Development of LIBS for Subterranean Chemical Sensing

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Abstract

The stability of different carbonate minerals is pH-dependent and their rates of dissolution vary. In the case of CO_2 leakage and upward migration from geologic carbon storage (GCS) sites, the reaction of available metal carbonates in bedrock may release specific metals useful as tracers in shallow groundwater aquifers. In this study, we used laser induced breakdown spectroscopy (LIBS) to examine in situ dissolution rates of various mineral carbonates ($MgCO_3$, $CaCO_3$, $SrCO_3$, and $MnCO_3$) in the presence of increasing CO_2 pressure ranging from 25 - 350 bar. The experiments were carried out using both pressed-carbonate and hydrogel-carbonate pellets. The gel pellets were formed by drying mixed suspensions of carbonate powder and 4% agarose gel. A pulsed Nd:YAG laser at 1064 nm was used to produce gaseous plasma in the fluid surrounding pellets. The ensuing plasma emission was spectrally analyzed, and the intensity of the Mg, Ca, Sr, and Mn emission lines were used to monitor their respective concentrations in aqueous solution. The dissolution of carbonates in CO_2-free aqueous HCl was also measured at ambient pressure over a pH range of 2 to 6 under the same experimental conditions. A kinetic model incorporating both results has been developed to represent the selective dissolution rates of carbonates used in this study. The results demonstrate that in situ monitoring of carbonate dissolution by LIBS may provide a useful indirect detection system indicative of CO_2 leakage from some storage sites.

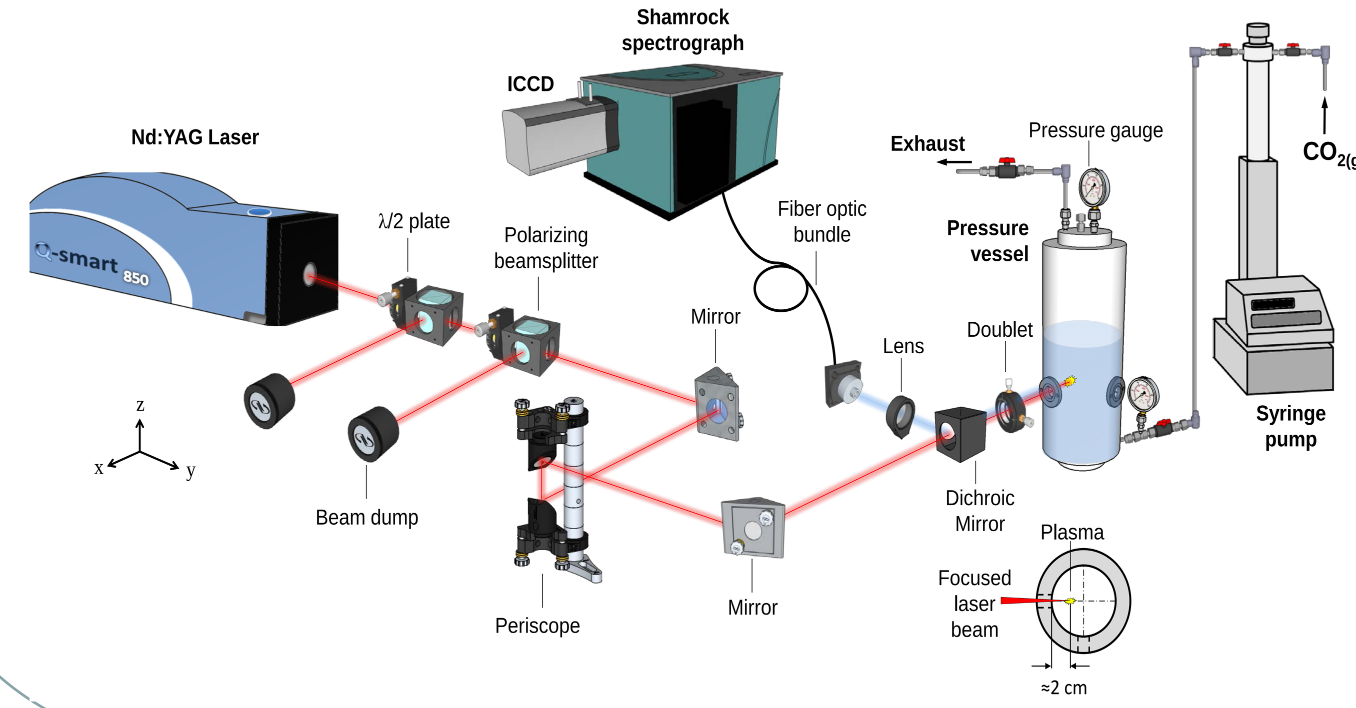
Laser-Induced Breakdown Spectroscopy (LIBS)

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

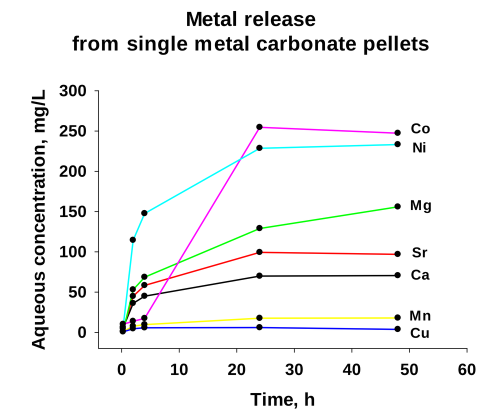
Experimental Samples

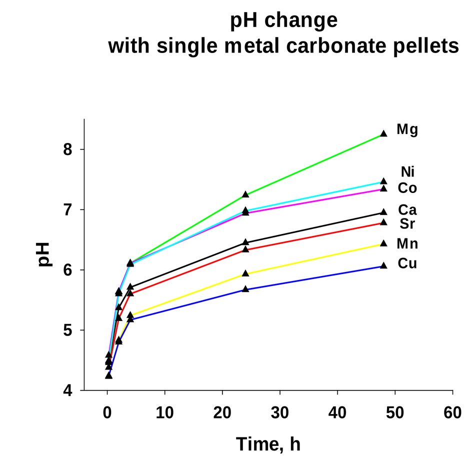
- Carbonate pellets were prepared from 4% agarose discs containing 0.5 g powder.
- Carbonates tested included Ca, Sr, Mg, Mn, Cu, Ni, Co, mixed carbonates and natural limestones.
- Pellets were shaken (150 rpm) in carbonated spring water for 2 d and monitored by ICP-OES.
- For LIBS, $CaCO_3$ (99.99%) Pellet was kept into a solution of 250 mL of 1 mM $BaCl_2H_2O$.

LIBS Experimental Set-Up

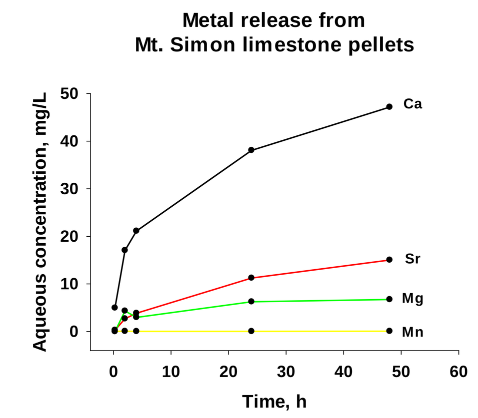


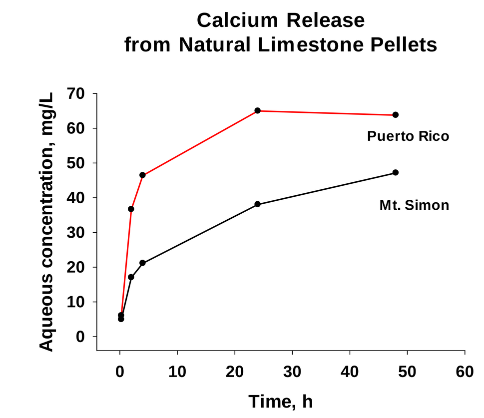
Overview of Pellet Dissolution Experiments





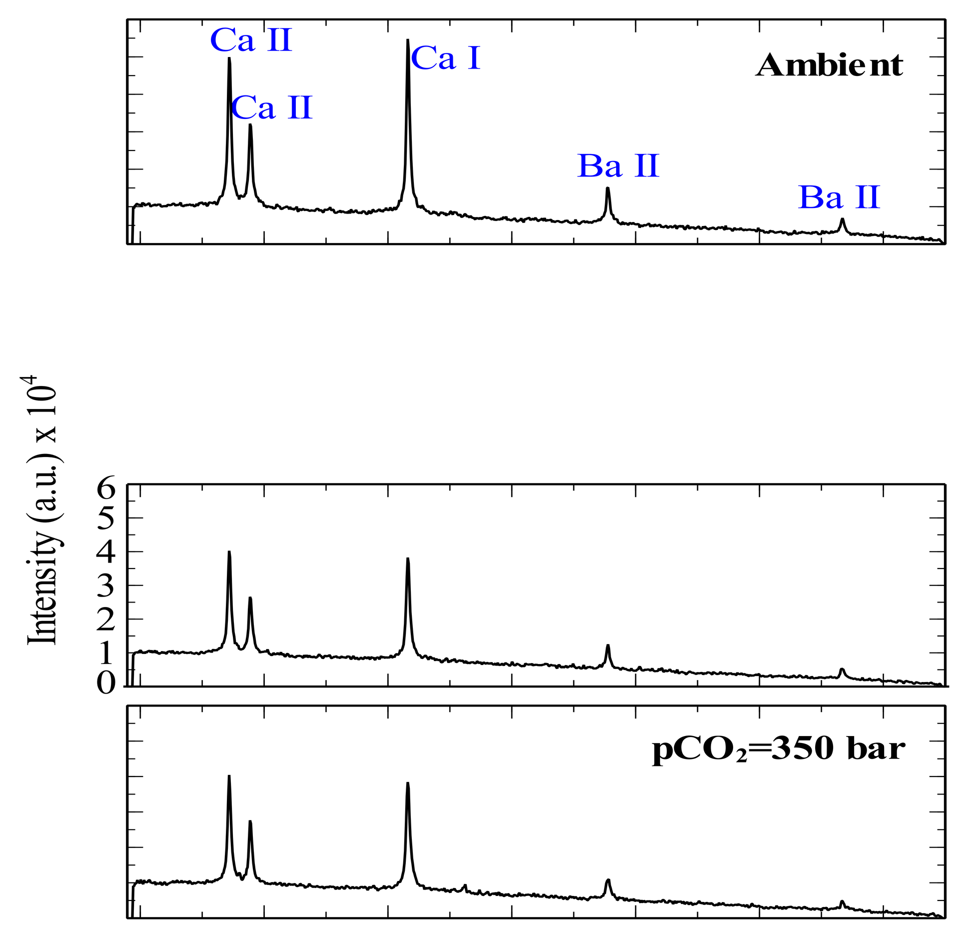
- Metal release rates from pellets prepared with reagent-grade carbonate powders differed in carbonated spring water. Co, Mg, and Ni pellets contained additional hydroxides, which influenced solubility and pH.
- The pH in all solutions rose over time, a combination of CO_2 degassing and selective buffering by carbonates and hydroxides.

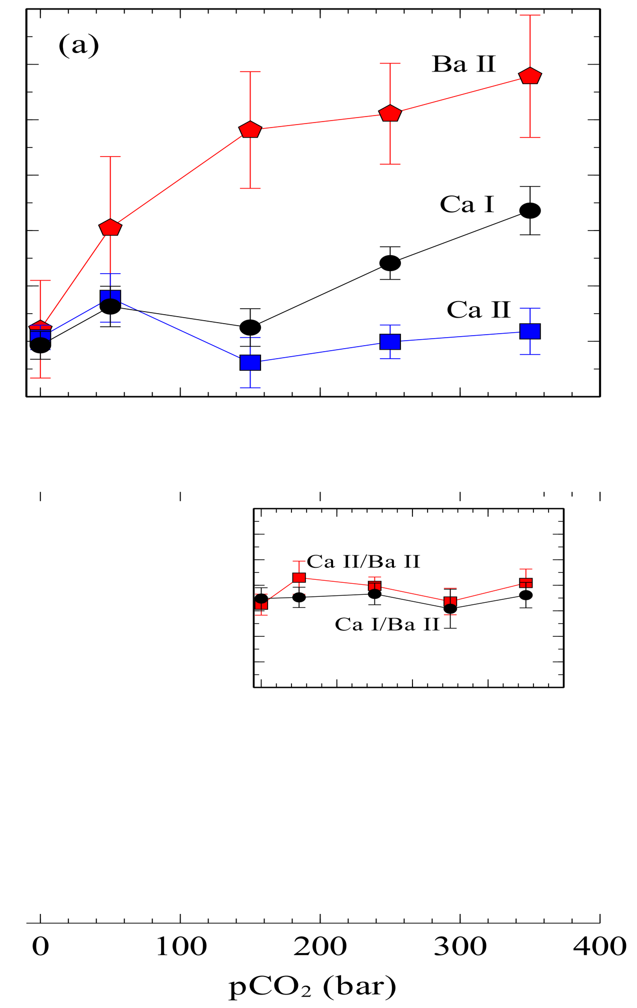




- Pellets prepared with limestone core (4288') above the Mt. Simon formation in the Illinois Basin showed selective release of Ca(II) in carbonated spring water.
- Comparison of Ca(II) release from pellets prepared using two different limestones (Mt. Simon and eogenetic limestone from Puerto Rico) suggests that solubility rates will be dependent on the source of the carbonate rock.

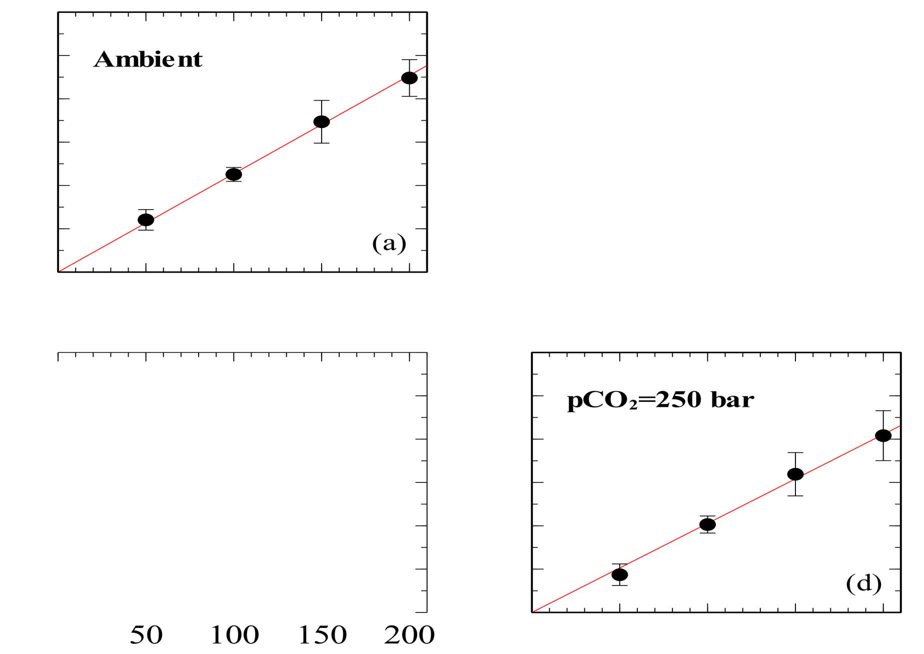
Influence of CO_2 Pressure on LIBS Spectra





- Pressure-induced line broadening: 20–37% increase of the full at width half maximum (FWHM) for Ca I and Ba II emission lines.
- CO_2 pressure has minimal adverse effects on the signal-to-background ratio (SBR), other than a small decrease at higher pressure.

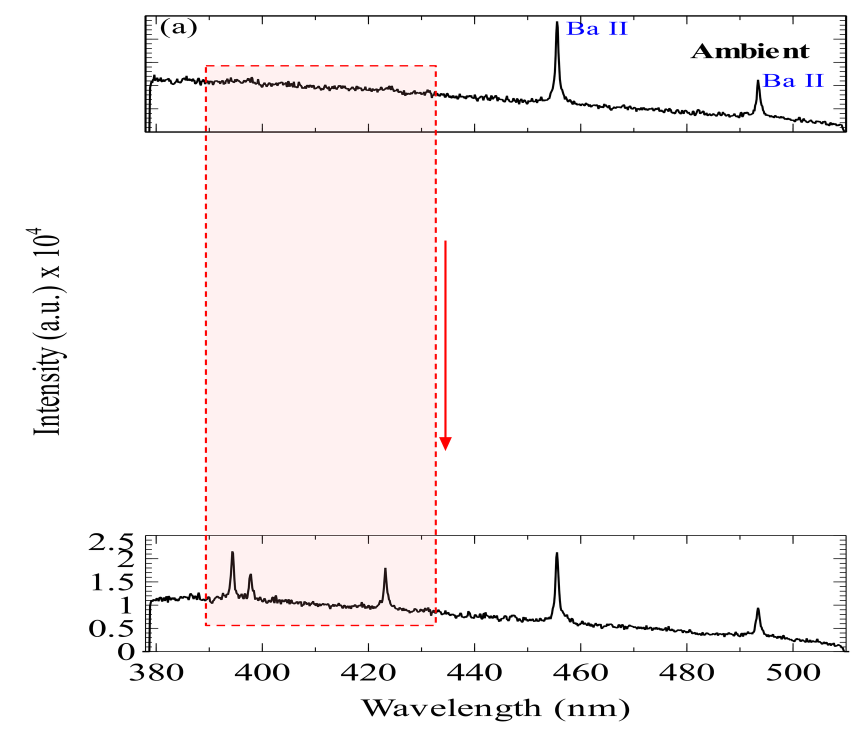
Calibrating LIBS System for Ca^{2+} Measurement

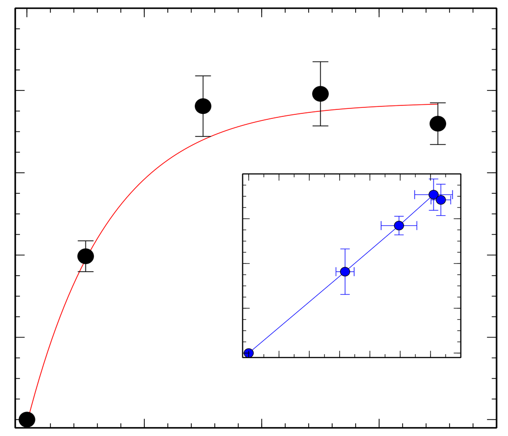


pCO_2 (bar)	R^2	DL (ppm)
Ambient	0.9997	7.35 ± 0.4
50	0.9977	9.21 ± 0.3
150	0.9962	9.37 ± 0.5
250	0.9988	9.03 ± 0.8
350	0.9994	9.58 ± 0.3

Increasing CO_2 pressure over the range 50–350 bar has little effects on Ca^{2+} detection limit (DL), which was estimated to be about 9 ppm.

In-situ Measurements of $CaCO_3$ Dissolution





Ca^{2+} released in water increases with pCO_2 up to 150 bars but remains nearly constant when pCO_2 was further increased to 350 bars, which may be related to lesser effects on the pH of the solution. Indeed, it is possible that the pH remains unchanged or varies slightly over the range 150–350 bars preventing further dissolution of $CaCO_3$.

Conclusions

- This work constitutes the first study that demonstrates the promising possibilities offered by LIBS for in situ quantitative analysis of CO_2-saturated water under pressures up to 350 bars.
- Carbonate dissolution can potentially provide a robust sensing device for CO_2 sequestration monitoring
- Elemental Information:
  - Can sense presence of Carbon dioxide (CO_2) leak
  - Can provide information about carbonate minerals leached from injection formations into ground water
- Future work:
  - Continue experiments on dissolution of other carbonates in HT/HP conditions.
  - Component integration towards field scale studies.
  - Laser and optical design for harsh environments.

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References

1. Christian Goueguel, et al. "In situ measurements of calcium carbonate dissolution under rising CO 2 pressure using underwater laser-induced breakdown spectroscopy." *Journal of Analytical Atomic Spectrometry* 31.7 (2016): 1374-1380.
2. P. K. Kennedy, et al., "Laser-induced breakdown in aqueous media," Progress in Quantum Electronics, vol. 21, pp. 155-248, 1997.