Direct measurements of seawater carbonate ion concentrations in the Gulf of Mexico: Implications for spatial mapping of CaCO₃ saturation states

Jonathan D. Sharp and Robert H. Byrne • University of South Florida College of Marine Science

Introduction

Total carbonate ion concentrations ([CO₃²⁻]) can be measured directly in lead-enriched seawater through observations of Pb(II) ultraviolet absorptions (Fig. A). A recently identified instrument-specific correction — detailed in Sharp et al., 2017 (submitted) — has improved the accuracy of these direct [CO₃²⁻] measurements. Furthermore, procedures outlined in the submitted manuscript (and in Section 3) allow for empirical calculation of in situ calcium carbonate saturation states (Ω) with respect to both calcite (ΩC) and aragonite (ΩA) from spectrophotometric measurements of [CO₃²⁻]. If the available data cover an adequate geographic extent, spatial mapping of saturation states and saturation horizons can thus be completed using only one measured parameter. This cheap, simple, and accurate method of evaluating Ω is increasingly useful for researchers and business (e.g., aquaculture) and natural resource managers as saturation states in the world’s oceans continue to decline. The technique has the potential to be applied to in situ instruments that can be deployed on gliders, moorings, profiling floats, and other platforms.

1. Theory

\[
\log([\text{CO}_3^{2-}]_{\text{spec}}) = \log([\text{Ca}^{2+}]_{\text{spec}}) + \log(R) + \log(e_2) + \log(S) + \log(T)
\]

where:
- \([\text{CO}_3^{2-}]_{\text{spec}}\): corrected absorbance ratio (Fig. B)
- \([\text{Ca}^{2+}]_{\text{spec}}\): corrected absorbance ratio (Fig. B)
- \(R\): wavelength offset correction factor
- \(e_2\): absorbance at 254 nm
- \(S\): salinity
- \(T\): temperature

2. Wavelength Offset Correction

- Wavelength calibration differences between different spectrophotometers can greatly influence measured Pb(II) absorbance ratios that are used to calculate [CO₃²⁻]_{spec} (Fig. B)
- Even sub-nanometer shifts significantly impact spectrophotometrically measured carbonate ion concentrations
- SRM 2034.4, a NIST wavelength standard, was used to determine wavelength offsets (Δλ_{254.1}), defined as differences between the location of the second SRM 2034 absorbance peak as defined by NIST (241.10 nm) and the location at which a given spectrophotometer reports that peak (Fig. C)
- Uncorrected absorbance ratios (R) of four distinct seawater samples were determined on each of five spectrophotometers (e.g., Fig. D, red dots)
- Using a linear correction, uncorrected absorbance ratios (R) were corrected to absorbance ratios that would be observed on an instrument with a Δλ_{254.1} equal to zero (R') (Fig. D, blue dots)
- Corrected ratios — and thus, calculated [CO₃²⁻]_{spec} values from corrected ratios — show far greater consistency between instruments

3. In situ Saturation State Model

- For instances where only [CO₃²⁻]_{spec} at 25°C and 1 atm total pressure is directly measured, a model was developed to calculate carbonate ion concentration at in situ temperature and pressure (P):

\[
[\text{CO}_3^{2-}]_{\text{spec}} = [\text{CO}_3^{2-}]_P + A + B \cdot t + C \cdot t^2
\]

For the 2012 GOMEC-2 cruise, the average difference was -0.0024 ± 0.041 (N = 1,057). In both cases, outliers were removed by eliminating data points greater than three standard deviations from the mean of each dataset.

4. Gulf of Mexico Cruises

The second Gulf of Mexico and East Coast Carbon Cruise of 2012 (GOMEC-2, Fig. H) sampled 93 stations from surface to seafloor across 8 transects in the Gulf of Mexico and the East Coast of the United States. Chemical variables measured included dissolved oxygen, nutrient concentrations, and all measurable CO₂ system parameters. Hydrographic data (temperature, depth, and salinity) were measured with a rosette-mounted CTD. Our lab group collected pH₅ and [CO₃²⁻]_{spec} data using spectrophotometric procedures detailed elsewhere. Absorbance ratios for [CO₃²⁻]_{spec} calculation were corrected according to the procedure detailed in Section 2. In situ calcium carbonate saturation states with respect to aragonite (ΩA) were determined using measured [CO₃²⁻]_{spec} data (Fig. E) and using measurements of pH₅ and total dissolved inorganic carbon (DIC) (Fig. F). A difference plot comparing these two calculation methods (Fig. G) demonstrates the accuracy of saturation states calculated from direct [CO₃²⁻]_{spec} measurements.

Three transects occupied on the GOMEC-2 cruise will be re-occupied this summer on the Gulf of Mexico Ecosystems and Carbon Cruise (GOMEC-3, Fig. I); the Louisiana transect (LA, Fig. I), the West Florida transect (WFL, Figs. E-G), and the East Florida transect (EFL, Fig. K). This re-occupation will allow for an assessment of temporal changes in the CO₂ system chemistry of the region in the context of both natural and anthropogenic influences.

5. Conclusions

The method detailed here allows for accurate determinations of seawater saturation states from simple spectrophotometric measurements of carbonate ion concentrations. Due to its speed, simplicity, low cost, and adaptability for use in situ, this method has the potential to become an extremely important tool for future assessments of the marine CO₂ system. These measurements will be utilized in the Summer of 2017 to assess ecosystem health in the Gulf of Mexico on the Gulf of Mexico Ecosystems and Carbon Cruise (GOMEC-3). Re-occupations of previously visited transects will allow for evaluation of chemical changes in the region — chiefly, changes in seawater saturation states with respect to calcite and aragonite — in the context of both natural and anthropogenic influences.

References

This material is based upon work supported the National Science Foundation Graduate Research Fellowship Program Grant No. 1144244.