Applications of Laser Induced Breakdown Spectroscopy (LIBS) in Elemental Analysis of varied Materials

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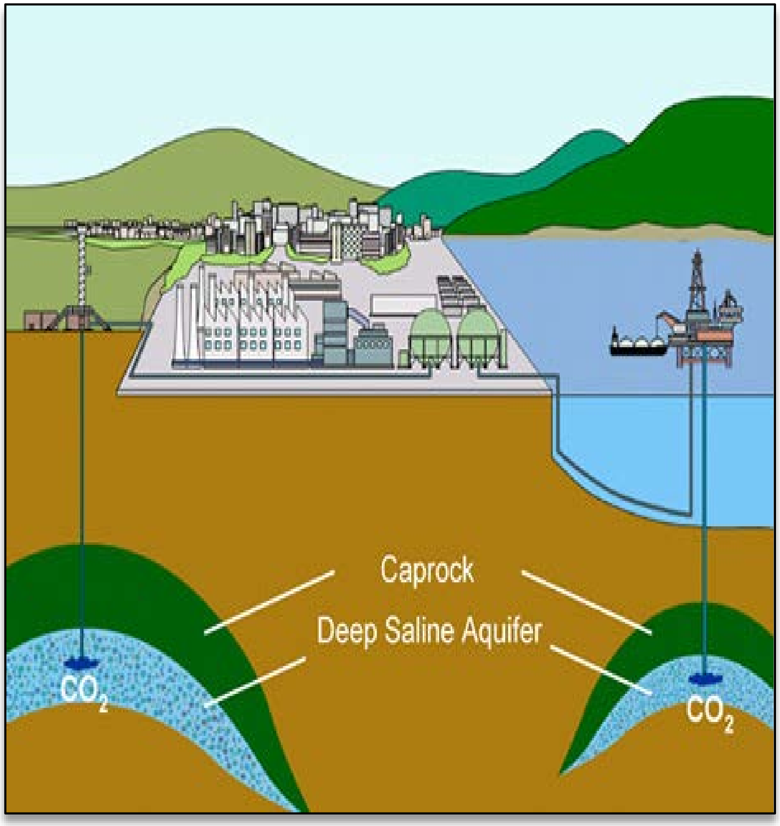
Solutions for Today | Options for Tomorrow

Outline

- LIBS overview
- Applications
  - Carbon sequestration
  - Rare Earth Elements
  - Oil and gas shales
- Isotope measurement
- Online measurement
- Conclusions

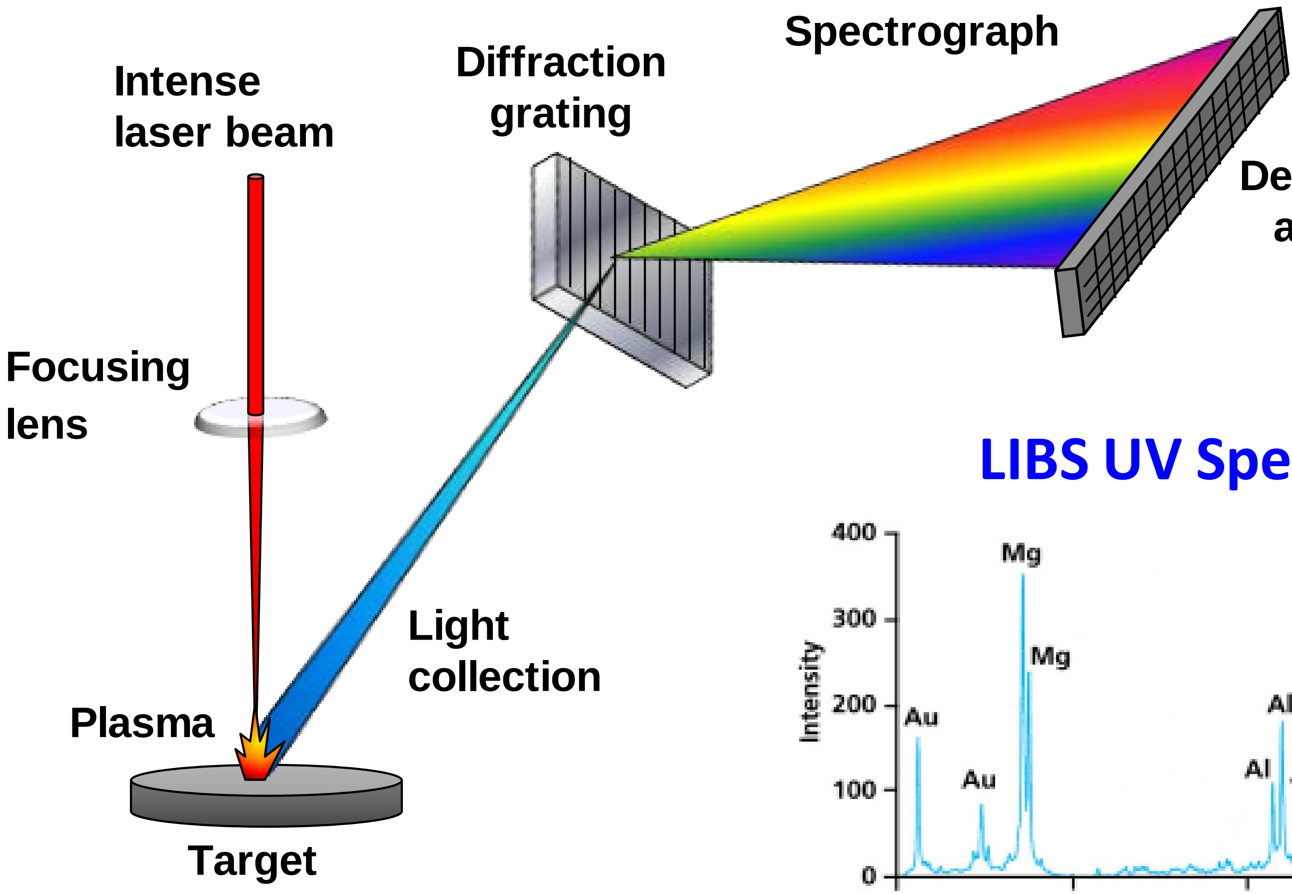


Laser Induced Breakdown Spectroscopy

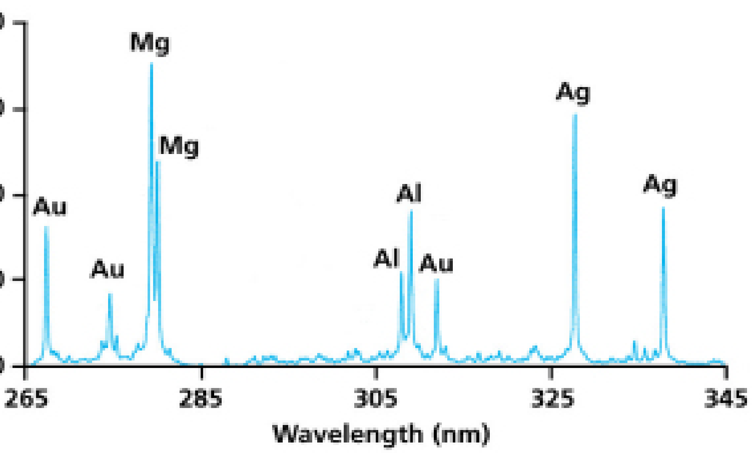
- Laser is fired upon a given sample and laser energy focused to a small spot
- A hot luminous plasma vaporizes the material, and leads to atomization and excitation of elements
- As plasma cools, emission occurs and the emitted light can be collected
- Every element in the Periodic Table gives off light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



Analysis on Soil Samples

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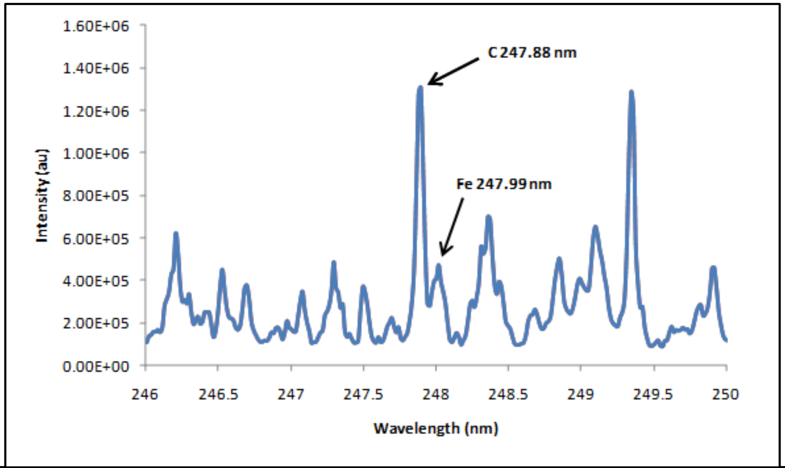
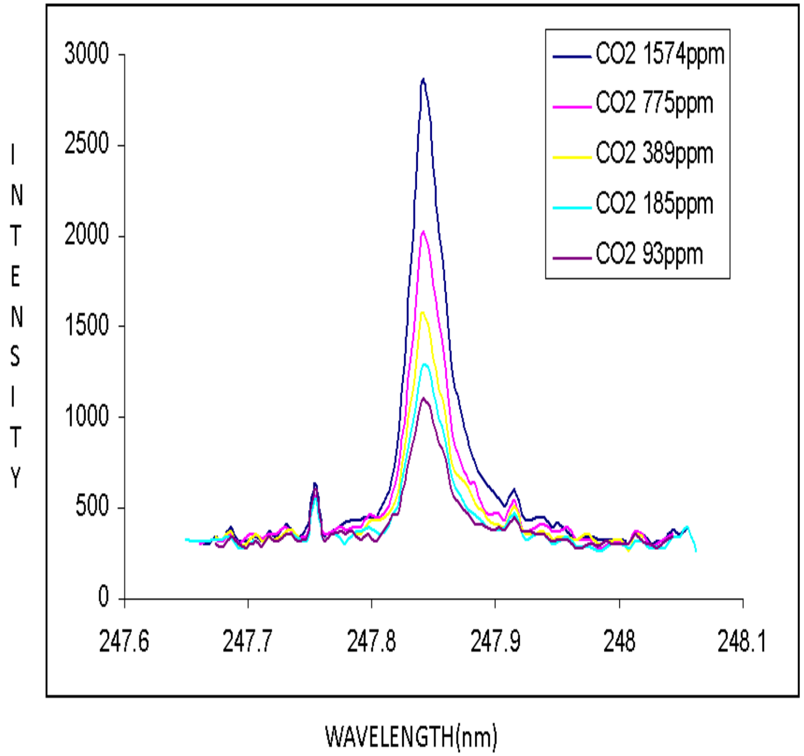
- **Total Carbon Measurement in Soil**



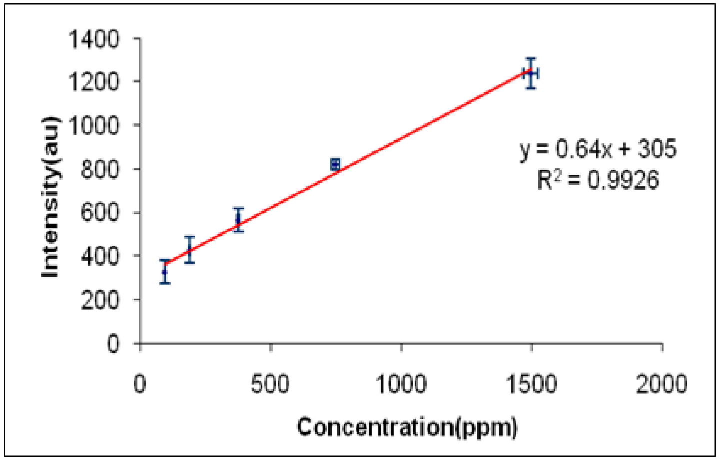
Sample	Carbon analyzer Value (wt. %)	LIBS value (wt. %)			
		SLR Model	RA%	MLR Model	RA%
1	2.43±0.05	2.49±0.44	2.41	2.54±0.43	4.47
2	3.74±0.04	3.76±0.42	0.58	3.55±0.62	5.14
3	5.22±0.14	5.40±0.69	3.31	5.13±0.55	1.72
4	6.88±0.18	6.53±0.49	4.98	6.96±0.31	1.28
5	8.31±0.07	8.50±0.84	2.33	8.38±0.70	0.86

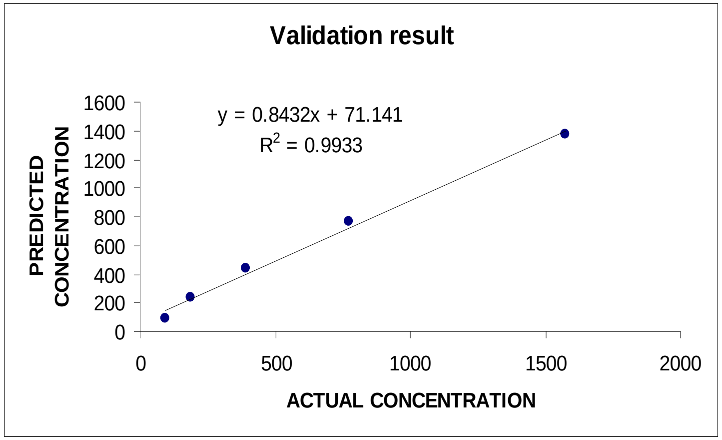
Analysis on Gas Samples

- **CO_2 Measurement in Air**



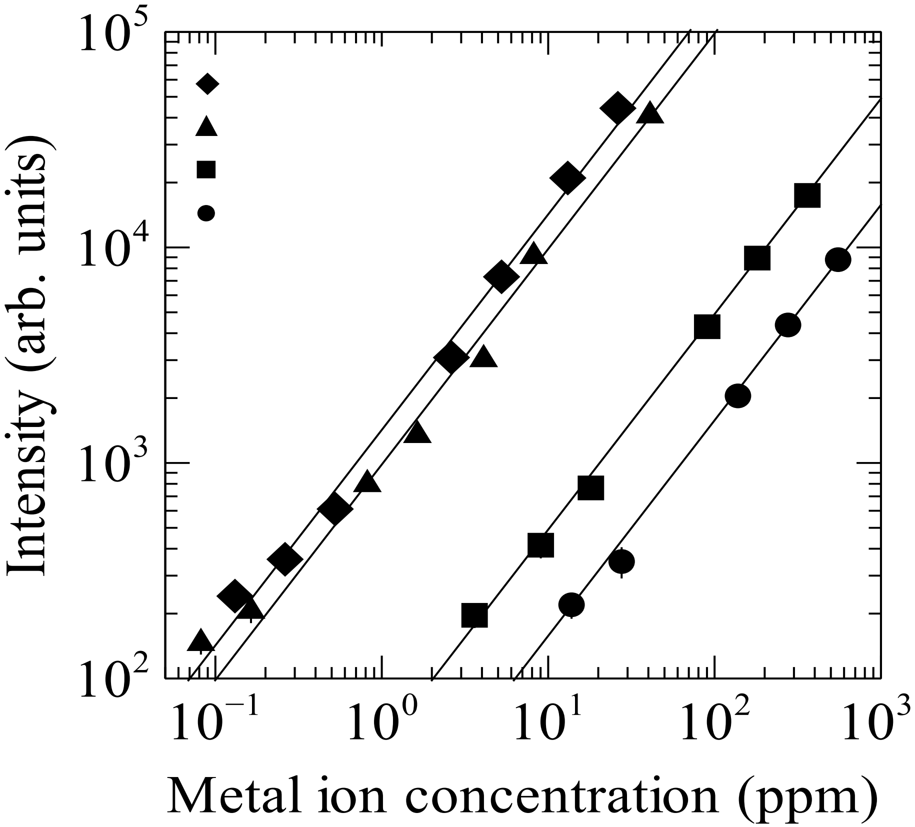
Calibration Curve





Underwater Analysis of Metal Ions (cont.)

- **Calibration Curves, Detection Limits, and Quantification Limits of K+, Li+, Ca_2+, and Sr_2+**

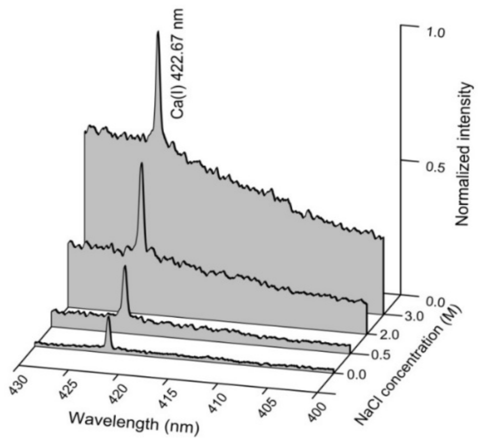


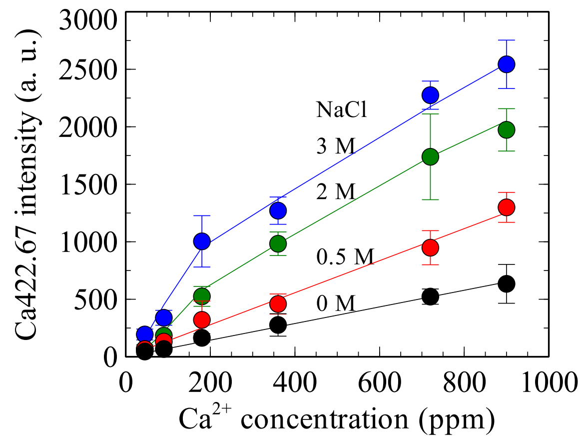
	R^2	DL	QL
Sr^{2+}	0.9990	2.89±0.11 ppm	9.63±0.39 ppm
Ca^{2+}	0.9997	0.94±0.14 ppm	3.11±0.07 ppm
Li^+	0.9988	60±2 ppb	0.19±0.01 ppm
K^+	0.9977	30±1 ppb	80±4 ppb

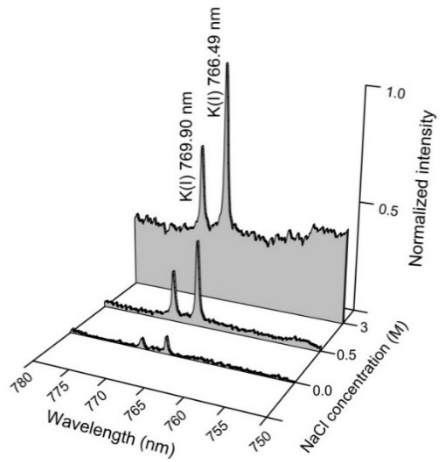
Easily ionized elements were detected in the ppb range, whereas elements with emission originating at higher energy levels were detected in the low ppm range

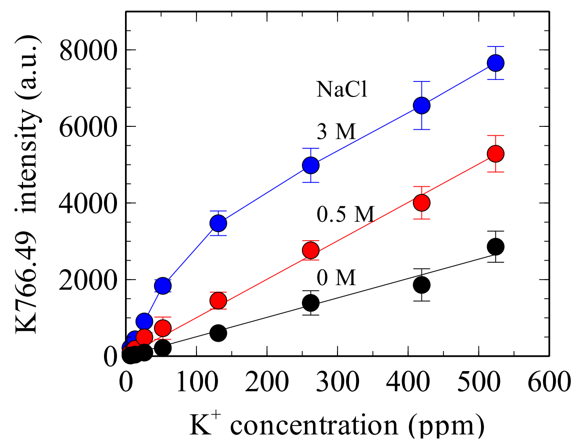
Underwater Analysis of Metal Ions (cont.)

- **Evaluating NaCl-induced Matrix Effects**



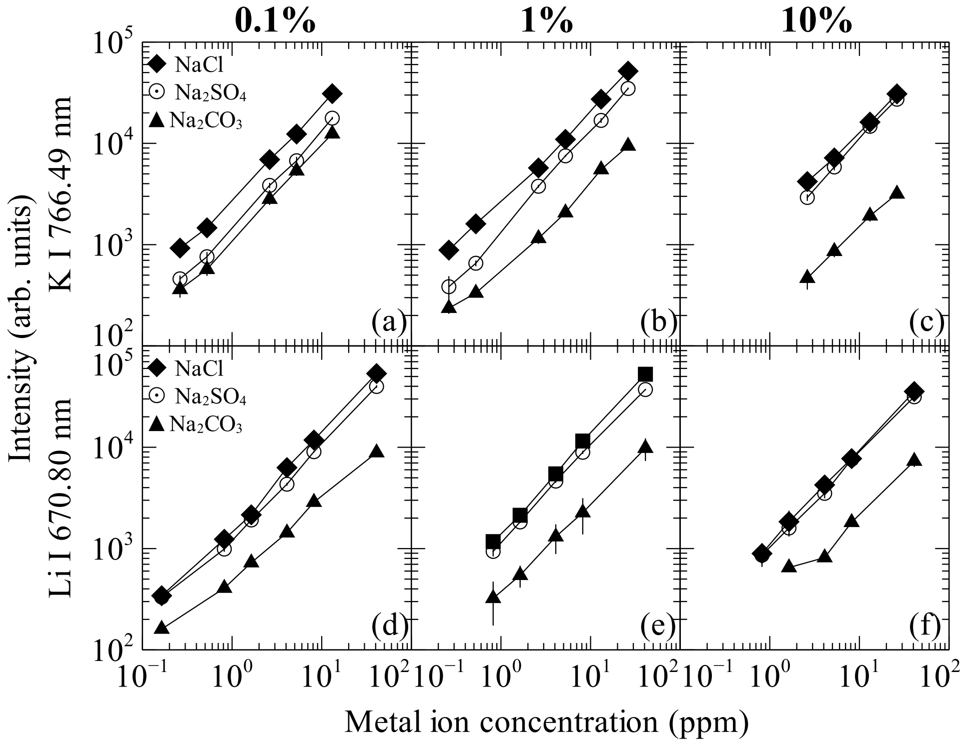


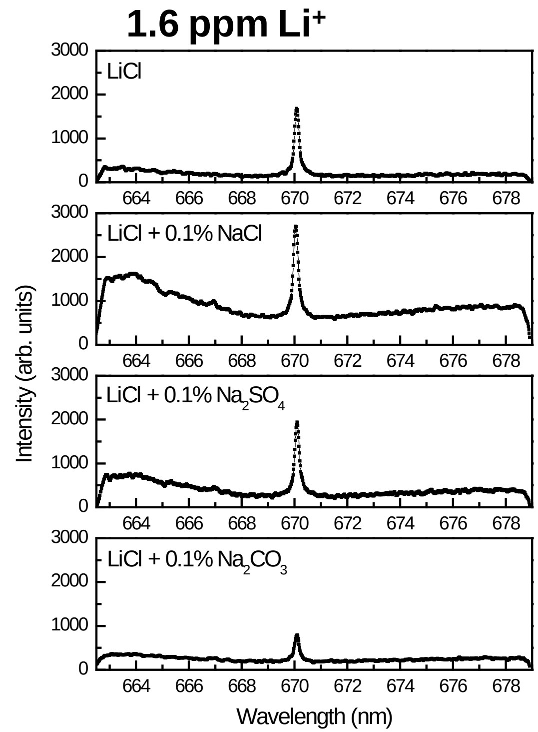




Underwater Analysis of Metal Ions (cont.)

- **Comparing Matrix Effects Induced by Common sodium compounds: NaCl, Na_2SO_4, and Na_2CO_3**





  - Increase in sodium compounds (from 0.1, 1, to 10 wt.%) affect detection of the elements
  - Must be accounted for with all measurements (Example: use of an internal standard)

High CO_2 Pressure Measurements (cont.)

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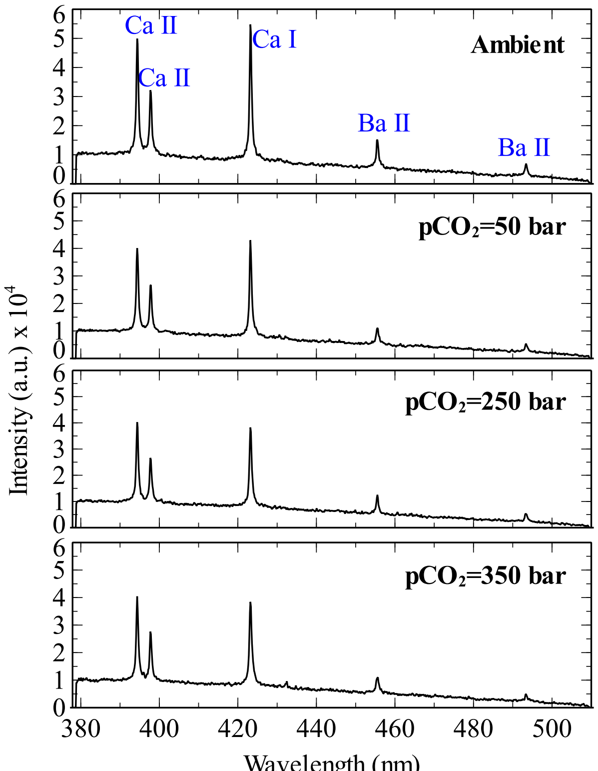
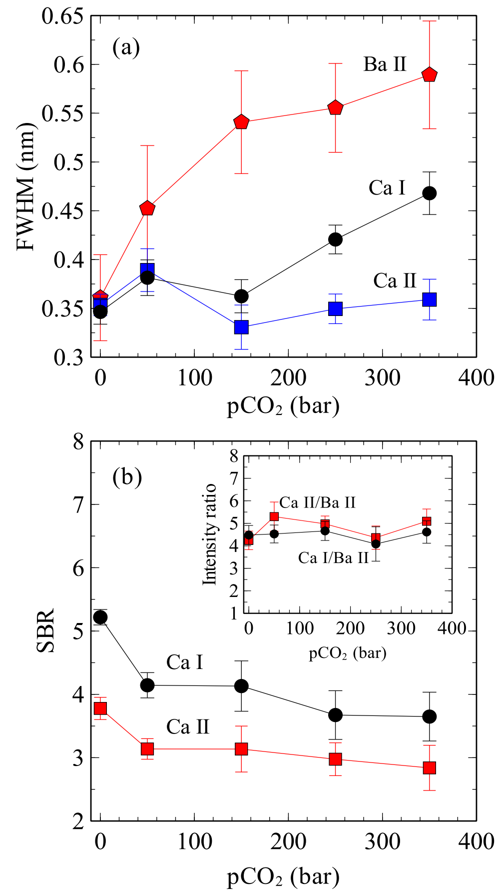
- **Effects of CO_2 Pressure on LIBS Spectra**



Strong and well-resolved spectral lines of Ca^{2+} and Ba^{2+} cations obtained in CO_2-saturated water over 50–350 bar



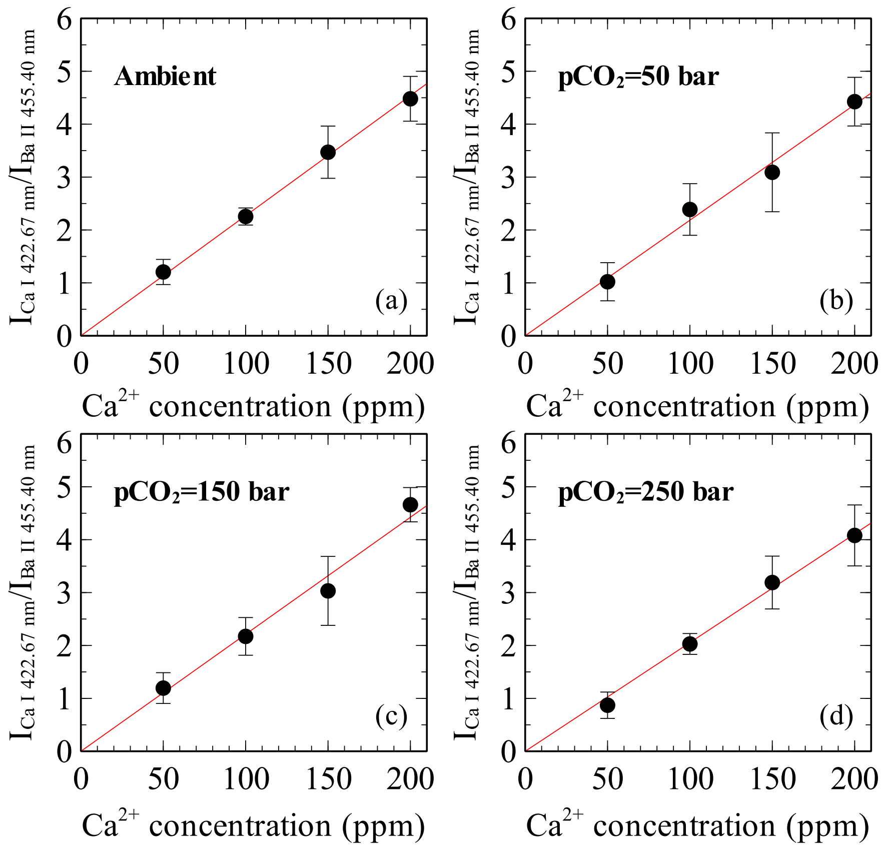
Pressure-induced line broadening:

20–37% increase of the full at width half maximum (FWHM) for Ca I and Ba II lines

CO_2 pressure has minimal adverse effects on the signal-to-background ratio (SBR), other than a small decrease at 350 bar

High CO_2 Pressure Measurements (cont.)

- **Calcium Calibration Curves and Detection Limits**



pCO_2 (bar)	R^2	DL (ppm)
Ambient	0.9997	7.35 ± 0.4
50	0.9977	9.21 ± 0.3
150	0.9962	9.37 ± 0.5
250	0.9988	9.03 ± 0.8
350	0.9994	9.58 ± 0.3

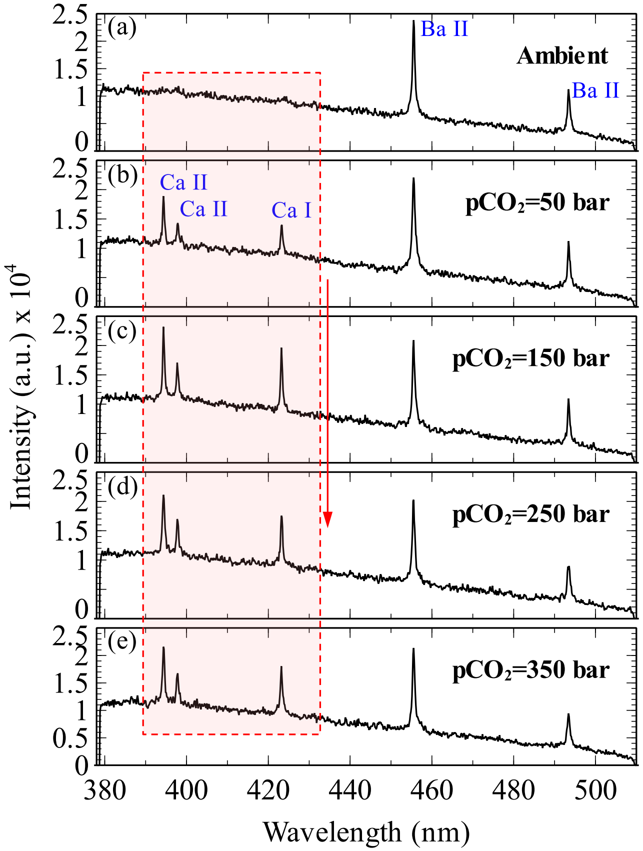
Increasing CO2 pressure over the range 50–350 bar has little effects on calcium detection limit (DL), which was estimated to **be about 9 ppm.**

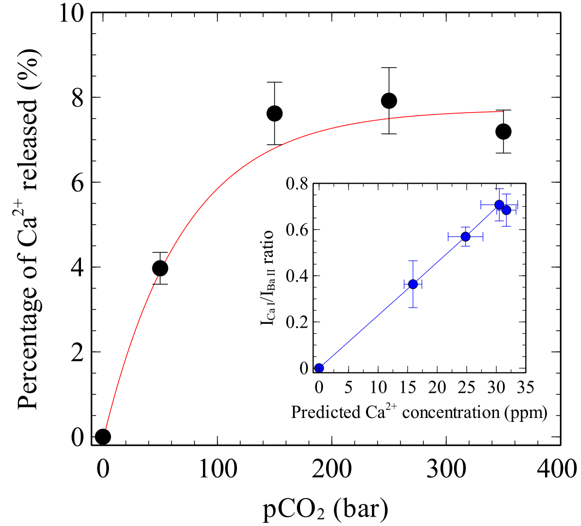
High CO_2 Pressure Measurements

- **Application: In-situ Measurements of $CaCO_3$ Dissolution as a Function of Rising CO_2 Pressure**

Pressed pellet of $CaCO_3$ powder (99.999%, trace metals basis) was introduced into a solution of 1 mM $BaCl_2{\cdot}2H_2O$

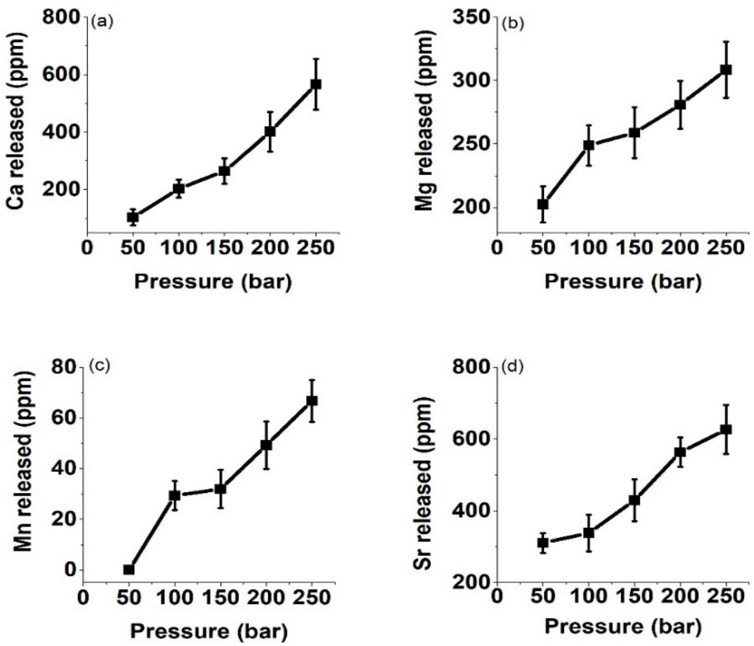
Measurements are based upon mass transport of dissolved Ca^{2+} by diffusion away from the liquid–carbonate boundary

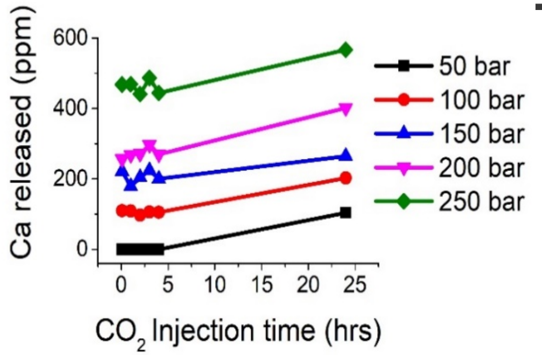


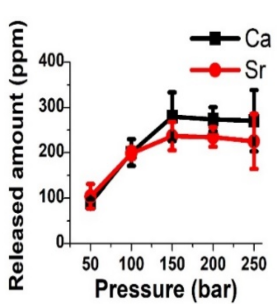


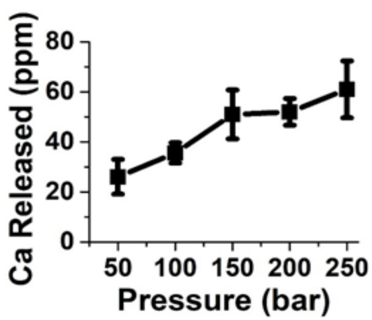
Ca^{2+} released in water increases with pCO_2 up to 150 bar but remains nearly constant when pCO_2 was further increased to 350 bar, which may be related to lesser effects on the pH of the solution.

Carbonates dissolution under CO_2 pressure



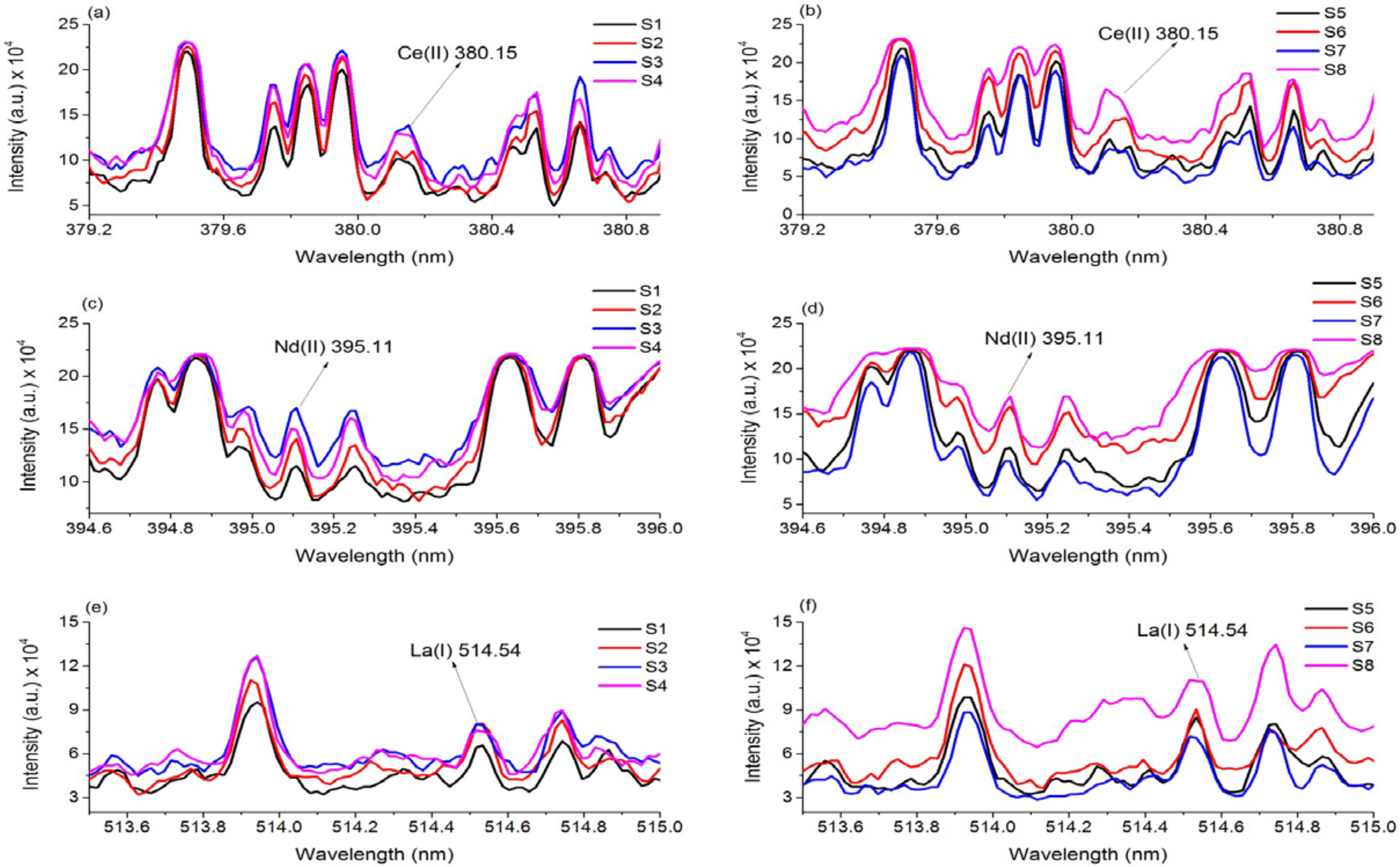






- Negligible difference in released amount for first 4 hrs
- Significant increase was observed at 24 hrs
- Released amount proportional to time of CO_2 injection and pressure.
- Different dissolution rates.
- At 50 bars, max. dissolution was for Sr ~300 ppm, and then Mg, Ca, and Mn with ~200, 100, and 0 ppm.
- At max. pressure 250 bars,
  Dissolution of Ca and Sr > 600 ppm, Mg > 300 ppm, Mn > 80 ppm .
- This difference in dissolution rates attributed to difference in their internal chemistry.
- Only Ca was detected from Mt. Simon dissolution.

Detection of REE Spectral Lines in Geological Sample



PLS-R: Predicted Vs Reference Plots for Geological Samples

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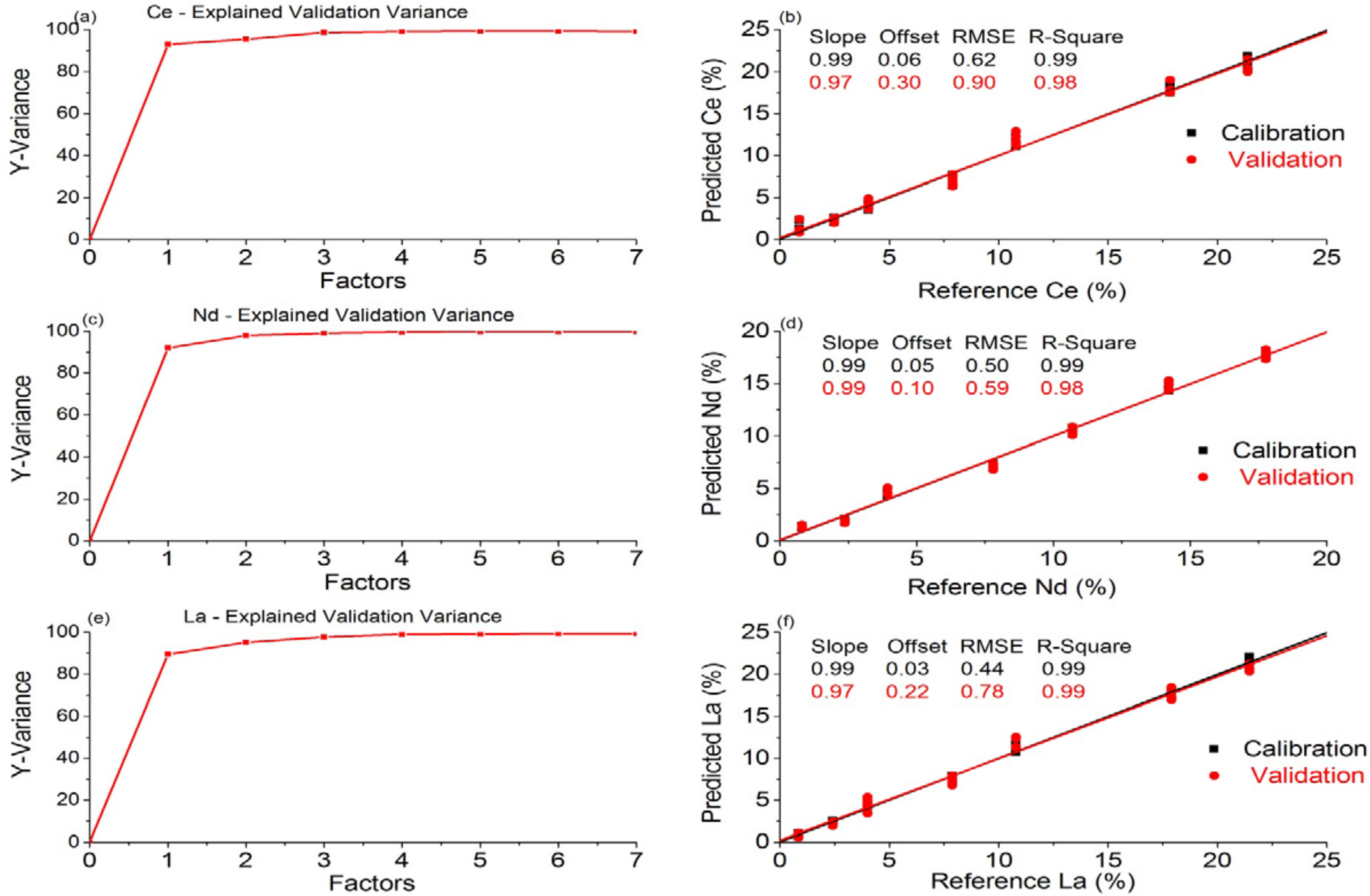
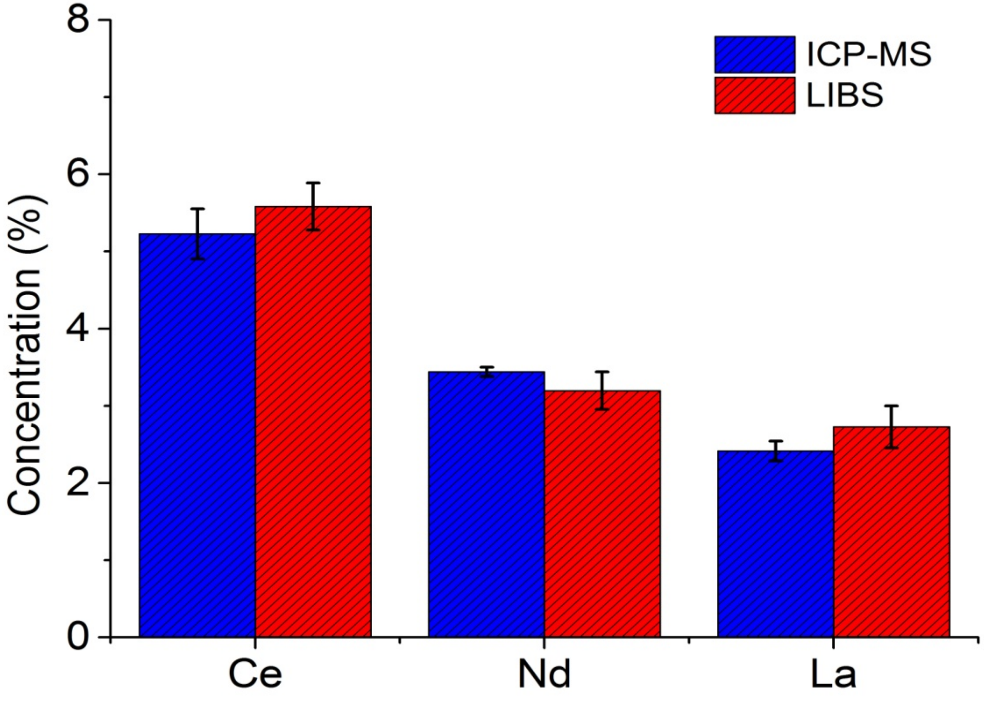


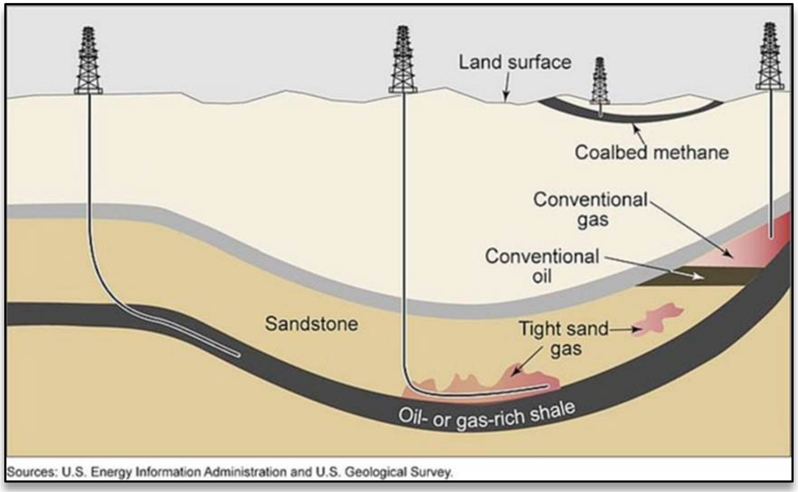
Evaluation of Calibration Models



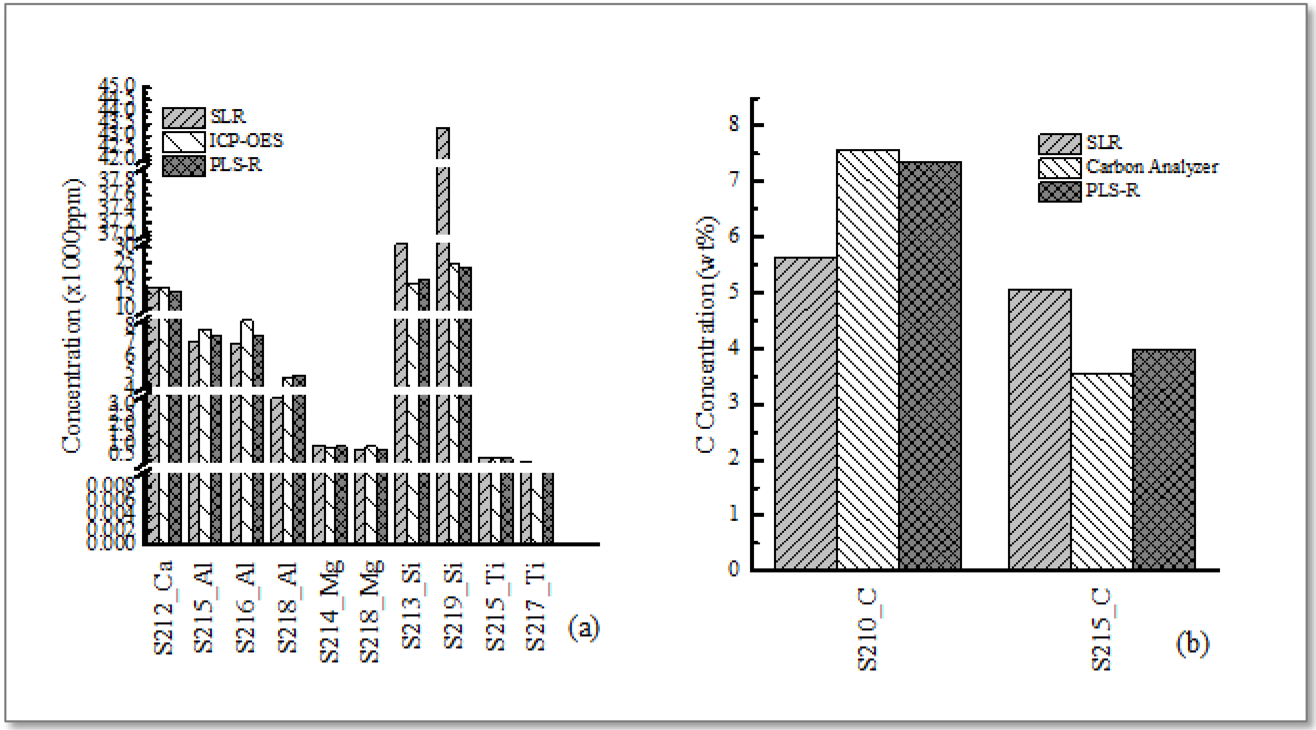
Analyte	Concentration %		Relative difference (%)
	ICP-MS	LIBS	
Ce	5.22	5.58	6.76
Nd	3.43	3.19	7.09
La	2.41	2.72	12.95

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

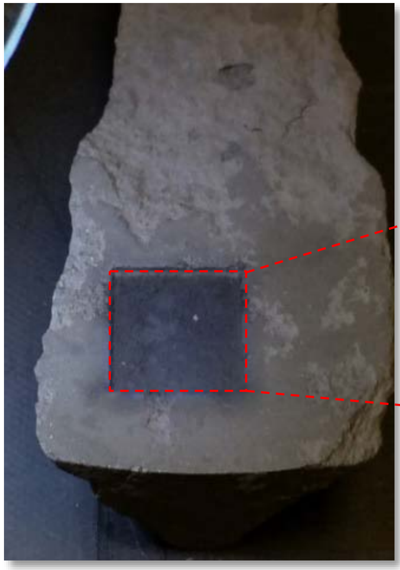


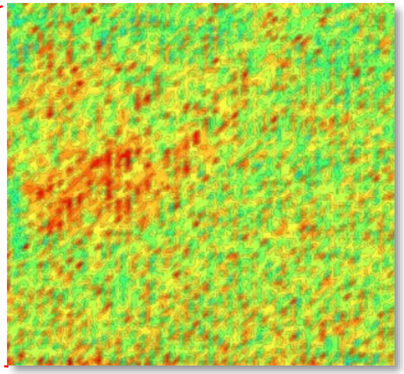
Shale Analysis



Shale Sample Mapped Area

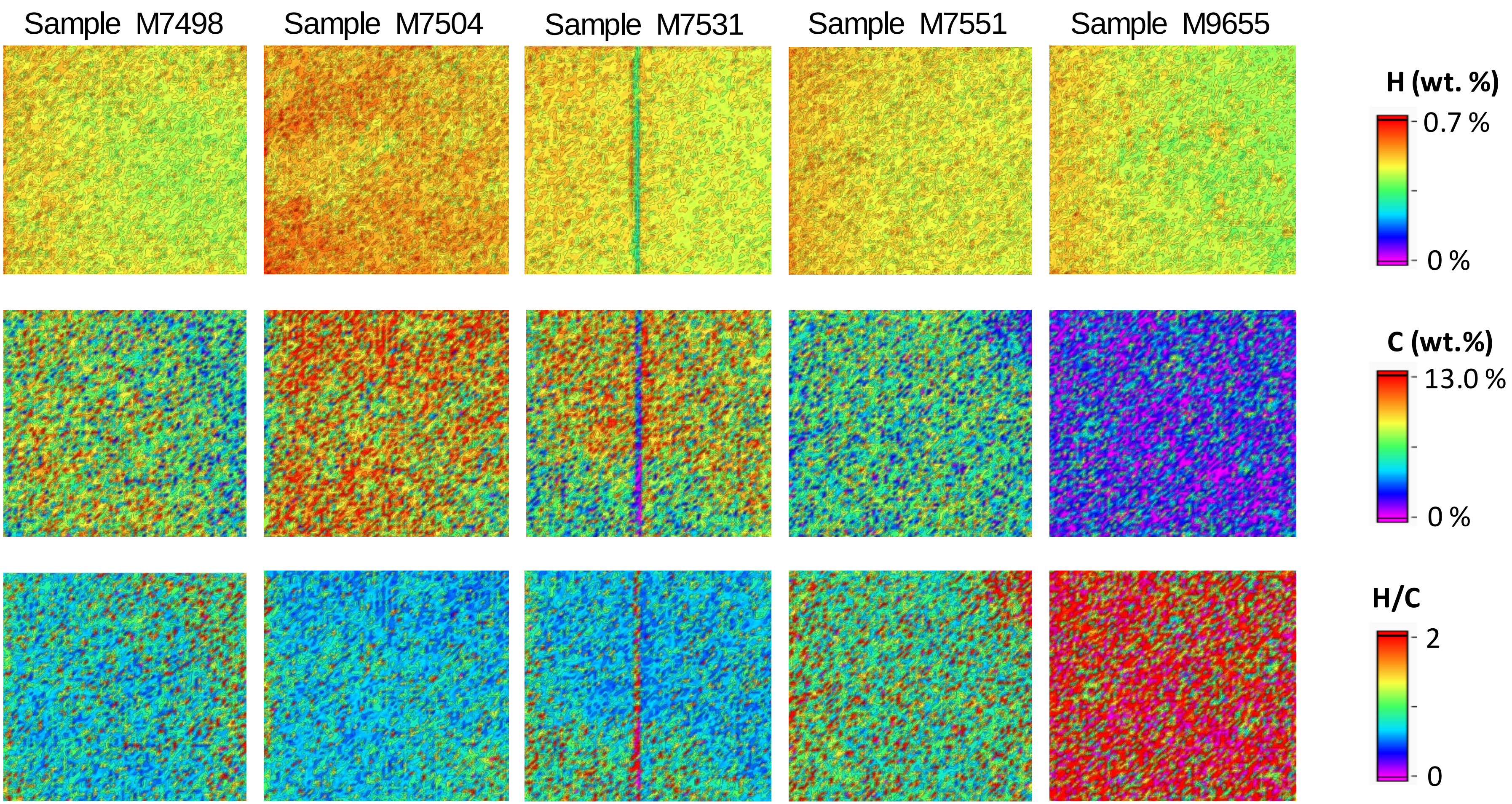
Sample M7504





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

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

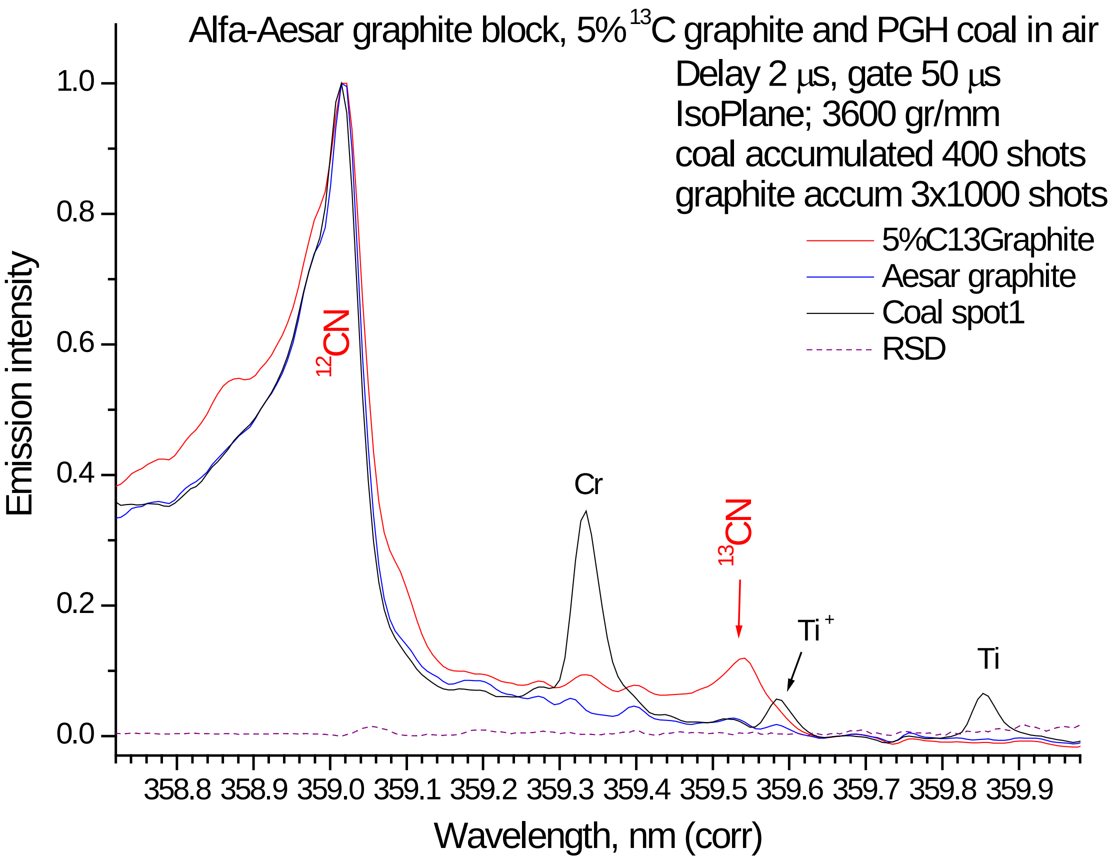
H/C < 1 – aromatic
H/C > 1 – aliphatic

	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

Isotopic Analysis

- **Carbon Isotope Analysis**



Field Deployable Unit

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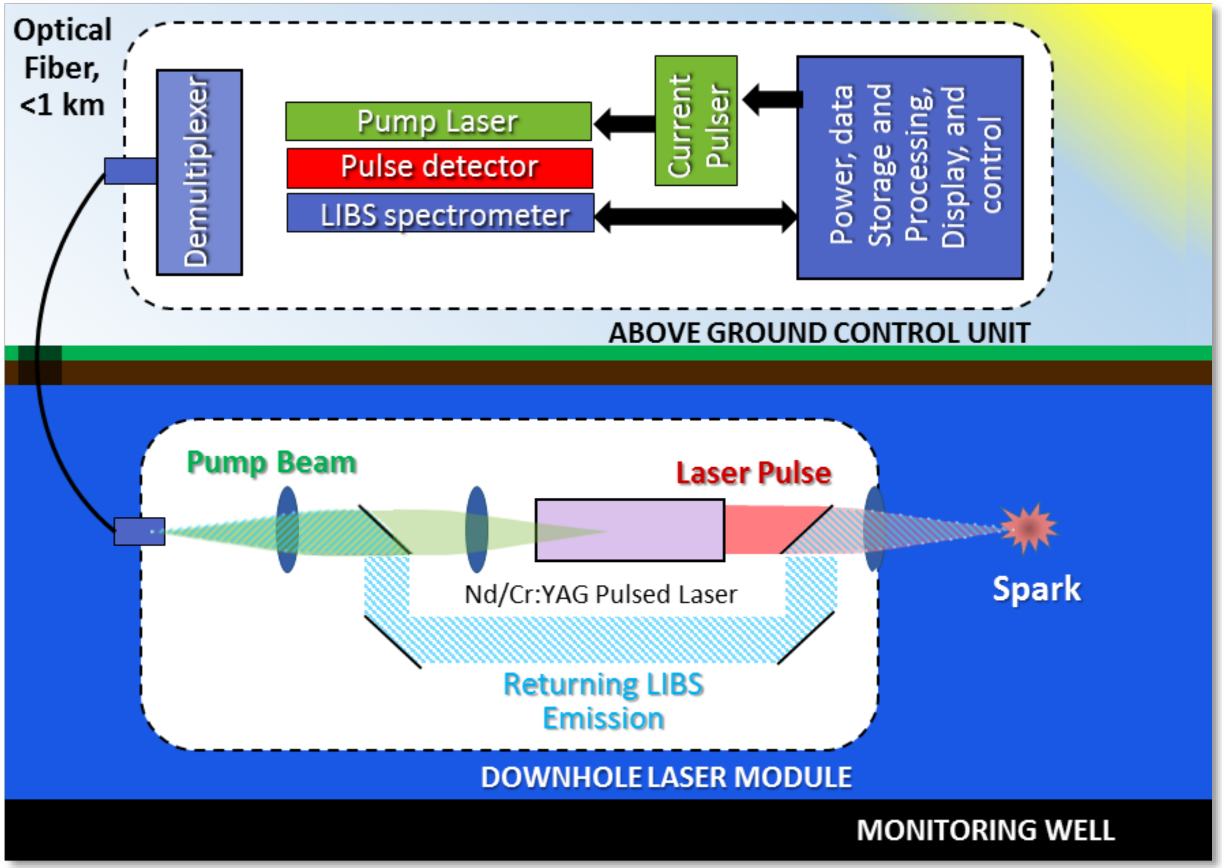
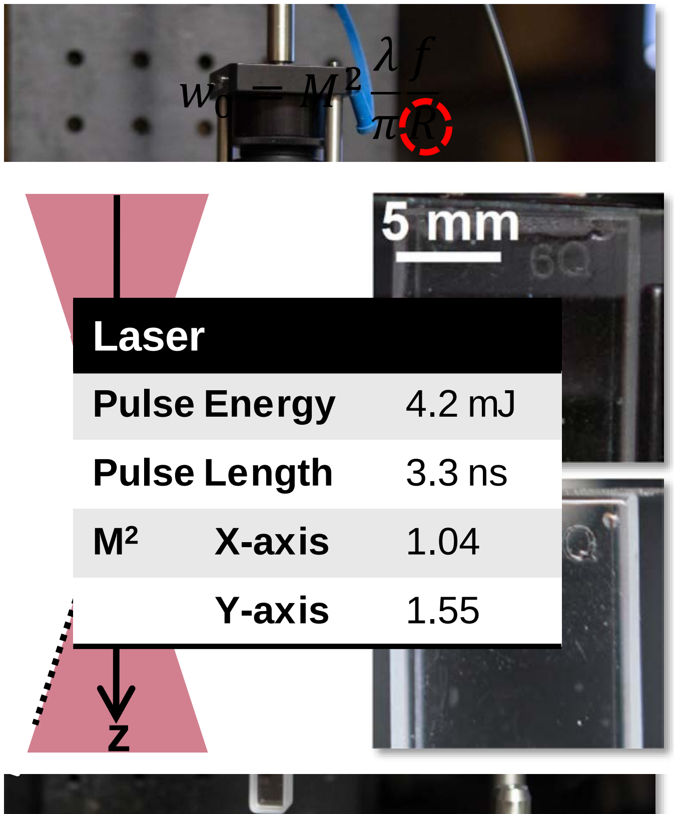
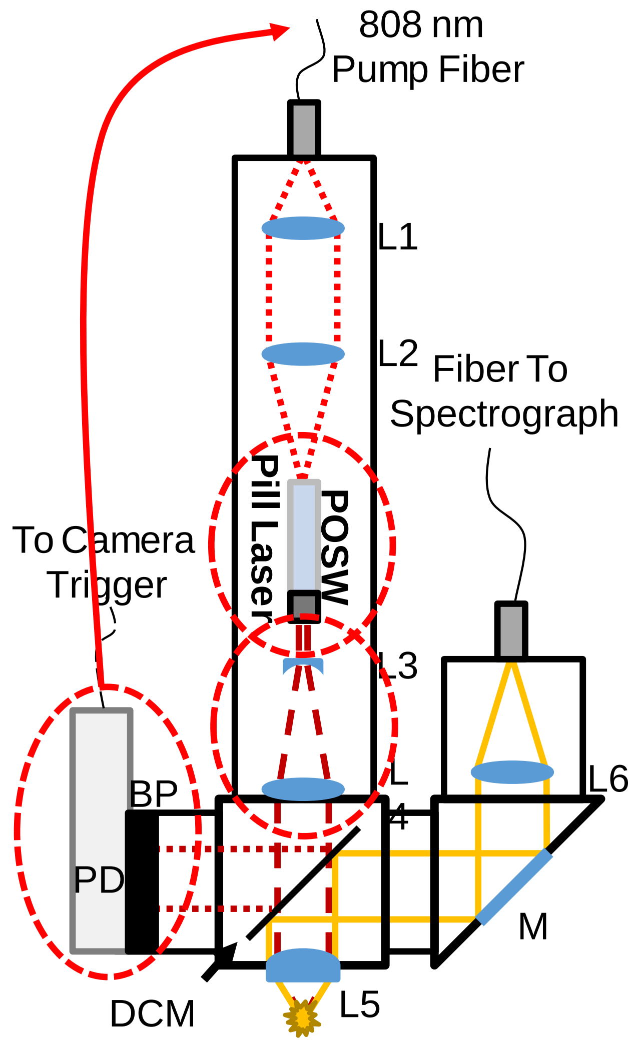


LIBS Prototype Schematic

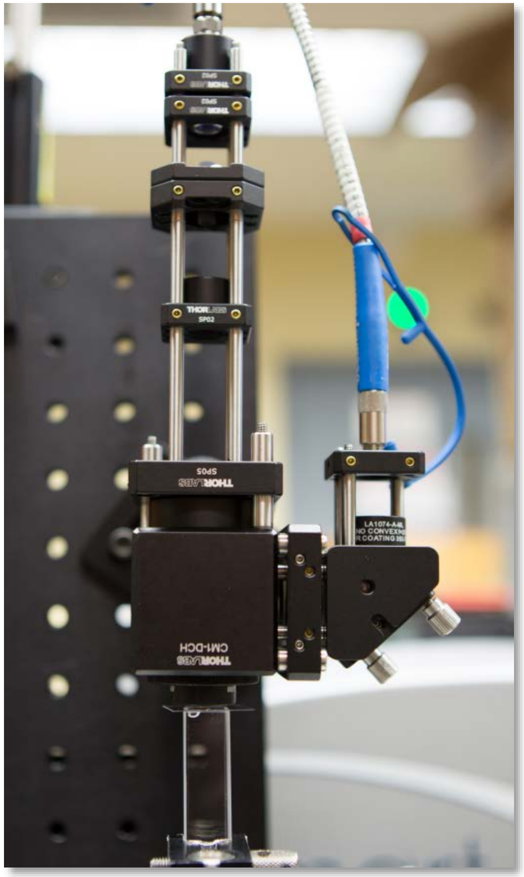


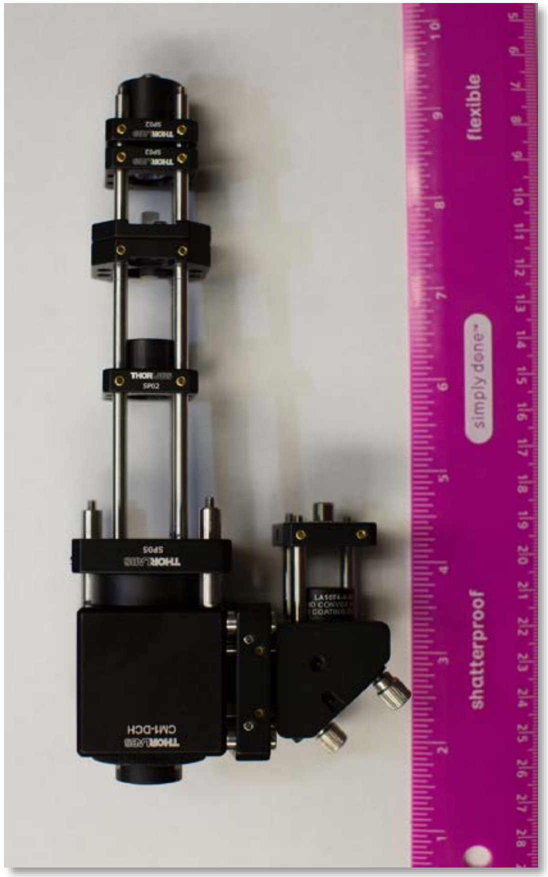
$$w_0 = M^2 \frac{\lambda f}{\pi R}$$

Laser		
Pulse Energy		4.2 mJ
Pulse Length		3.3 ns
M^2	X-axis	1.04
	Y-axis	1.55



LIBS prototype Sensor head





Performance – Alkali / Alkaline Metals

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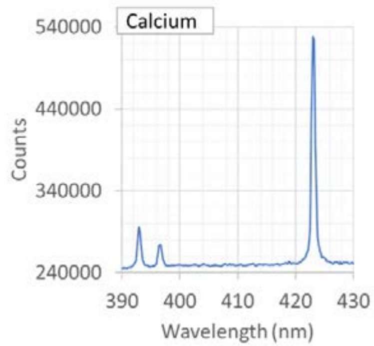
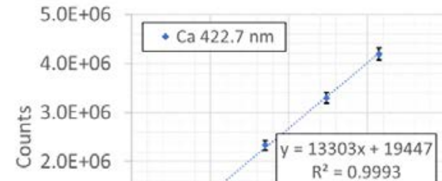
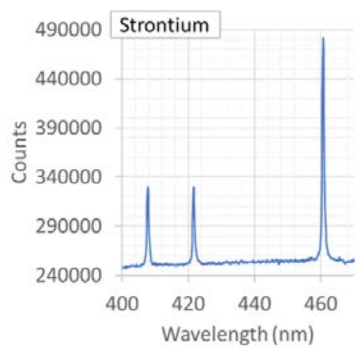
- $CaCl_2$ in DI water
  - 25.1 ppm Ca
  - 450 shots
  - Gate:
    - Delay = 250 ns
    - Width = 3 μs

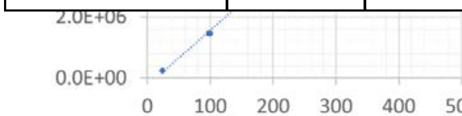




Element	Line (nm)	LOD (ppm)	LOD (literature) (ppm)		
Calcium	422.7	0.10[A]	0.94[B]	0.047[C]	0.13[E]
Strontium	460.7	0.04[A]	2.89[B]		
Potassium	766.6	0.009[A]	0.03[B]	0.006[D]	1.2[F]
	769.9	0.069[A]			

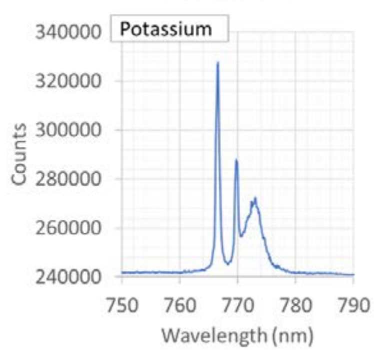
- $SrCl_2$ in DI water
  - 24.1 ppm Sr
  - 450 shots
  - Gate:
    - Delay = 300 ns
    - Width = 3 μs

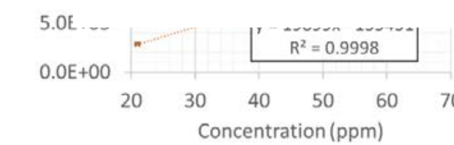




A – Hartzler et. al. **2019**, Scientific Reports, Vol. 9, 4430
B – Goueguel et. al. **2015**, Applied Optics, Vol. 54, 6071-6079
C – Pearman et. al. **2003**, Applied Optics, Vol. 42, 6085-6093
D – Golik et. al. **2012**, Journal of Applied Spectroscopy, Vol. 79, 471-476
E – Knopp et. al. **1996**,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

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





Conclusions

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- **Laser induced breakdown spectroscopy (LIBS) can provide elemental (including light elements) and isotopic analysis of solid, liquid , and gases**
- The technique provides accurate data with reasonable detection limits for most of the elements
- Minimum to no sample preparation makes this technique an attractive option to avoid lengthy sample preparation procedures
- LIBS can be a robust field deployable device for real time measurement purposes
- High pressure high temperature measurement capability makes LIBS a suitable tool for downhole applications

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