Determination of rare earth elements in geological minerals by laser induced breakdown spectroscopy

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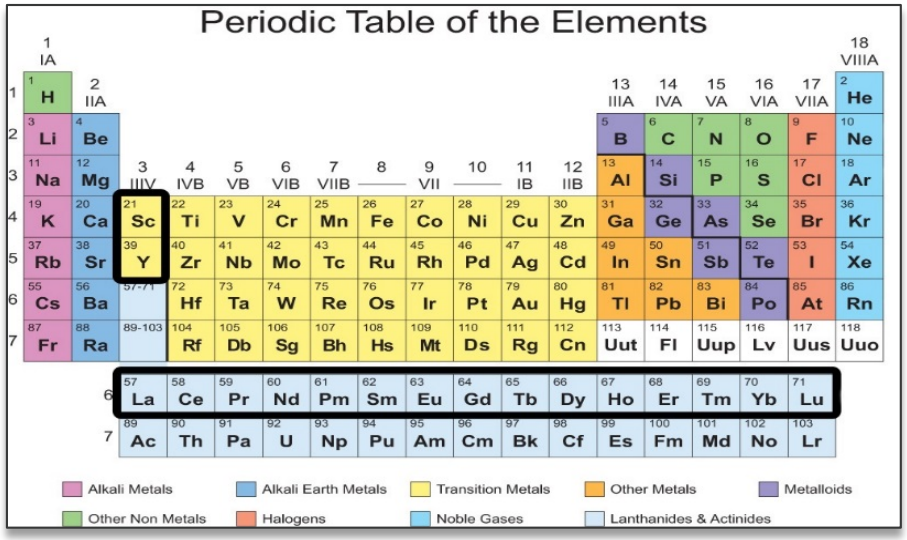
Rare Earth Elements



- 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
- 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.

Working Samples to Study REE

- **Three different types of samples:**

1) Standard REE oxides in powder form: (Six REEs' oxides) CeO2, Eu2O3, Gd2O3, Nd2O3, Sm2O3, and Y2O3.

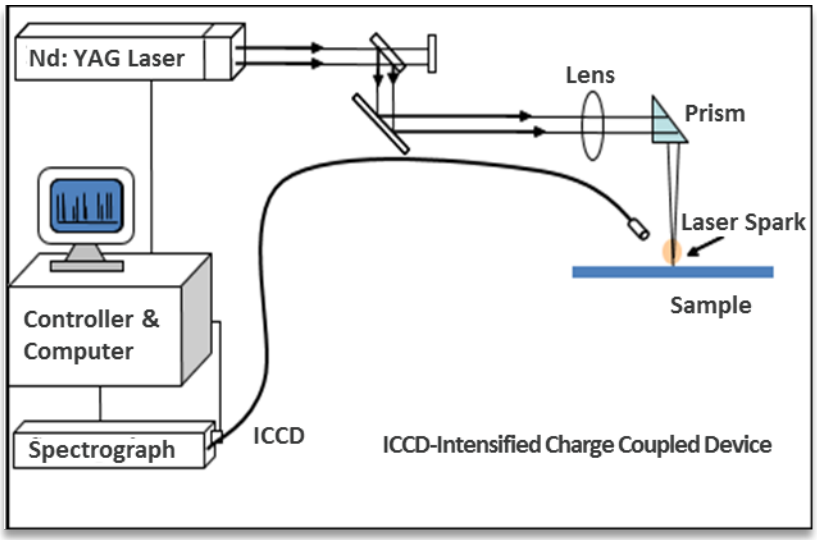
2) REE in geological samples: (16 REEs)
Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Sc, Tb, Tm, Yb and Y.

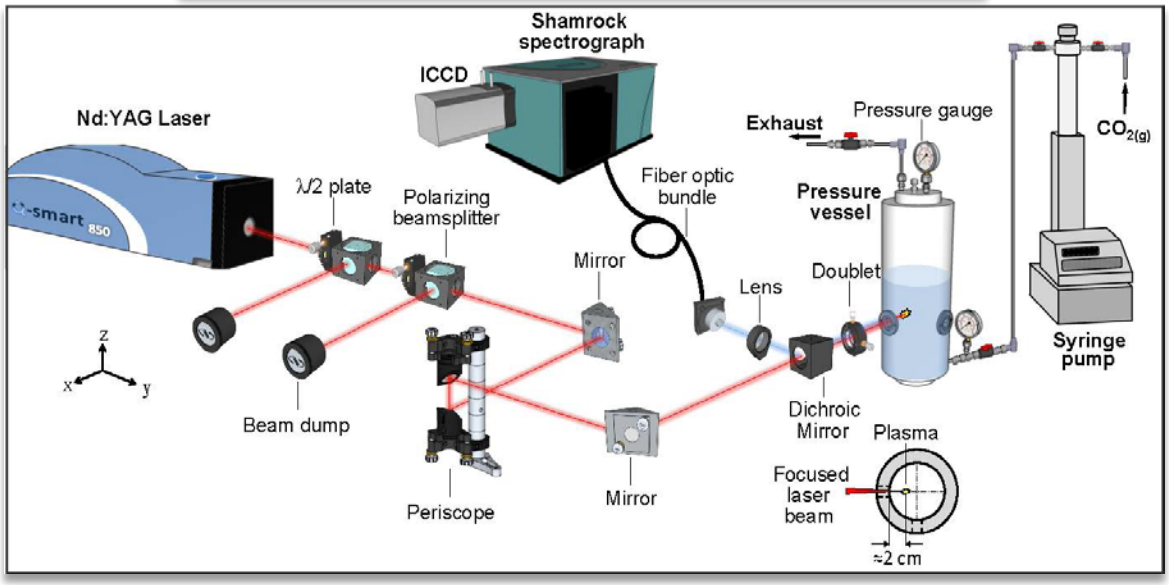
3) REE in aqueous solutions: Eu and Yb





Experimental Set-up

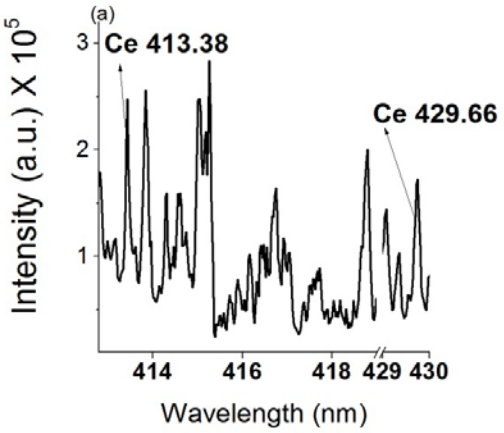


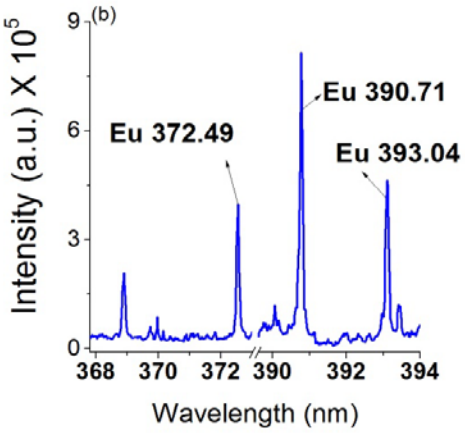


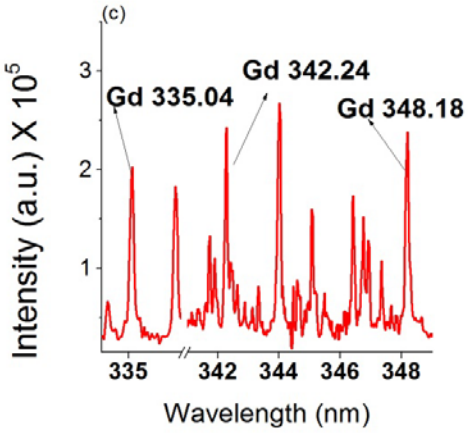
Geological Samples: REEs Composition

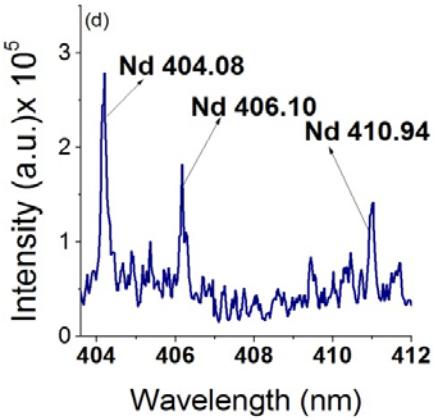
Samples	Concentrations (ppm)															
	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
S1	39	100	814	1367	118	429	55	14	51	6	28	4	12	1.4	9	1.3
S2	43	136	1103	1880	165	590	78	19	72	8	37	5	16	1.8	12	1.6
S3	71	293	1366	2193	212	740	89	22	93	11	63	11	32	3.9	24	3.2
S4	45	169	1479	2284	221	786	102	25	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

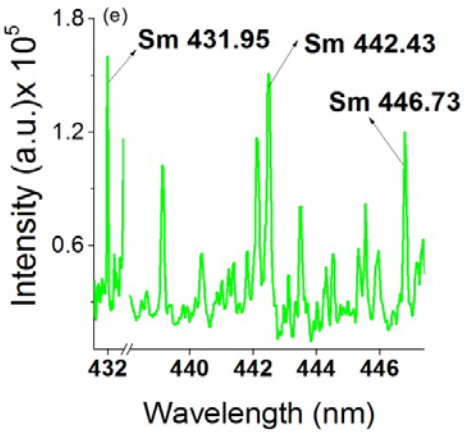
Qualitative Analysis: Detection of Spectral Lines in Standard Samples

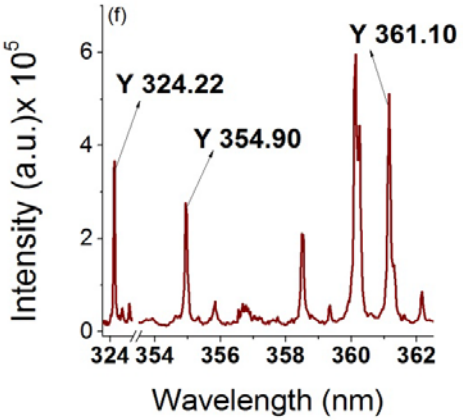




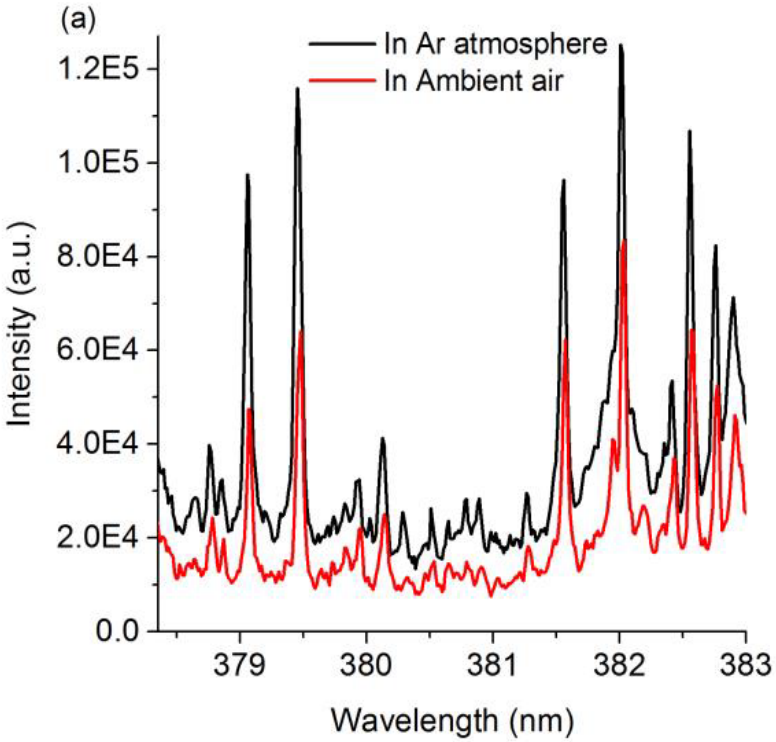


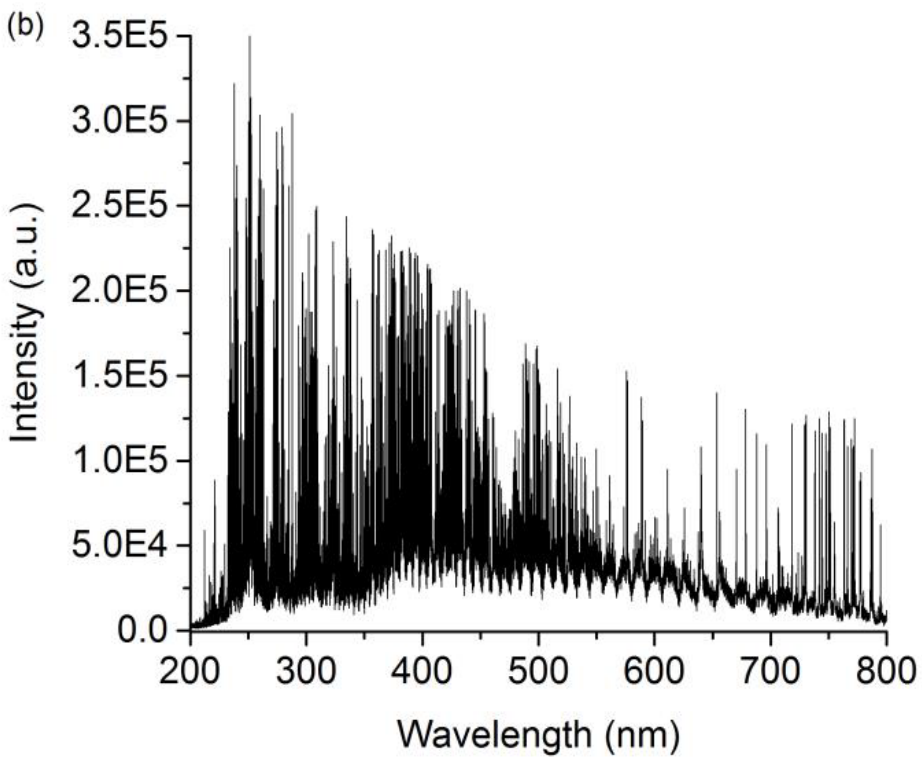






Enhancement of Signal Intensity in Ar Atmosphere



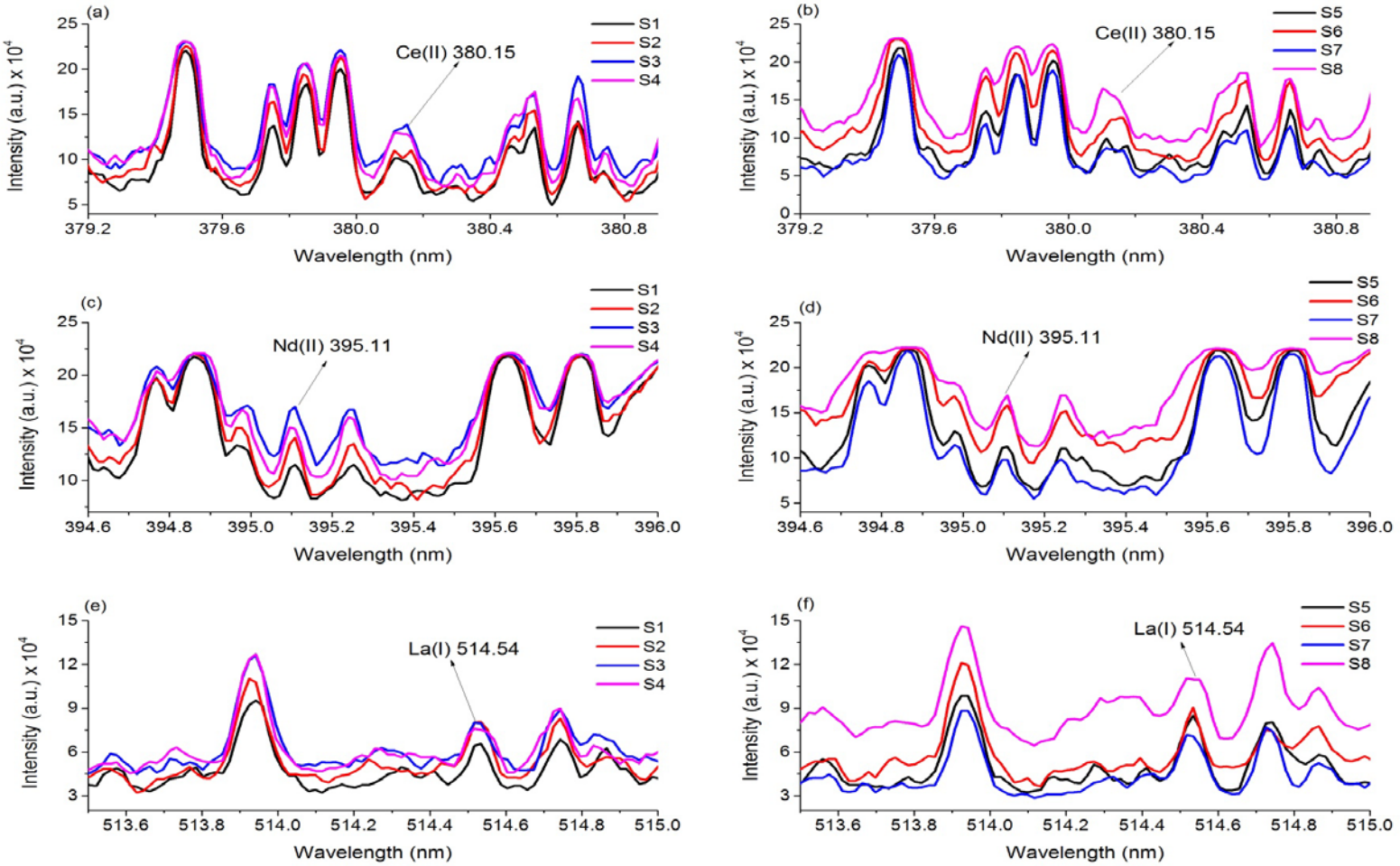


Detection of Spectral Lines in Geological Samples

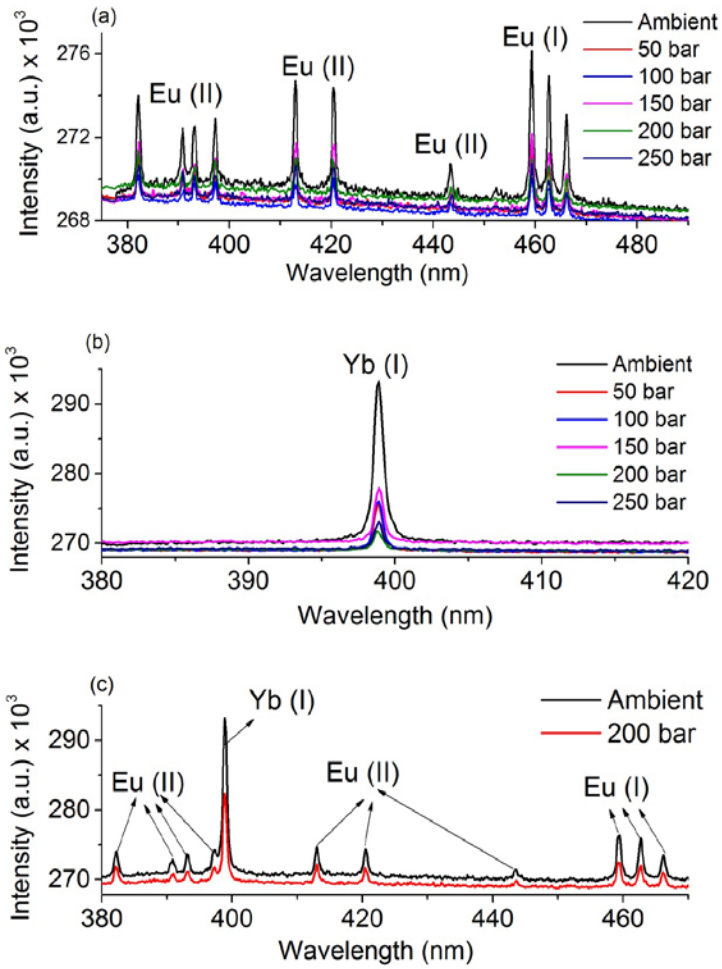
Identified lines	Samples in which these lines were detected
Ce I 560.12	S1, S2, S3, S4, S5, S6, S7, S8
Ce I 571.90	S2, S3, S4, S5, S6, S7, S8
Ce I 594.08	S1, S2, S3, S4, S5, S6, S8
Ce II 380.15	S1, S2, S3, S4, S5, S6, S7, S8
Ce II 413.76	S1, S2, S3, S4, S5, S6, S7, S8
Ce II 418.65	S1, S2, S3, S4, S5, 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

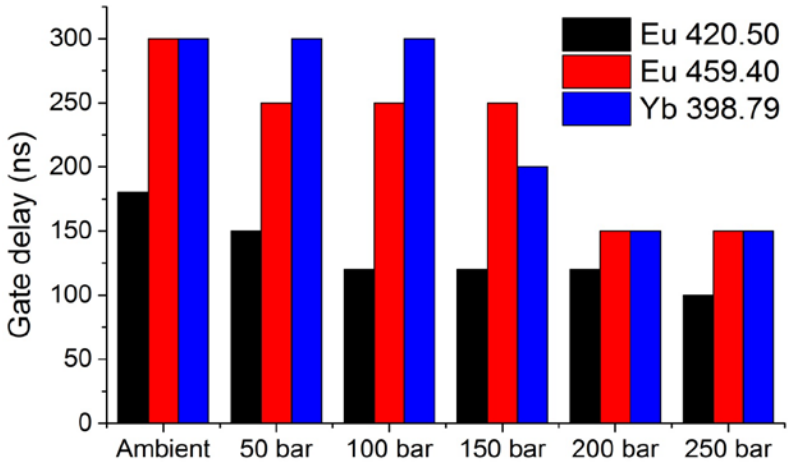
Elements	Spectral lines detected in the sample S-8
Y	324.22, 354.90, 360.07, 361.10, 363.31, 371.02, 377.43, 407.73, 412.82, 417.75, 437.49, 488.36, 490.01, 508.741 nm
Pr	417.93, 420.67, 422.29, 495.13 nm
Sm	356.82, 359.26, 363.42, 369.39 , 442.43, 446.73, 447.08 nm
Eu	372.49, 381.96, 390.71, 397.19, 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

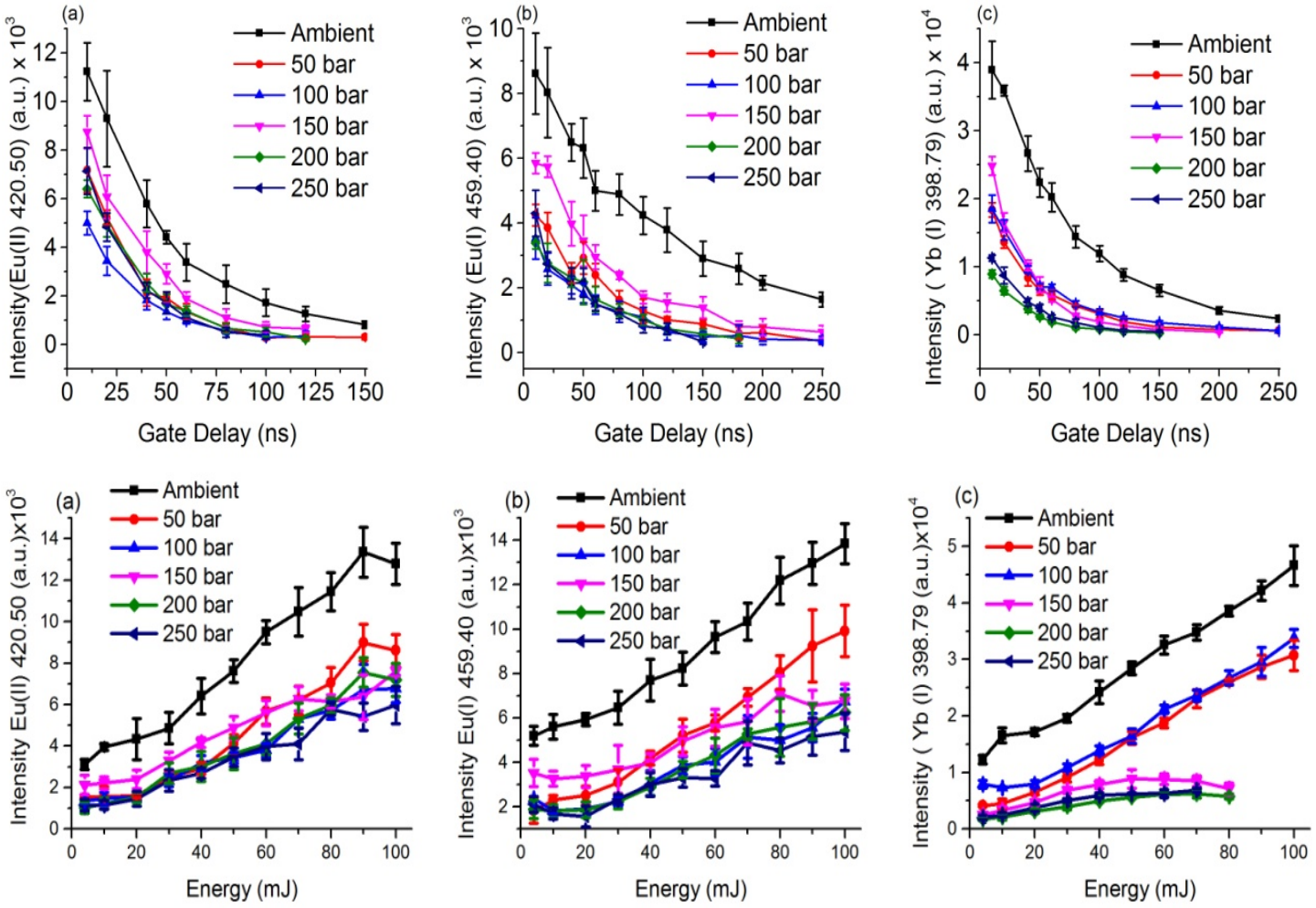


Detection of Spectral Lines in Liquid Samples





Plasma Evolution and Effect of laser Energy



Effect of Pressure on Plasma Emission

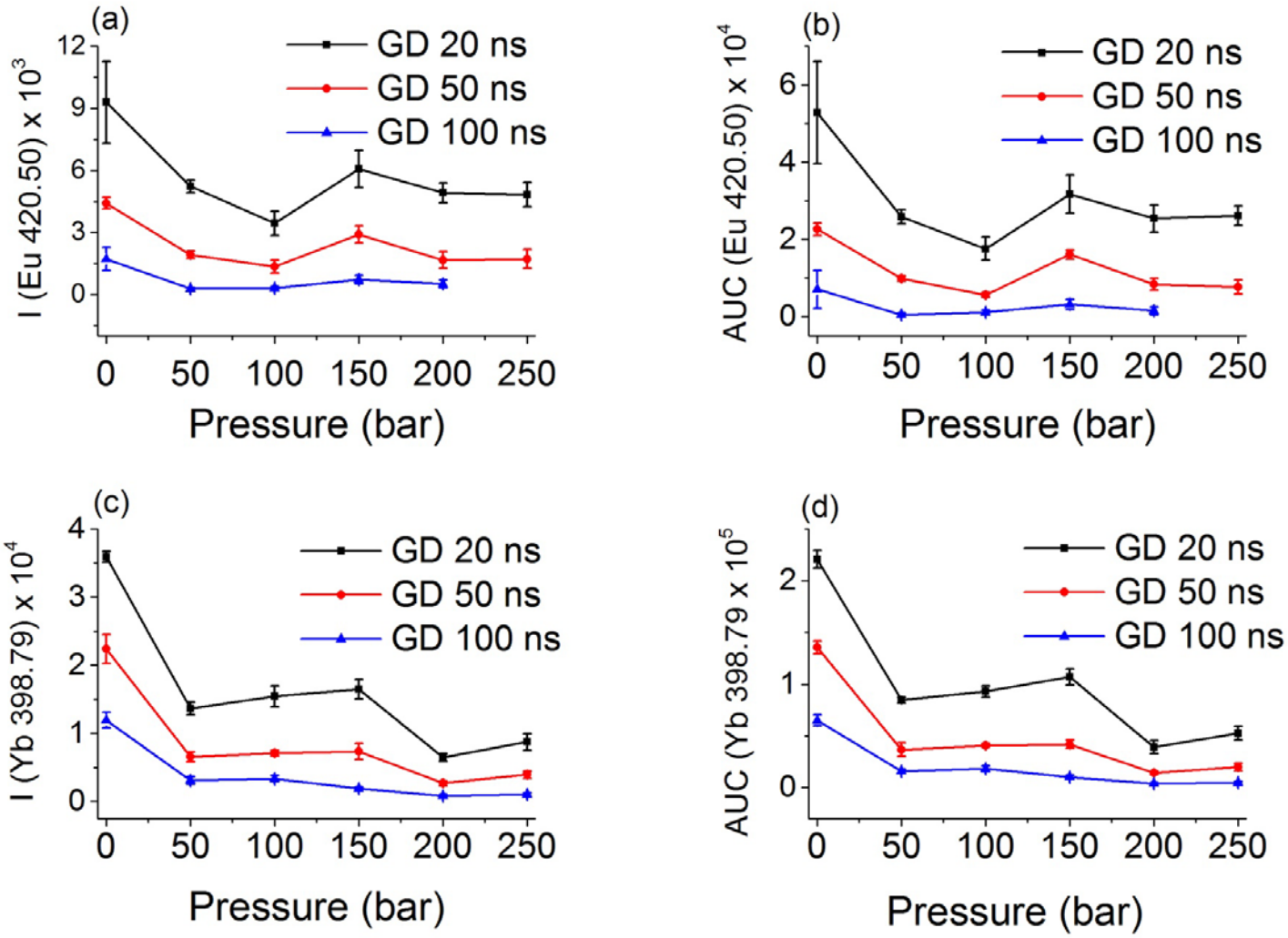
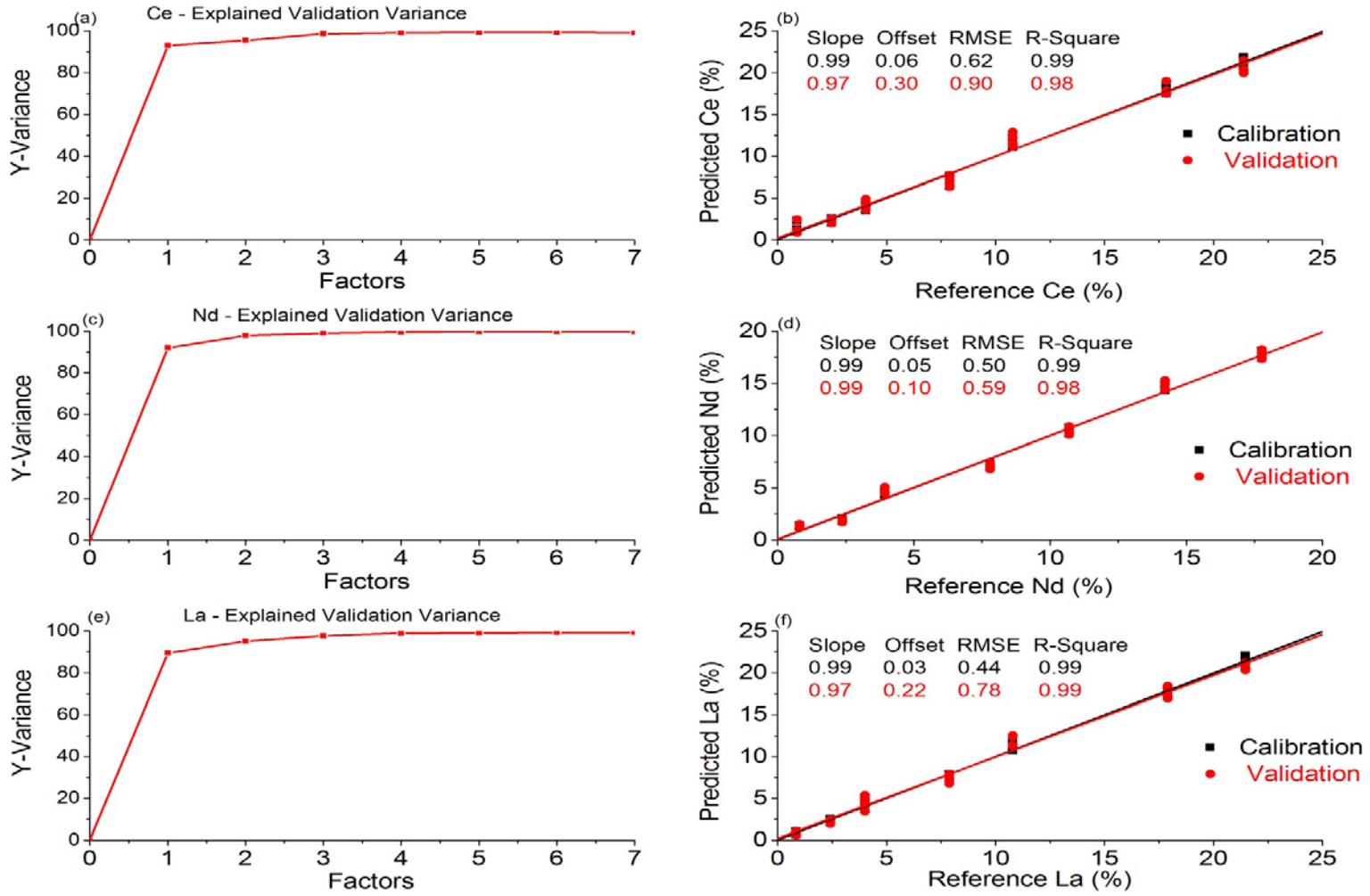


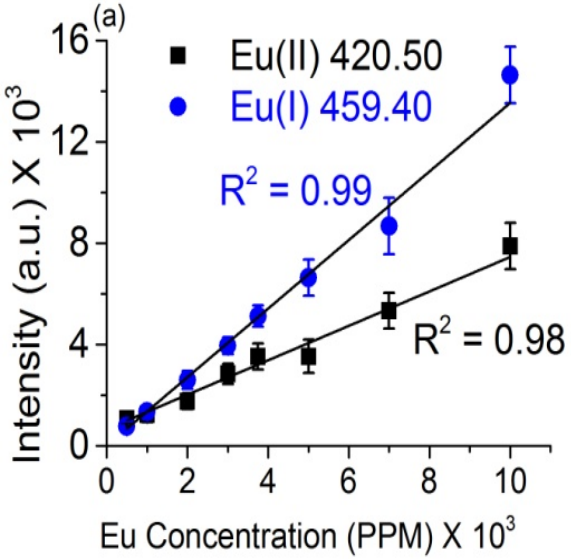
Table 2. Concentration of Ce, La, and Nd in pellets prepared for quantitative analysis.

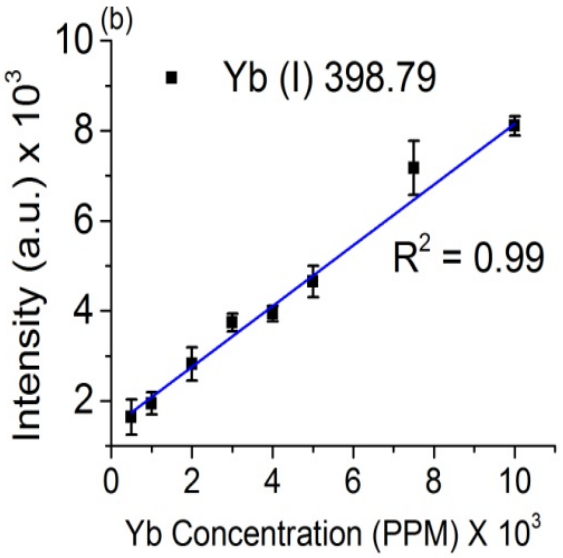
Samples	Concentration (%)		
	Ce	La	Nd
S1-M	0.89	0.85	0.81
S2-M	2.48	2.42	2.37
S3-M	4.05	4.00	3.93
S4-M	7.90	7.88	7.80
S5-M	10.79	10.79	10.70
S6-M	17.84	17.89	17.78
S7-M	21.39	21.46	14.22
S8	5.22	2.41	3.43

PLS-R: Predicted Vs Reference Plots for Geological Samples



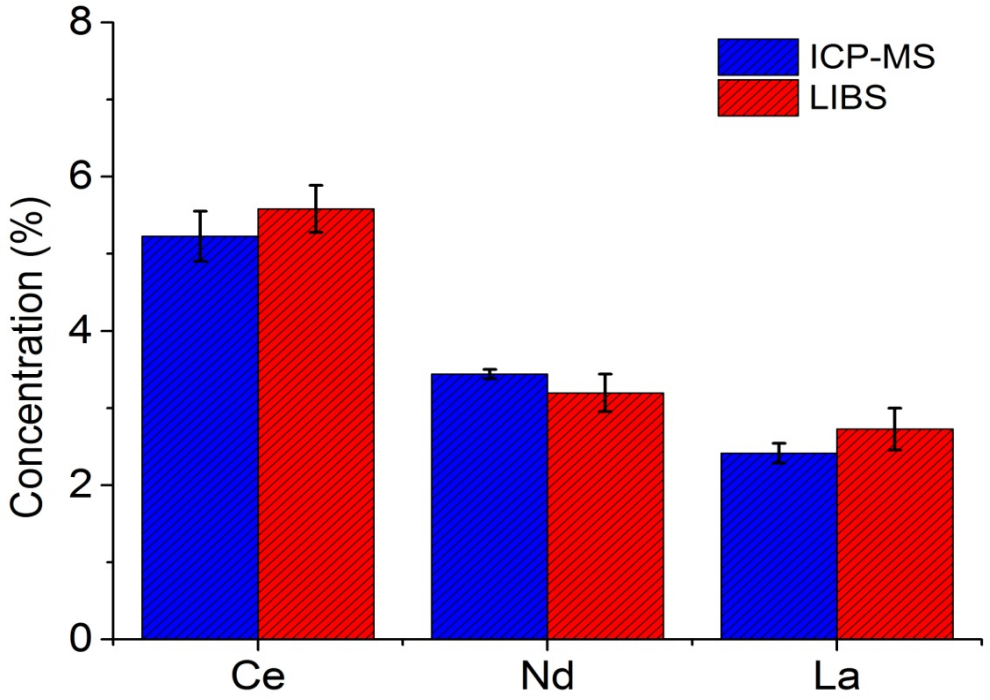
SLR Calibration Models for REE in Liquid Samples





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

Conclusions

- Designed LIBS system is a useful tool in detecting and quantifying REEs in geological minerals and liquid samples.
- The signal intensity decreased initially but stabilized later on with increasing CO2 pressures.
- Simple linear regression (SLR) calibration method yielded acceptable results for liquid samples.
- PLS-R calibration models were preferred for complex matrix geological samples.
- The predicted results for Ce, Nd, and La were found to be comparable to those obtained by ICP-MS measurements.

Acknowledgment

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