Use of LIBS Technology for CO_2 Leak Detection in Carbon-Sequestration

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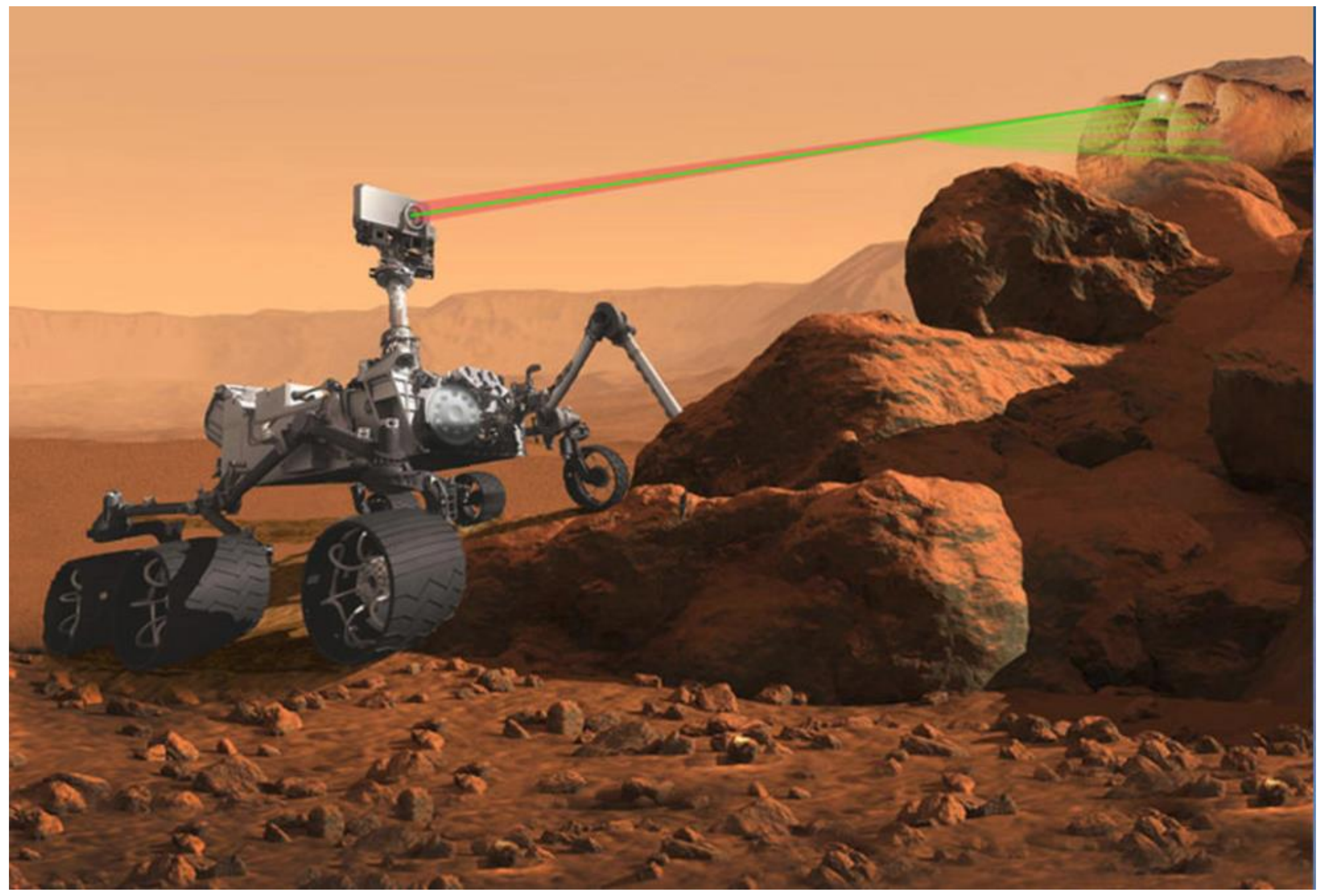
LIBS is an atomic emission spectroscopy-based analytical technique to obtain qualitative and quantitative information of the material.

LIBS for Mars mission

NASA's Curiosity rovers:
ChemCam-2012 and SuperCam-2020.



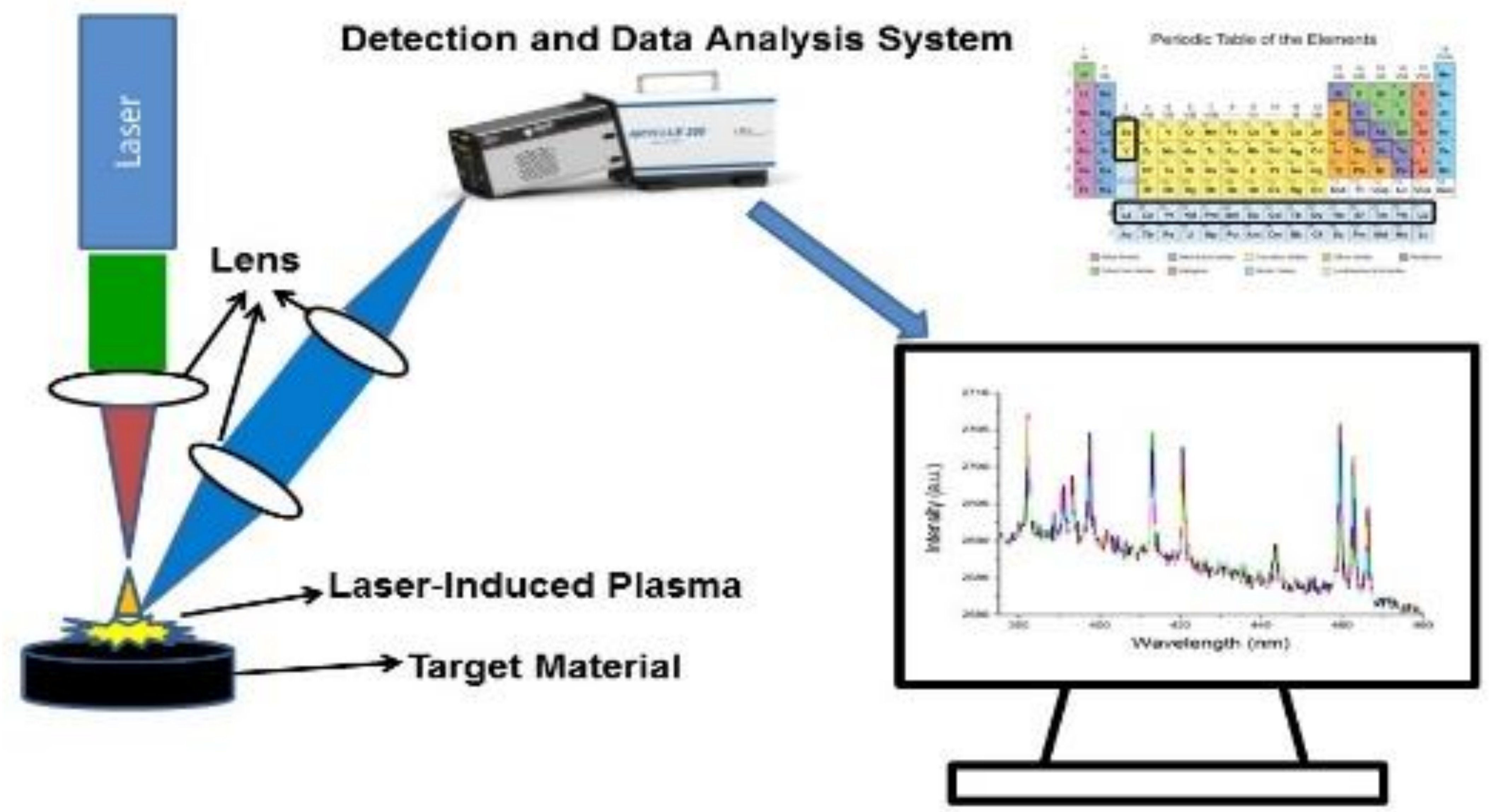
Advantages of LIBS

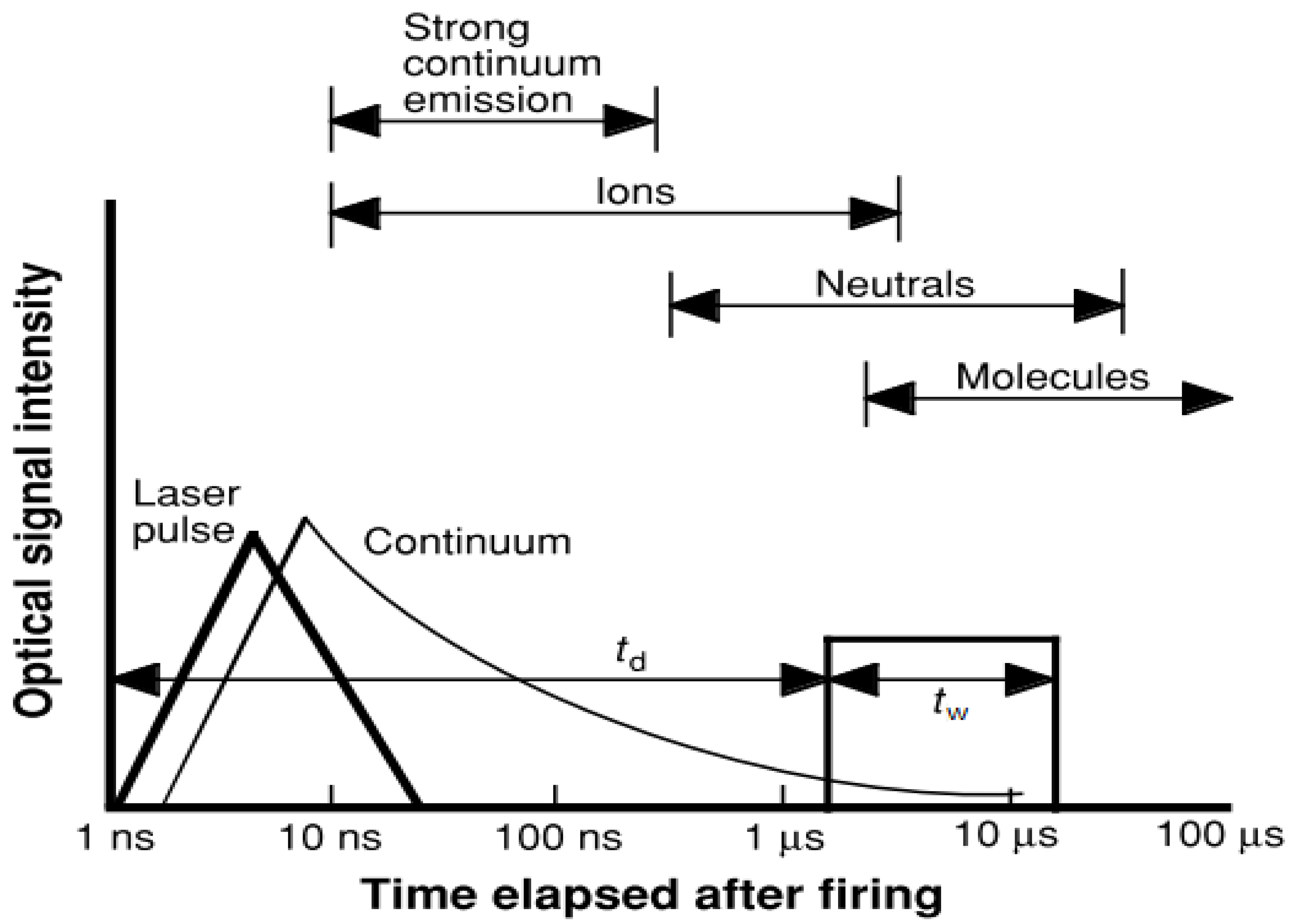
- LIBS is in situ technique.
- Needs minimal or no sample preparation.
- Can analyze any matter regardless of its physical state; solid, liquid, gas, aerosol.
- Broad elemental analysis - including Light elements of Z < 12 (e.g. C, H, O, N, Li, B, Be) and heavy elements.
- Feasibility of using in harsh environments generally unattainable with other techniques.

How Does LIBS Work?

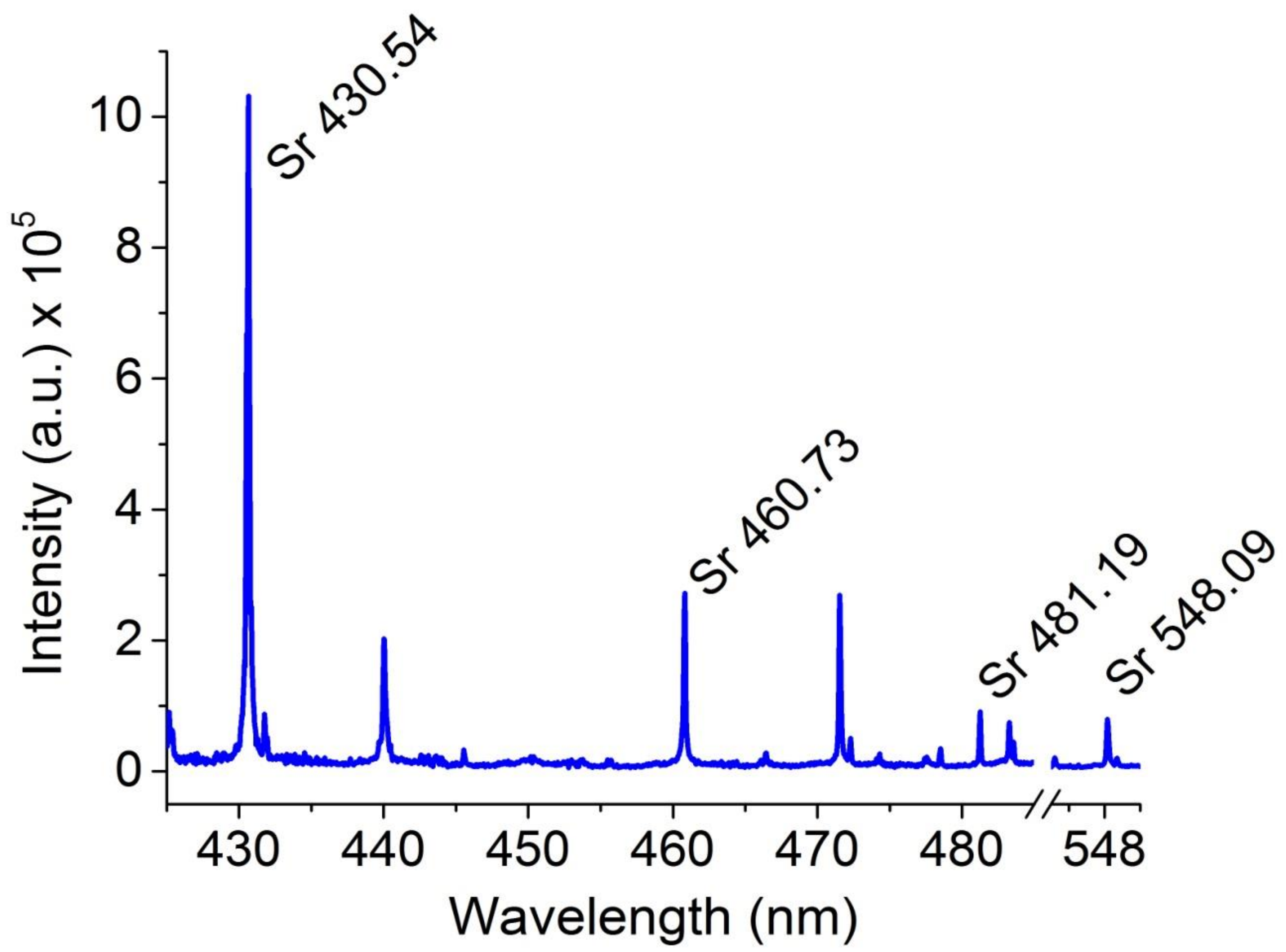
LIBS is an atomic emission spectroscopy-based analytical technique to obtain qualitative and quantitative information of the material.

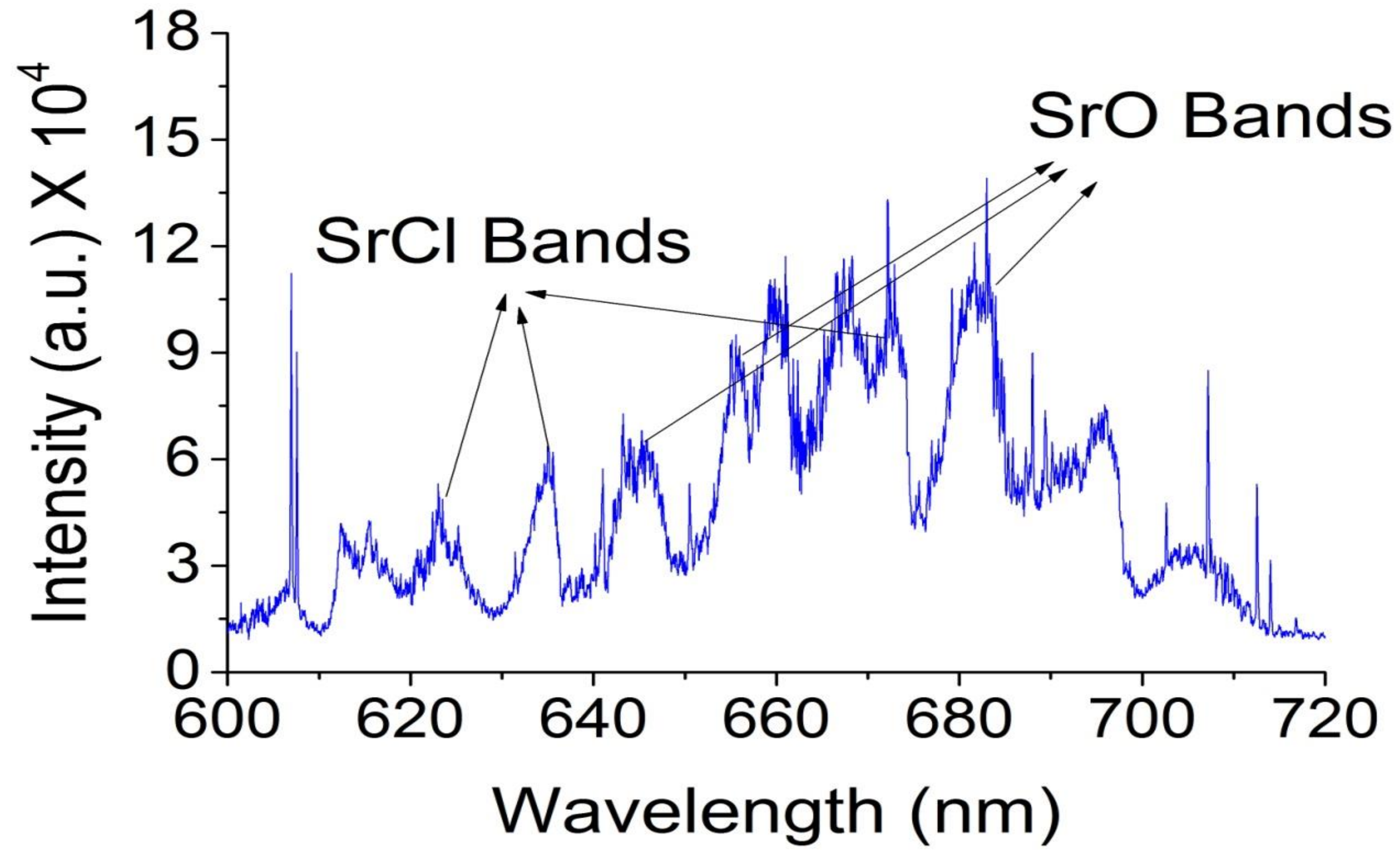
- High energy laser pulse creates micro plasma plume on the sample by ablating a very small amount of material.
- The ablated material dissociates into excited ionic and atomic species.
- The excited atoms/ions present in the plasma emit light at their characteristic wavelengths.
- Spectral analysis of the emission spectrum from the plasma is used to infer the elemental composition of the sample.

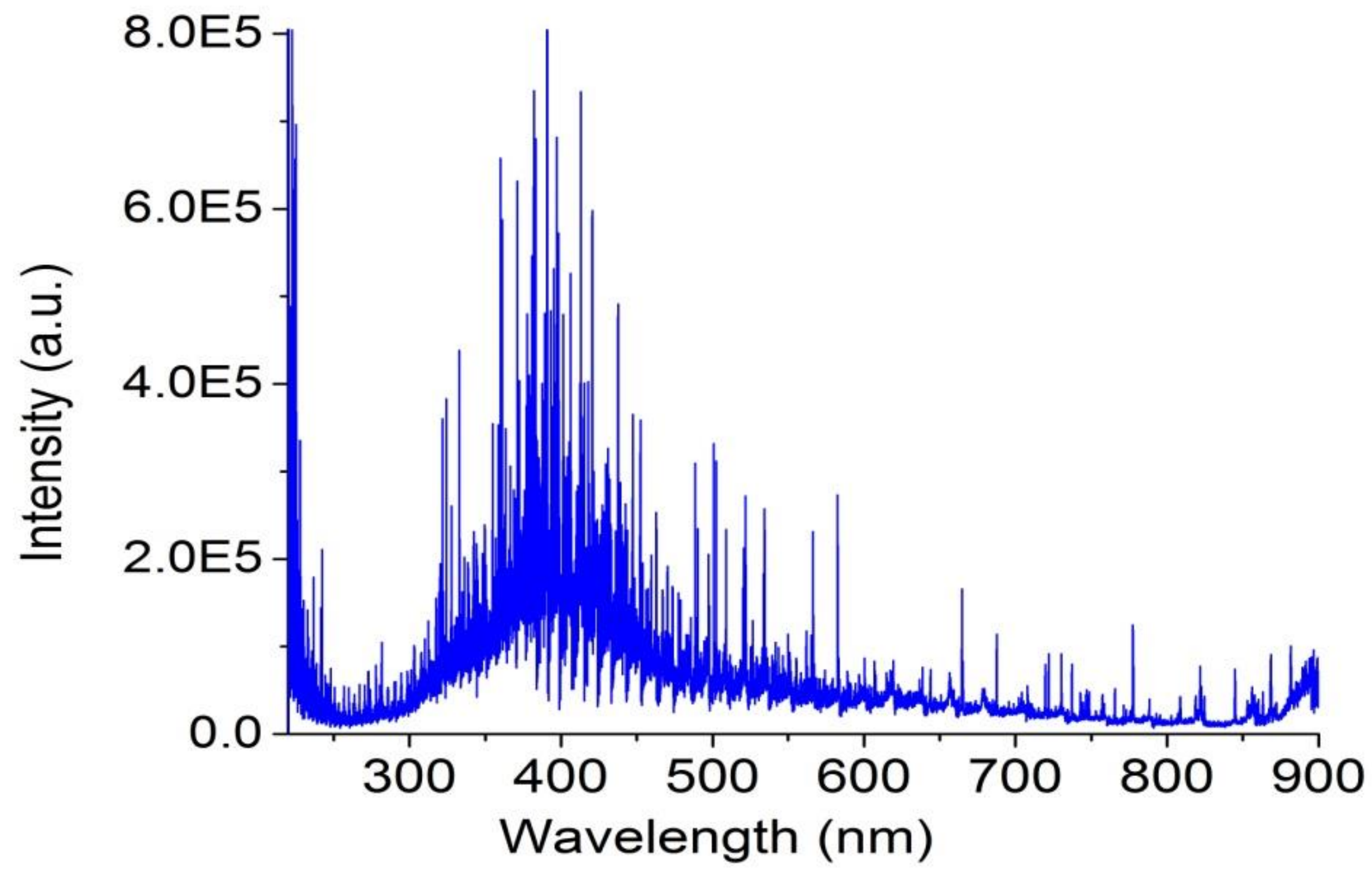




Univariate & Multivariate Analysis







Univariate Analysis: SLR
Multivariate Analysis: PLS, PCA

CCS: DOE-NETL’s one of the projects

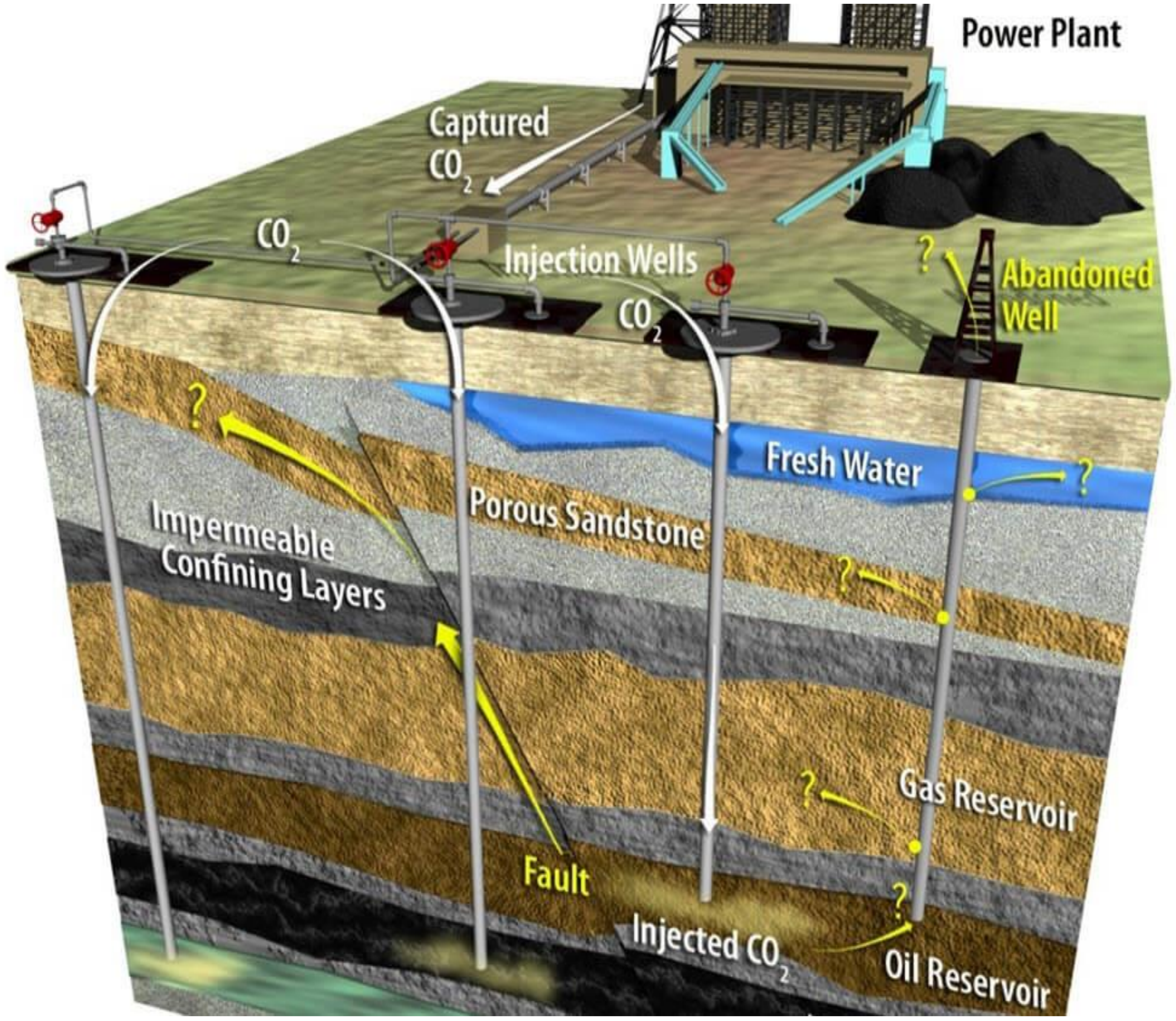
- Carbon Capture and Storage
- Research Gaps
- Need of online monitoring

- At NTP, carbonates are almost insoluble.
- As pCO_2 increases, the pH drops, carbonate ions (CO_3^{2-}) are converted into bicarbonate (HCO_3^-) ions.

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$

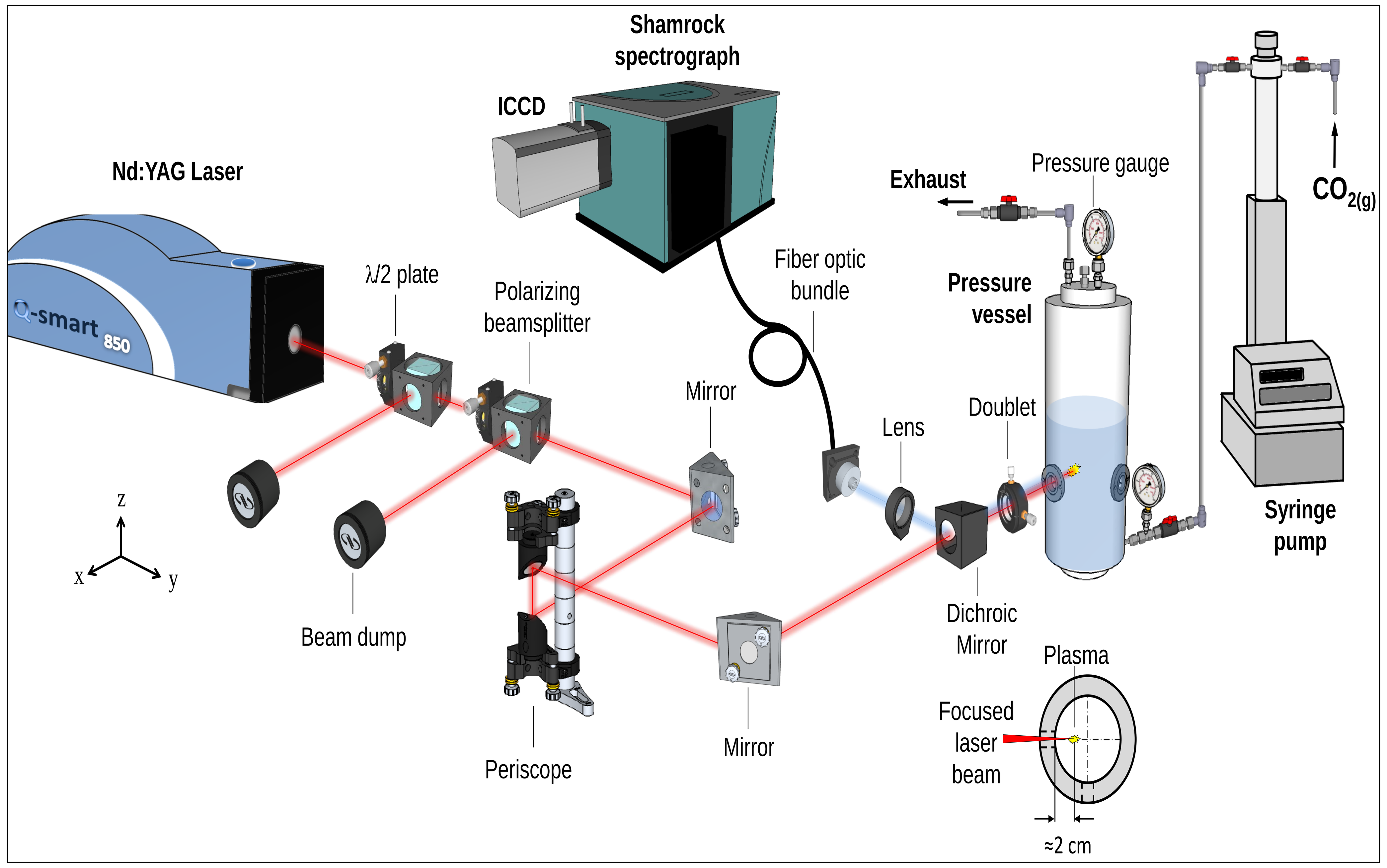
$$H^+ + SrCO_3 \leftrightarrow Sr^{2+} + HCO_3^-$$

$$H^+ + CaCO_3 \leftrightarrow Ca^{2+} + HCO_3^-$$



Picture: GoldSim Technology Group, Los Alamos National Laboratory (LANL)

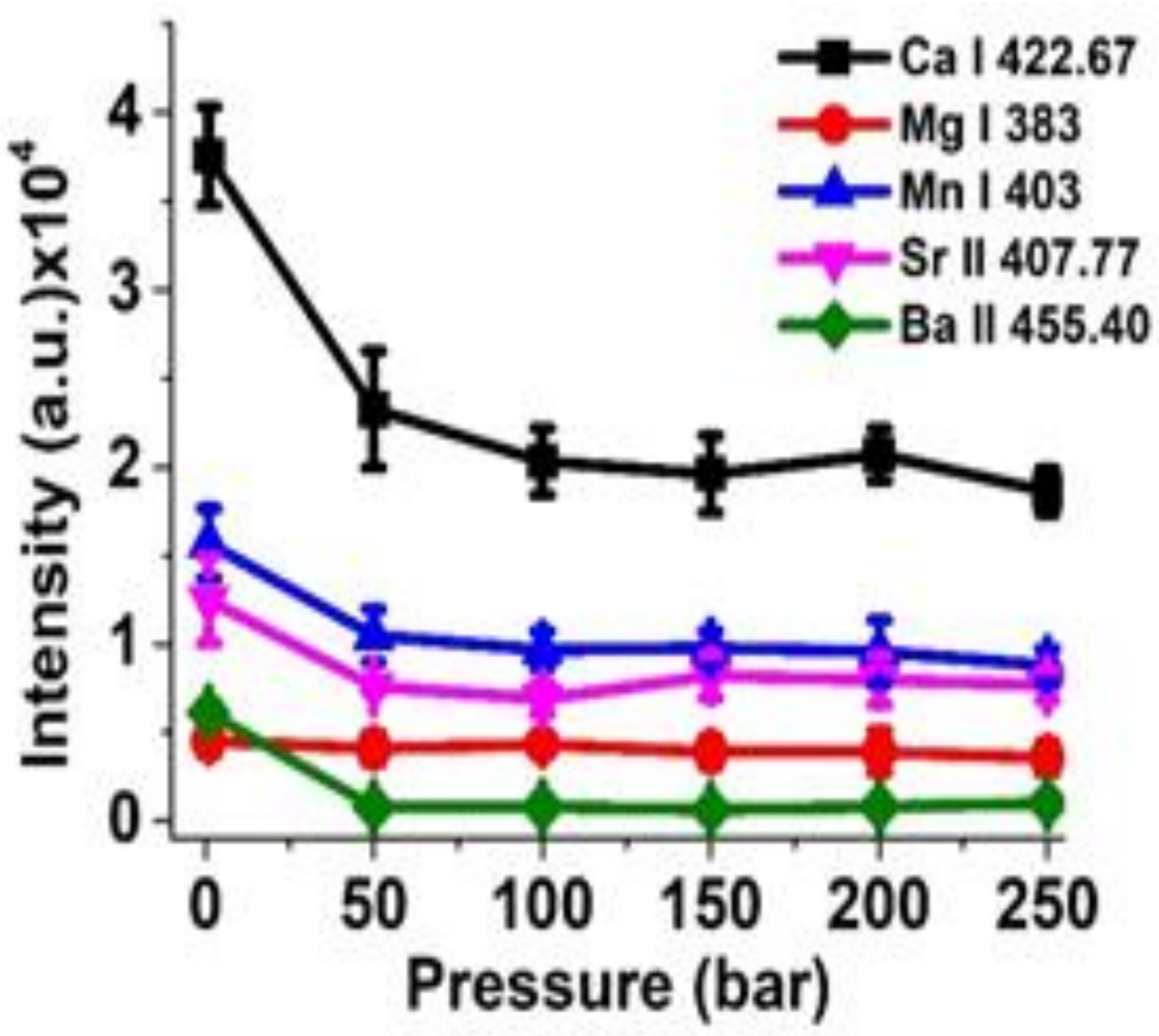
Working Samples & Experimental Set-up



- Samples: $CaCO_3$, $SrCO_3$, $MnCO_3$, $MgCO_3$, Mt. Simon.
- Pellet composition: Carbonate powder and 4% agarose.
- Pellet size and weight: 15 mm diameter, 0.5 g.

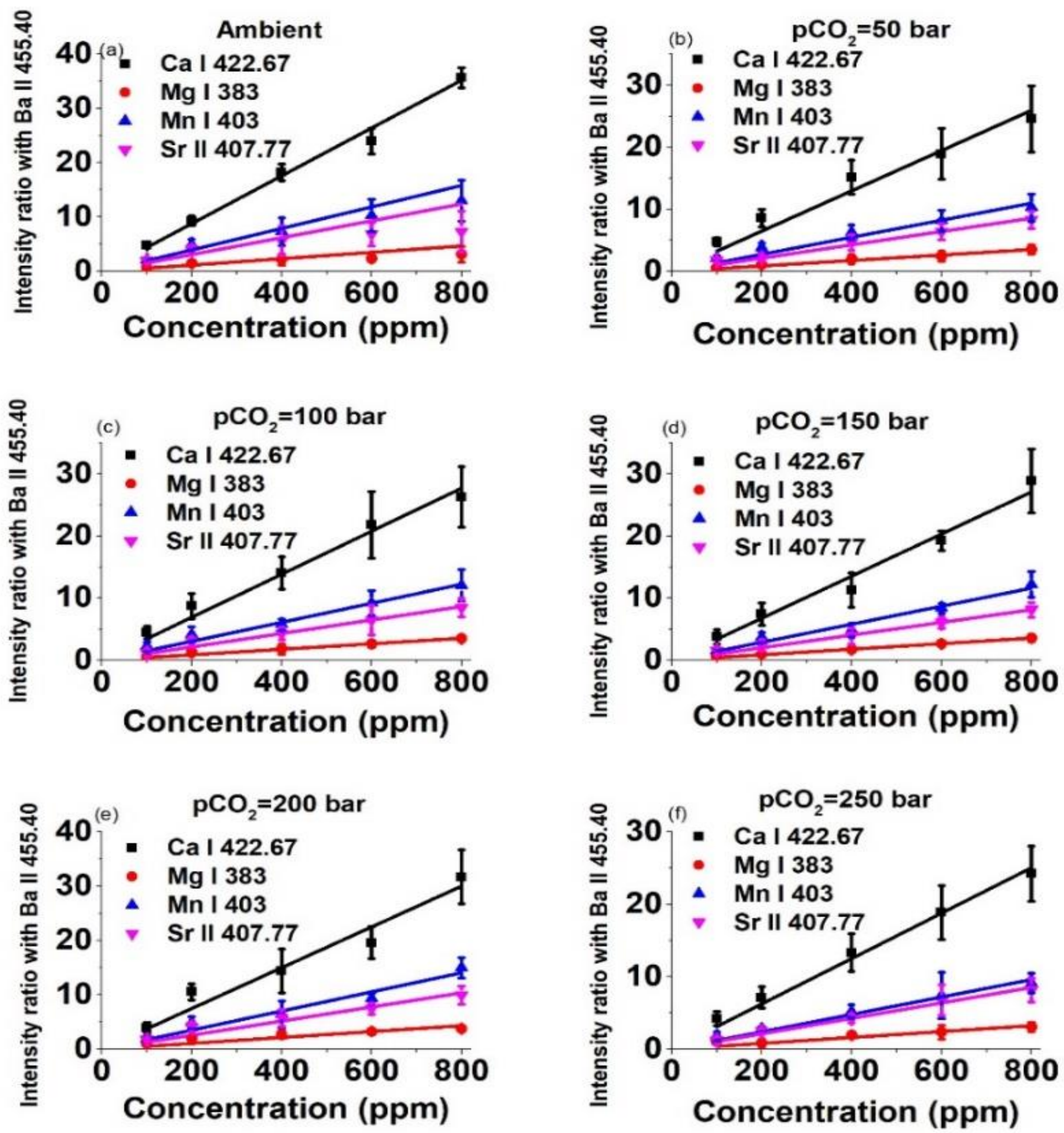
Experimental parameters
Laser: Nd:YAG (Q-smart 850, Quantel),
Wavelength: 1064 nm, Pulse duration: 6ns
Gate delay: 100 ns and 160 ns,
Gate width: 400 ns and 800 ns,
Laser energy: 25 mJ with 10 Hz repetition rate

CO_2 Pressure Effect on Underwater LIBS



- Sample: 200 ppm each Ca, Mg, Mn, and Sr in 1mM $BaCl_2.2H_2O$ solution (250 ml)
- CO_2 Pressure: Ambient -250 bar ~ 8000 ft.
- Ambient to 50 bars: Significant effect on Ca, Mn, Sr, Ba lines
- 50 to 250 bars: Almost negligible effect.
- Mg doublet: no significant change in intensity but change in intensity profile.
- Significant effect in the beginning (<50 bar) of the injection of the CO_2.
- Increased pressure confines the plasma and intensity reduced due to confinement.
- Once the CO_2 absorption reaches to saturation, intensity remains unaffected.

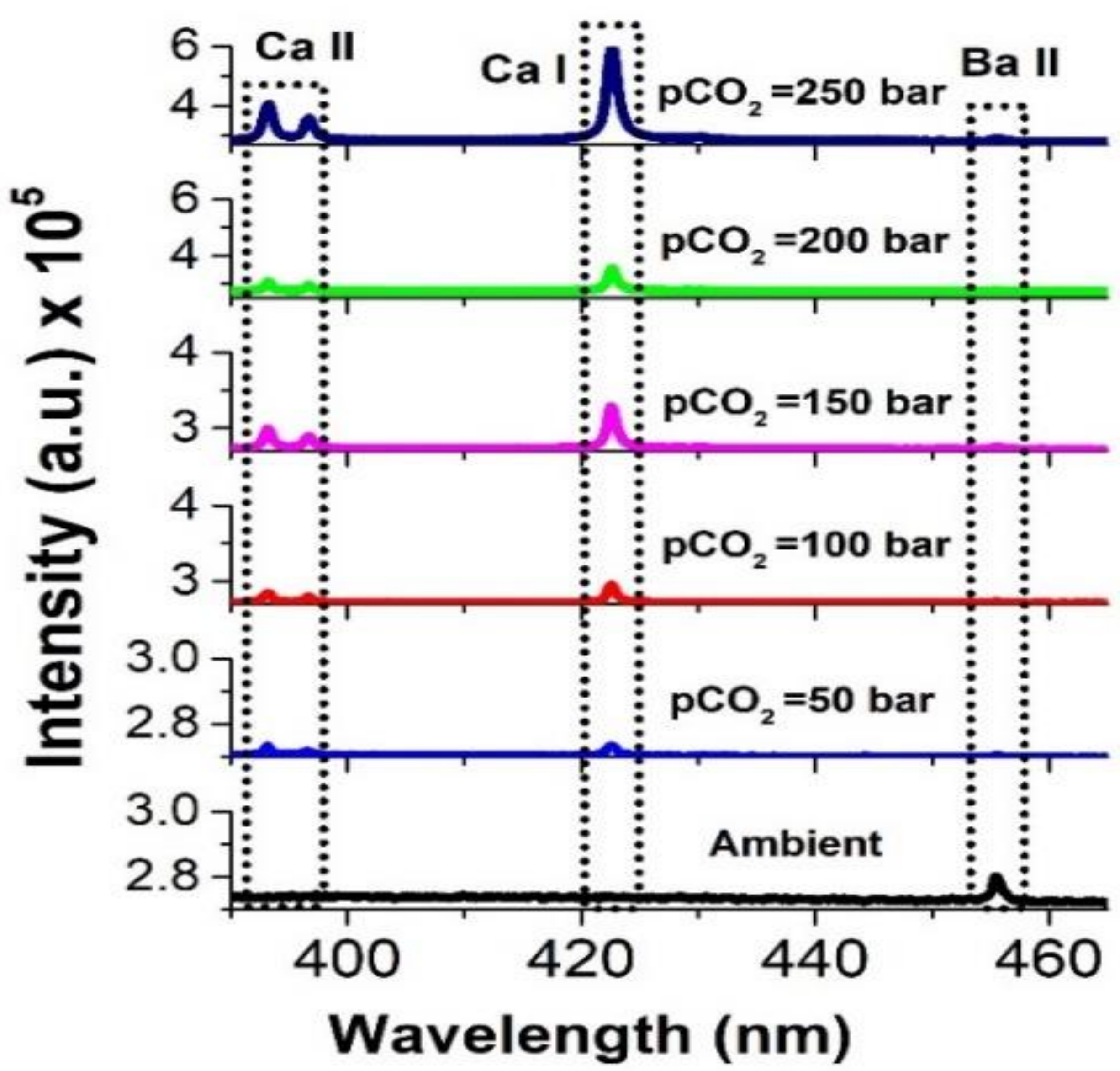
Calibration Curves and LOD

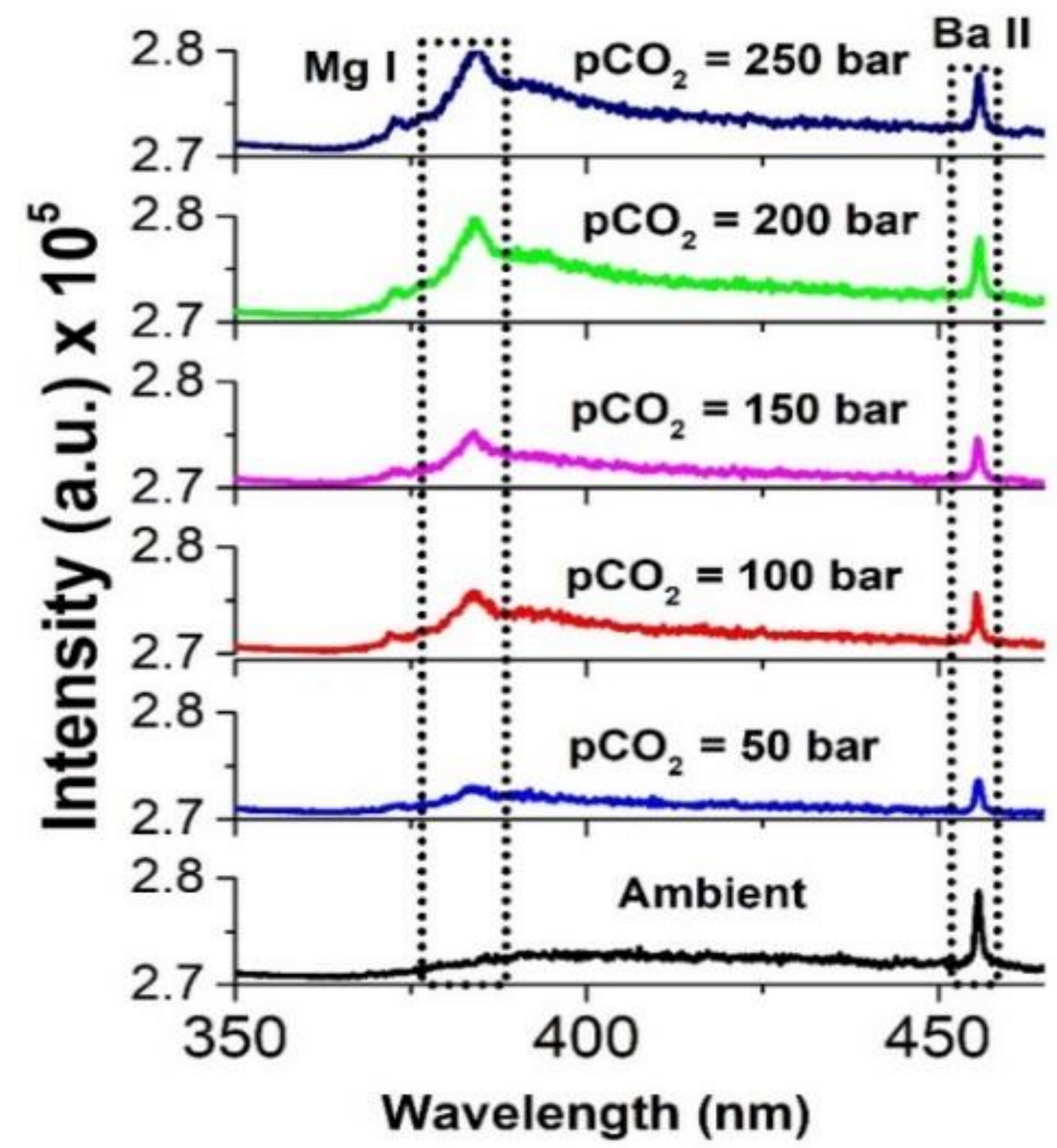


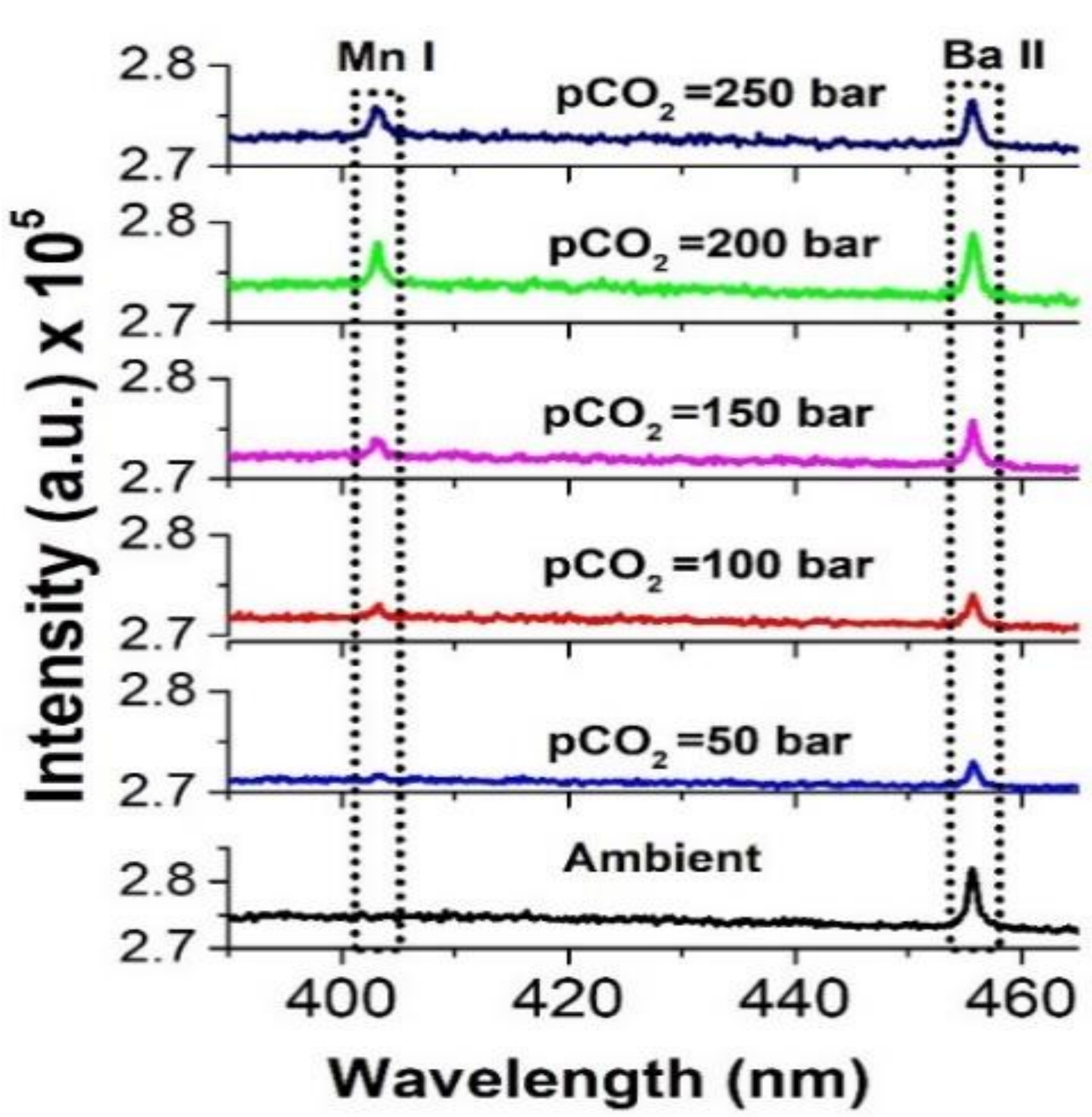
CO_2 Pressure	LOD (ppm)			
	Ca I 422.67	Sr II 407.77	Mn I 403	Mg I 383
Ambient	1	2	2	6
50 bar	5	10	4	10
100 bar	4	9	4	8
150 bar	4	9	4	11
200 bar	4	9	4	10
250 bar	4	11	5	11

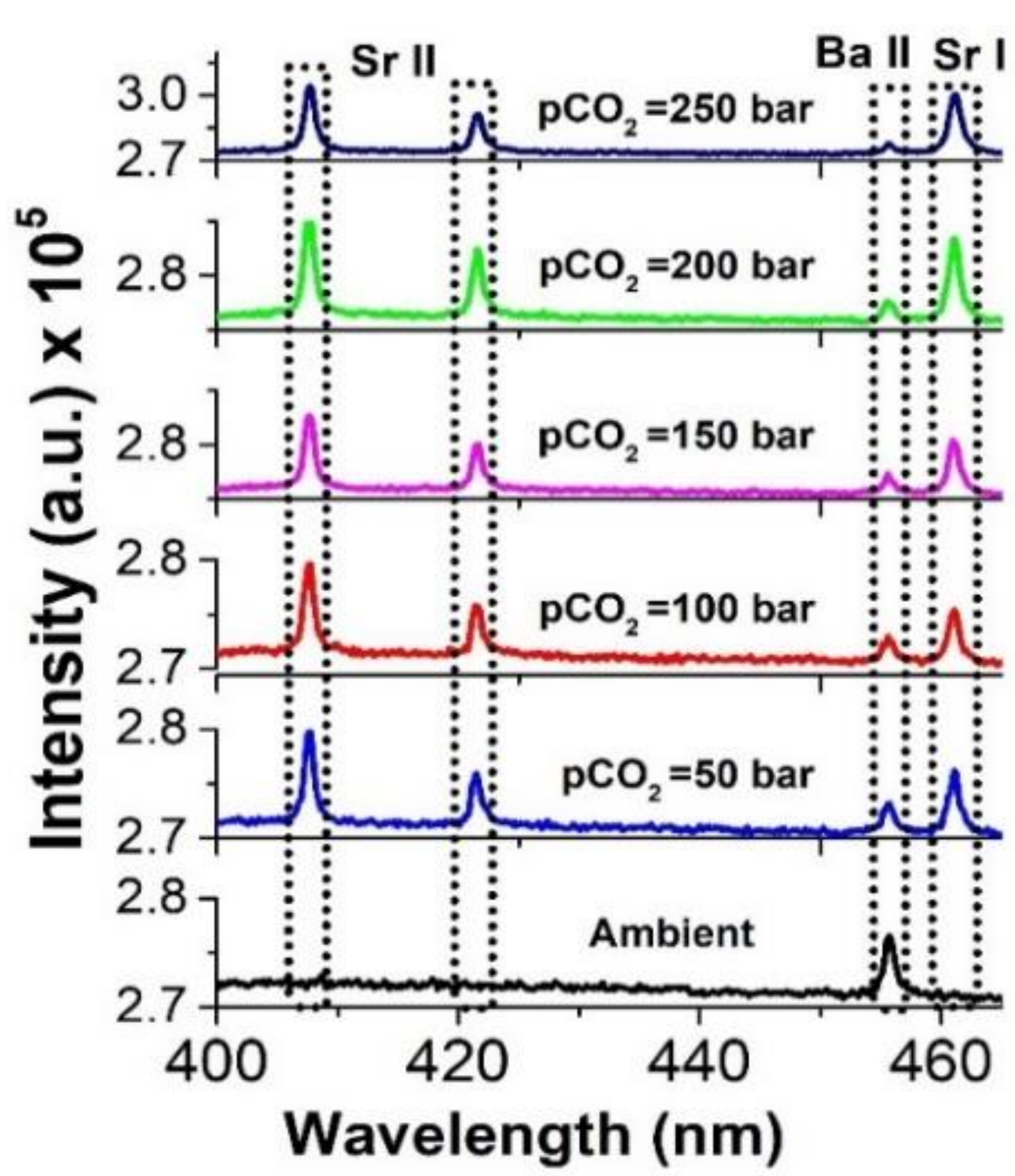
Note: CO_2 Pressure affected LOD

Dissolution from Carbonates



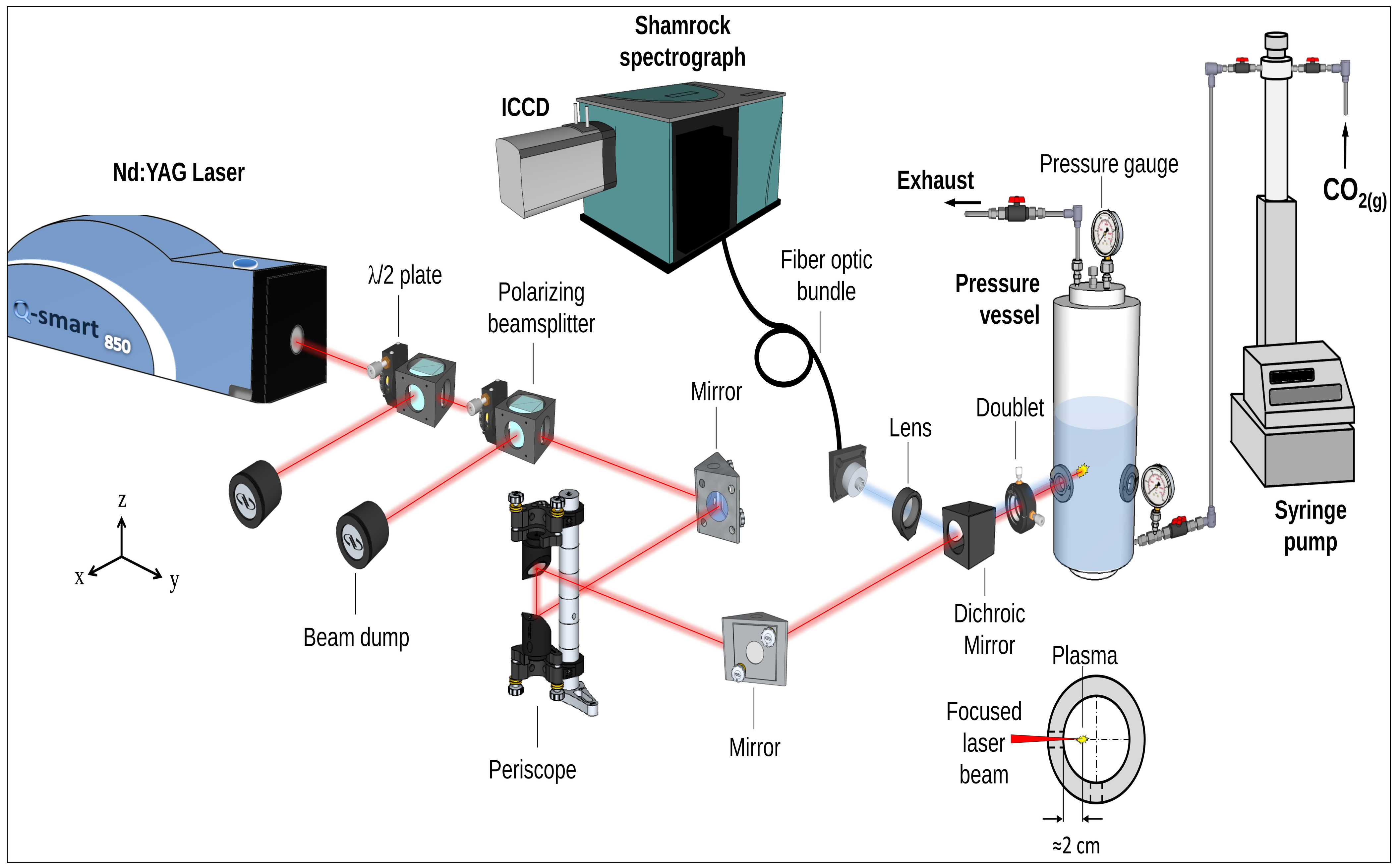


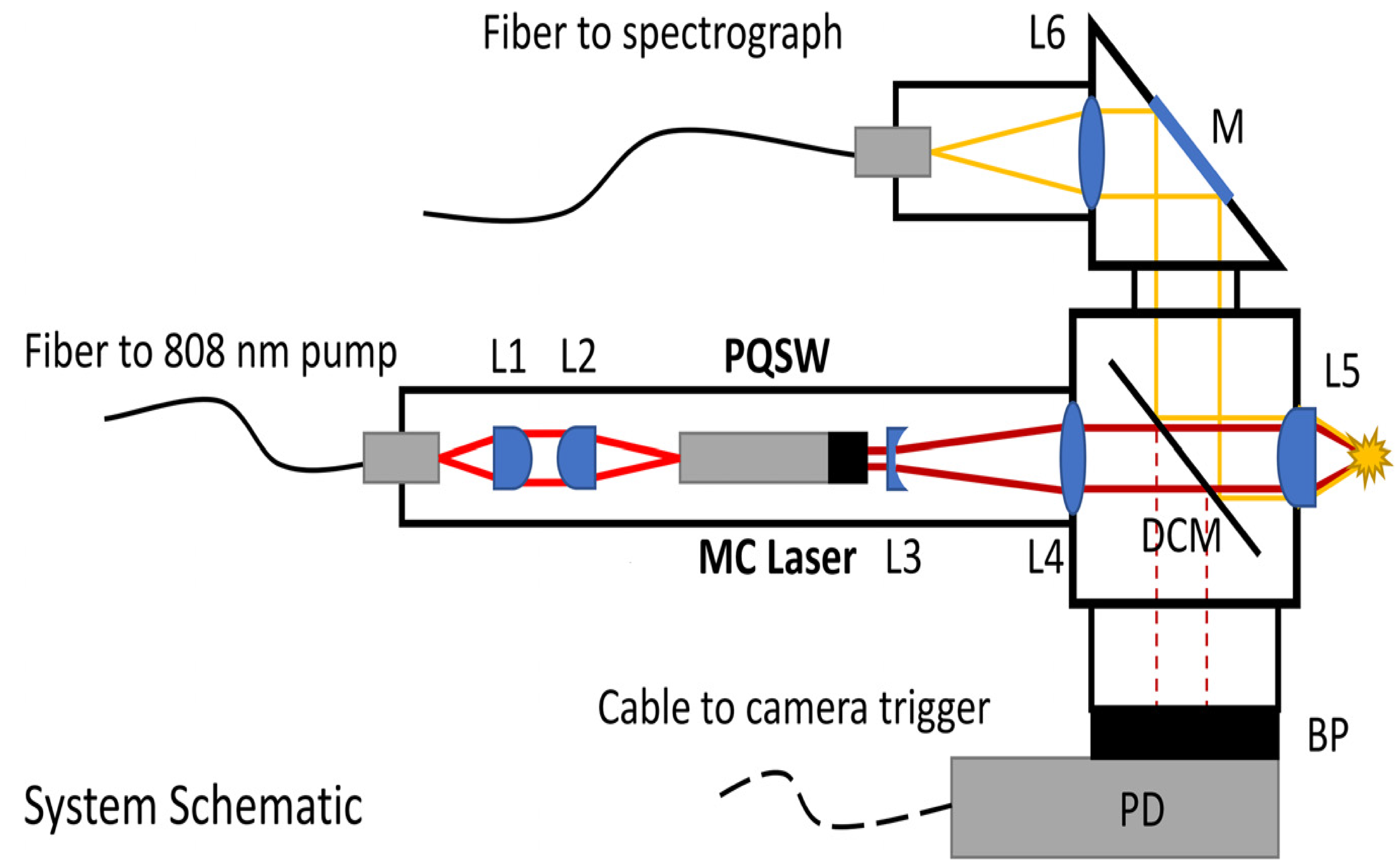




- pCO_2: 50, 100, 150, 200, 250 bars
- Each pressure was continuously maintained for 24 hours.
- LIBS spectra were recorded: in 5 min, 1 hr, 2 hr, 3hr, 4 hr and 24 hrs.
- At 50 bars, no distinguishable signals for first four hours.
- After 24 hrs, Ca, Mg, and Sr was detected.
- Lines detected:
  Ca (Ca II 393.36, Ca II 396.84, Ca I 422.67 nm),
  Unresolved doublet Mg I 383 nm, Sr II 407.77, Sr II 421.55, Sr I 460.73)
- No signal of Mn at 50 bars.
- Unresolved triplet Mn I 403 nm detected after 24 hrs of 100 bars.
- Either no dissolution or very small; no detection due to very weak signal/limitation of set up or pressure effect.

Miniaturization





Picture: Hand-held LIBS spectrometer | Spectroscopy Europe/Asia

Conclusions

- LIBS methodology was developed to detect dissolution of four carbonates, $CaCO_3$, $SrCO_3$, $MnCO_3$, $MgCO_3$, and Mt. Simon in high pressure CO_2 liquid environment.

- This study shows that LIBS can be used to detect CO_2 leakage during its geological storage by monitoring carbonate dissolution.

- Water contamination due carbon storage in underground reservoirs can be assessed.

- LIBS Sensor can be developed for online monitoring of CO_2 leak detection and water quality assessment.

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Questions?