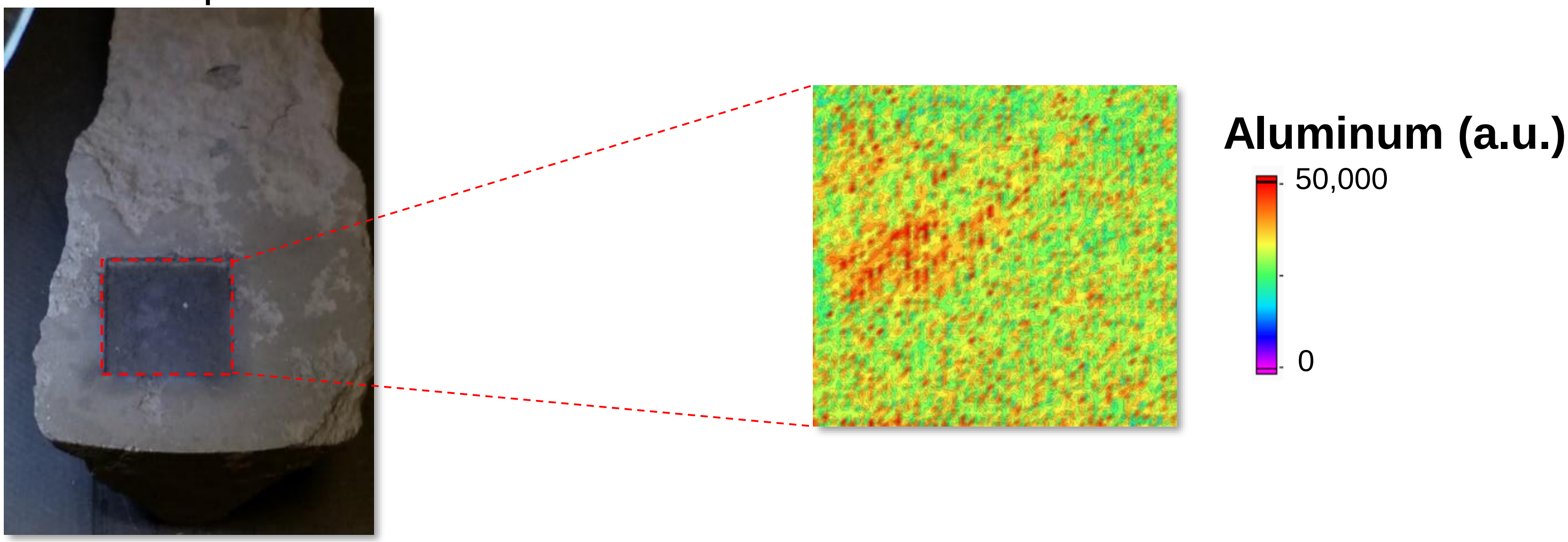


Sample B9655



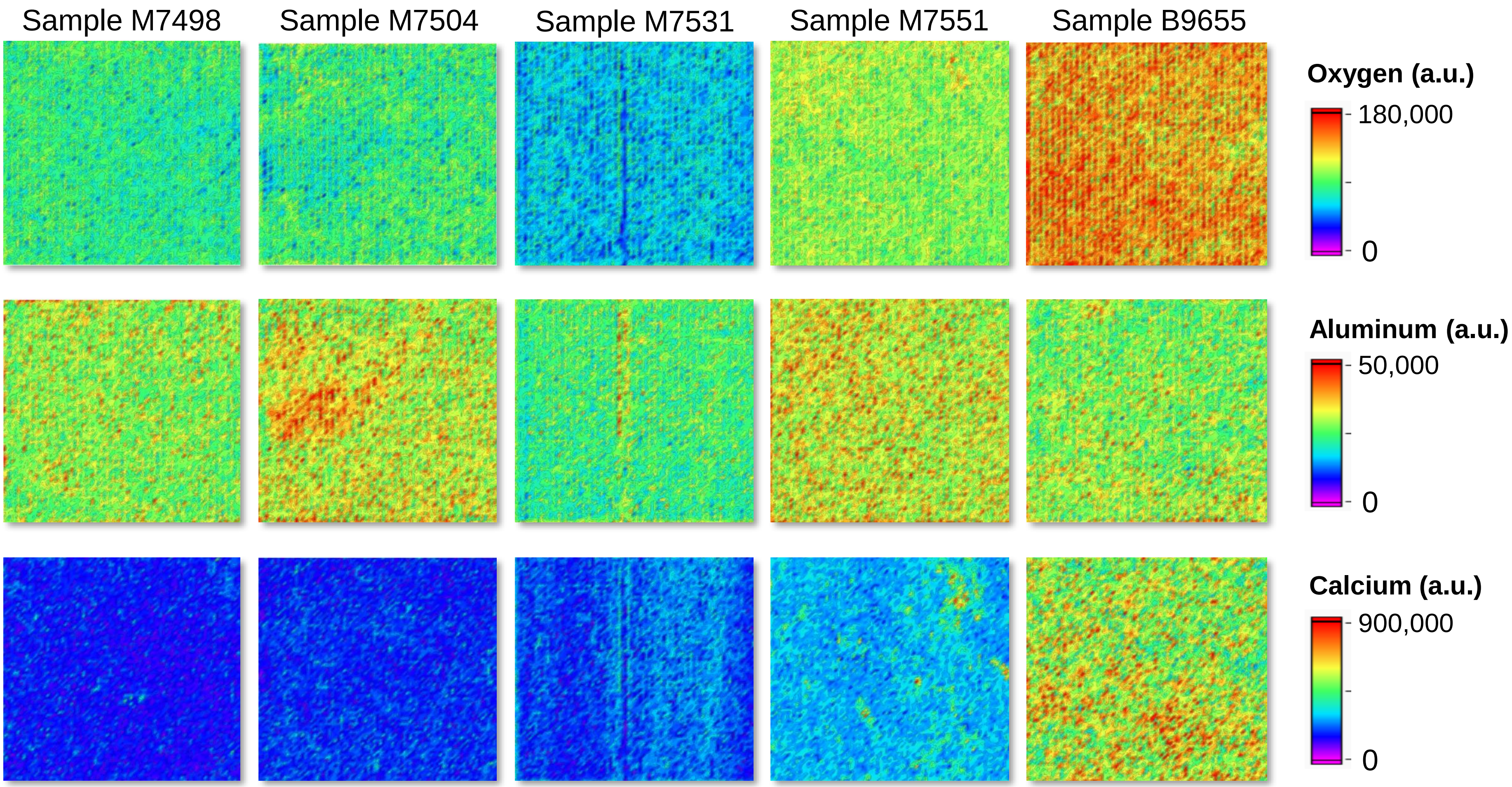
Shale Sample Mapped Area

Sample M7504

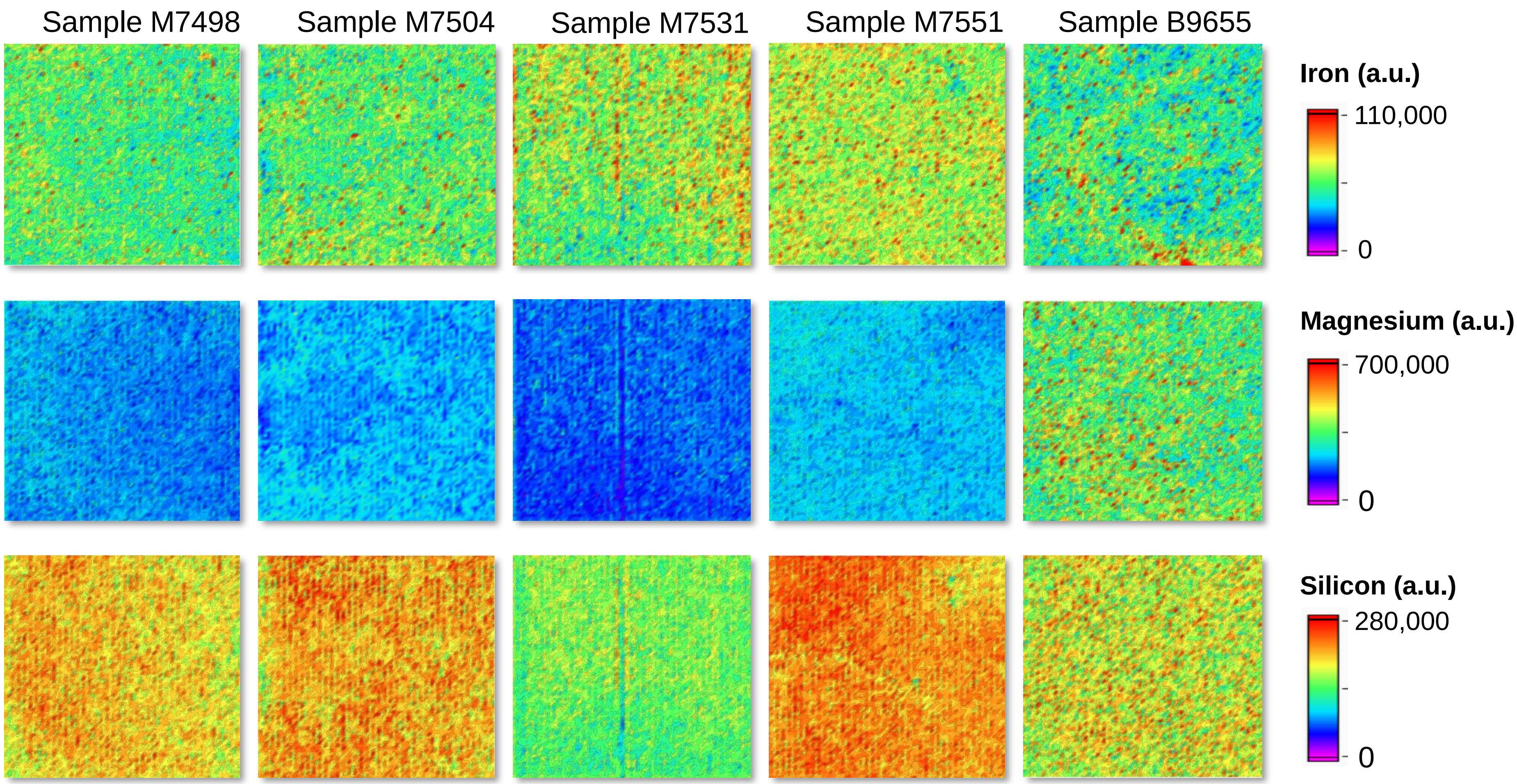


C193, H656, O777, Ca393, Mg280, Al394, Fe275, Si288, Ba493, K766, Sr407, Ti334, Na589

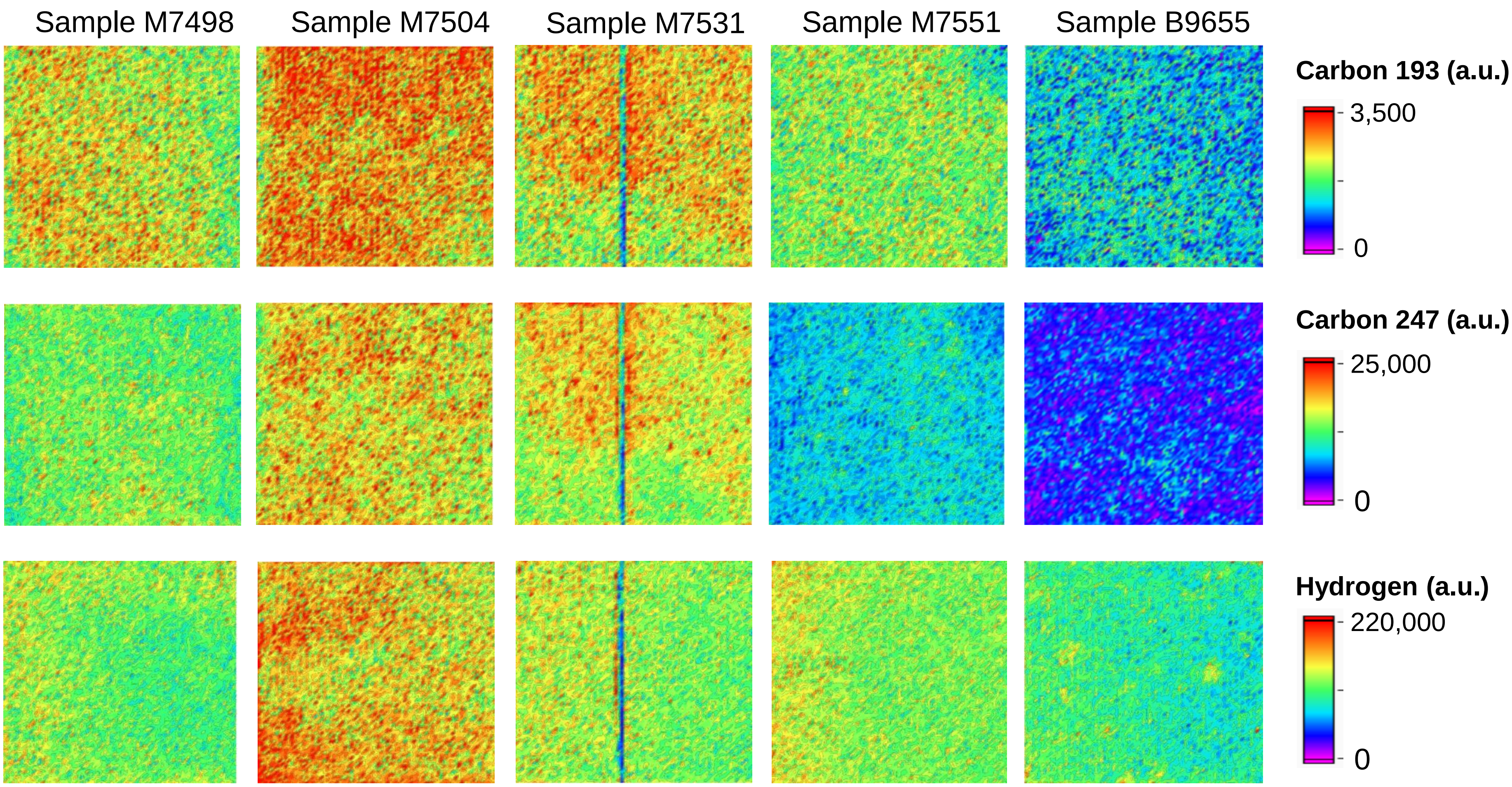
Shale Elemental Maps



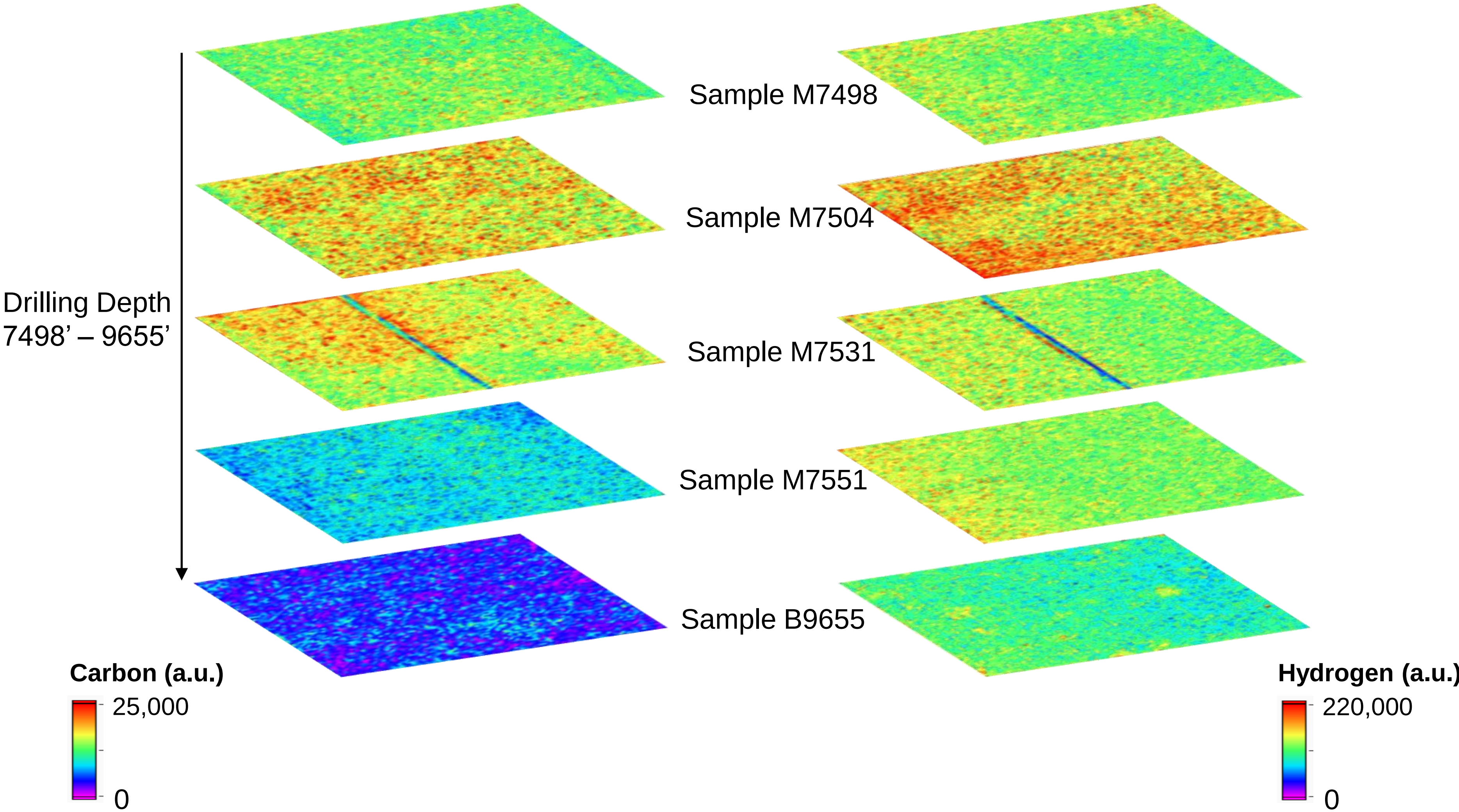
Shale Elemental Maps



Shale Elemental Maps



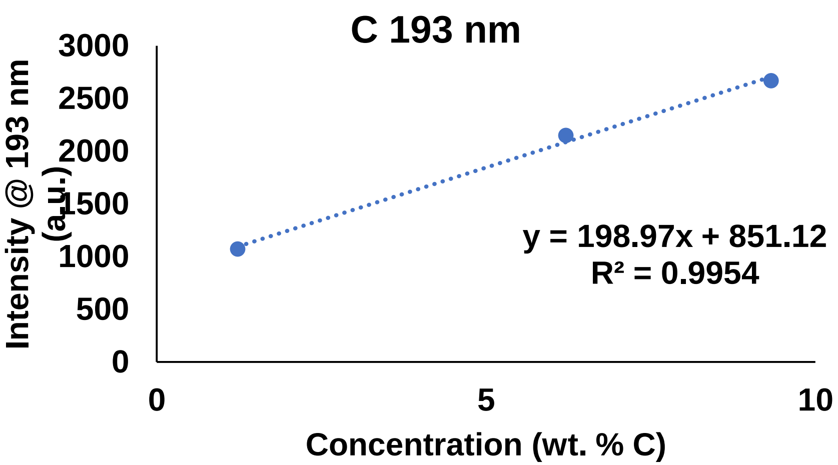
Shale C &H Maps Depth Profile

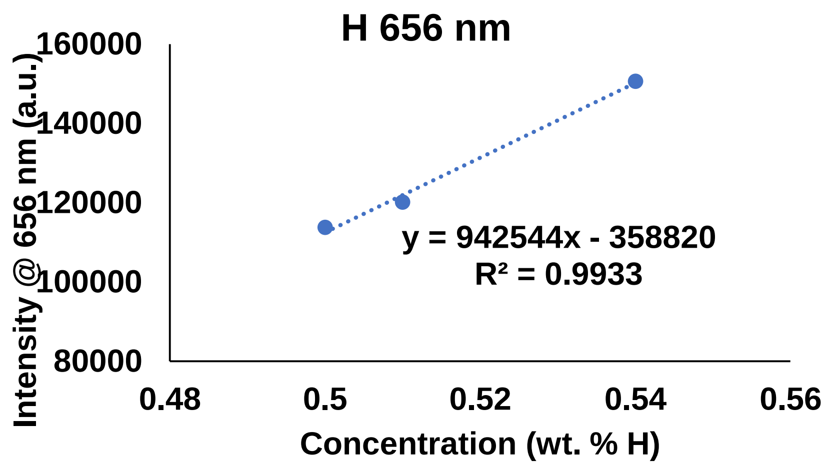


Calibration Standards

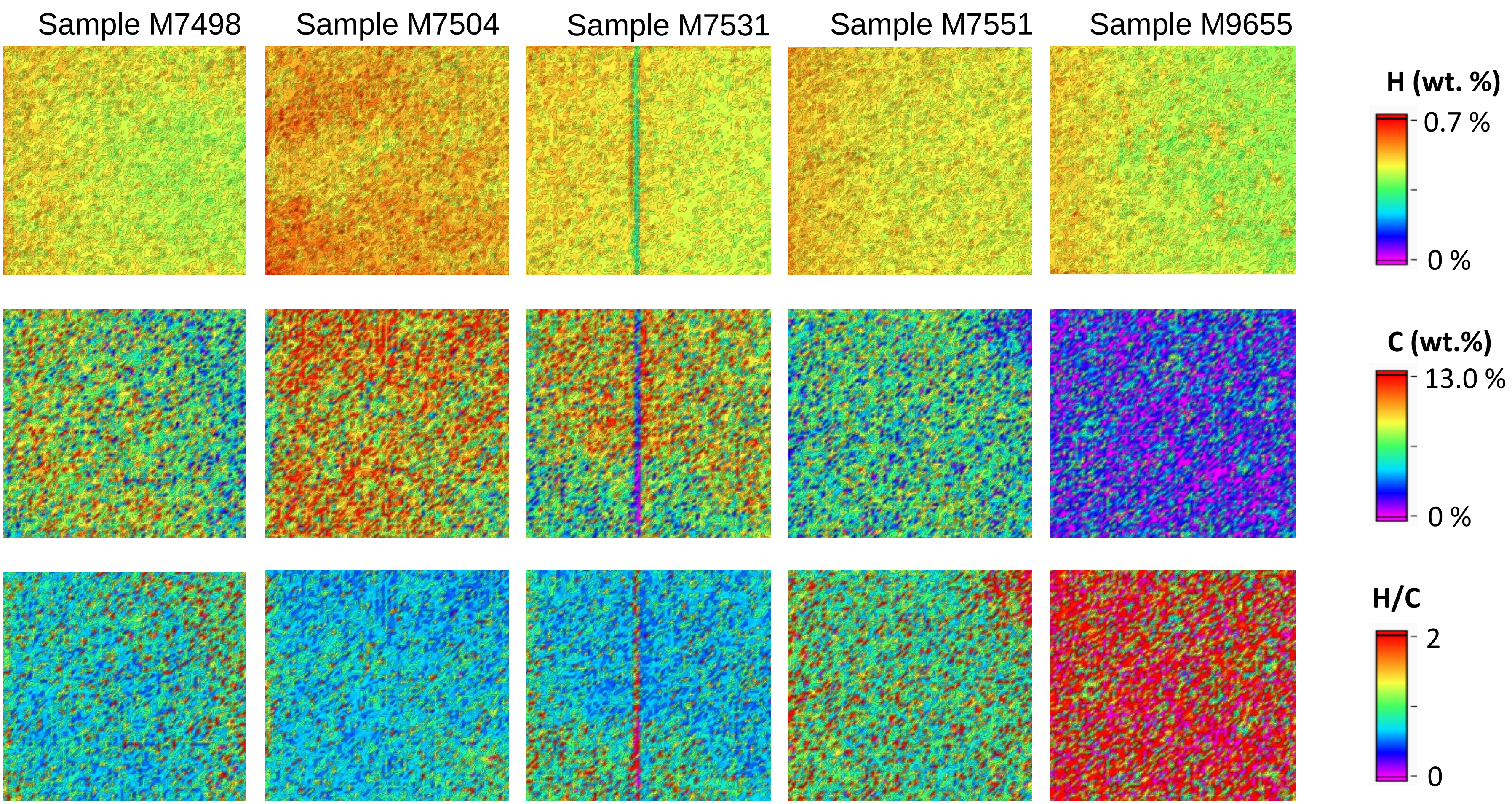
- Availability of matrix matched calibration standards is limited
- Shale samples characterized in our previous study (Spectrochimica Acta B, 122, 2016, 9-14) by ICP-OES and LIBS were used to calibrate the instrument
- C and H analysis was performed at the Western Kentucky University using Leco CHN TrueSpec analyzer
- Calibration standards were mapped along with samples to create calibration curves

Calibration Curves





Concentration Maps



C & H Concentrations

Total concentration of 8 mm x 8 mm area analyzed (n = 6,561)

	C 193	%RSD	H 656	%RSD
M7498	7.13 %	8.4	0.46 %	8.1
M7504	9.26 %	5.1	0.53 %	9.2
M7531	7.93 %	8.1	0.47 %	9.4
M7551	5.89 %	21.0	0.48 %	7.3
B9655	2.39 %	54.0	0.45 %	9.3

	H/C
7498'	0.85
7504'	0.76
7531'	0.84
7551'	1.05
9655'	1.70

H/C < 1 – aromatic
H/C > 1 – aliphatic

	C H N Analyzer	***LIBS***	
	Reference Value	**LIBS**	**% BIAS**
M7504	9.33 wt. % C	9.26 % C	-0.8
M7504	0.51 wt. % H	0.53 % H	3.9

Sample	**TC**	**TOC**	**TOC/TC**
M7498	7.13	4.78	0.67
M7504	9.26	5.92	0.64

Elemental Concentrations

	Depth (')	Al 394	Ca 393	Fe 275	Mg 280	Si 288
		Concentration Average Value (Wt.% ± 1 SD)				
M7498	**7498**	0.71 ± 0.52	1.22 ± 0.20	1.74 ± 0.11	0.65 ± 0.4	21.7 ± 0.99
M7504	**7504**	1.63 ± 0.75	1.53 ± 0.19	1.82 ± 0.11	0.68 ± 0.03	22.6 ± 1.06
M7531	**7531**	0.8 ± 0.29	2.12 ± 0.50	1.99 ± 0.19	0.58 ± 0.04	17.26 ± 1.05
M7551	**7551**	1.67 ± 0.62	3.32 ± 0.48	2.06 ± 0.09	0.70 ± 0.03	23.60 ± 1.05
B9655	**9655**	0.73 ± 0.59	7.67 ± 0.66	1.72 ± 0.14	1.06 ± 0.07	20.09 ± 0.90

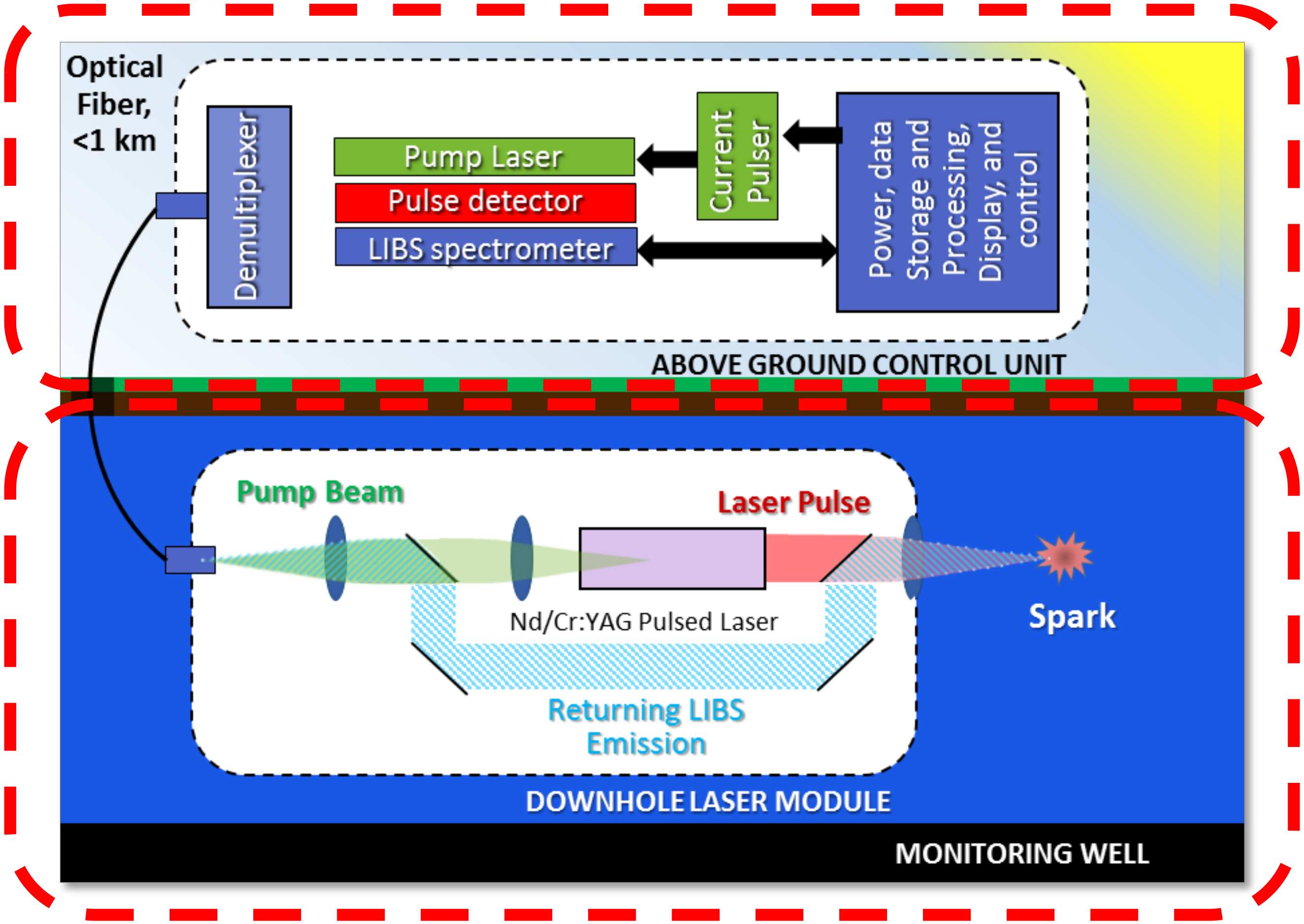
Comparison of XRF and LIBS values (Wt.% ± 1 SD)

Sample		Al	Ca	Fe	Si
M7498	XRF	5.18 ± 0.13	1.60 ± 0.01	3.85 ± 0.03	21.27 ± 0.12
	LIBS	0.71 ± 0.52	1.22 ± 0.20	1.74 ± 0.11	21.7 ± 0.99
M7504	XRF	3.39 ± 0.97	1.48 ± 0.01	2.75 ± 0.02	22.1 ± 0.11
	LIBS	1.63 ± 0.75	1.53 ± 0.19	1.82 ± 0.11	22.6 ± 1.06
M7531	XRF	2.16 ± 0.11	0.84 ± 0.01	3.21 ± 0.03	15.44 ± 0.11
	LIBS	0.8 ± 0.29	2.12 ± 0.50	1.99 ± 0.19	17.3 ± 1.05
M7551	XRF	2.13 ± 0.09	3.21 ± 0.02	3.55 ± 0.03	21.72 ± 0.12
	LIBS	1.67 ± 0.62	3.32 ± 0.48	2.06 ± 0.90	23.6 ± 1.05

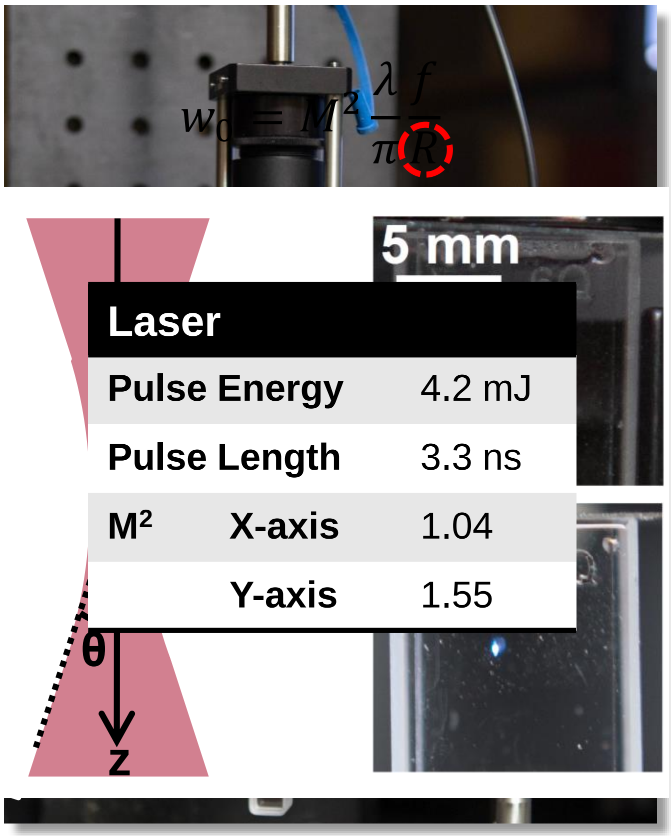
Elements	Calibration Curves
Al	y = 3.698 x + 26528
Ca	y = 61.8 x + 86709
Fe	y = 41.28 x - 16559
Mg	**y = 440.4 x - 86648**
Na	y = 514.6 x + 49061
Si	y = 11.778 x - 52464
Sr	y = 579.7 x - 1871
Ti	y = 231.3 x - 46293

Downhole Deployment

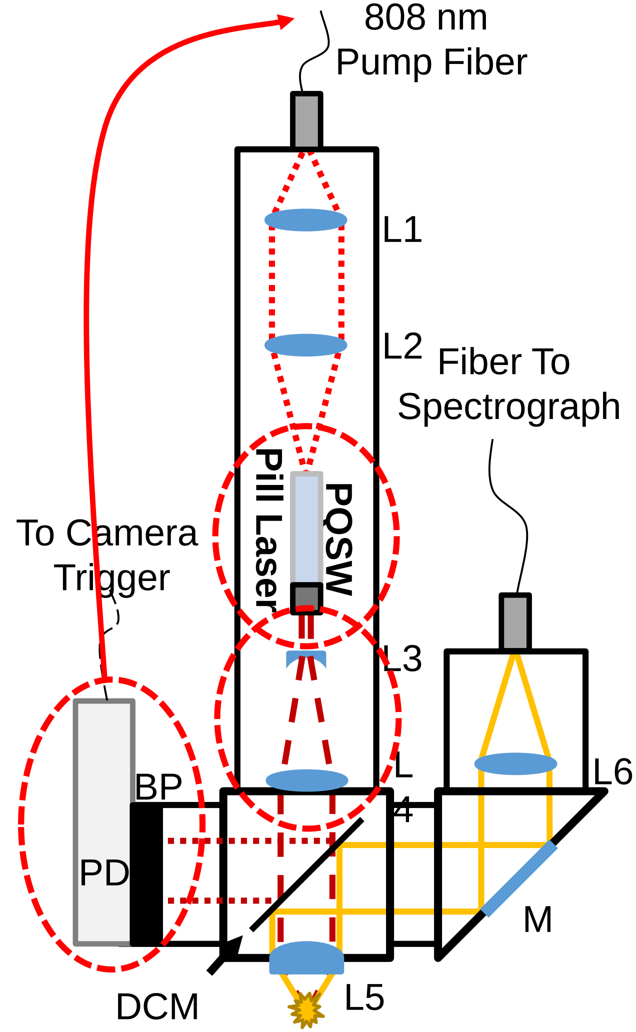
NATIONAL ENERGY TECHNOLOGY LABORATORY



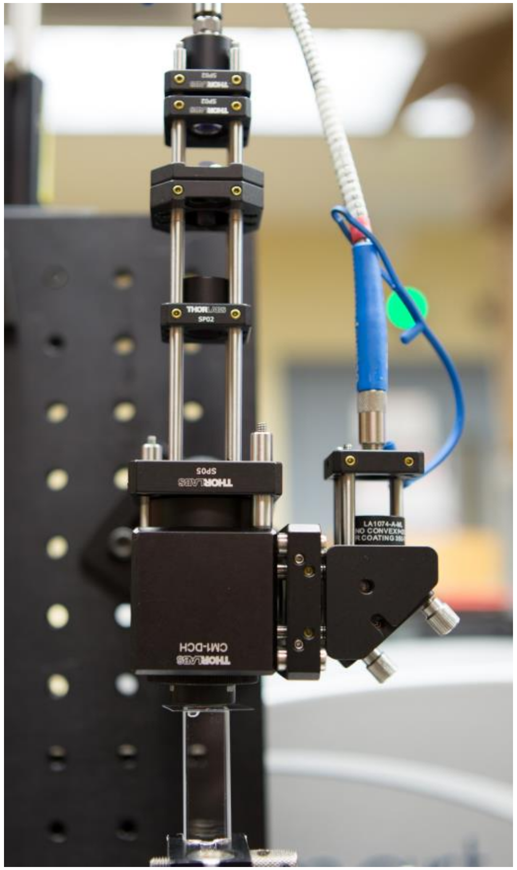
LIBS Prototype Schematic

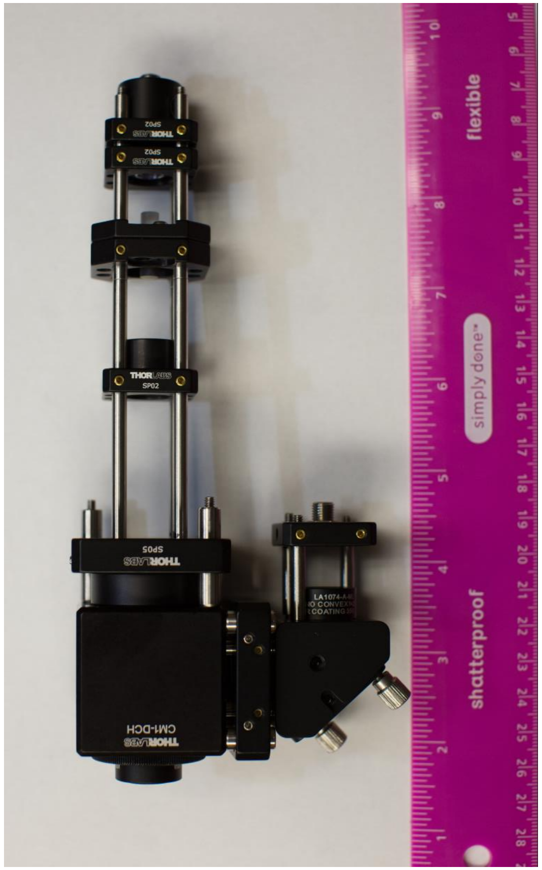


Laser		
Pulse Energy		4.2 mJ
Pulse Length		3.3 ns
M²	**X-axis**	1.04
	Y-axis	1.55



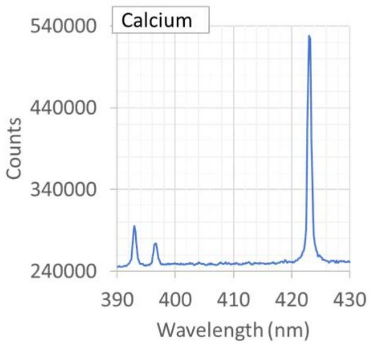
LIBS prototype Sensor head

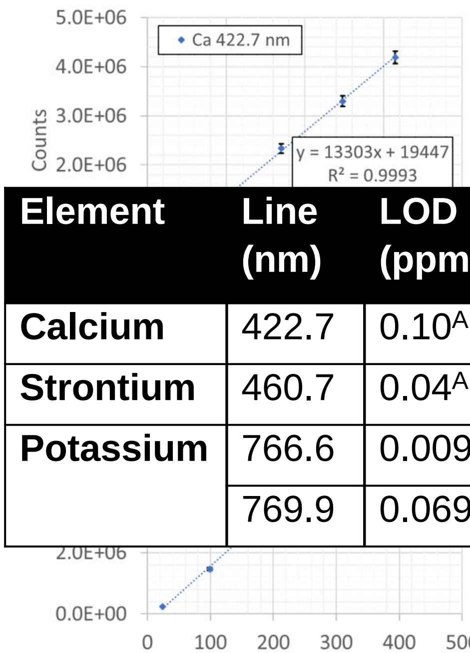




Performance – Alkali / Alkaline Metals

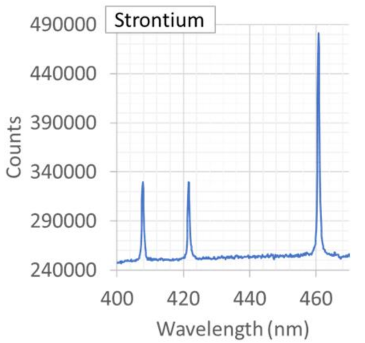
- $CaCl_2$ in DI water
  - 25.1 ppm Ca
  - 450 shots
  - Gate:
    - Delay = 250 ns
    - Width = 3 μs



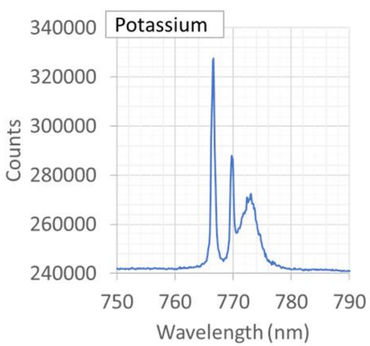


Element	Line (nm)	LOD (ppm)	LOD (literature) (ppm)		
Calcium	422.7	0.10[A]	0.94[B]	0.047[C]	0.13[E]
Strontium	460.7	0.04[A]	2.89[B]		
Potassium	766.6	0.009[A]	0.03[B]	0.006[D]	1.2[F]
	769.9	0.069[A]			

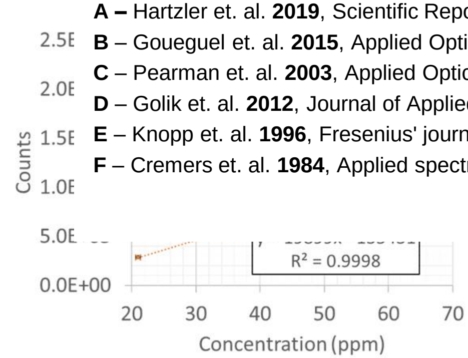
- $SrCl_2$ in DI water
  - 24.1 ppm Sr
  - 450 shots
  - Gate:
    - Delay = 300 ns
    - Width = 3 μs



- KCl in DI water
  - 5.2 ppm K
  - 450 shots
  - Gate:
    - Delay = 300 ns
    - Width = 3 μs



A – Hartzler et. al. **2019**, Scientific Reports, Vol. 9, 4430
B – Gougeguel et. al. **2015**, Applied Optics, Vol. 54, 6071-6079
C – Pearman et. al. **2003**, Applied Optics, Vol. 42, 6085-6093
D – Golik et. al. **2012**, Journal of Applied Spectroscopy, Vol. 79, 471-476
E – Knopp et. al. **1996**, Fresenius' journal of analytical chemistry, Vol. 355, 16-20
F – Cremers et. al. **1984**, Applied spectroscopy, Vol. 38, 721-729



Conclusions

- Laser induced Breakdown Spectroscopy (LIBS) can provide mineral composition and distribution in shale
- The technique provides accurate data with reasonable detection limits for most of the elements
- It can analyze light elements including C and H.
- LIBS can determine H/C ratio to predict the presence and type of gaseous hydrocarbons and impurities in scanned area
- Minimum to no sample preparation makes this technique an attractive option to avoid lengthy sample preparation procedures
- LIBS can be a robust device for in-situ shale core mapping and exploration purposes

Acknowledgment

This work was performed in support of the US Department of Energy's Fossil Energy Crosscutting Technology Research Program. Research performed by Leidos Research Support Team staff was conducted under the RSS contract 89243318CFE000003.

Disclaimer