Laser Induced Breakdown Spectroscopy (LIBS): A Potential Technique for in-situ Geochemical Characterization of Gas-Producing Shales

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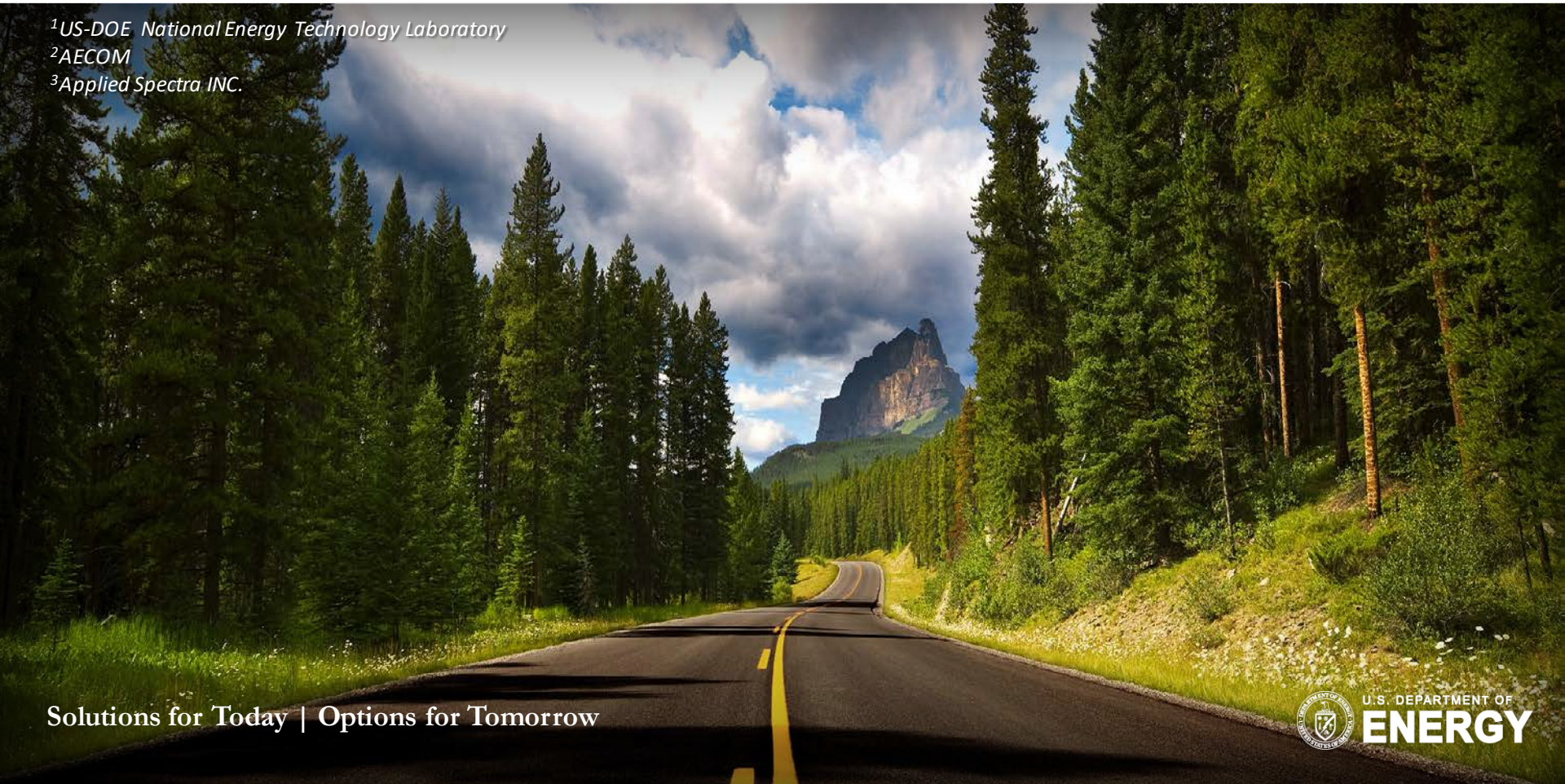
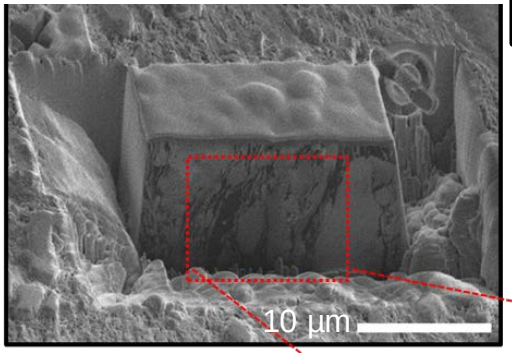


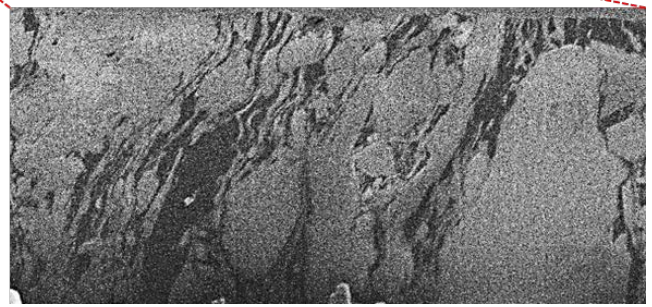
Solutions for Today | Options for Tomorrow

U.S. DEPARTMENT OF ENERGY

Unconventional Shale

- **Fine grained**
  - < 2 microns
- **High Clay Content**
  - Generally > 50%
- **High Organic Content**
- **Low Permeability**
  - Nano-Darcy
- **Hydrocarbon Generation**
- **Susceptible to hydraulically induced fractures**
  - E.g. generally behaves in a brittle manner





Circe Verba, *2017*

Core Samples – Marcellus Shale Energy and Environmental Laboratory

- **Marcellus Well drilled in Morgantown, West Virginia in 2015**
  - Purpose:
    - Provide a stable source of natural gas to the city of Morgantown
    - Give researchers access to a highly instrumented and technologically advanced production well
    - Cradle to grave access to all data
  - Consists of one scientific monitoring well and 4 production wells
  - Approximately 100 feet of vertical core used in this study came from well MIP-3H
    - 7440 to 7514 feet depth

XRF in Use at NETL

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Benefits

Portable

High spatial resolution

Reproducibility

Ease of Use

Low Cost

Limitations

Core/Rock/Material must be at surface temperature and pressure for measurement

Material needs to be a semi-solid to solid and generally dry

Requires planar surface to prevent energetic losses

Mode selection limits which elements are reported

Low atomic mass and high atomic mass elements are not measureable

Laser Induced Breakdown Spectroscopy

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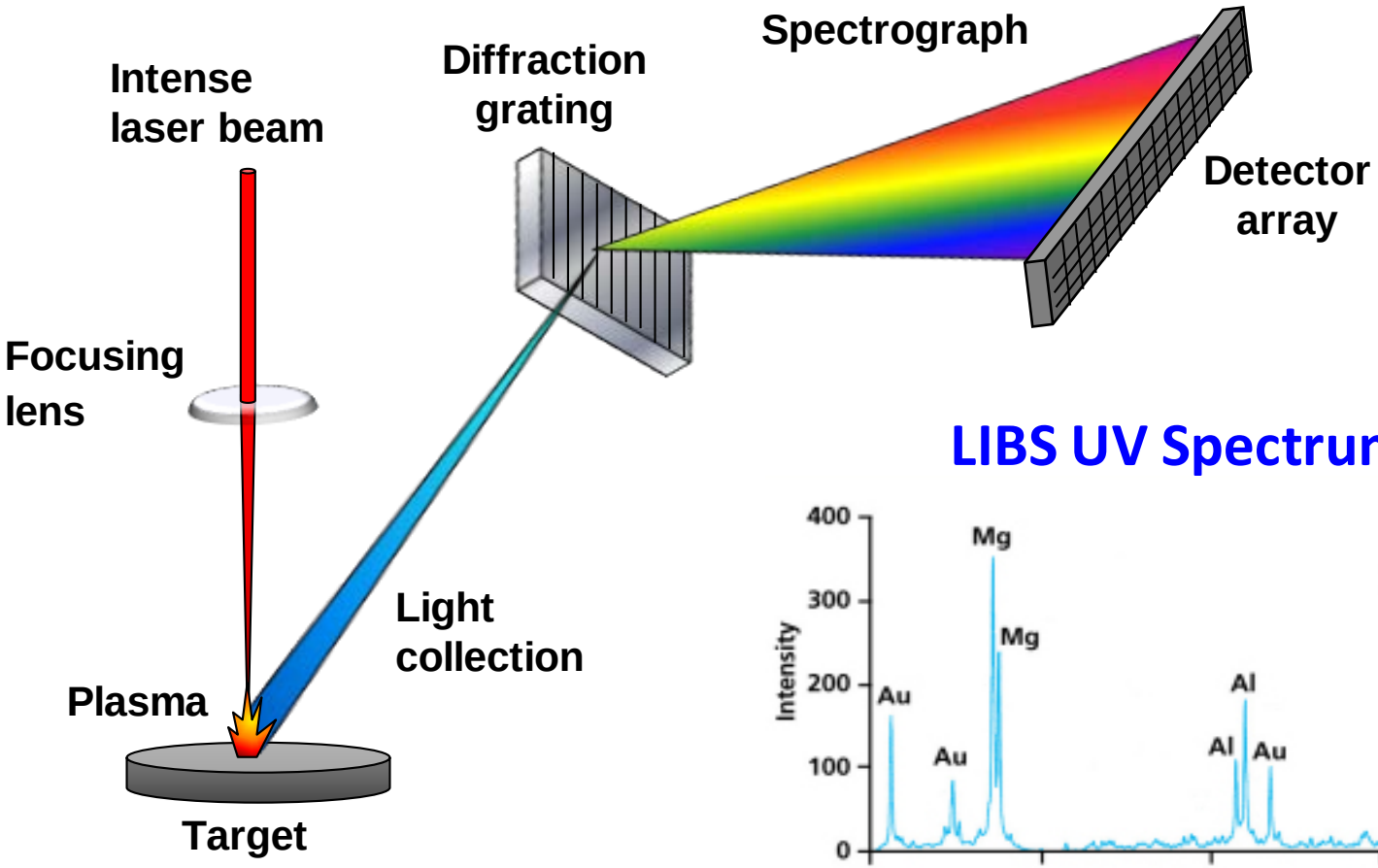
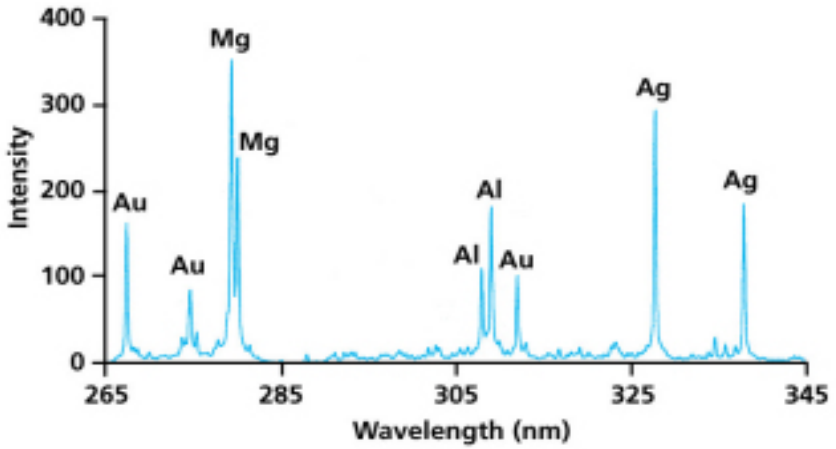
- **Laser is fired upon a given sample and laser energy focused to a small spot**
- **A hot luminous plasma vaporizes the material, and leads to atomization and excitation of elements**
- **As plasma cools, emission occurs and the emitted light can be collected**
- **Every element in the Periodic Table 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)
- **Flexibility of probe design, and use of fiber optics make it a suitable for real-time and stand-off measurements in harsh conditions and at hard to reach places.**

Principle of LIBS



LIBS UV Spectrum



LIBS Instrument & Method parameters

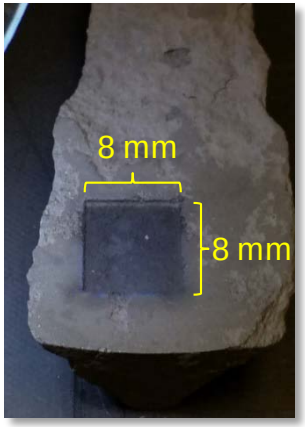
- **Experimental Conditions**
  - 266 nm Nd:YAG nanosecond laser
  - 50 um laser spot size
  - 81 x 81 grid pattern map
  - 8 X 8 mm (64 mm2)
  - 5 shots per location – Accumulated
  - 6561 data points per map
  - ~ 390 minutes per map

J 200 Applied Spectra LIBS system

Shale samples Analyzed

PARA2 7498

PARA1 7504



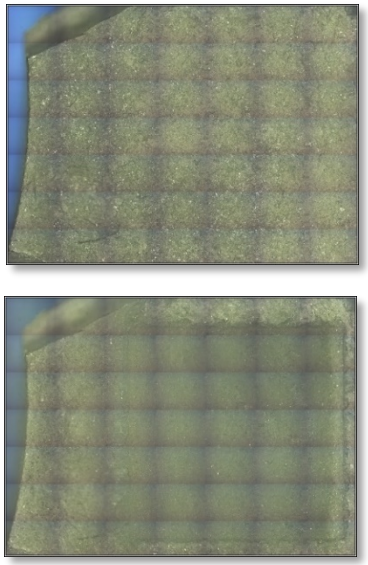
MSEEL 7531

MSEEL 7551

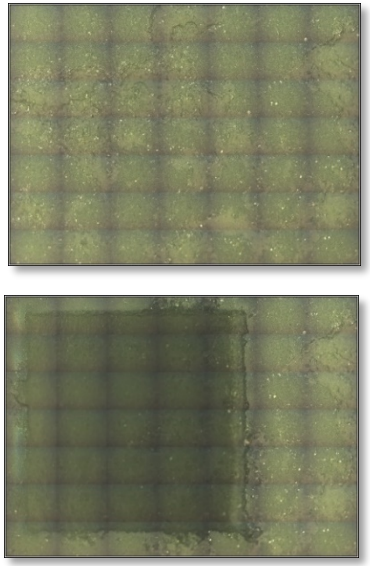
Bakken 9655

Shale Samples Analyzed

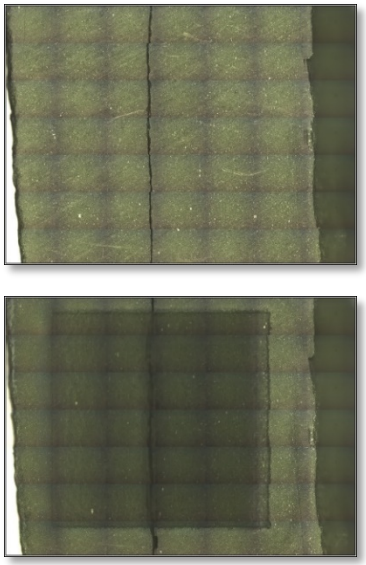
PARA2 7498



PARA1 7504



MSEEL 7531



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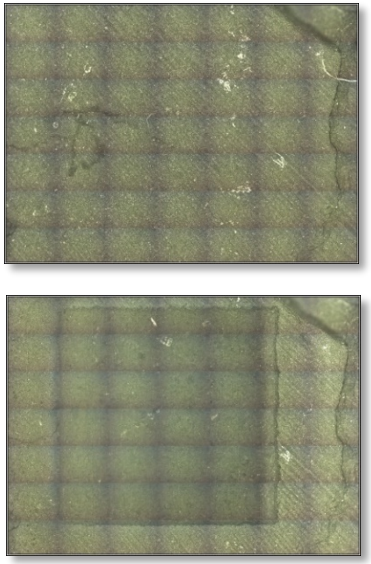
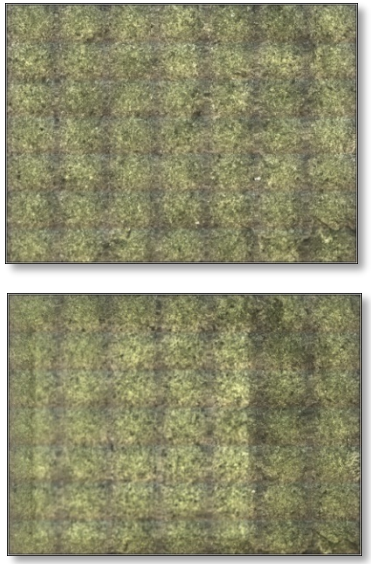
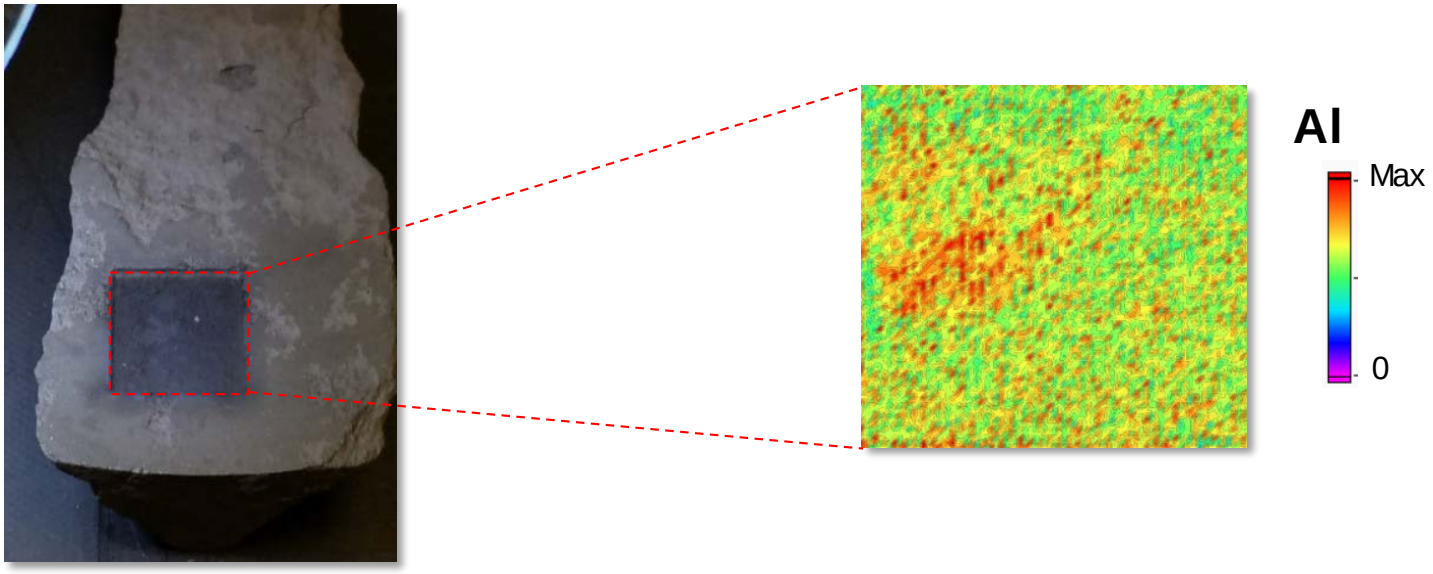


Bakken 9655

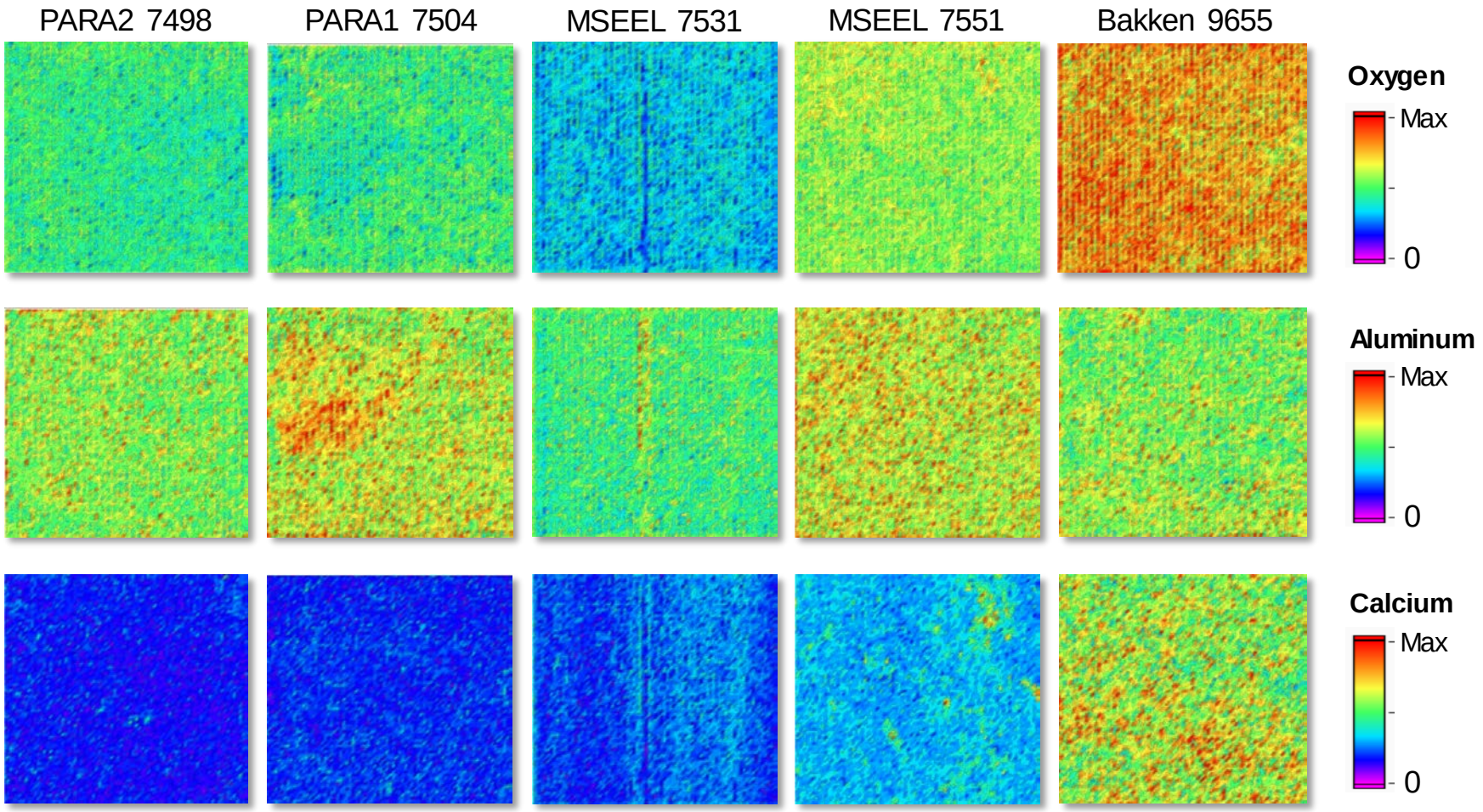


Shale Sample Mapped Area

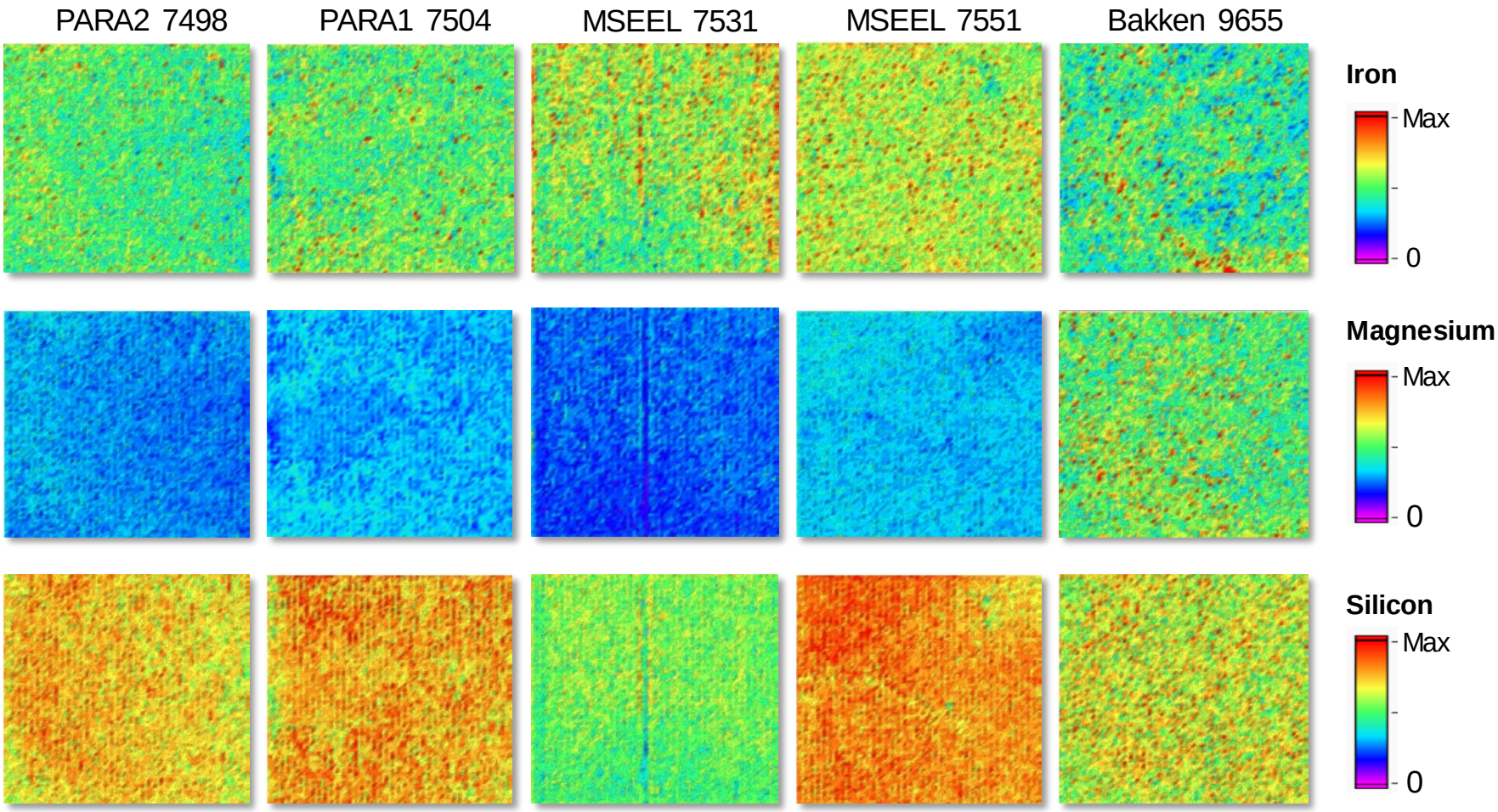


C, H, O, Ca, Mg, Al, Fe, Si

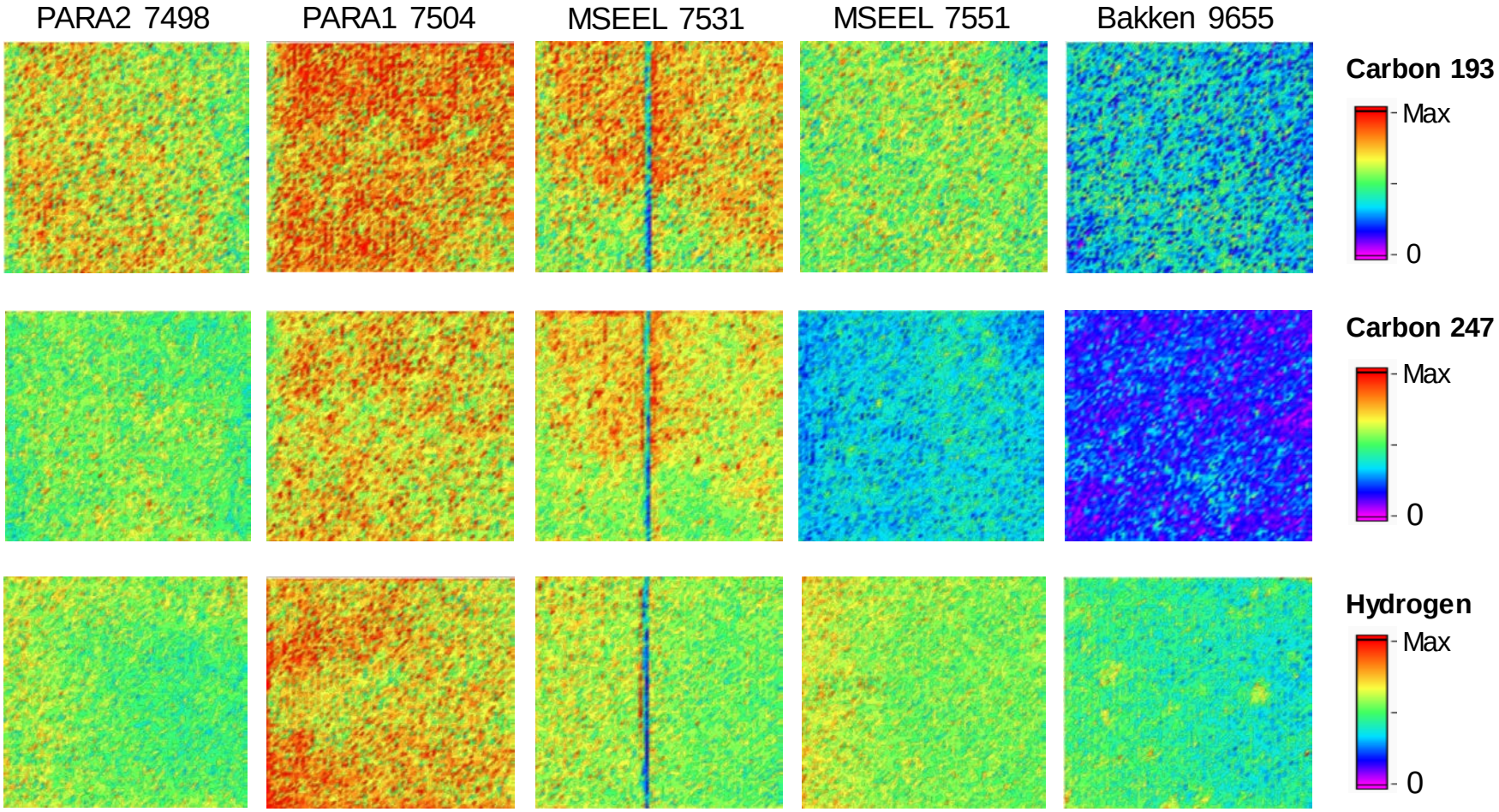
Shale Elemental Maps



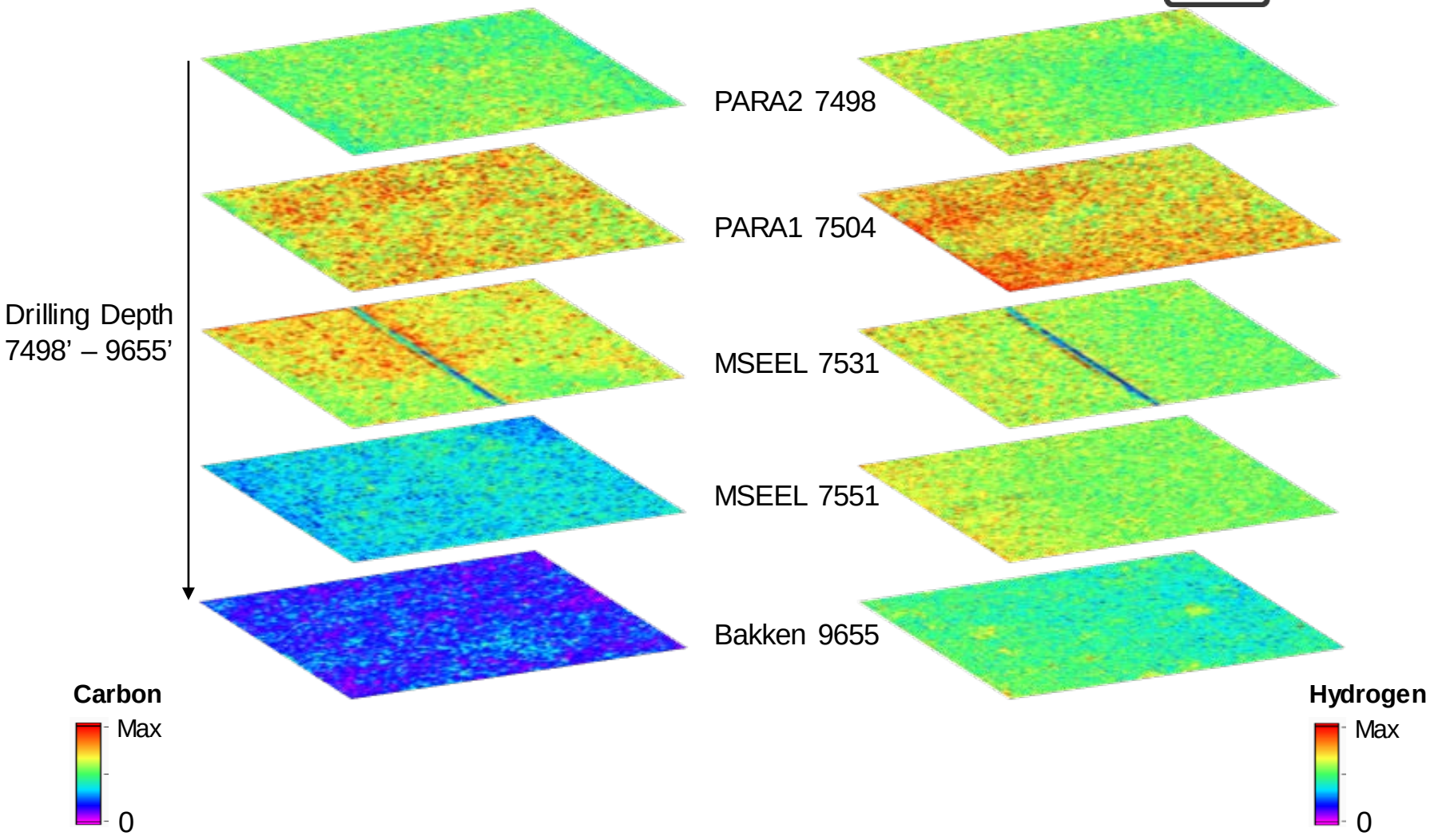
Shale Elemental Maps



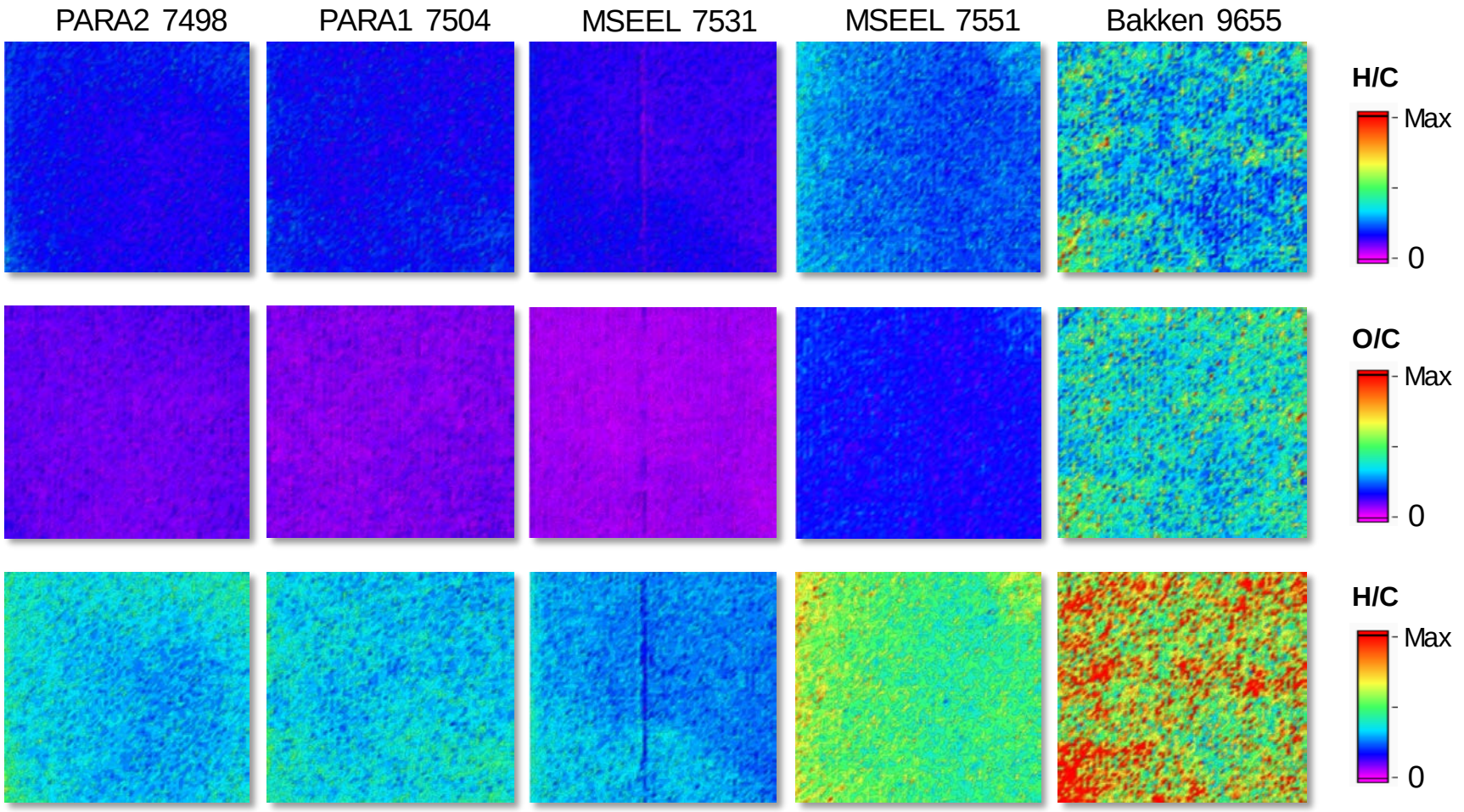
Shale Elemental Maps



Shale C &H Maps Depth Profile



Shale Maps Elemental Ratios



Elemental Concentrations

		Concentration Average Value (ppm)									
	Depth (')	Al 394	Ca 393	Ba 493	Fe 275	K 766	Mg 280	Si 288	Sr 407	Ti 334	Na 589
PARA2 7498	7498	708	1215	80	1741	2970	648	21647	11	312	267
PARA1 7504	7504	1634	1531	82	1816	2999	677	22573	9	314	295
MSEEL 7531	7531	75	2118	86	1986	2975	579	17262	8	279	238
MSEEL 7551	7551	1667	3316	77	2058	2999	703	23603	9	346	268
Bakken 9655	9655	728	7671	90	1716	3034	1057	20094	9	315	361

	Concentration Average Value (ppm ± 1 SD)					
	Depth (')	Al 394	Ca 393	Fe 275	Mg 280	Si 288
PARA2 7498	7498	708 ± 520	1215 ± 199	1741 ± 113	648 ± 35	21647 ± 991
PARA1 7504	7504	1634 ± 754	1532 ± 192	1816 ± 108	678 ± 32	22573 ± 1063
MSEEL 7531	7531	75 ± 286	2118 ± 504	1986 ± 190	579 ± 42	17262 ± 1053
MSEEL 7551	7551	1667 ± 624	3316 ± 477	2058 ± 91	703 ± 28	23603 ± 1045
Bakken 9655	9655	728 ± 596	7671 ± 660	1716 ± 138	1057 ± 72	20094 ± 902

	%RSD				
	Depth (')	Al 394	Ca 393	Fe 275	Mg 280	Si 288
PARA2 7498	7498	73.4	16.4	6.5	5.5	4.6
PARA1 7504	7504	46.2	12.5	6.0	4.8	4.7
MSEEL 7531	7531	379.4	23.8	9.6	7.3	6.1
MSEEL 7551	7551	37.4	14.4	4.4	4.0	4.4
Bakken 9655	9655	81.8	8.6	8.0	6.8	4.5

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

Conclusions

- Laser induced Breakdown Spectroscopy (LIBS) can provide mineral composition and distribution in shale
- **It can analyze light elements including C and H.**
- LIBS can determine C/H ratio to predict the presence and type of gaseous hydrocarbons in scanned area
- **Minimum to no sample preparation makes this technique an attractive option for field measurements**
- LIBS can be a suitable technique for analysis in harsh environments and can provide a robust sensing device for in-situ shale core mapping and exploration purposes

Acknowledgment

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