Direct measurements of seawater carbonate ion concentrations in the Gulf of Mexico: Implications for spatial mapping of $CaCO_3$ saturation states

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

Introduction

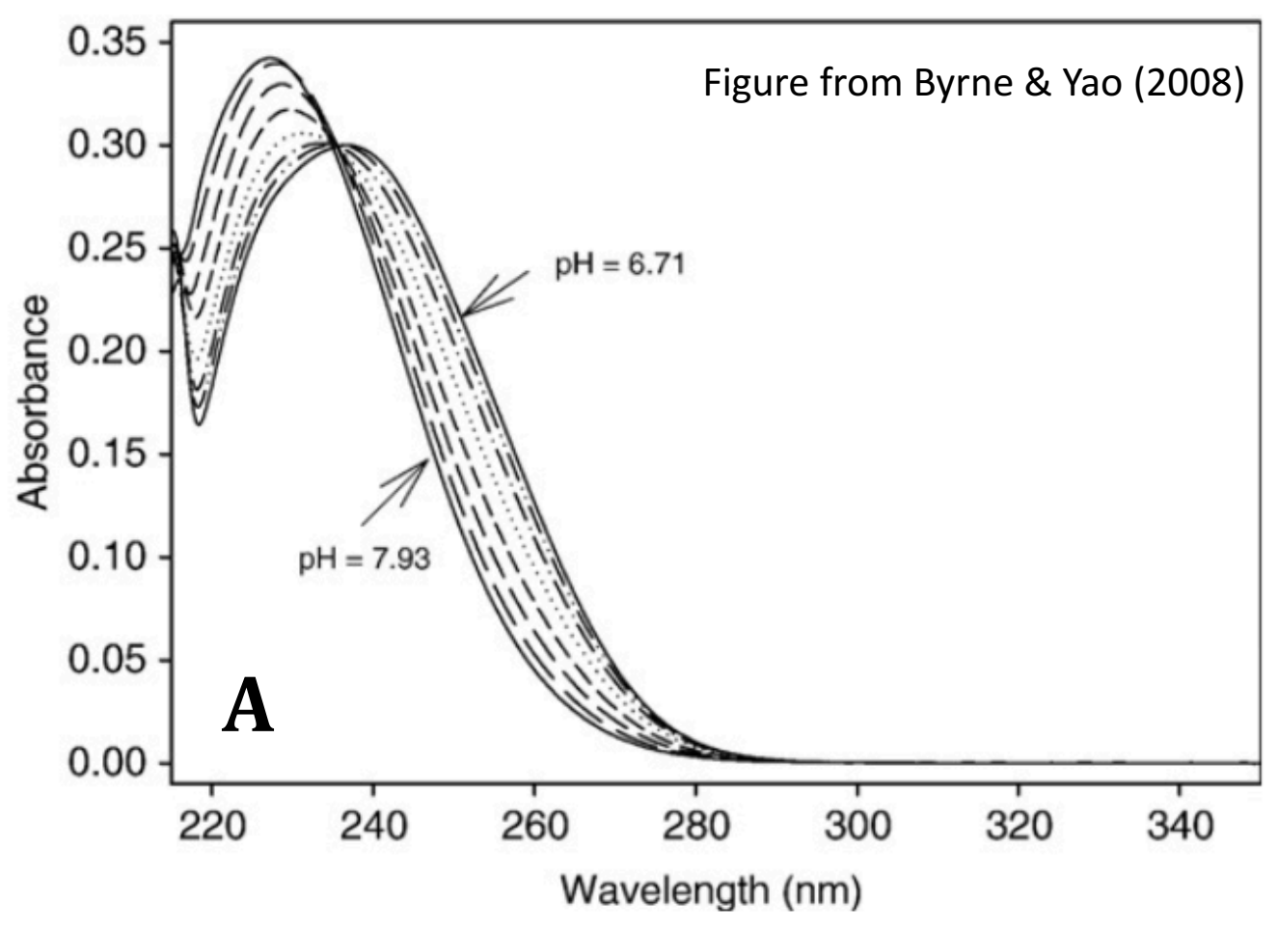
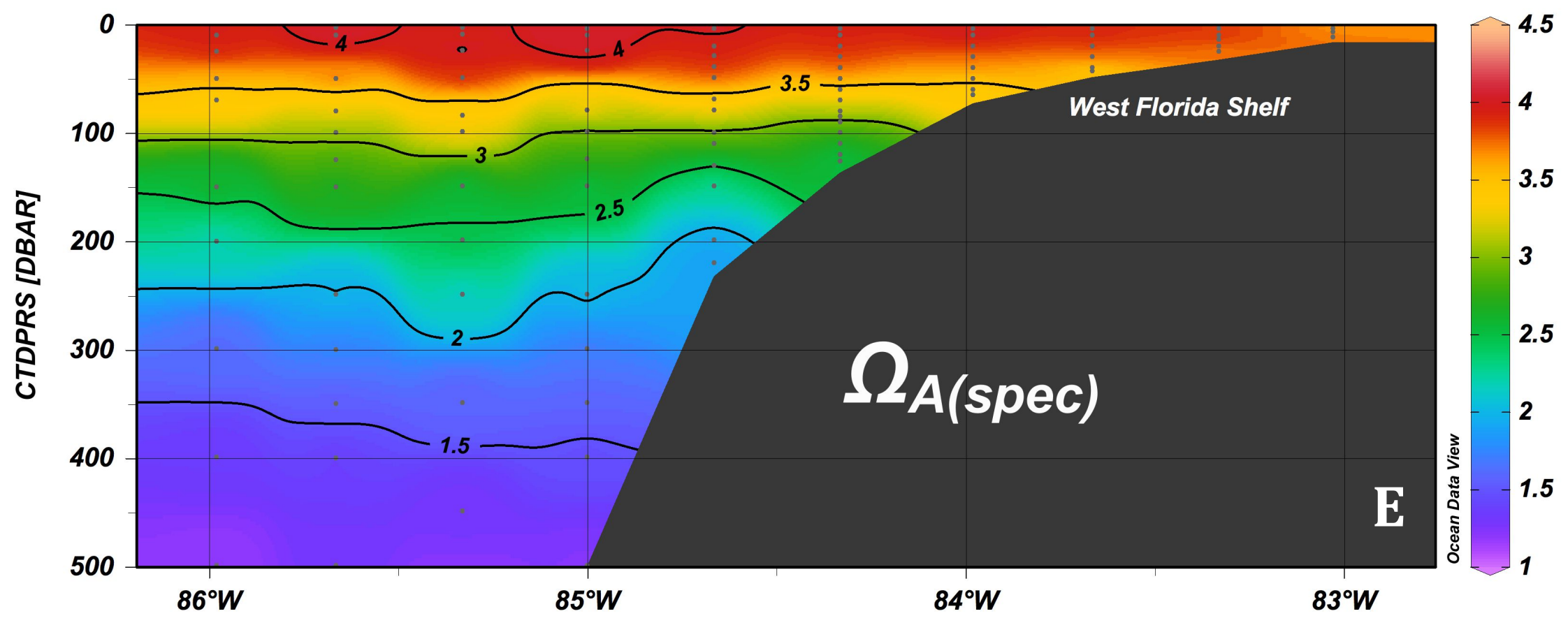
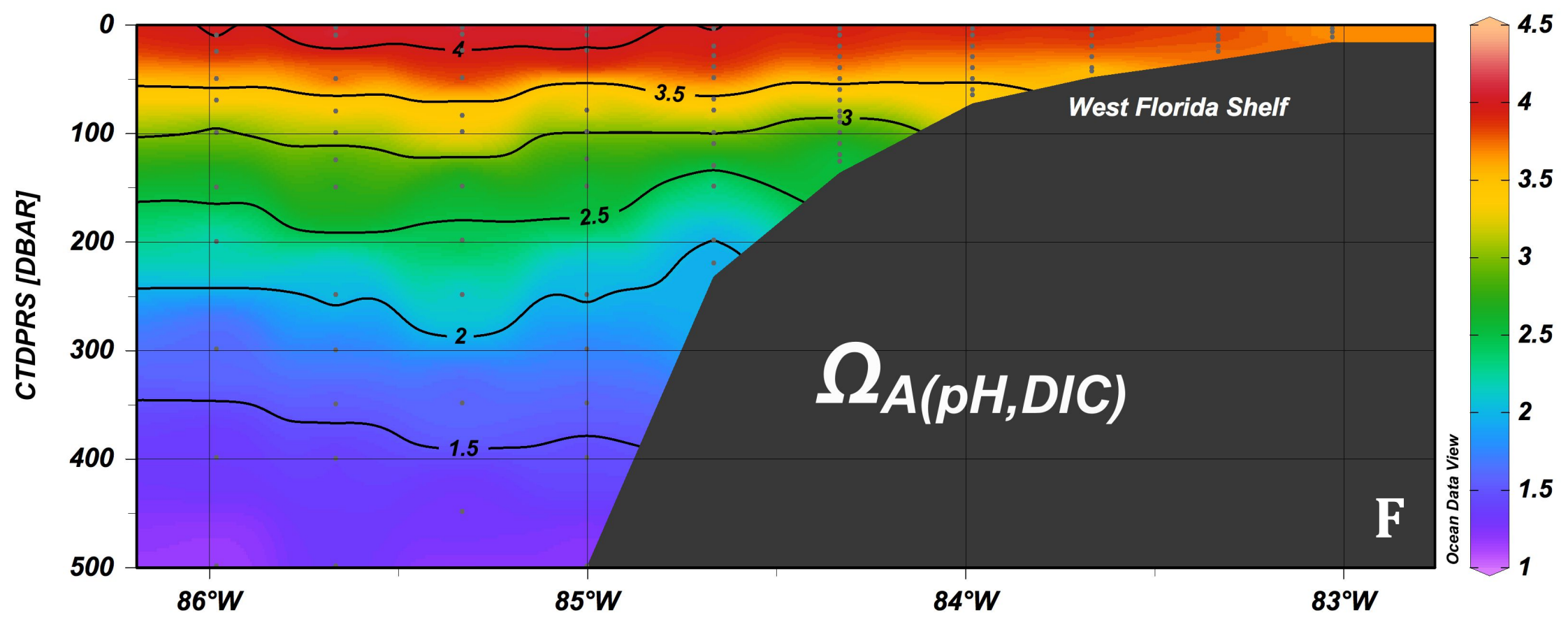


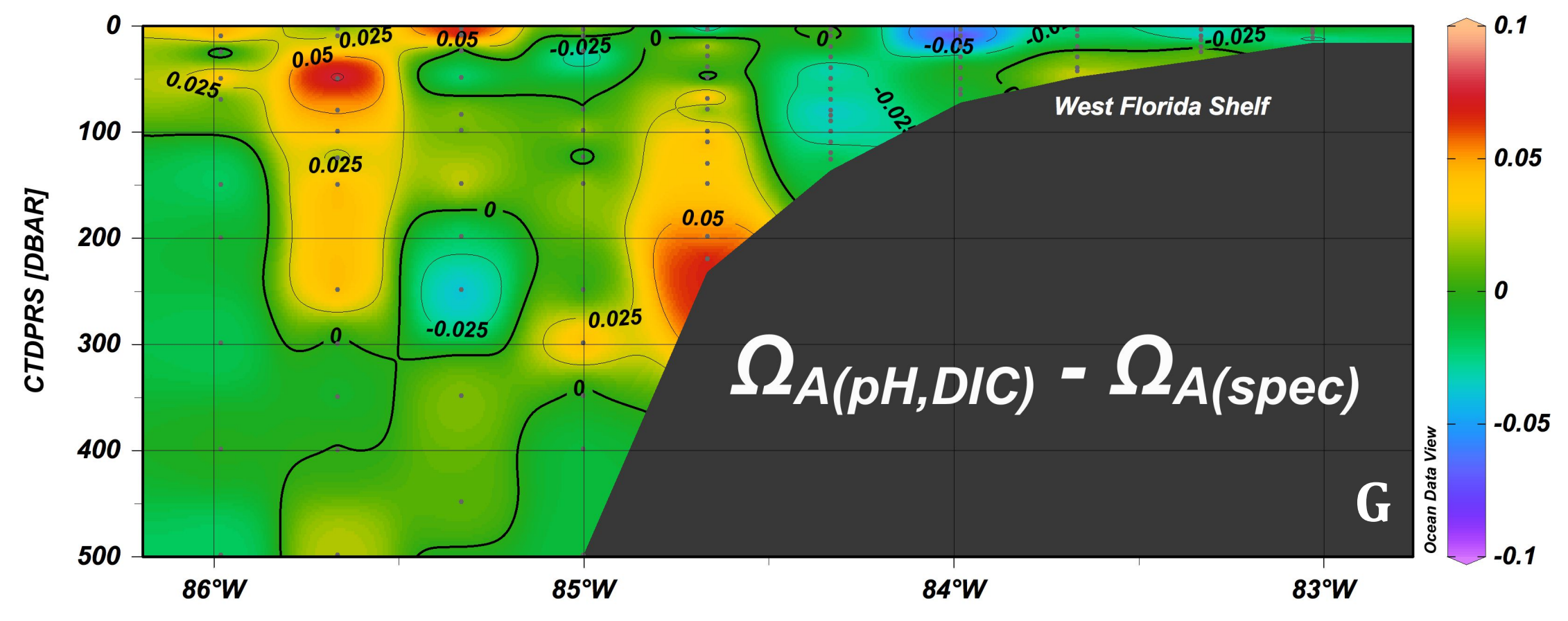
Figure from Byrne & Yao (2008)

Total carbonate ion concentrations ($[CO_3^{2-}]$) can be measured directly in lead-enriched seawater through observations of Pb(II) ultraviolet absorbances (**Fig. A**).[1] A recently identified instrument-specific correction — detailed in Sharp et al., 2017 (submitted)[2] and in Section 2 — has improved the accuracy of these direct $[CO_3^{2-}]$ 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 (Ω_C) and aragonite (Ω_A) from spectrophotometric measurements of $[CO_3^{2-}]$. 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 adapted to in situ instruments that can be deployed on gliders, moorings, profiling floats, and other platforms.







3. In situ Saturation State Model[2]

- For instances where only $[CO_3^{2-}]_{spec}$ 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 ($[CO_3^{2-}]^*_{spec}$):

$$[CO_3^{2-}]^*_{spec} = [CO_3^{2-}]_{spec} + A + B \cdot t + C \cdot t^2$$

$$10^2 \cdot A = 310.245 - 26.9211 \cdot S - 26.3699 \cdot (P/100) - 3.02769 \cdot [CO_3^{2-}]_{spec}$$
$$10^3 \cdot B = -44.9562 + 5.75068 \cdot S + 4.15720 \cdot (P/100) + 2.01654 \cdot [CO_3^{2-}]_{spec}$$
$$10^4 \cdot C = 5.81804 + 1.71105 \cdot S - 0.429245 \cdot (P/100) - 0.502054 \cdot [CO_3^{2-}]_{spec}$$

- $[CO_3^{2-}]_{spec}$ is measured carbonate ion concentration (µmol/kg) at 25°C and one atmosphere total pressure, t is temperature in degrees Celsius, S is salinity, P is gauge pressure in decibars, and$[CO_3^{2-}]^*_{spec}$ is in situ carbonate ion concentration.
- Aragonite saturation states ($\Omega_A = ([Ca^{2+}]_T[CO_3^{2-}]^*_{spec})/K'_{spA}$) determined with this model ($\Omega_{A(spec)}$) and by conventional calculation ($\Omega_{A(pH,DIC)}$) from paired measurements of pH_T and DIC were compared extensively.
- For the recently completed 2016 West Coast Ocean Acidification Cruise, the average difference between the two characterizations of Ω_A was −0.0061 ± 0.023 (N = 1,679). For the 2012 GOMECC-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.

1. Theory[1,2]

$$-log[CO_3^{2-}]_{spec} = log\{_{CO_3}\beta_1/e_2\} + log\{(R^0 - e_1)/(1 - R^0 \cdot e_3/e_2)\}$$

$$log\{_{CO_3}\beta_1/e_2\} = 6.87057 - 0.142142 \cdot S + 0.00190892 \cdot S^2$$

$$_{CO_3}\beta_1 = \frac{[PbCO_3^0]}{[Pb^{2+}]_T[CO_3^{2-}]_T}$$

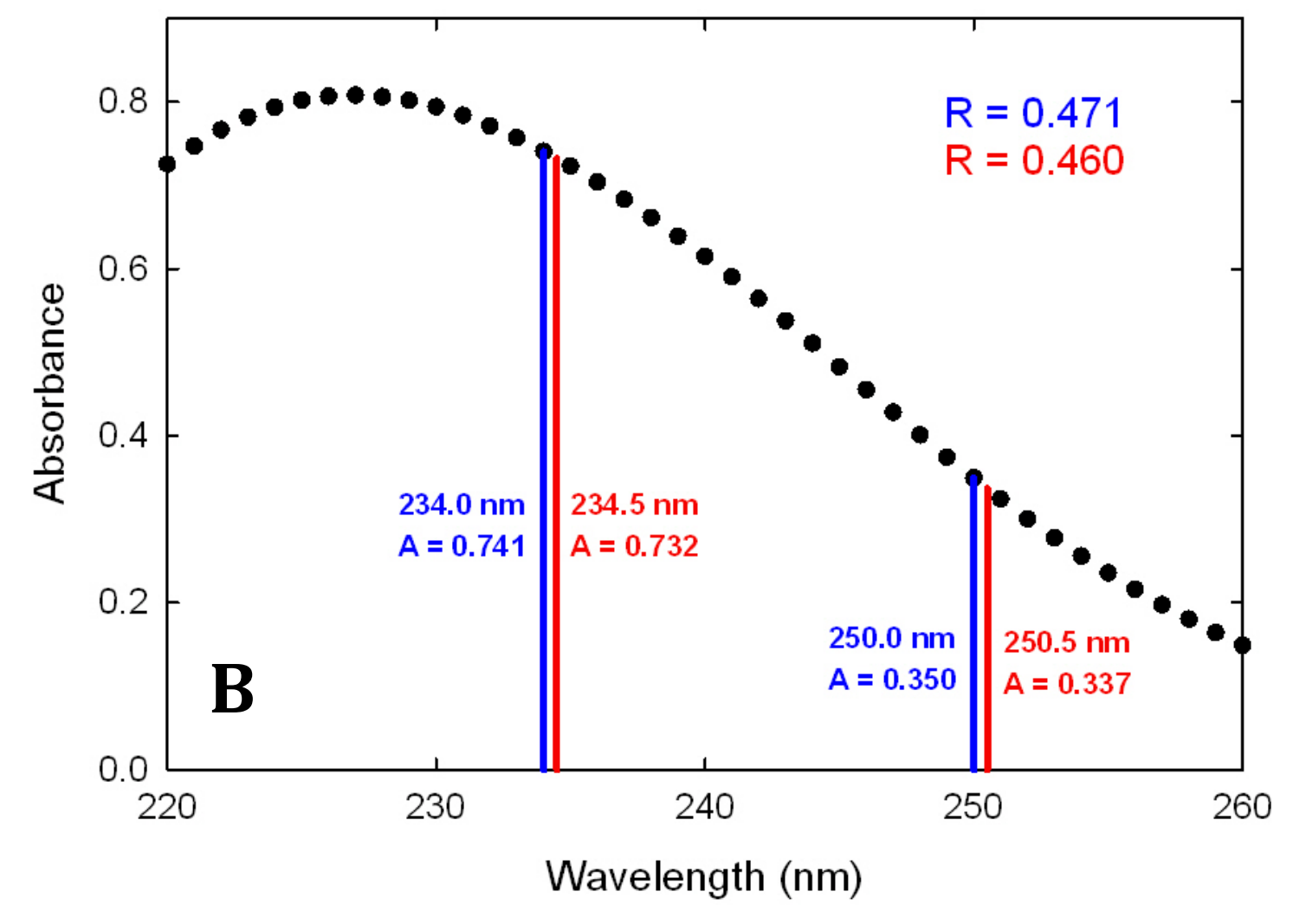
$$e_1 = 0.787458 - 0.0339648 \cdot S + 0.000583574 \cdot S^2$$

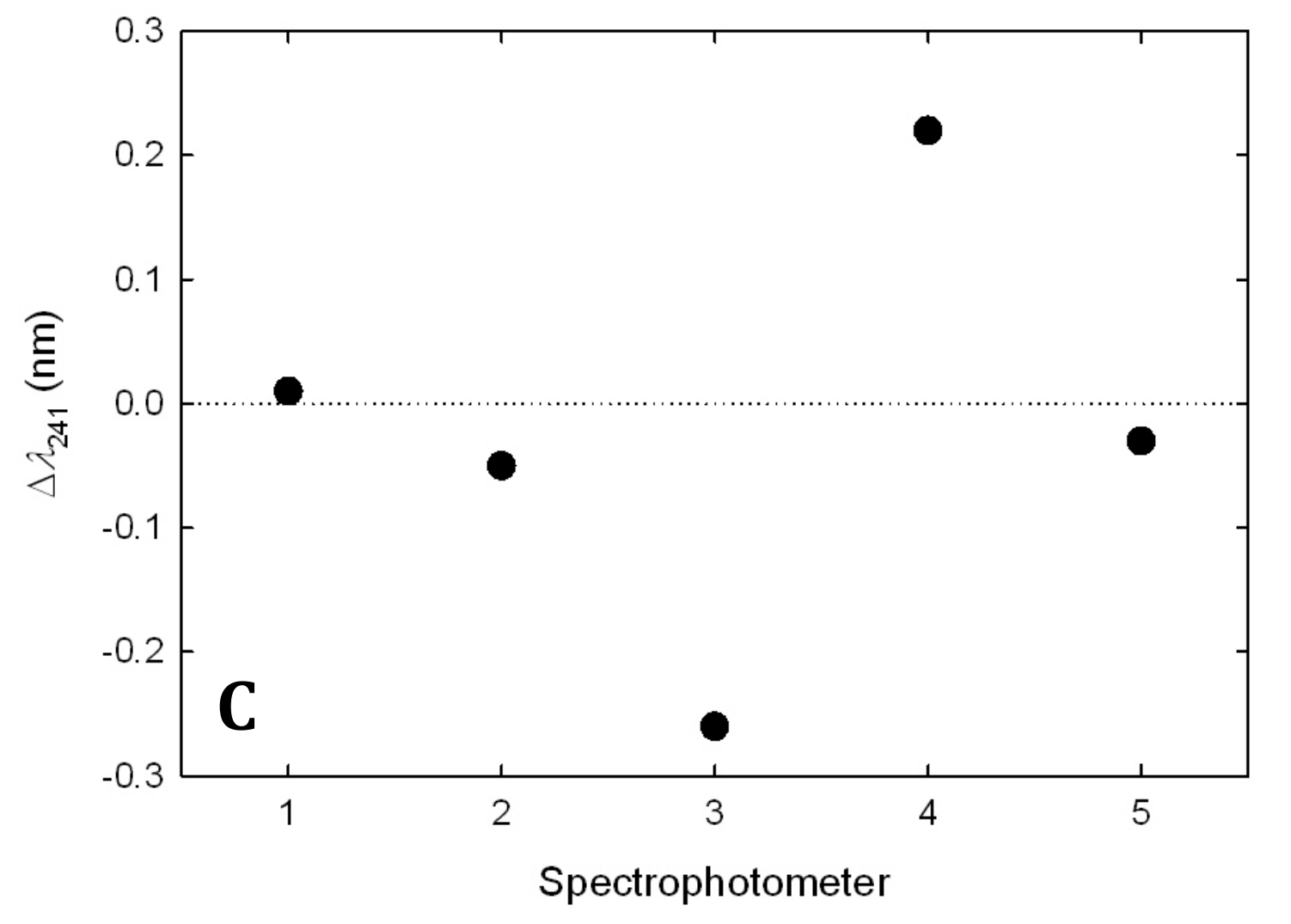
$$R = \frac{(_{250}A - _{350}A)}{(_{234}A - _{350}A)}$$

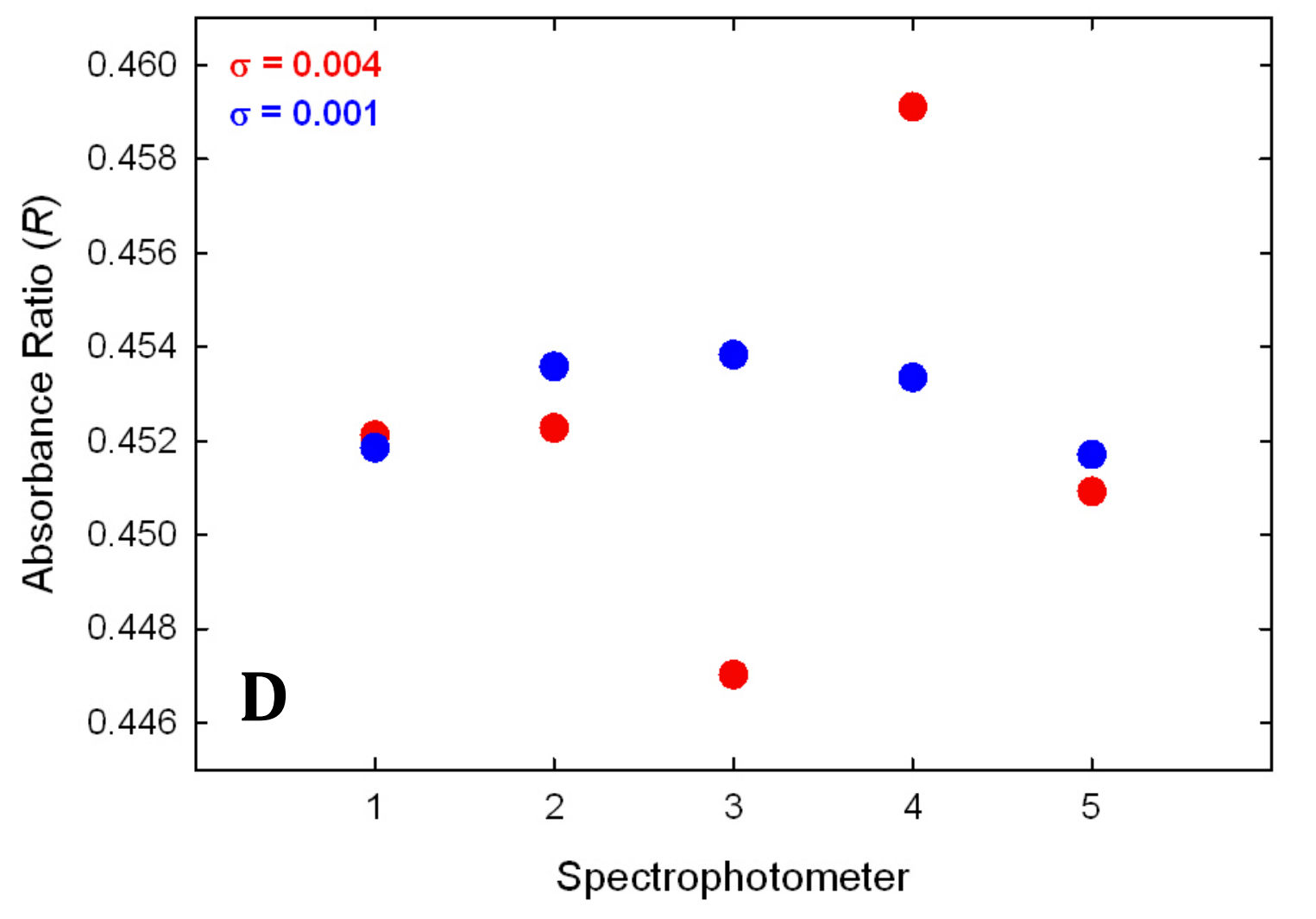
$$R^0 = R - 0.265 \cdot \Delta\lambda_{241.1}$$

$$e_3/e_2 = 2.52288 - 0.0383205 \cdot S$$

2. Wavelength Offset Correction[2]

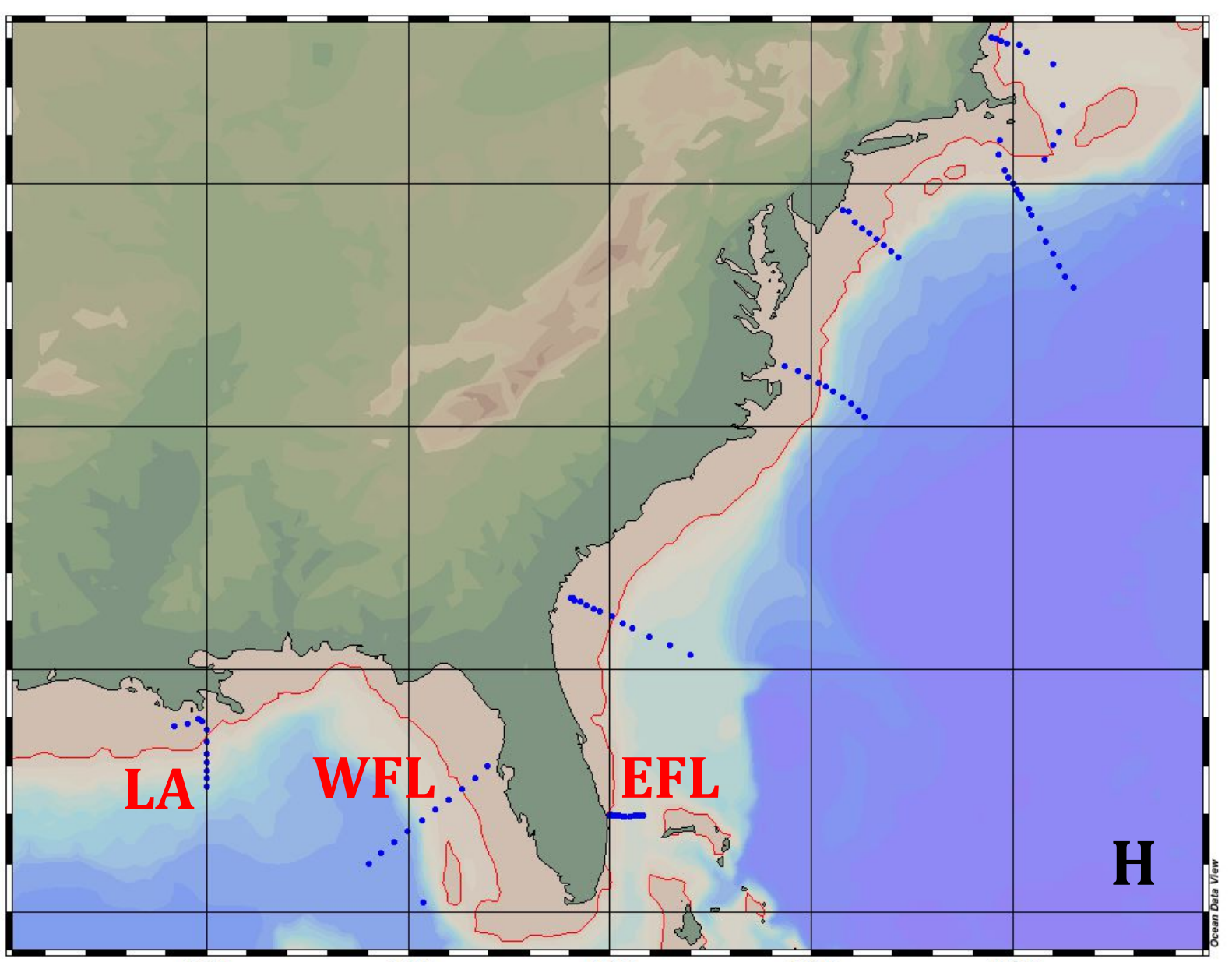




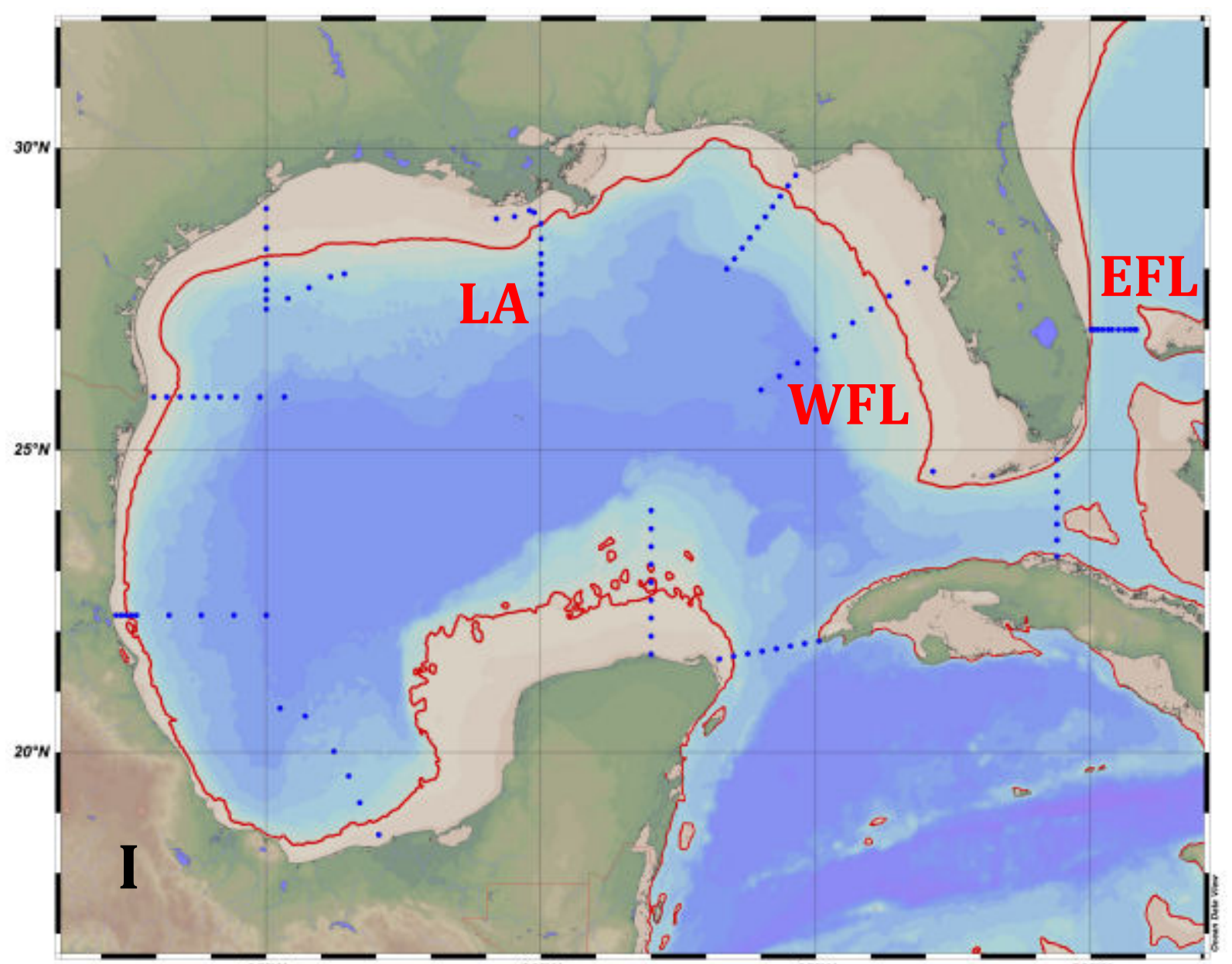


- Wavelength calibration differences between different spectrophotometers can greatly influence measured Pb(II) absorbance ratios that are used to calculate $[CO_3^{2-}]_{spec}$ (**Fig. B**)
- Even sub-nanometer shifts significantly impact spectrophotometrically measured carbonate ion concentrations
- SRM 2034,[3] a NIST wavelength standard, was used to determine wavelength offsets ($\Delta\lambda_{241.1}$), 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 $\Delta\lambda_{241.1}$equal to zero (R^0) (e.g. **Fig. D**, blue dots)
- Corrected ratios — and thus, calculated $[CO_3^{2-}]_{spec}$ values from corrected ratios— show far greater consistency between instruments

GOMECC-2 Cruise Plan (2012)



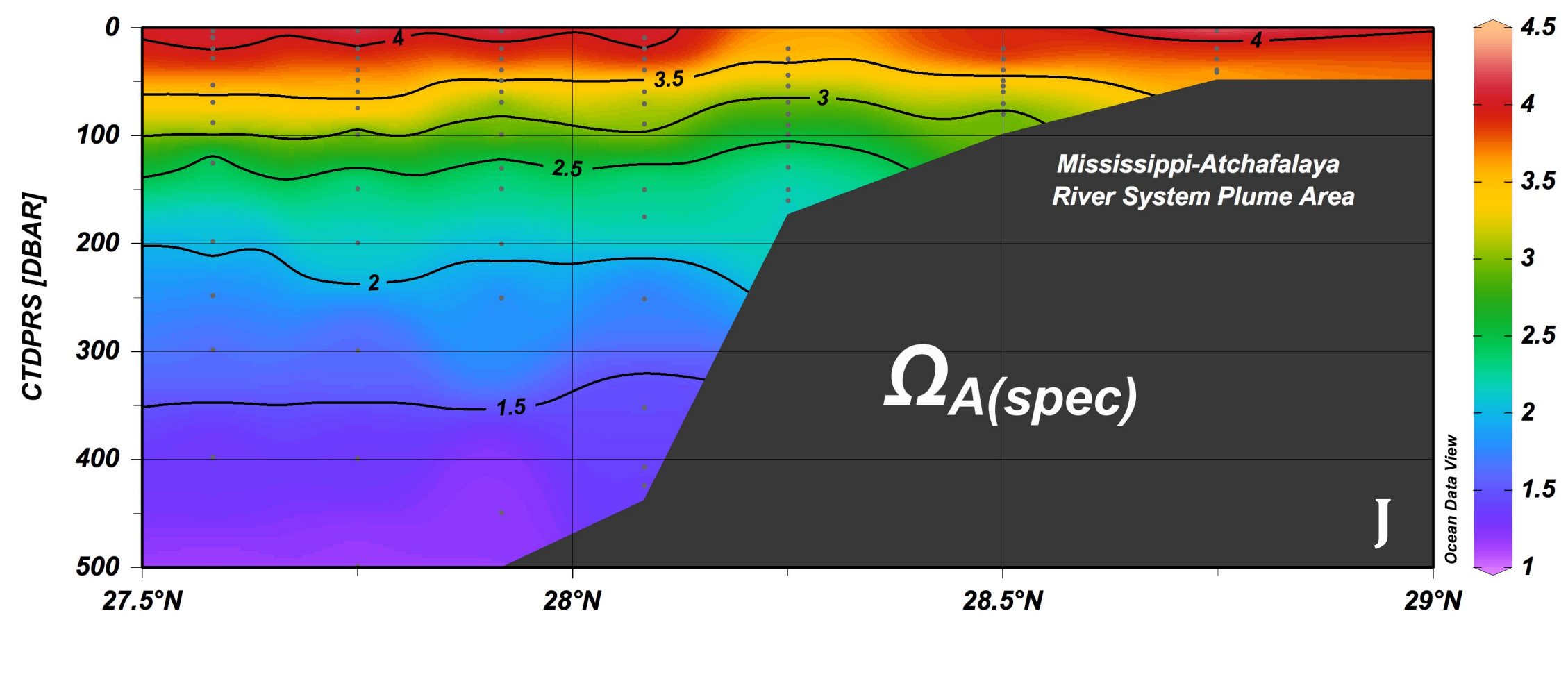
GOMECC-3 Cruise Plan (2017)

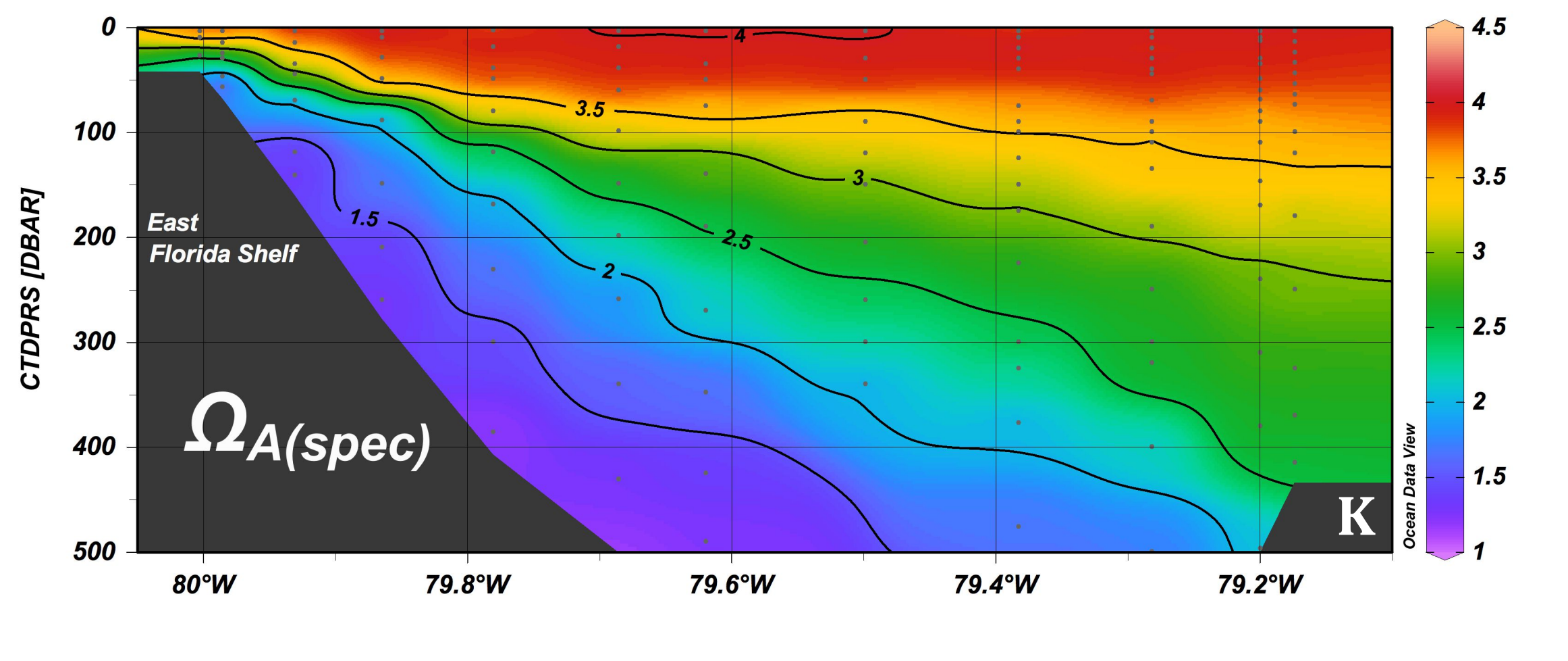


4. Gulf of Mexico Cruises

The second Gulf of Mexico and East Coast Carbon Cruise of 2012 (GOMECC-2, **Fig. H**) sampled 93 stations from surface to seafloor across 8 transects in the Gulf of Mexico and off the East Coast of the United States. Chemical variables measured included dissolved oxygen, nutrient concentrations, and all measurable CO_2 system parameters. Hydrographic data (temperature, depth, and salinity) were measured with a rosette-mounted CTD. Our lab group collected pH_T and $[CO_3^{2-}]_{spec}$ data using spectrophotometric procedures detailed elsewhere.[4–6] Absorbance ratios for $[CO_3^{2-}]_{spec}$ calculation were corrected according to the procedure detailed in Section 2. In situ calcium carbonate saturation states with respect to aragonite (Ω_A) were determined using measured $[CO_3^{2-}]_{spec}$ data[2] (**Fig. E**) and using measurements of pH_T 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 $[CO_3^{2-}]_{spec}$ measurements.

Three transects occupied on the GOMECC-2 cruise will be re-occupied this summer on the Gulf of Mexico Ecosystems and Carbon Cruise (GOMECC-3, **Fig. I**): the Louisiana transect (LA, **Fig. J**), 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 CO_2 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 be an extremely important tool for future assessments of the marine CO_2 system. These procedures 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 (GOMECC-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

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(6) Patsavas, M.C., et al., 2015. Mar. Chem. 168, 80–85.

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