

# In-situ measurement of calcium carbonate dissolution under rising $pCO_2$ using underwater laser induced breakdown spectroscopy

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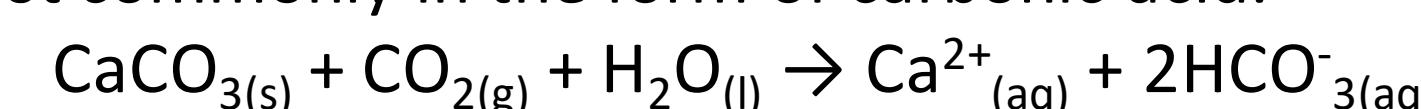
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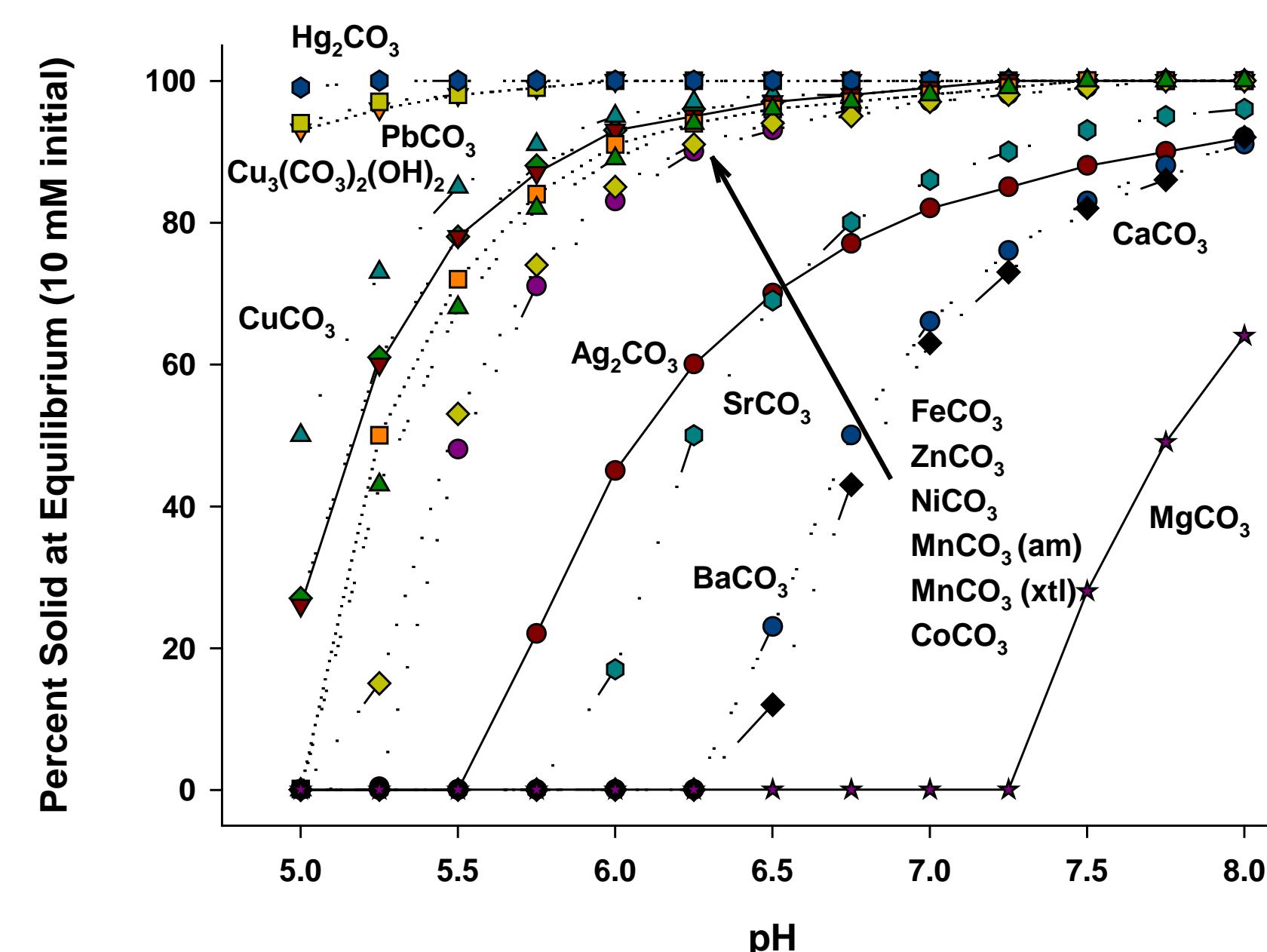
## Introduction

Geological formations associated with carbon sequestration generally contain carbonate minerals that can release cations upon dissolution when reacting with  $CO_2$ , and could provide pathways for  $CO_2$  to leak to the surface. In this study, we applied underwater laser-induced breakdown spectroscopy (underwater LIBS) for rapid in-situ measurement of calcium carbonate ( $CaCO_3$ ) dissolution as a function of  $CO_2$  pressure ( $pCO_2$ ). A pulsed Nd:YAG laser at 1064 nm was used to produce gaseous plasma in the fluid surrounding a pressed pellet of  $CaCO_3$  powder. The ensuing plasma emission was spectrally analyzed, and the intensity of the calcium emission line at 422.67 nm was used to monitor  $Ca^{2+}$  cation released to the water. The barium emission line at 455.40 nm was simultaneously recorded as an internal standard to calibrate the Ca line intensity. The study showed that relatively strong and well-resolved spectral lines of both  $Ca^{2+}$  and  $Ba^{2+}$  cations could be obtained in  $CO_2$ -saturated water. More importantly, the results showed that underwater LIBS is capable of performing quantitative analysis at elevated  $pCO_2$ , with an estimated  $Ca^{2+}$  detection limit of about 9 ppm over  $50 \text{ bar} \geq pCO_2 \leq 350 \text{ bar}$ . In the solution with initially added  $CaCO_3$  pellet, the concentration of  $Ca^{2+}$  increased by a factor of 2 with increasing  $pCO_2$  from 50 to 150 bar and remained nearly constant when  $pCO_2$  was further increased up to 350 bar. This study could potentially benefit the monitoring of  $CO_2$  leakage in carbon sequestration.

In aquifers, limestone is a common buffering rock that releases  $Ca^{2+}$  upon dissolution when reacting with acids, most commonly in the form of carbonic acid:



MINTEQ-Modeled Stability of Various Carbonates (pH only; pH 5–8)



Typically,  $CaCO_3$  is slightly soluble in water, but its solubility increases with a decreasing pH of the solution. Dissolution of  $CO_2$  in water forms  $H_2CO_3$ , which is a controlling factor for the solubility of  $CaCO_3$ . As  $pCO_2$  increases, the pH of the solution drops, carbonate ions ( $CO_3^{2-}$ ) are converted into bicarbonate ( $HCO_3^-$ ) ions.

## Objectives

LIBS has real-time monitoring capability and can be used for elemental analysis of solid, liquid, and gas samples. We used the technique to conduct laboratory-scale experiments to measure calcium cation in aqueous samples during carbonate dissolution reactions. Stability fields for a wide range of carbonate minerals over a pH range of 5–8 were determined by geochemical modeling. Experiments detected increases in dissolved divalent ions due to incremental  $CO_2$  gas in the presence of their respective carbonates. The ultimate aim of using this technology to develop a field-deployable underwater LIBS instrument for *in situ* monitoring of  $CO_2$  leakage into groundwater aquifers is presented.

## Method

### Experimental setup

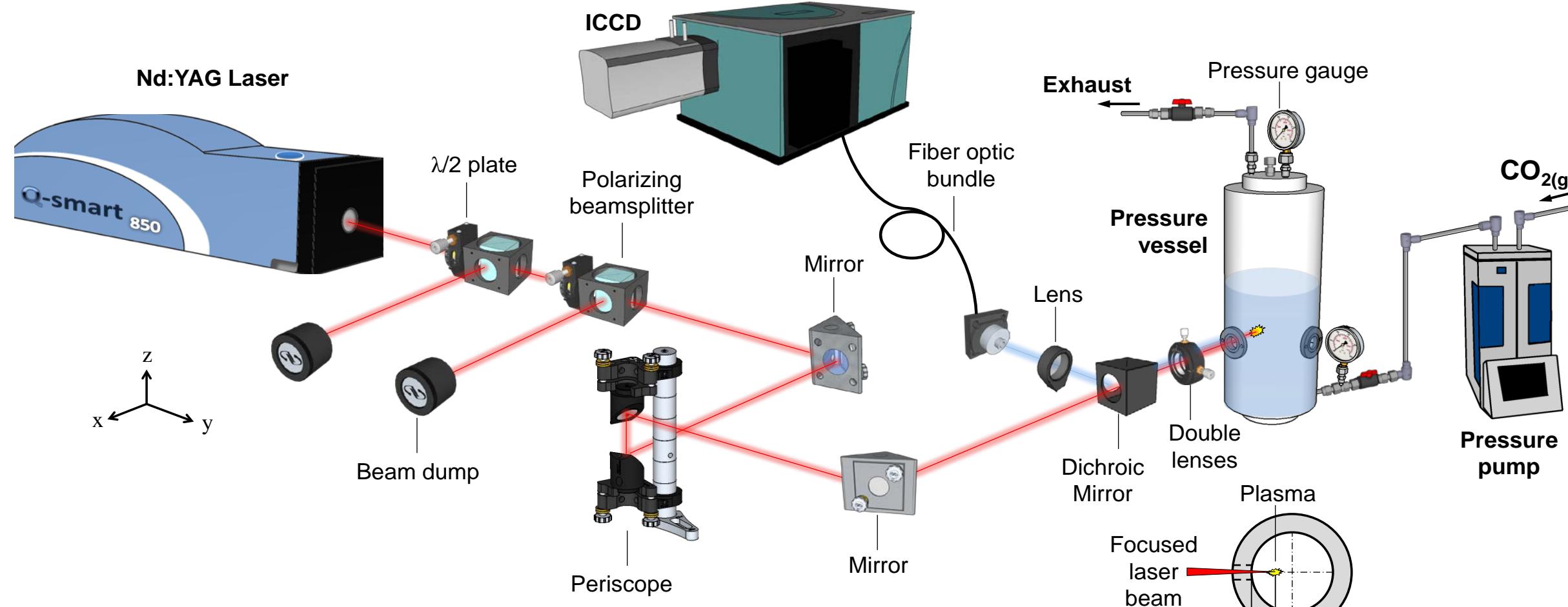


FIG. 1: Underwater LIBS experimental setup to study *in situ* dissolution of carbonate minerals in the presence of  $CO_2$ . The pressure vessel used as reaction chamber is optically accessible through transparent sapphire windows. Laser beam is directed by a set of lenses and is focused inside the solution to make spark. Plasma emission is collected using an optical fiber.

### Standard calibration curves

Strong and well-resolved spectral lines of  $Ca^{2+}$  and  $Ba^{2+}$  cations obtained in  $CO_2$ -saturated water over 50–350 bar. Barium was chosen as internal standard.

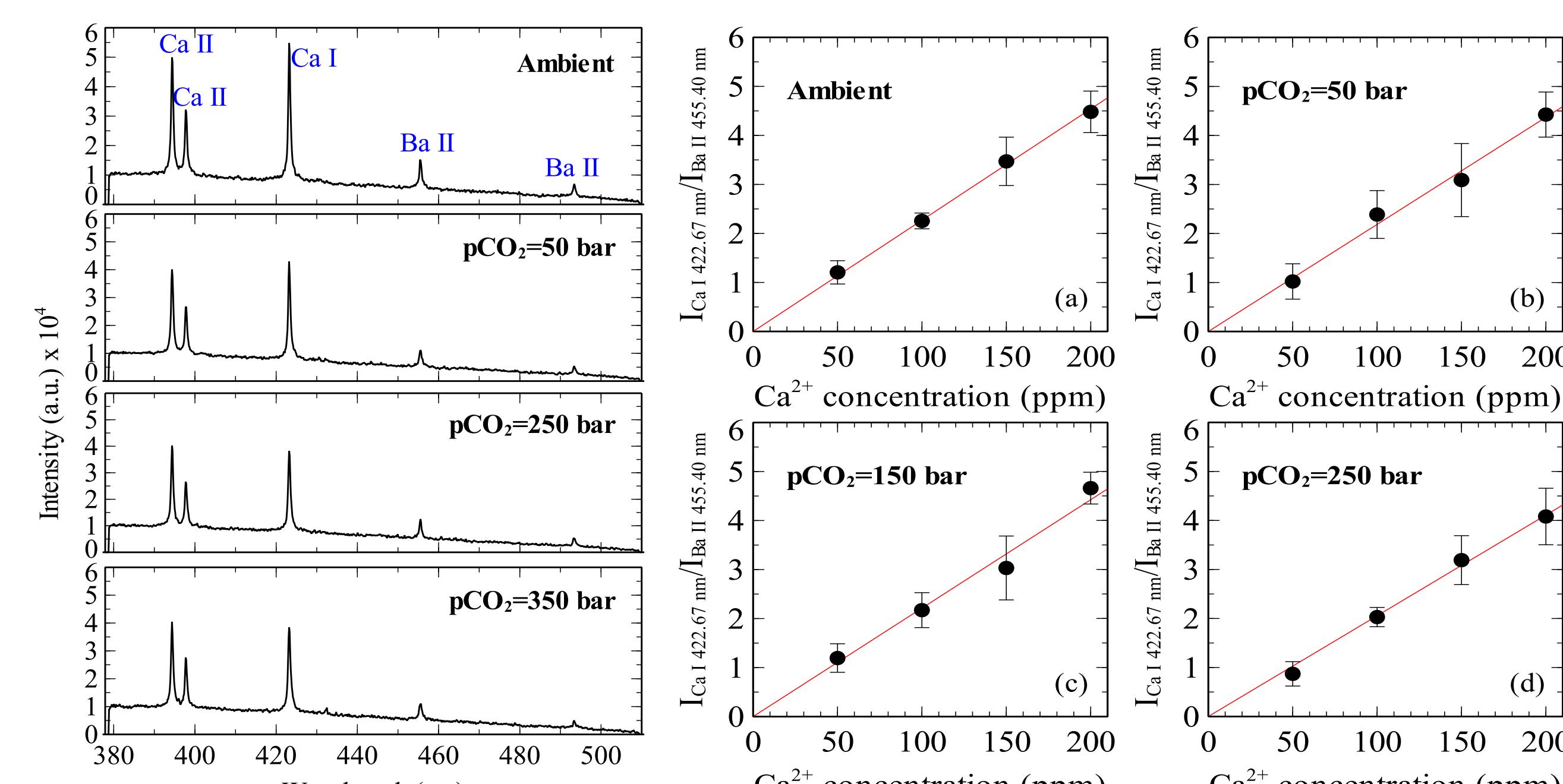


FIG. 2: Underwater LIBS spectra obtained for 200 ppm  $Ca^{2+}$  in standard solution. Standard calibration curves of  $Ca^{2+}$  at ambient pressure and  $pCO_2$  of 50, 150, and 250 bar, plotted as the  $Ca\text{ I }422.67\text{ nm}/Ba\text{ II }455.40\text{ nm}$  intensity ratio.

### Limit of detections

Increasing  $CO_2$  pressure over the range 50–350 bar has little effects on calcium detection limit (DL), which was estimated to be about 9 ppm.

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

## Results and discussion

- 1.25 g of pressed pellet of  $CaCO_3$  powder (99.999%, trace metals basis) was introduced into a solution of 250 mL 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.

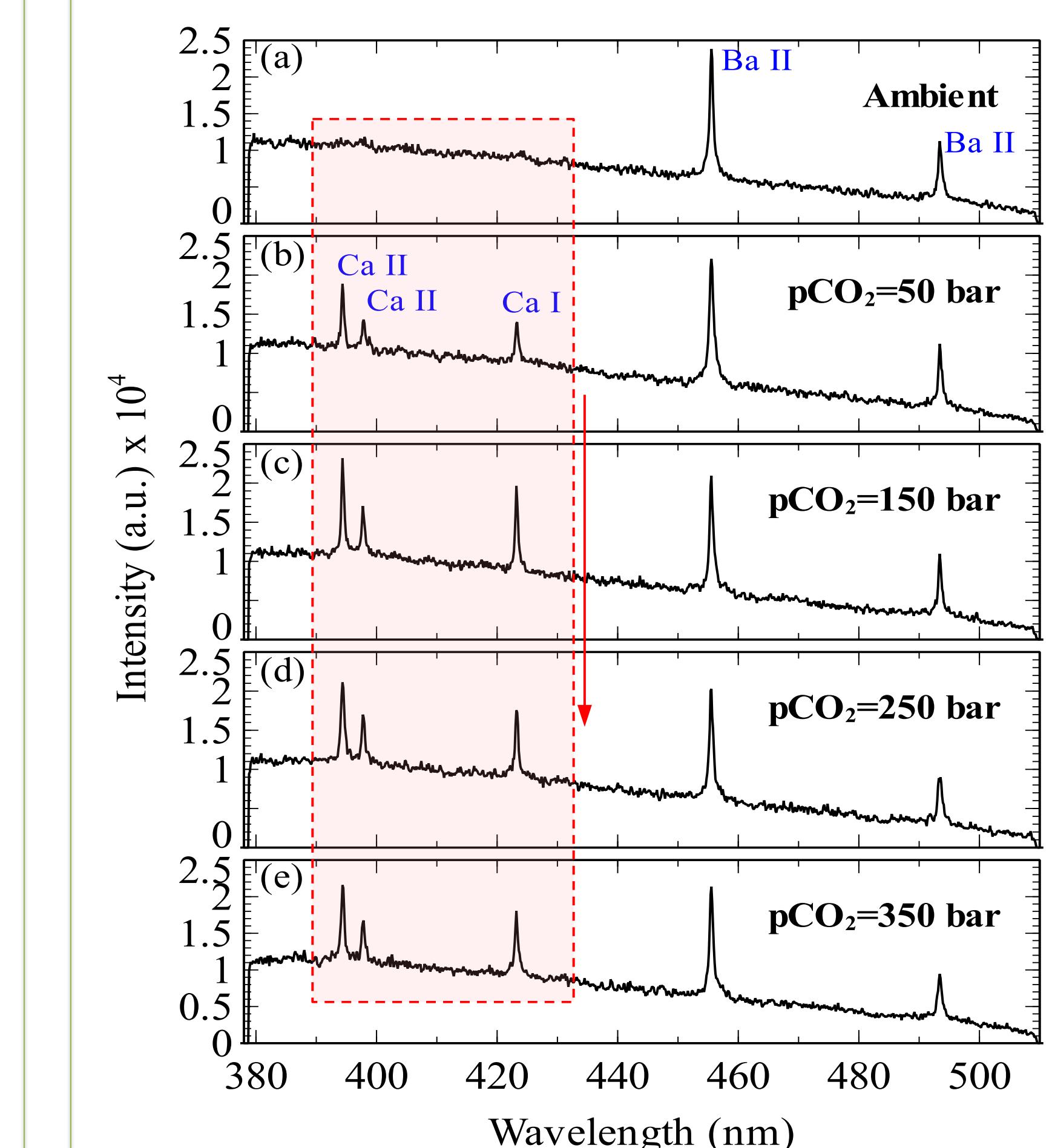


FIG. 3: Leaching of  $Ca^{2+}$  cation from  $CaCO_3$  by  $CO_2$ -enriched water. The shaded red box highlights Ca ionic and neutral emission lines whereas the arrow symbol indicates rising  $CO_2$  pressure.

$Ca^{2+}$  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. Indeed, it is possible that the pH remains unchanged or varies slightly over the range 150–350 bar preventing further dissolution of  $CaCO_3$ .

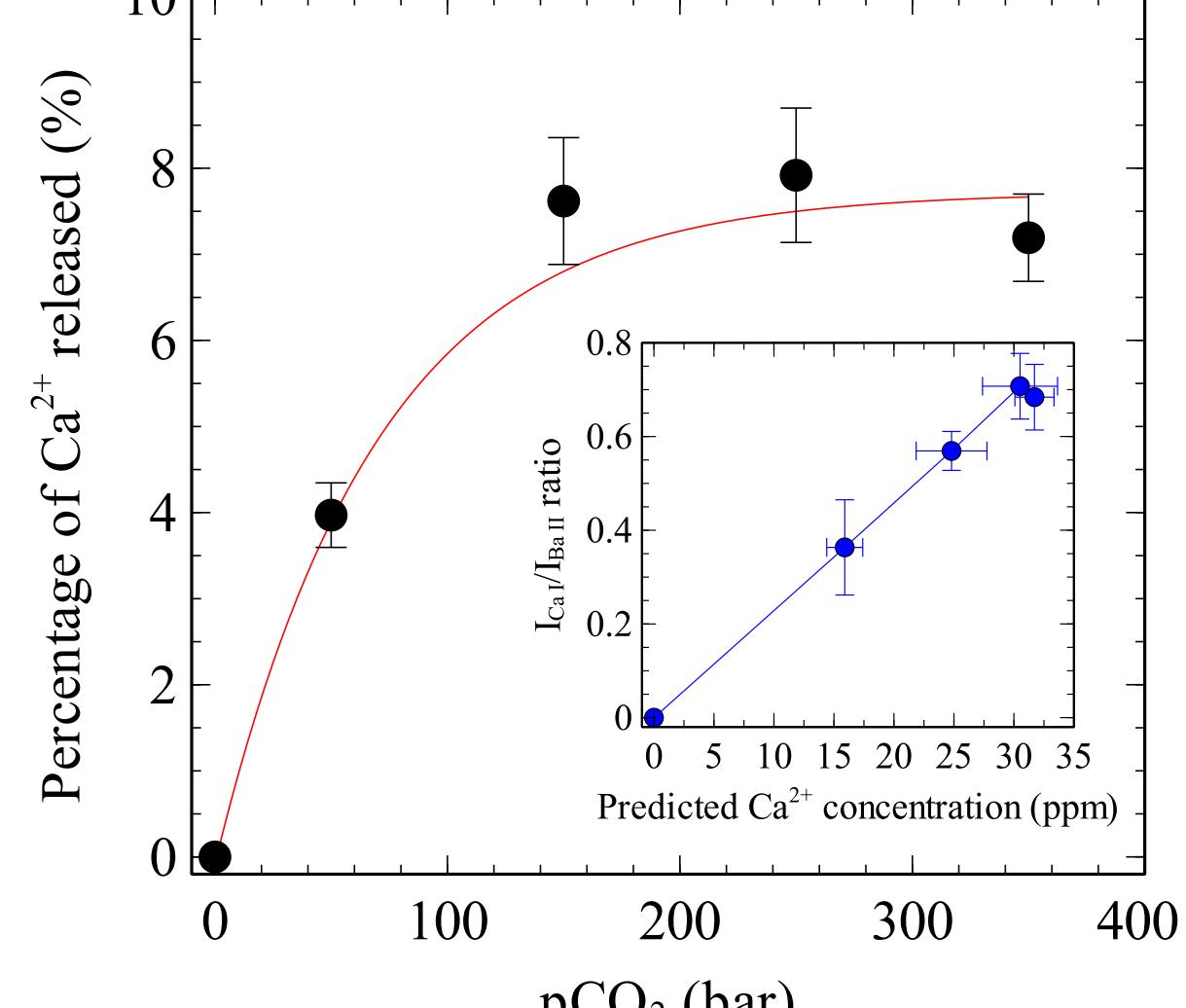


FIG. 4: Percentage of  $Ca^{2+}$  released to the water as a function of  $CO_2$  pressure ( $pCO_2$ ). The inset shows the relation between the observed  $Ca\text{ I }422.67\text{ nm}/Ba\text{ II }455.40\text{ nm}$  intensity ratio and the predicted  $Ca^{2+}$  concentration.

## Conclusions and geological applications

In this work, we have presented a comprehensive case study for directing *in-situ* measurement of  $CaCO_3$  dissolution at elevated  $pCO_2$  using underwater LIBS. This constitutes the first study that demonstrates the promising possibilities offered by underwater LIBS for quantitative *in situ* analysis of  $CO_2$ -saturated water under pressures up to 350 bar, which equates to depths of 3470 and 3569 m for seawater and freshwater, respectively.

This study could potentially benefit the monitoring of  $CO_2$  leakage in geologic  $CO_2$  storage (GCS). Soluble cations such as  $Ca^{2+}$  may migrate ahead of  $CO_2$  in some geological settings and provide the earliest warning of approaching  $CaCO_3$  dissolution in deep monitoring wells. The ability of reservoirs to retain stored  $CO_2$  is important in GCS and the alteration of cement used for sealing injection wells may compromise the seal integrity. Our findings suggest that underwater LIBS can potentially provide a practical means to perform real-time measurement of elements released during carbonate dissolution resulting from the degradation of such cement seals.

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