

# Laser induced breakdown spectroscopy (LIBS): A potential technology for online process monitoring of rare earth elements (REE) recovery



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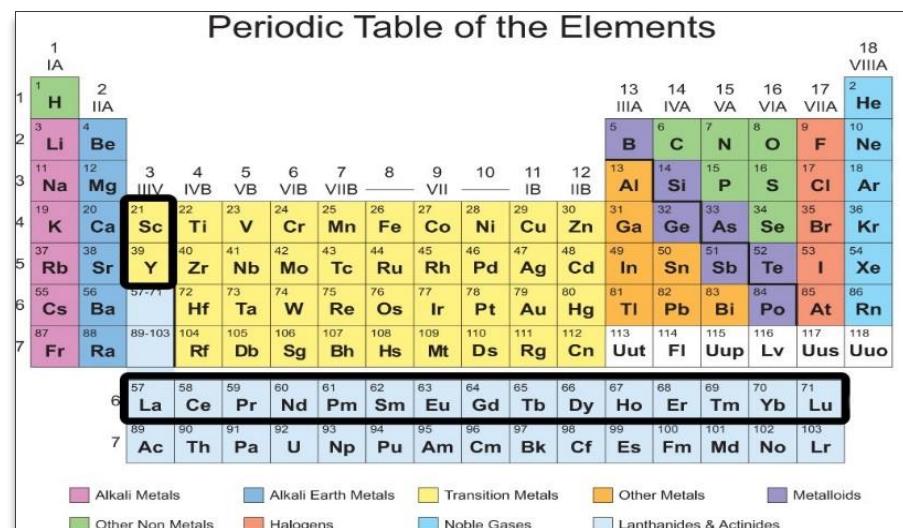


Solutions for Today | Options for Tomorrow



# Rare Earth Elements

- Use of REE in high-tech products, including cell phones, computers, batteries, and lasers.
- REE distribution & mobilization can be used to sort out important geochemical and petrogenetic processes
- REE-enriched ores are predominant mining source but industrial waste and aqueous byproducts appear to be an inexpensive alternative sources
- Current analytical methods include ICP-MS, NAA, ICP-OES, XRF.
- Advantages of LIBS technique over traditional ones.
- Prior LIBS Work with REE
  - There is prior LIBS work on REEs.
  - All the studies are done with standard samples.
  - No work is reported with natural geological samples.
  - No work is reported with under water LIBS.

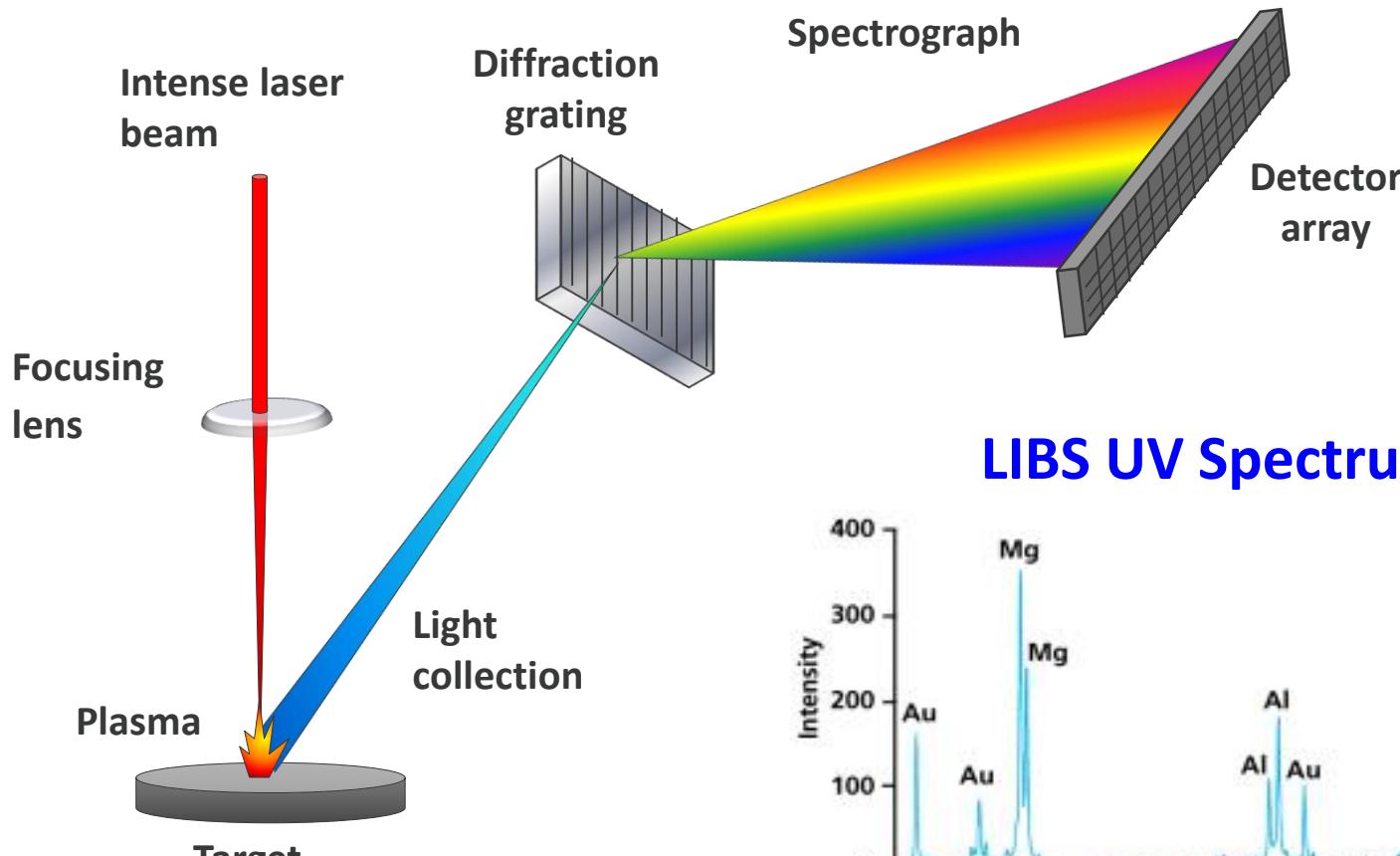


# Laser Induced Breakdown Spectroscopy (LIBS)

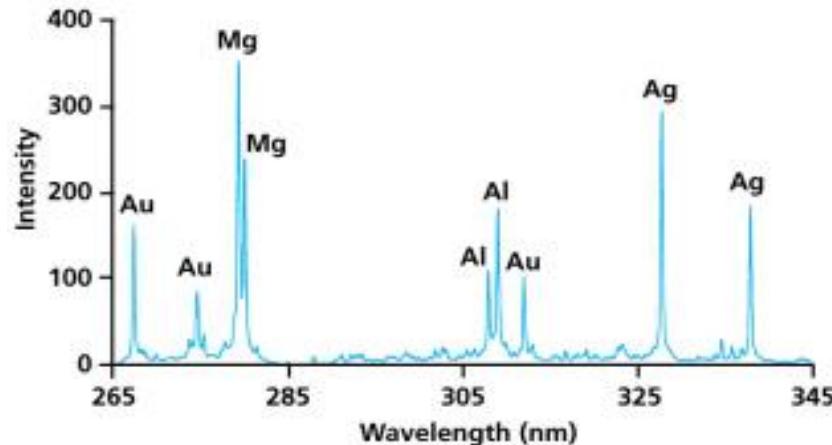


- Laser is fired upon a given sample and laser energy focused to a small spot
- A hot luminous plasma vaporizes the material, and leads to atomization and excitation of elements
- As plasma cools, emission occurs and the emitted light can be collected
- Every element in the Periodic Table gives off light at a distinct wavelength
- LIBS can perform in-situ elemental and isotopic analysis of liquid samples and is capable of making underwater measurements
- Flexibility of probe design, and use of fiber optics make it a suitable technique for real-time and stand-off measurements in harsh conditions and at hard to reach places.

# Principle of LIBS



**LIBS UV Spectrum**

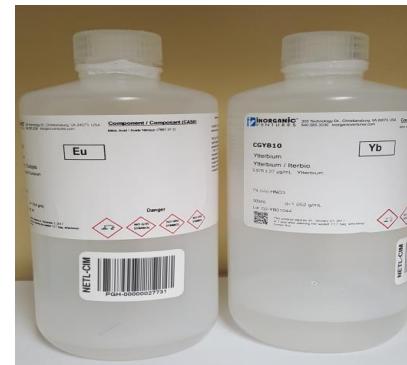
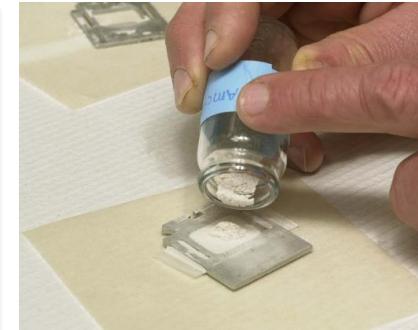


# Working Samples to Study REE

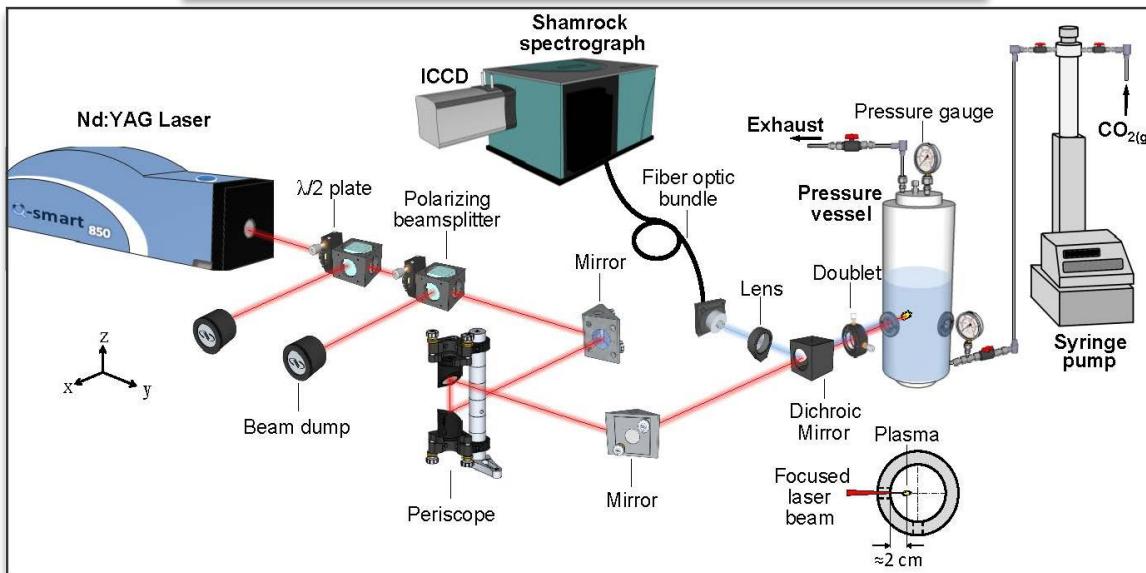
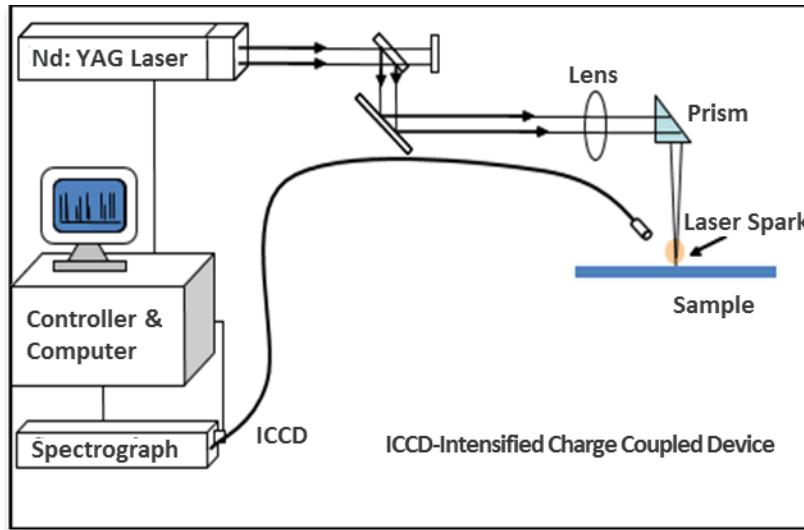


Three different types of samples:

- 1) Standard REE oxides in powder form: (Six REEs' oxides)  $\text{CeO}_2$ ,  $\text{Eu}_2\text{O}_3$ ,  $\text{Gd}_2\text{O}_3$ ,  $\text{Nd}_2\text{O}_3$ ,  $\text{Sm}_2\text{O}_3$ , and  $\text{Y}_2\text{O}_3$ .
- 2) REE in geological samples: (16 REEs)  
Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Sc, Tb, Tm, Yb and Y.
- 3) REE in aqueous solutions: Eu and Yb



# Experimental Set-up

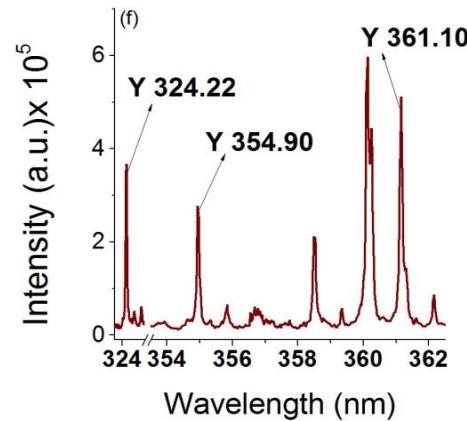
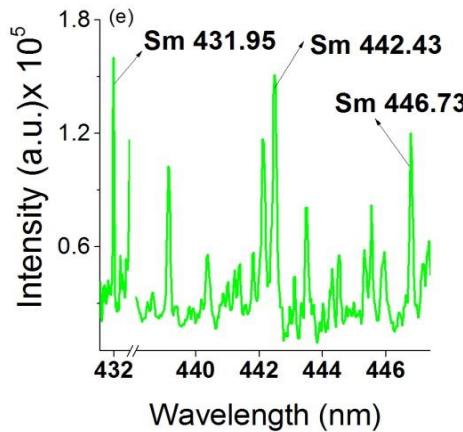
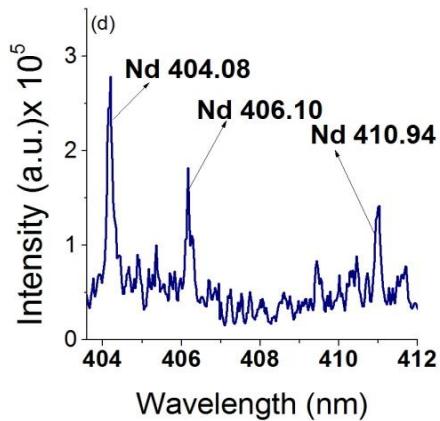
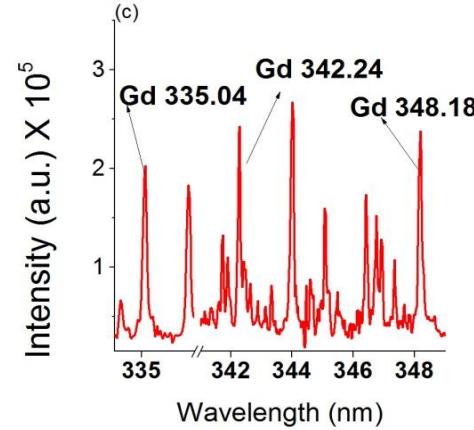
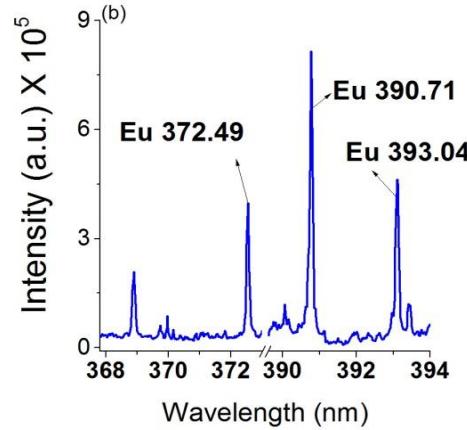
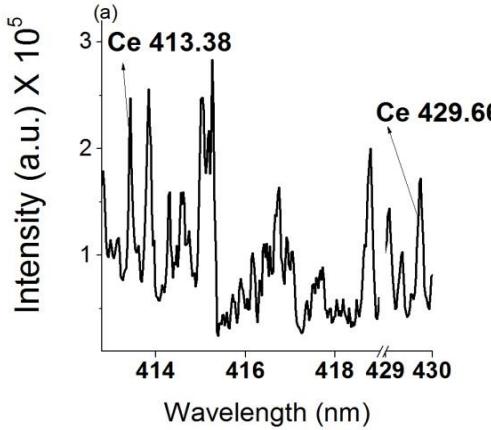


# Geological Samples: REEs Composition

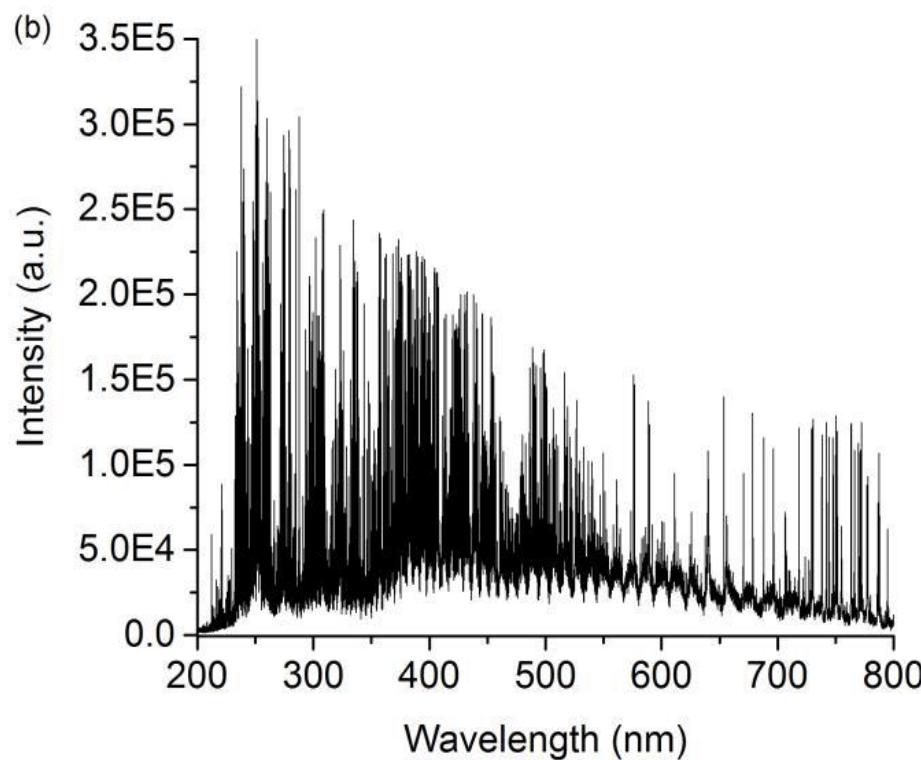
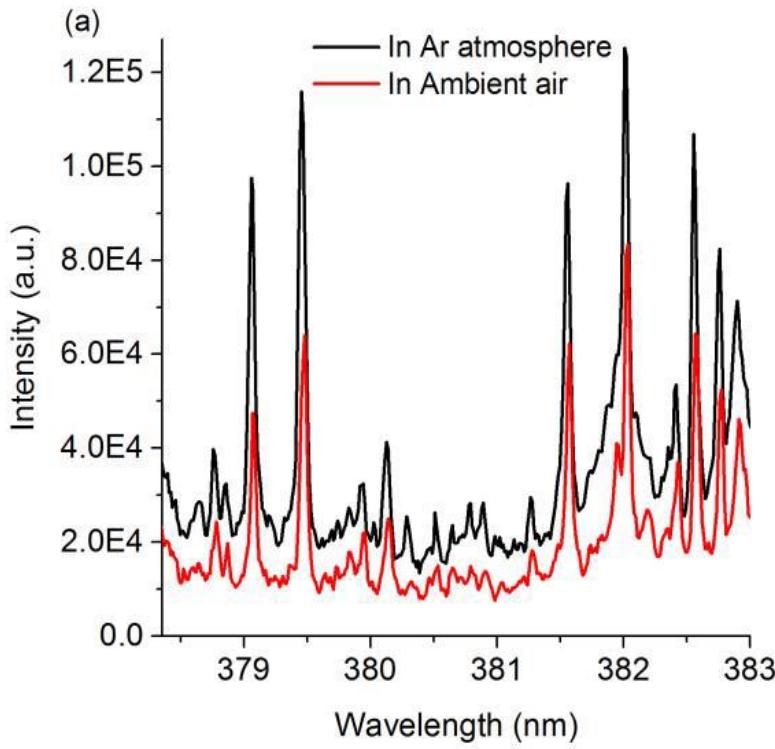


Samples	Concentrations (ppm)															
	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
S1	39	100	814	1367	118	429	55	14	51	6	28	4	12	1.4	9	1.3
S2	43	136	1103	1880	165	590	78	19	72	8	37	5	16	1.8	12	1.6
S3	71	293	1366	2193	212	740	89	22	93	11	63	11	32	3.9	24	3.2
S4	45	169	1479	2284	221	786	102	25	92	10	48	7	20	2.2	14	1.9
S5	45	196	1779	2685	265	957	126	31	113	12	59	8	23	2.5	16	2.1
S6	51	202	1794	2751	265	964	126	31	113	12	58	8	23	2.7	16	2.3
S7	44	206	1922	2861	285	1027	136	33	119	12	60	9	24	2.7	17	2.3
S8	43	204	1915	2878	286	1039	136	33	120	12	61	9	24	2.5	16	2.2
S9	52	202	1813	2770	271	990	128	32	115	12	61	8	24	2.7	17	2.3
S10	14	750	26556	57513	7710	37833	4835	633	2552	201	711	36	199	5.1	32	3.5

# Qualitative Analysis: Detection of Spectral Lines in Standard Samples



# Enhancement of Signal Intensity in Ar Atmosphere



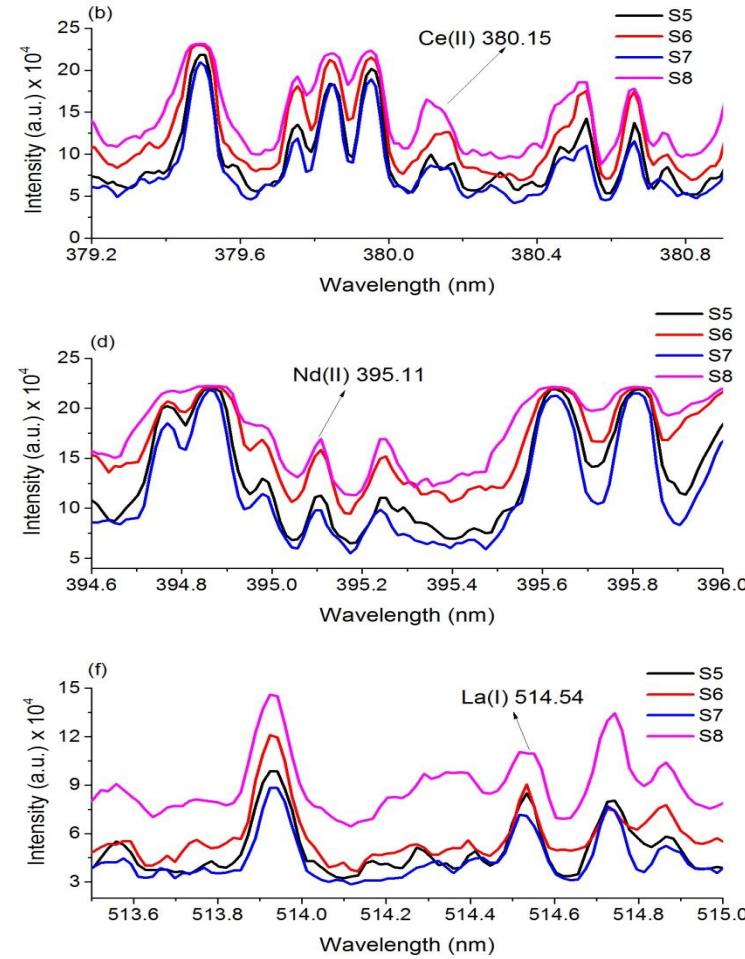
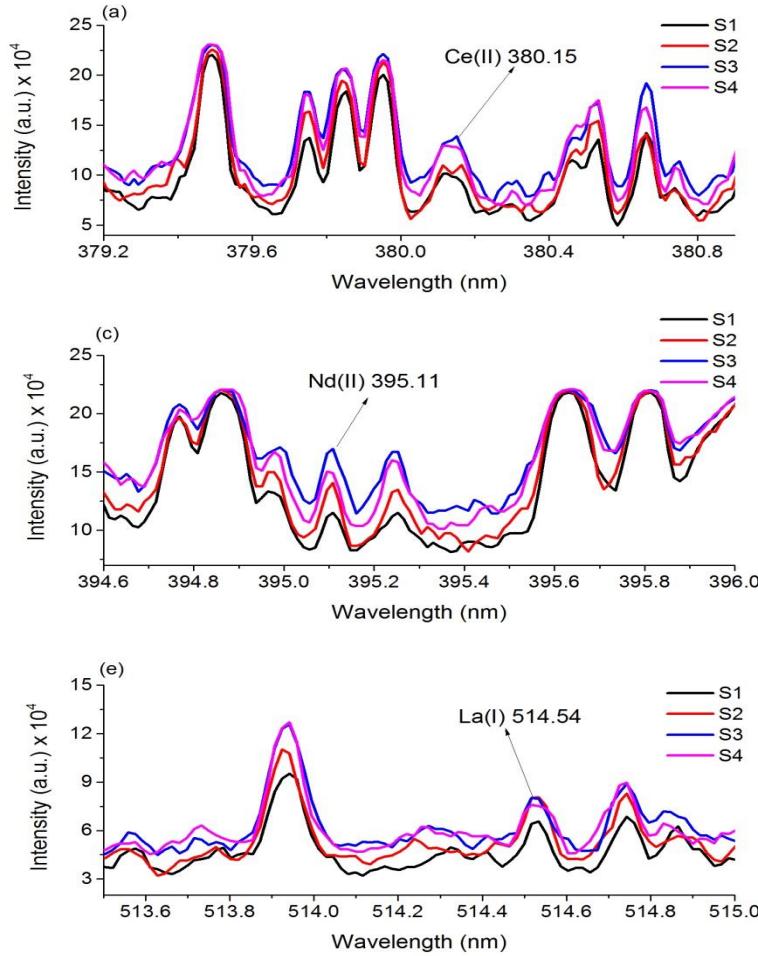
# Detection of Spectral Lines in Geological Samples



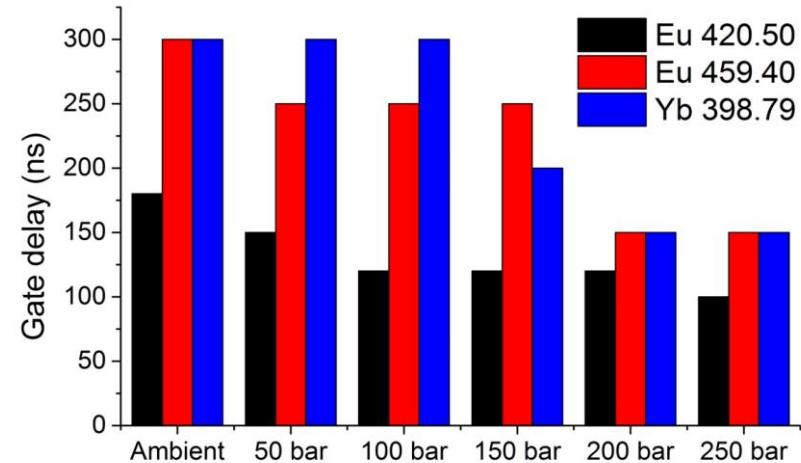
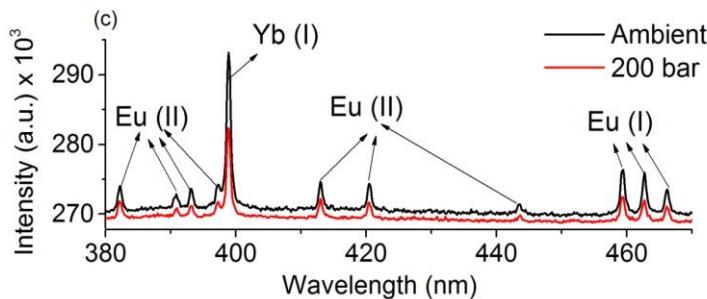
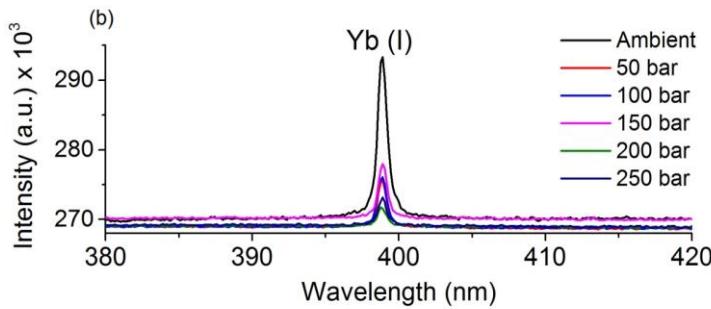
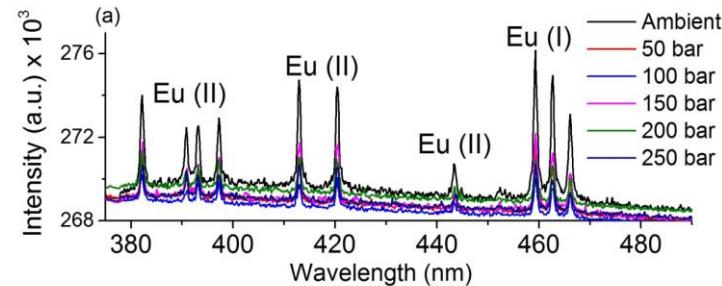
Identified lines	Samples in which these lines were detected
Ce I 560.12	S1, S2, S3, S4, S5, S6, S7, S8
Ce I 571.90	S2, S3, S4, S5, S6, S7, S8
Ce I 594.08	S1, S2, S3, S4, S5, S6, S8
Ce II 380.15	S1, S2, S3, S4, S5, S6, S7, S8
Ce II 413.76	S1, S2, S3, S4, S5, S6, S7, S8
Ce II 418.65	S1, S2, S3, S4, S5, S6, S7, S8
Ce II 446.02	S1, S2, S3, S4, S5, S6, S7, S8
Ce II 456.23	S1, S2, S3, S4, S5, S6, S7, S8
Nd II 378.42	S3, S6, S7, S8
Nd II 380.53	S1, S2, S3, S4, S5, S6, S7, S8
Nd II 386.34	S2, S3, S4, S5, S6, S8
Nd II 394.15	S6, S8
Nd II 395.11	S1, S2, S3, S4, S5, S6, S7, S8
Nd II 401.22	S1, S2, S3, S4, S5, S6, S7, S8
Nd II 415.60	S4, S6, S8
La I 428.02	S1, S2, S3, S4, S5, S6, S7, S8
La I 514.54	S1, S2, S3, S4, S5, S6, S7, S8
La I 521.18	S1, S2, S3, S4, S5, S6, S8
La I 550.13	S1, S2, S3, S4, S5, S6, S7, S8
La I 624.99	S3, S4, S5, S8
La II 379.08	S1, S3, S4, S5, S6, S8
La II 399.57	S1, S2, S3, S4, S5, S6, S7, S8
La II 404.29	S1, S2, S3, S4, S5, S6, S7, S8
La II 408.67	S1, S2, S3, S4, S5, S6, S7, S8
La II 433.37	S1, S2, S3, S4, S5, S6, S7, S8

Elements	Spectral lines detected in the sample S-8
Y	324.22, 354.90, 360.07, 361.10, 363.31, 371.02, 377.43, 407.73, 412.82, 417.75, 437.49, 488.36, 490.01, 508.741 nm
Pr	417.93, 420.67, 422.29, 495.13 nm
Sm	356.82, 359.26, 363.42, 369.39, 442.43, 446.73, 447.08 nm
Eu	372.49, 381.96, 390.71, 397.19, 412.97, 420.50, 459.40, 462.72, 466.18 nm
Gd	335.04, 335.86, 342.24, 354.58, 358.49, 371.35, 374.34, 376.83, 379.63, 404.98, 405.36, 417.55, 451.96 nm
Dy	353.17, 364.53, 396.83, 404.59, 418.68 nm

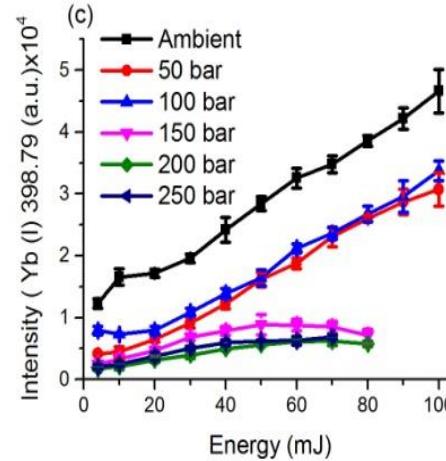
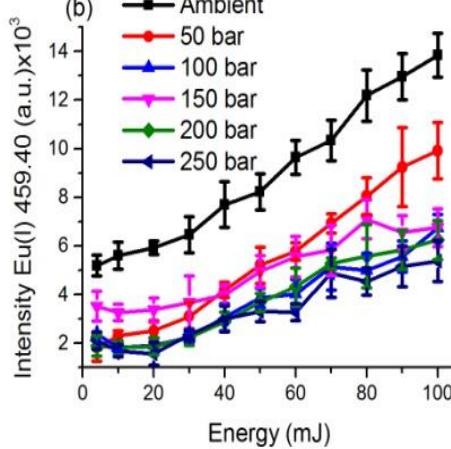
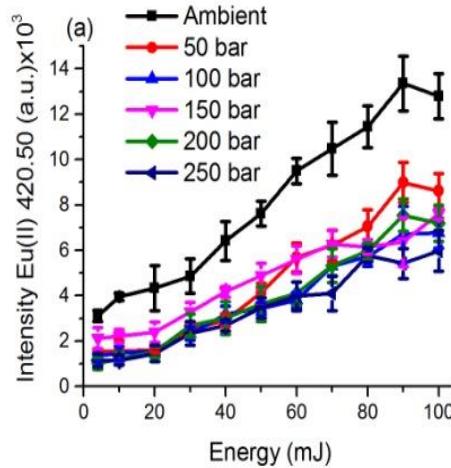
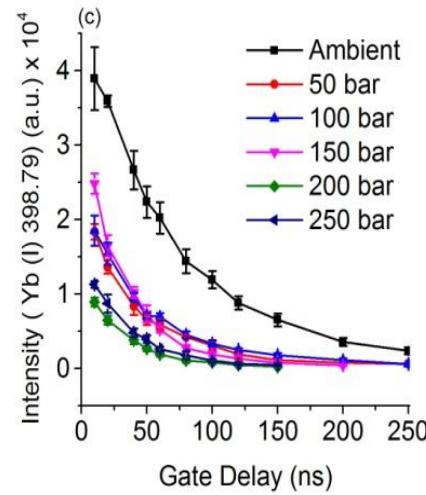
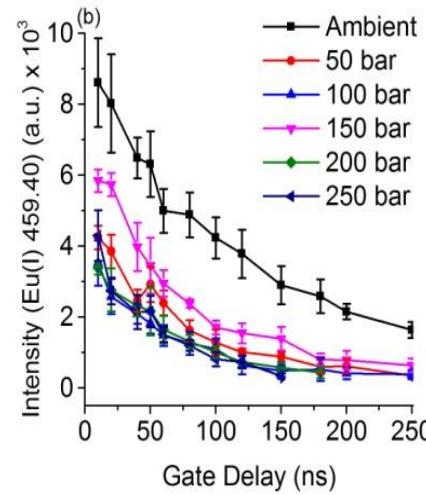
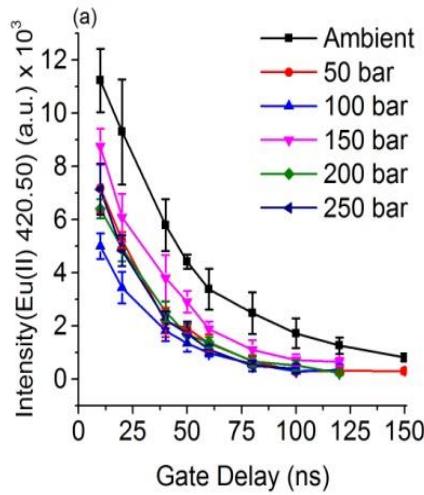
# Detection of Spectral Lines in Geological Samples



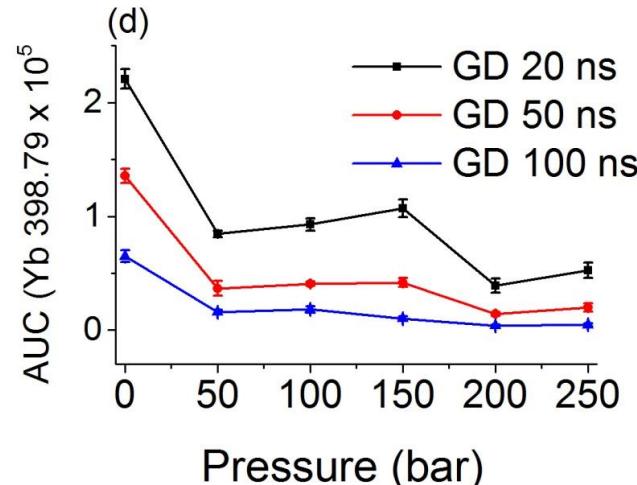
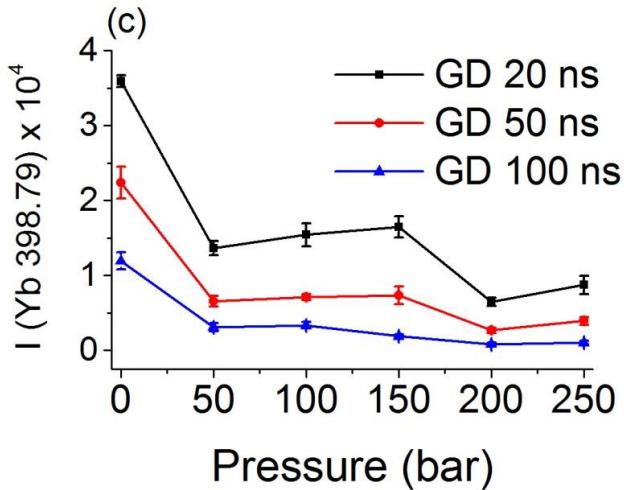
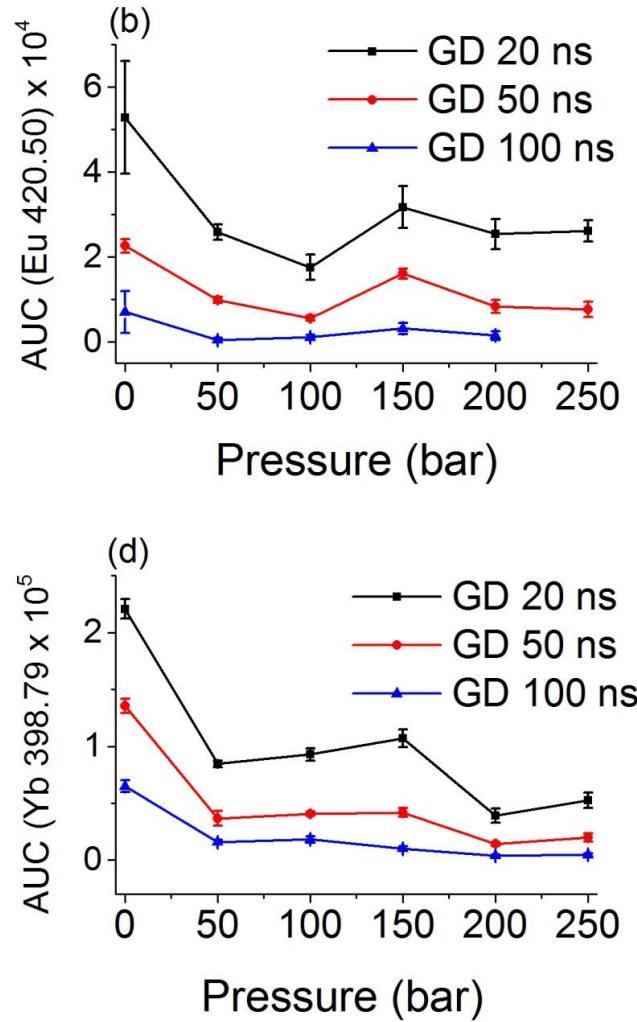
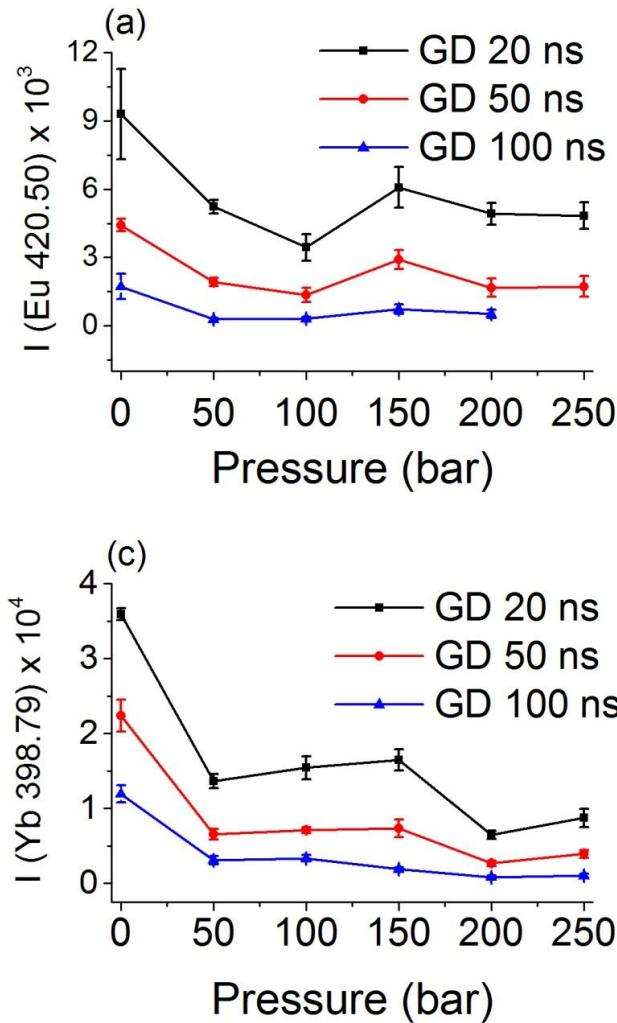
# Detection of Spectral Lines in Liquid Samples



# Plasma Evolution and Effect of Laser Energy



# Effect of Pressure on Plasma Emission

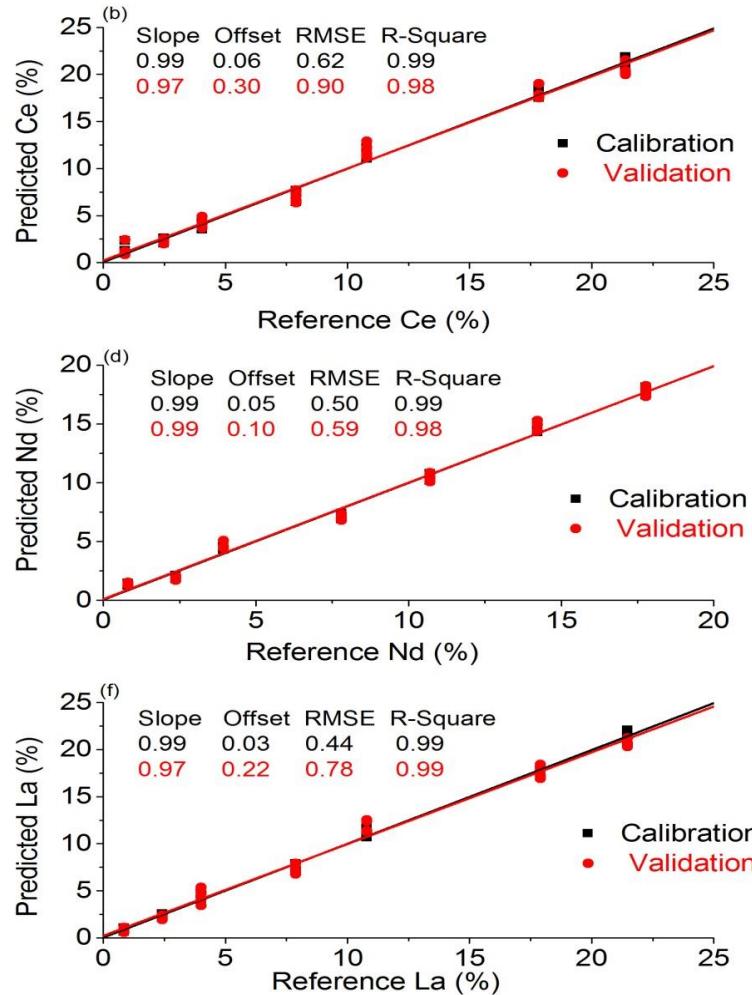
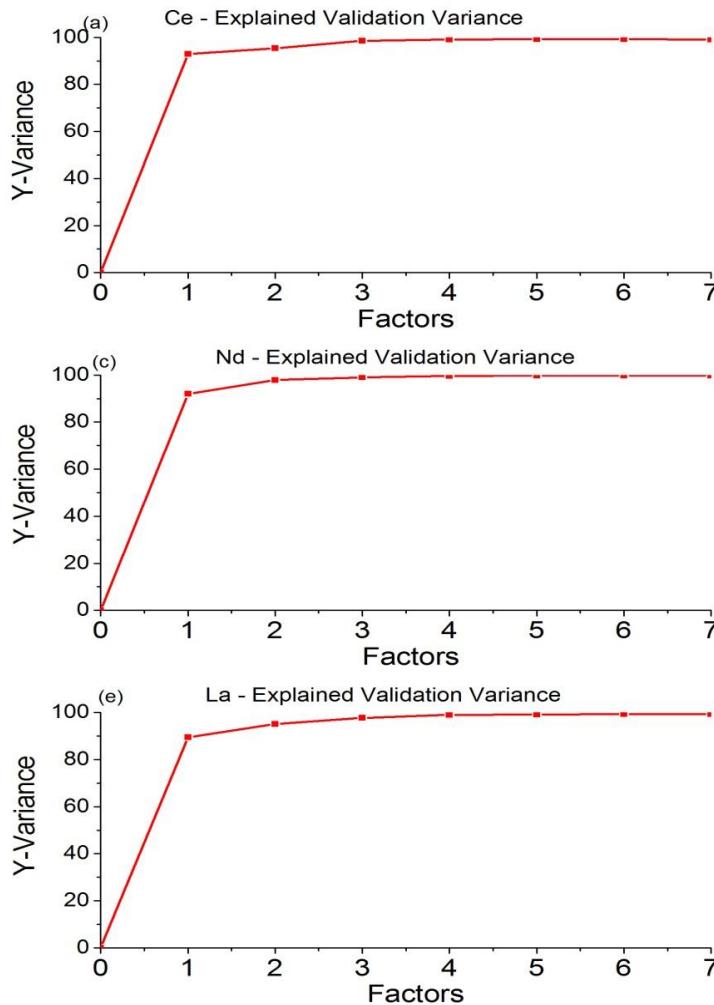


# Concentration of Ce, La, and Nd in Pellets Prepared for Quantitative Analysis

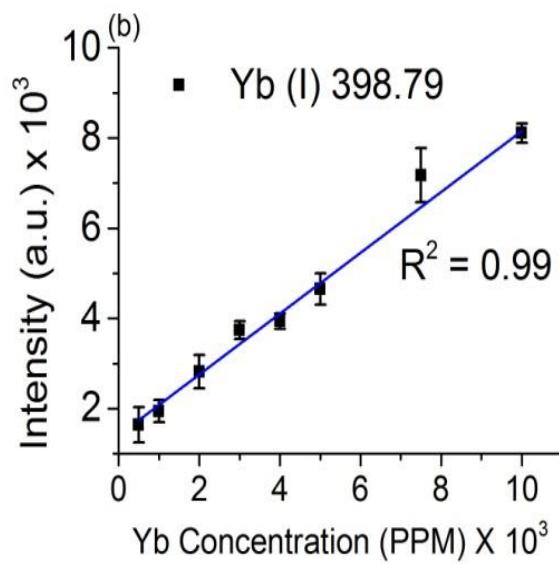
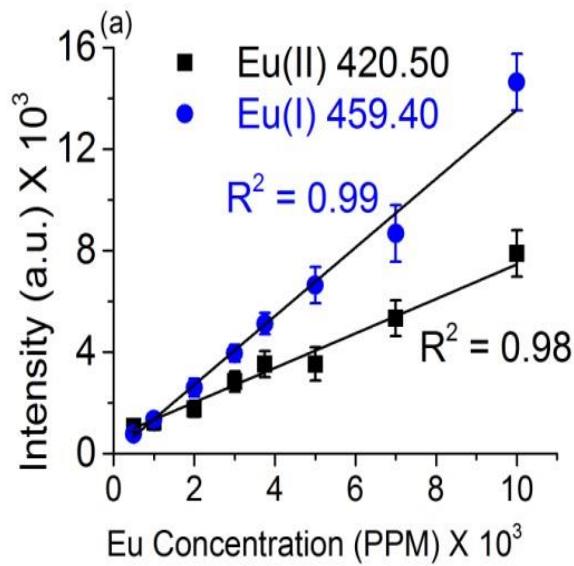


Samples	Concentration (%)		
	Ce	La	Nd
S1-M	0.89	0.85	0.81
S2-M	2.48	2.42	2.37
S3-M	4.05	4.00	3.93
S4-M	7.90	7.88	7.80
S5-M	10.79	10.79	10.70
S6-M	17.84	17.89	17.78
S7-M	21.39	21.46	14.22
S8	5.22	2.41	3.43

# PLS-R: Predicted vs Reference Plots for Geological Samples

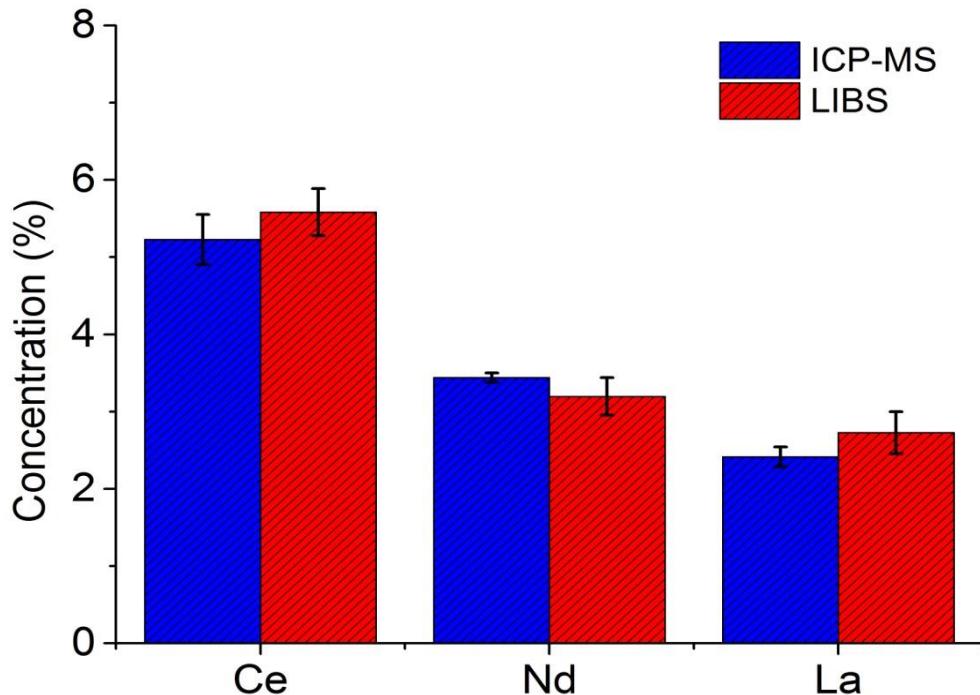


# SLR Calibration Models for REE in Liquid Samples



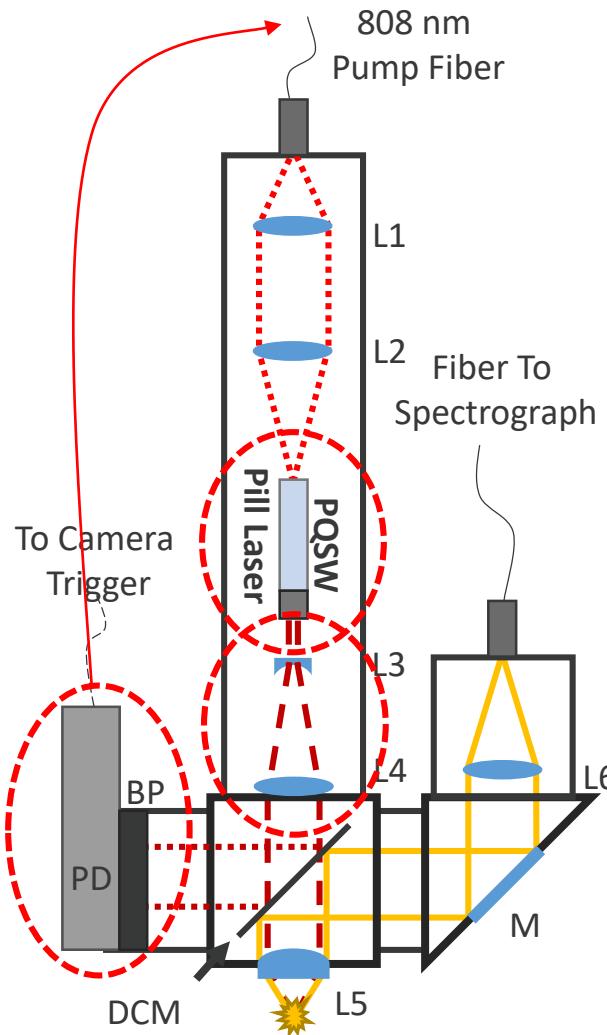
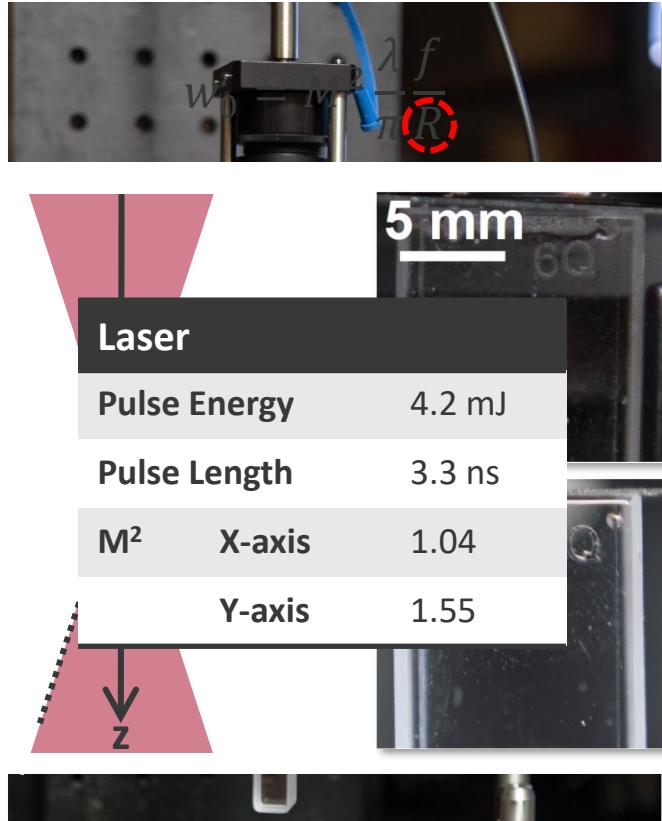
Elements	LOD (ppm)
Eu	209
Yb	156

# Evaluation of Calibration Models

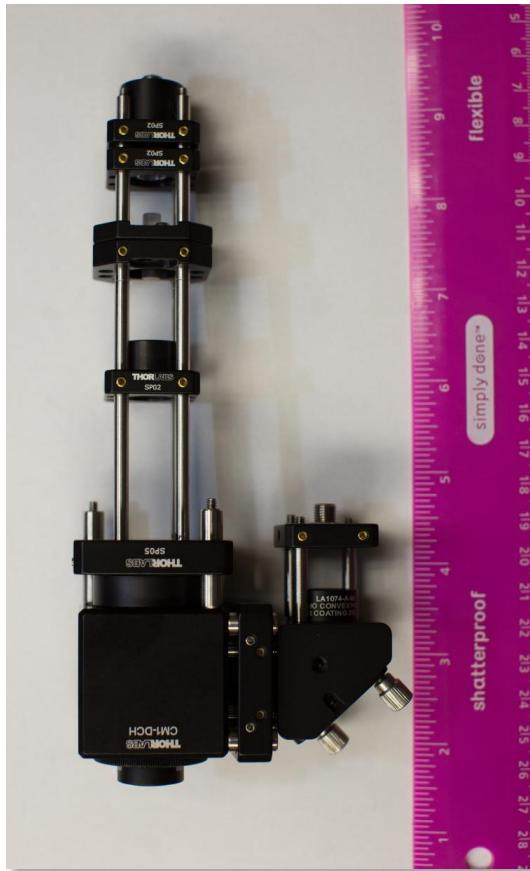
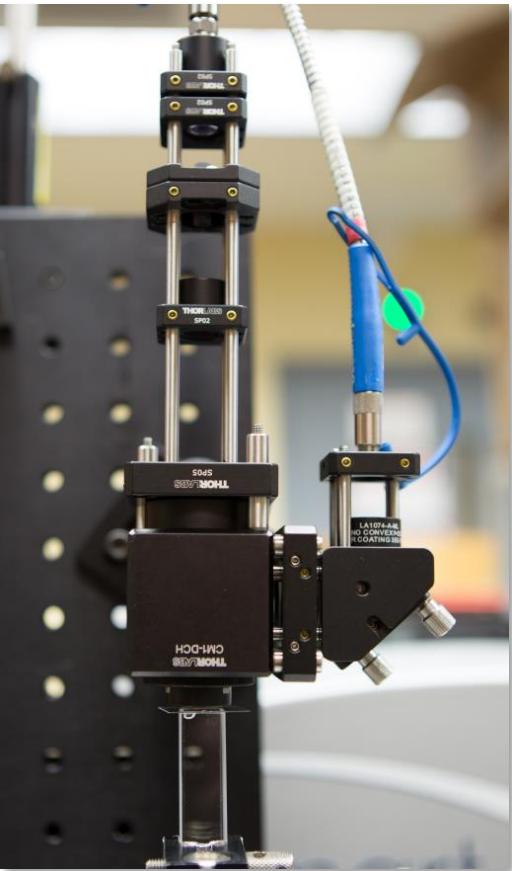


Analyte	Concentration (%)		Relative difference (%)
	ICP-MS	LIBS	
Ce	5.22	5.58	6.76
Nd	3.43	3.19	7.09
La	2.41	2.72	12.95

# LIBS Prototype Schematic

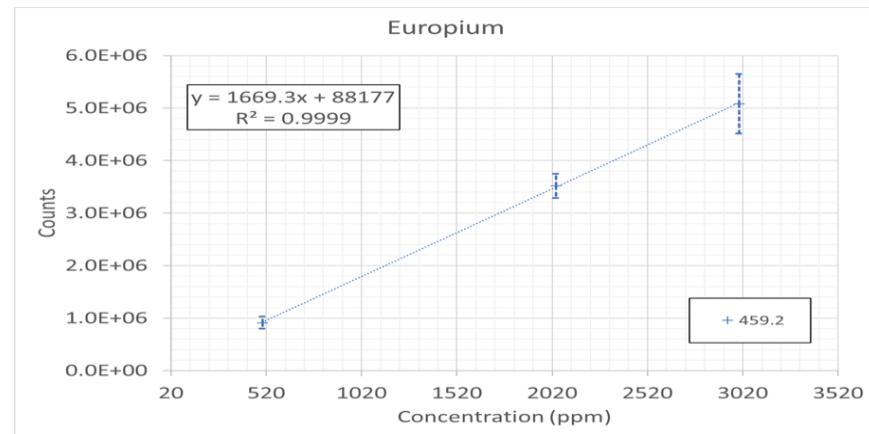
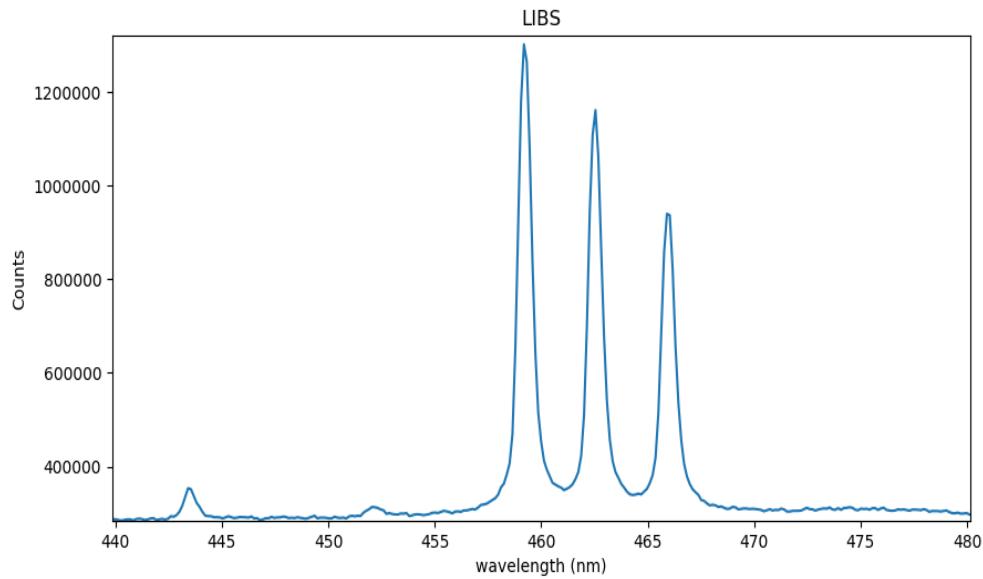


# LIBS prototype Sensor head



# Europium Emission Spectra

- Eu LIBS Spectra 440-480 nm
  - Eu 459.2 nm, Eu 462.5 nm, and Eu 465.9 nm lines
  - Underwater LIBS in Eu Solution
- Eu 459.2 Calibration curve (all lines can be used for calibration)
  - Error bars are  $\pm 1 \sigma$  of 6 spectra
- LOD 2.61 PPM, LOQ 8.71 PPM



# Conclusions

- LIBS is a useful tool in detecting and quantifying REEs in geological minerals and liquid samples.
- The technique provides accurate data with reasonable detection limits for most of the elements. No sample preparation is required.
- Simple linear regression (SLR) calibration method yielded acceptable results for liquid samples.
- PLS-R calibration models were preferred for complex matrix geological samples.
- Field deployable and real-time monitoring capabilities of LIBS makes it a suitable tool for REE process monitoring.

# Acknowledgment

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