

In-situ measurement of calcium carbonate dissolution under rising pCO₂ using underwater laser induced breakdown spectroscopy

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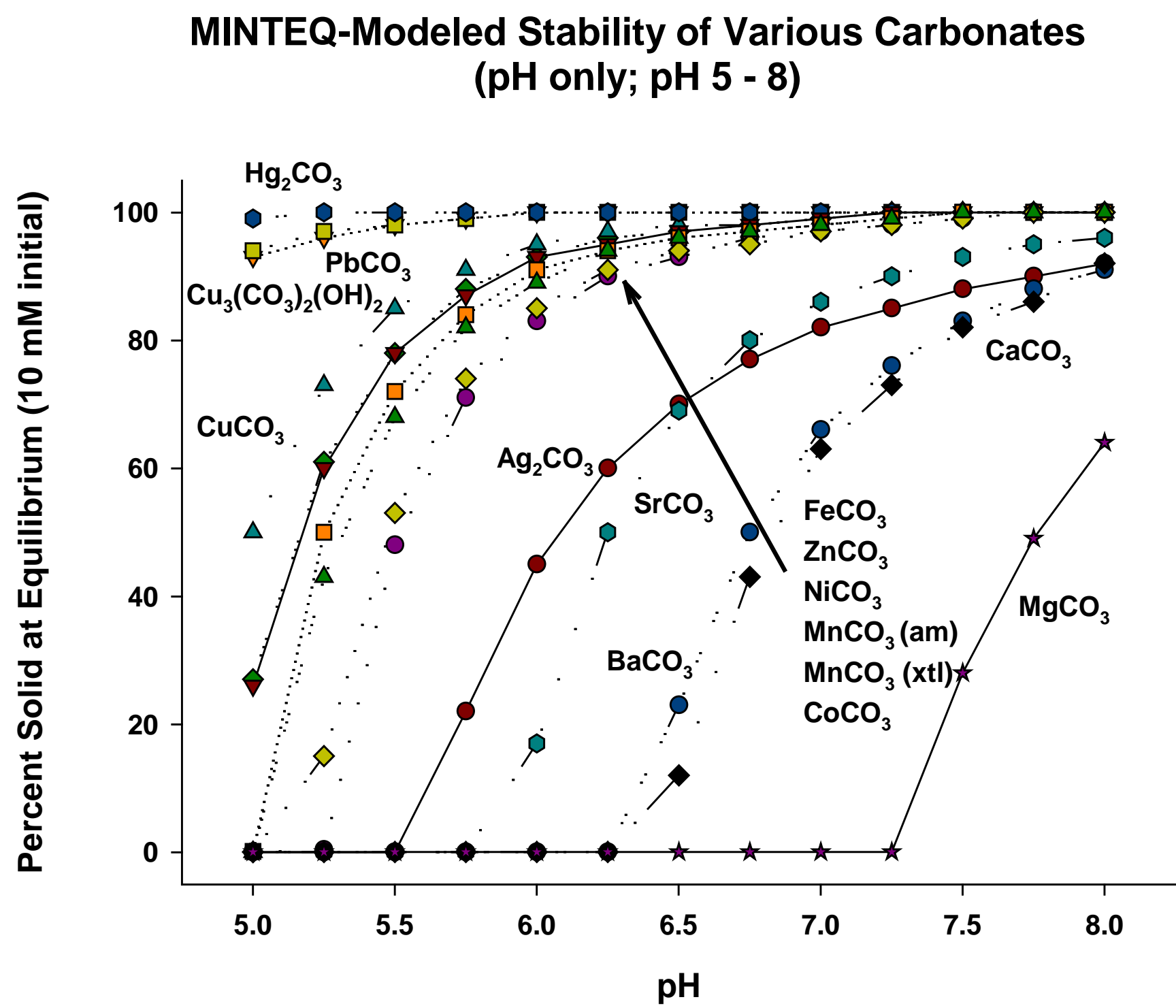
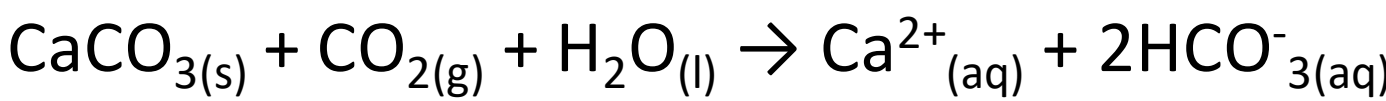
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Introduction

Geological formations associated with carbon sequestration generally contain carbonate minerals that can release cations upon dissolution when reacting with CO₂, and could provide pathways for CO₂ 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 (CaCO₃) dissolution as a function of CO₂ pressure (pCO₂). A pulsed Nd:YAG laser at 1064 nm was used to produce gaseous plasma in the fluid surrounding a pressed pellet of CaCO₃ powder. The ensuing plasma emission was spectrally analyzed, and the intensity of the calcium emission line at 422.67 nm was used to monitor Ca²⁺ 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 Ca²⁺ and Ba²⁺ cations could be obtained in CO₂-saturated water. More importantly, the results showed that underwater LIBS is capable of performing quantitative analysis at elevated pCO₂, with an estimated Ca²⁺ detection limit of about 9 ppm over 50 bar ≤ pCO₂ ≤ 350 bar. In the solution with initially added CaCO₃ pellet, the concentration of Ca²⁺ increased by a factor of 2 with increasing pCO₂ from 50 to 150 bar and remained nearly constant when pCO₂ was further increased up to 350 bar. This study could potentially benefit the monitoring of CO₂ leakage in carbon sequestration.

In aquifers, limestone is a common buffering rock that releases Ca²⁺ upon dissolution when reacting with acids, most commonly in the form of carbonic acid:



Typically, CaCO₃ is slightly soluble in water, but its solubility increases with a decreasing pH of the solution. Dissolution of CO₂ in water forms H₂CO₃, which is a controlling factor for the solubility of CaCO₃. As pCO₂ increases, the pH of the solution drops, carbonate ions (CO₃²⁻) are converted into bicarbonate (HCO₃⁻) 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 CO₂ 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 CO₂ leakage into groundwater aquifers is presented.

Method

Experimental setup

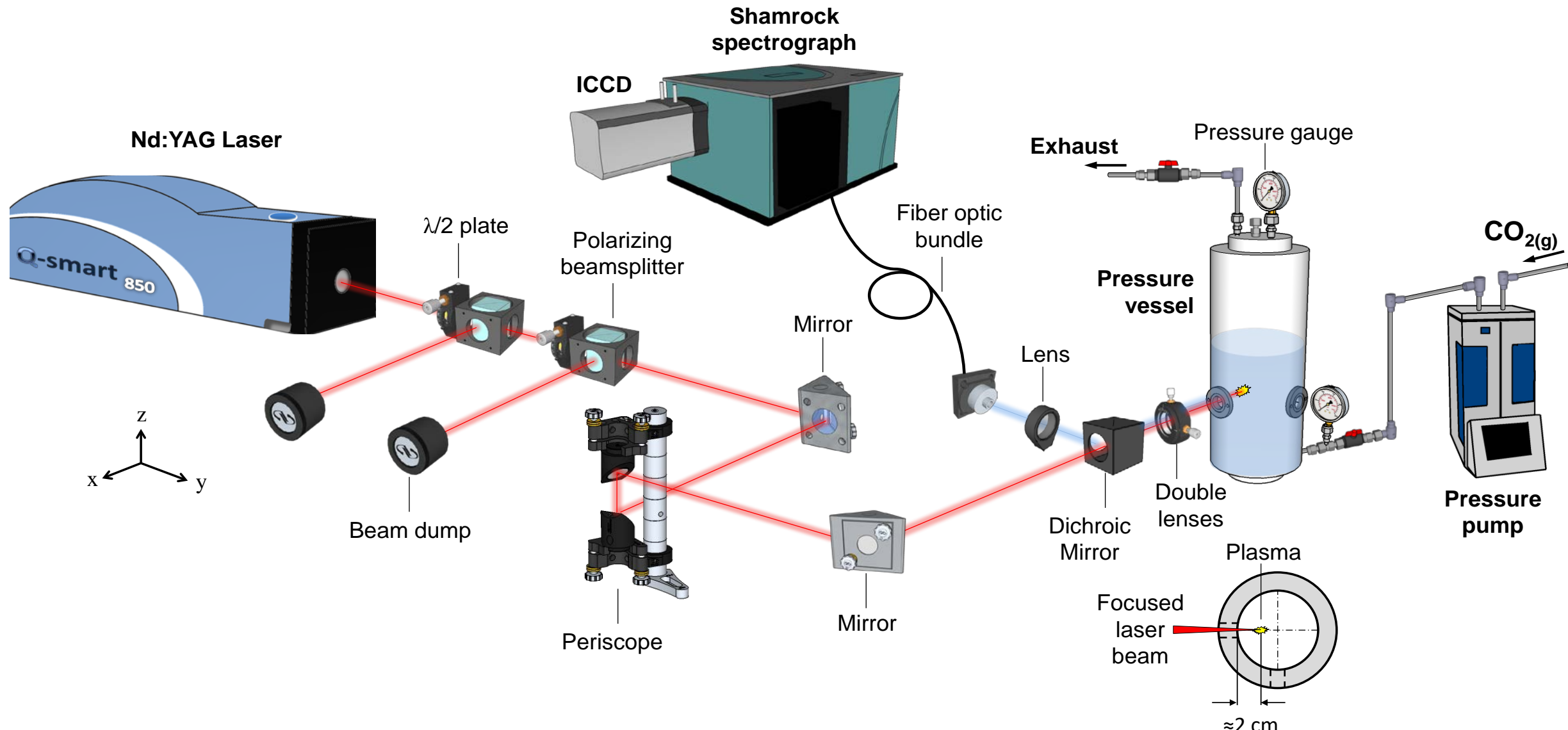


FIG. 1: Underwater LIBS experimental setup to study in situ dissolution of carbonate minerals in the presence of CO₂. The pressure vessel used as reaction chamber is optically accessible through transparent sapphire windows. Laser beam is directed by a set of lenses and is focused inside the solution to make spark. Plasma emission is collected using an optical fiber.

Standard calibration curves

Strong and well-resolved spectral lines of Ca²⁺ and Ba²⁺ cations obtained in CO₂-saturated water over 50–350 bar. Barium was chosen as internal standard.

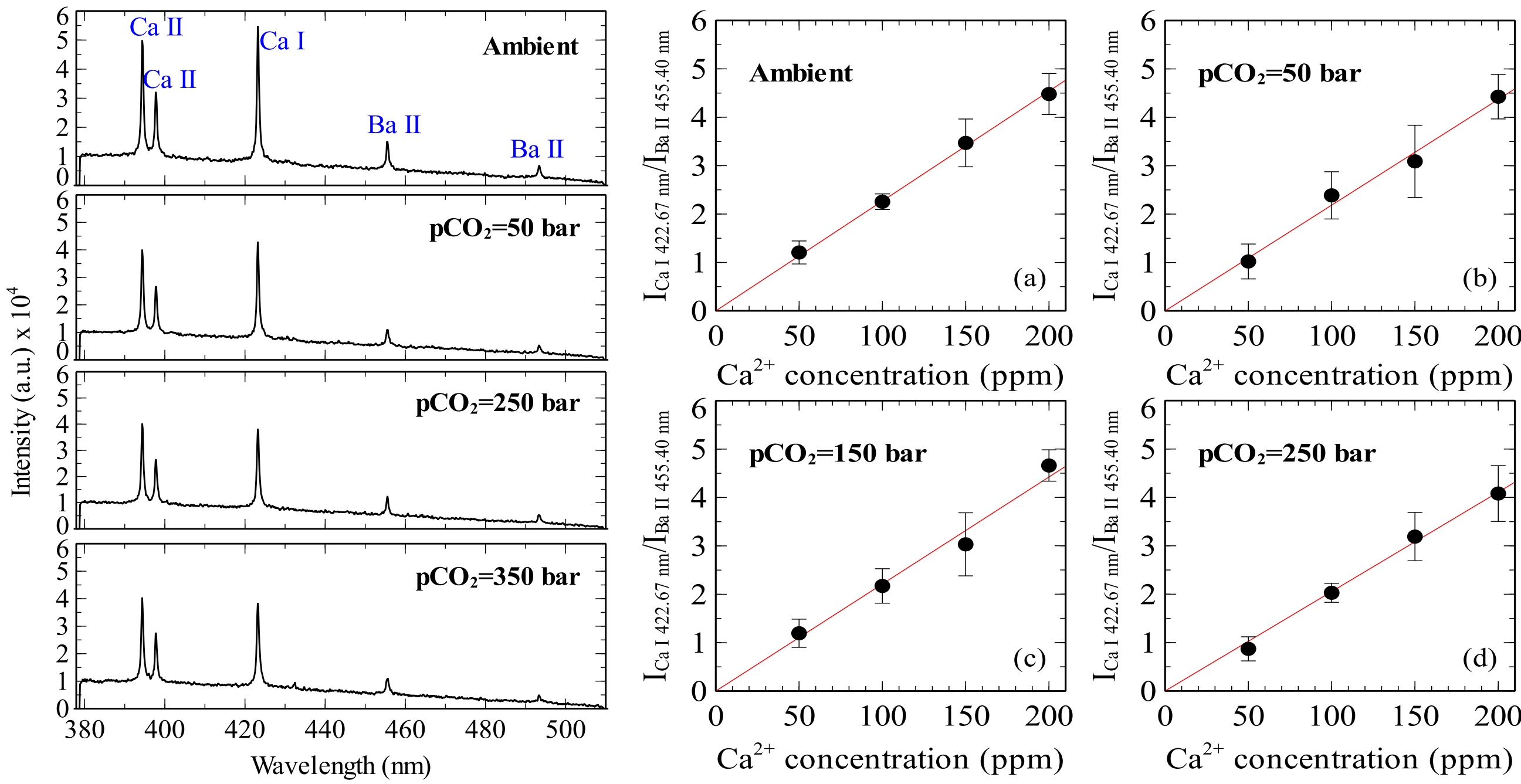


FIG. 2: Underwater LIBS spectra obtained for 200 ppm Ca²⁺ in standard solution. Standard calibration curves of Ca²⁺ at ambient pressure and pCO₂ of 50, 150, and 250 bar, plotted as the Ca I 422.67 nm/Ba II 455.40 nm intensity ratio.

Limit of detections

Increasing CO₂ 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 ± 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

Results and discussion

- 1.25 g of pressed pellet of CaCO₃ powder (99.999%, trace metals basis) was introduced into a solution of 250 mL of 1 mM BaCl₂·2H₂O.
- Measurements are based upon mass transport of dissolved Ca²⁺ by diffusion away from the liquid–carbonate boundary.

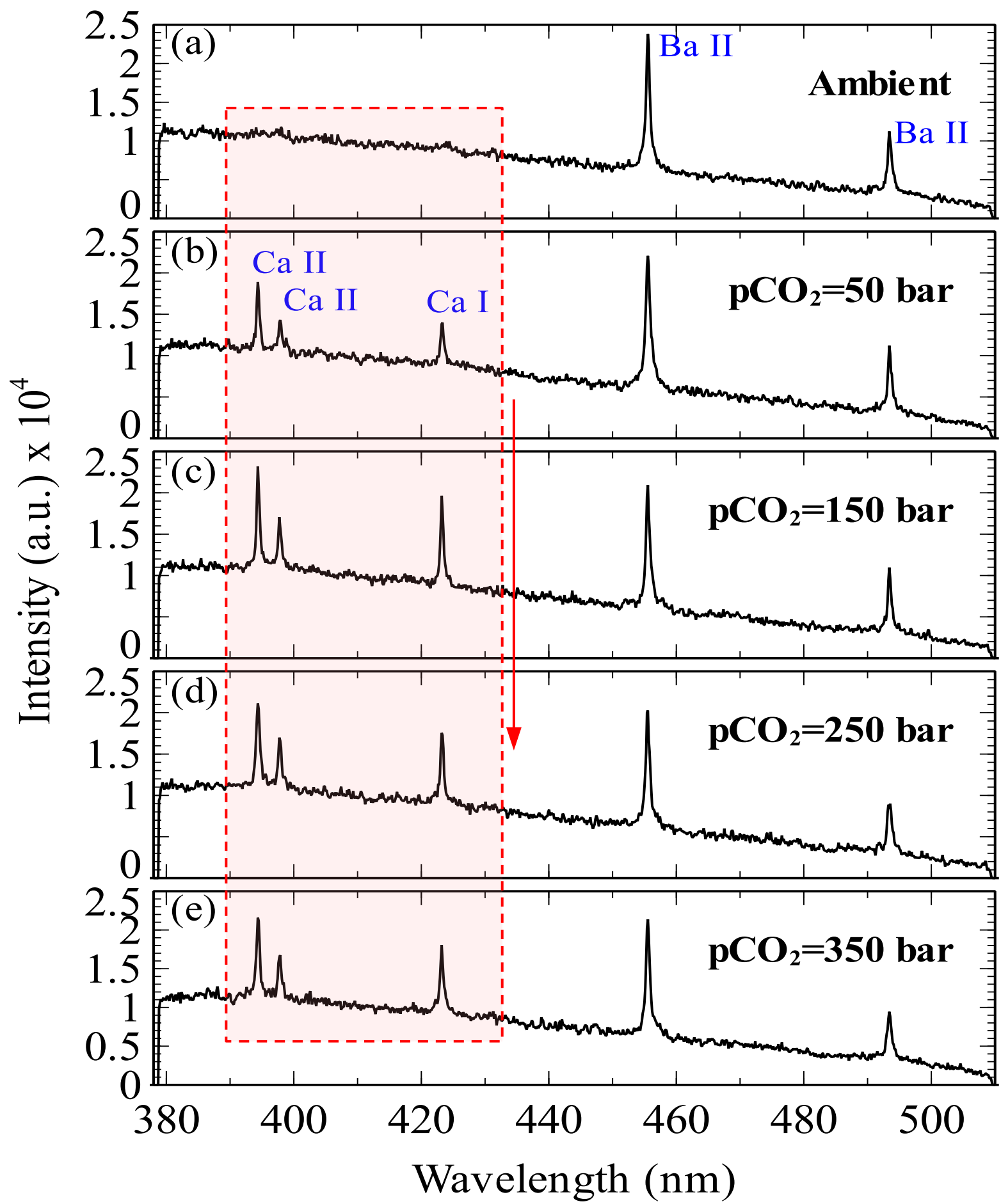


FIG. 3: Leaching of Ca²⁺ cation from CaCO₃ by CO₂-enriched water. The shaded red box highlights Ca ionic and neutral emission lines whereas the arrow symbol indicates rising CO₂ pressure.

Ca²⁺ released in water increases with pCO₂ up to 150 bar but remains nearly constant when pCO₂ 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 CaCO₃.

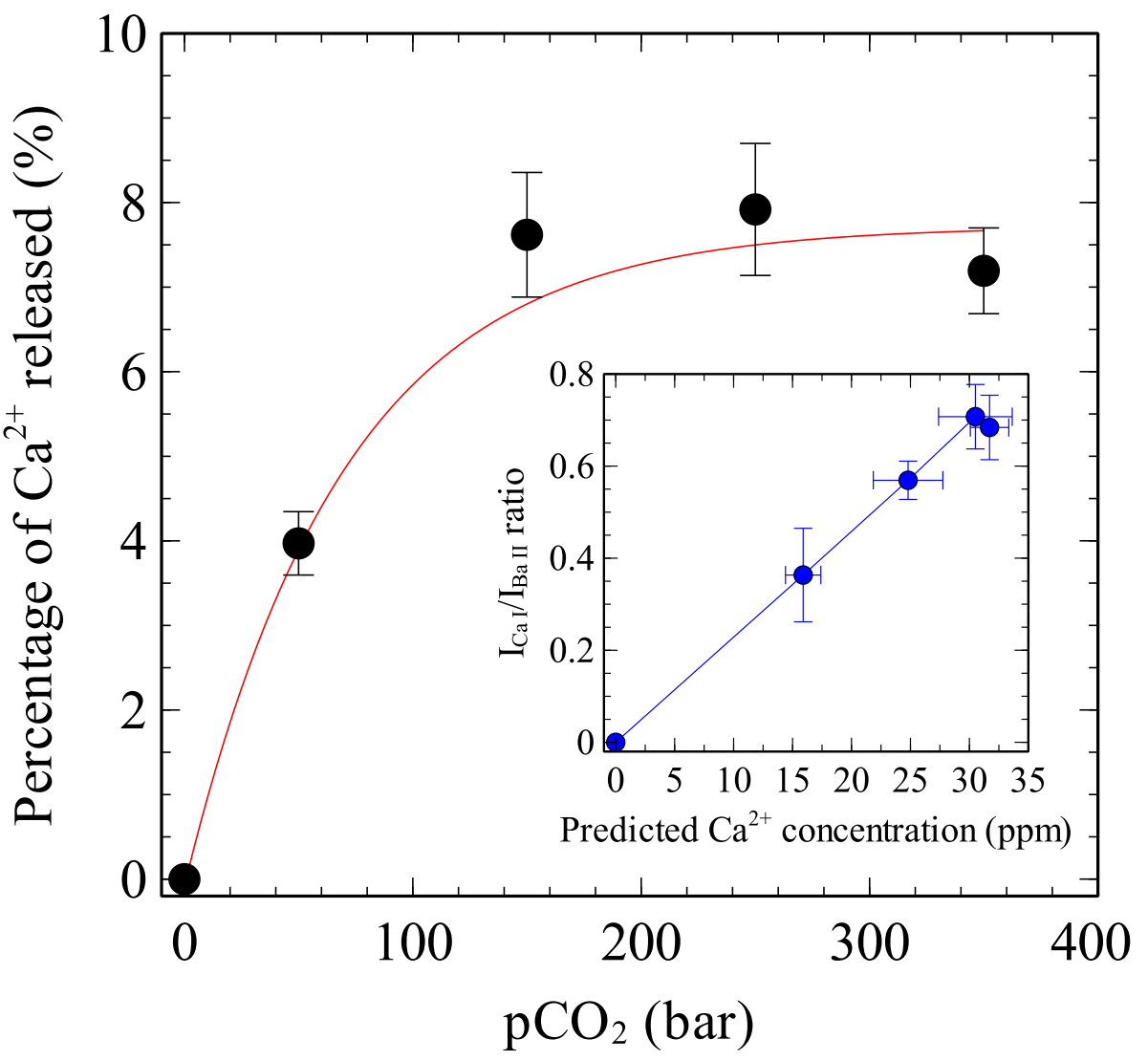


FIG. 4: Percentage of Ca²⁺ released to the water as a function of CO₂ pressure (pCO₂). The inset shows the relation between the observed Ca I 422.67 nm/Ba II 455.40 nm intensity ratio and the predicted Ca²⁺ concentration.

Conclusions and geological applications

In this work, we have presented a comprehensive case study for directing in-situ measurement of CaCO₃ dissolution at elevated pCO₂ using underwater LIBS. This constitutes the first study that demonstrates the promising possibilities offered by underwater LIBS for quantitative in situ analysis of CO₂-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 CO₂ leakage in geologic CO₂ storage (GCS). Soluble cations such as Ca²⁺ may migrate ahead of CO₂ in some geological settings and provide the earliest warning of approaching CaCO₃ dissolution in deep monitoring wells. The ability of reservoirs to retain stored CO₂ 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.