



# Internal consistency of marine carbonate system measurements and assessments of aragonite saturation state: Insights from two U.S. coastal cruises



Mark C. Patsavas<sup>a</sup>, Robert H. Byrne<sup>a,\*</sup>, Rik Wanninkhof<sup>b</sup>, Richard A. Feely<sup>c</sup>, Wei-Jun Cai<sup>d</sup>

<sup>a</sup> College of Marine Science, University of South Florida, 140 7th Avenue South, St. Petersburg, FL 33701, United States

<sup>b</sup> NOAA Atlantic Oceanographic and Meteorological Laboratory, 4301 Rickenbacker Causeway, Miami, FL 33149, United States

<sup>c</sup> NOAA Pacific Marine Environmental Laboratory, 7600 Sand Point Way NE, Seattle, WA 98115, United States

<sup>d</sup> School of Marine Science and Policy, University of Delaware, Newark, DE 19716, United States

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## ABSTRACT

This research assesses the thermodynamic consistency of recent marine CO<sub>2</sub> system measurements in United States coastal waters. As one means of assessment, we compared aragonite saturation states calculated using various combinations of measured parameters. We also compared directly measured and calculated values of total alkalinity and CO<sub>2</sub> fugacity. The primary data set consists of state-of-the-art measurements of the keystone parameters of the marine CO<sub>2</sub> system: dissolved inorganic carbon (DIC), total alkalinity (TA), CO<sub>2</sub> fugacity (*f*CO<sub>2</sub>), and pH. This study is the first thermodynamic CO<sub>2</sub> system intercomparison based on measurements obtained using purified meta cresol purple as a pH indicator. The data are from 1890 water samples collected during NOAA's West Coast Ocean Acidification Cruise of 2011 (WCOA2011) and NOAA's Gulf of Mexico and East Coast Carbon Cruise of 2012 (GOMECC-2).

Calculations of in situ aragonite saturation states ( $\Omega_A$ ) near the saturation horizon exhibited differences on the order of  $\pm 10\%$  between predictions based on the (DIC, TA) pair of measurements vs. the (pH, DIC), (*f*CO<sub>2</sub>, DIC), or (*f*CO<sub>2</sub>, pH) pairs. Differences of this magnitude, which are largely attributable to the imprecision of  $\Omega_A$  calculated from the (DIC, TA) pair, are roughly equivalent to the magnitude of  $\Omega_A$  change projected to occur over the next several decades due to ocean acidification. These observations highlight the importance of including either pH or *f*CO<sub>2</sub> in saturation state calculations.

Calculations of TA from (pH, DIC) and (*f*CO<sub>2</sub>, DIC) showed that internal consistency could be achieved if minor subtractions of TA ( $\leq 4 \mu\text{mol kg}^{-1}$ ) were applied to samples of salinity  $< 35$ . The extent of thermodynamic consistency is also exemplified by the small offset between TA calculated from (DIC, pH) and that calculated from (DIC, *f*CO<sub>2</sub>):  $\sim 3 \mu\text{mol kg}^{-1}$ , which is similar to the accuracy of the TA measurements. Systematic trends can be detected in the offsets between measured and calculated parameters, but for this high-quality data set the magnitude of methodological improvements required to achieve exact thermodynamic consistency is quite small.

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## 1. Introduction

Ocean biogeochemistry is now being strongly influenced by the oceanic uptake of anthropogenic carbon dioxide (CO<sub>2</sub>) from the atmosphere. Dissolution of CO<sub>2</sub> in seawater increases the hydrogen ion concentration (i.e., decreases pH) and alters the relative proportions of the inorganic carbon species, in particular decreasing the carbonate ion concentration. This process is commonly referred to as “ocean acidification.” Many pH-dependent biogeochemical processes in open and coastal waters are therefore being affected by seawater uptake of

CO<sub>2</sub> (Anthony et al., 2011; Cai et al., 2011; Doney et al., 2009; Dore et al., 2009; Feely et al., 2004, 2008, 2010; Gledhill et al., 2008; Guinotte and Fabry, 2008; Honisch et al., 2012; Ilyina et al., 2009; Kleypas and Yates, 2009; Orr et al., 2005; Steinacher et al., 2009). Documentation of today's rapidly changing ocean chemistry is essential for understanding this acidity perturbation and its consequences.

Routinely measured CO<sub>2</sub> system parameters in seawater include dissolved inorganic carbon (DIC), total alkalinity (TA), and, increasingly, pH or carbon dioxide fugacity (*f*CO<sub>2</sub>).

Dissolved inorganic carbon is defined as:

$$\text{DIC} = [\text{CO}_2^*] + [\text{HCO}_3^-]_{\text{T}} + [\text{CO}_3^{2-}]_{\text{T}} \quad (1)$$

\* Corresponding author.

E-mail address: [rhbyrne@usf.edu](mailto:rhbyrne@usf.edu) (R.H. Byrne).

where  $\text{CO}_2^*$  is the sum of aqueous  $\text{CO}_2$  and carbonic acid:  $[\text{CO}_2^*] = [\text{CO}_2] + [\text{H}_2\text{CO}_3]$ . Total alkalinity and pH are defined as:

$$\text{TA} = [\text{HCO}_3^-]_{\text{T}} + 2[\text{CO}_3^{2-}]_{\text{T}} + [\text{B}(\text{OH})_4^-]_{\text{T}} + [\text{OH}^-]_{\text{T}} + [\text{HPO}_4^{2-}]_{\text{T}} + 2[\text{PO}_4^{3-}]_{\text{T}} + [\text{SiO}(\text{OH})_3^-]_{\text{T}} - [\text{H}^+]_{\text{T}} - [\text{H}_3\text{PO}_4^0] + [\text{organic bases}] \quad (2)$$

$$\text{pH}_{\text{T}} = -\log[\text{H}^+]_{\text{T}} \quad (3)$$

Brackets ( $[\ ]_{\text{T}}$ ) denote the total concentrations of each species. Carbonate alkalinity is given by  $[\text{HCO}_3^-]_{\text{T}} + 2[\text{CO}_3^{2-}]_{\text{T}}$ . As our sampling was restricted to depths >15–20 m, the contributions of parameters uniquely tied to sediments, such as  $\text{NH}_3$ , were not included in our calculations. Seitzinger and Gliblin (1996) showed that the effect of  $\text{NH}_3$  was small in water depths >20 m.

Due to limited resources, investigators sometimes measure only two of the four keystone parameters. Some researchers choose the (DIC, TA) pair because samples can be conveniently preserved using mercuric chloride (thus halting photosynthesis and respiration) and then stored for later analysis. Others choose the (pH, DIC) pair because pH measurements are rapid and precise and the DIC measurement is free of matrix effects (i.e., the influence of organics). Typical carbon system research cruises involve measurement of three of the four parameters. Simultaneous measurement of all four parameters is rare.

Investigators typically rely on the fact that the four parameters are related by thermodynamic models such that only two are required to calculate any of the others (Dickson et al., 2007). Equilibrium constants for these calculations include:

$$K_0 = \frac{[\text{CO}_2^*]}{f\text{CO}_2} \quad (4)$$

$$K_1' = \frac{[\text{HCO}_3^-]_{\text{T}}[\text{H}^+]_{\text{T}}}{[\text{CO}_2^*]} \quad (5)$$

$$K_2' = \frac{[\text{CO}_3^{2-}]_{\text{T}}[\text{H}^+]_{\text{T}}}{[\text{HCO}_3^-]_{\text{T}}} \quad (6)$$

Other relationships between measured and calculated parameters are described in Dickson et al. (2007).

Saturation states ( $\Omega$ ) for the polymorphs of calcium carbonate (e.g., calcite, aragonite) are currently not measured directly. These quantities can, however, be calculated from measurable parameters, in various combinations, via the following relationship (Morse et al., 2007):

$$\Omega = \frac{[\text{Ca}^{2+}]_{\text{T}}[\text{CO}_3^{2-}]_{\text{T}}}{K_{\text{SP}}} \quad (7)$$

Here  $[\text{Ca}^{2+}]_{\text{T}}$  is the total calcium concentration, which is generally calculated from salinity. The apparent solubility product ( $K'_{\text{SP}}$ ) of the polymorph is a function of salinity ( $S$ ), temperature ( $T$ ), and pressure (Zeebe and Wolf-Gladrow, 2001). Carbonate ion concentrations,  $[\text{CO}_3^{2-}]_{\text{T}}$ , can be directly determined from observations of Pb(II) ultraviolet absorbance spectra (Easley et al., 2013; Patsavas et al., 2015) but are routinely calculated with greater precision from measurements of two  $\text{CO}_2$  system parameters (e.g., DIC and either pH or  $f\text{CO}_2$ ). When  $\Omega > 1$ , precipitation of solid calcium carbonate,  $\text{CaCO}_3(\text{s})$  is favored; when  $\Omega < 1$ , conditions are thermodynamically favorable for  $\text{CaCO}_3(\text{s})$  dissolution.

In the open ocean, carbonate saturation states are typically high at the sea surface, and decrease with depth. The three-dimensional horizon (saturation horizon, SH) defined by the depths where  $\Omega = 1$  serves as a common indicator or metric of potential biological impacts of ocean acidification (Barton et al., 2012; Bednaršek et al., 2012,

2014). In recent years, SH shoaling due to ocean acidification has been reported, and this change is expected to profoundly affect marine ecosystems (Doney et al., 2009; Feely et al., 2002, 2004, 2008, 2012; Guinotte and Fabry, 2008; Tanhua et al., 2007). Accurate mapping of saturation states in the ocean is therefore imperative. Because  $\Omega$  is not directly measured, a thorough understanding of the implications of choosing different parameter pairs as the basis for  $\Omega$  calculations is necessary. Use of different parameter pairs creates differences in the precisions and accuracies of calculated saturation states because imperfections in both  $\text{CO}_2$  system parameter measurements and the equilibrium characterizations that relate them (Eqs. (4)–(7)) produce nonlinear outcomes in  $\text{CO}_2$  system calculations.

This work highlights the consequences of alternative methods of calculating aragonite saturation state and explores the internal inconsistencies that give rise to differences in calculated  $\Omega$ . This investigation of the internal consistency of  $\text{CO}_2$  system calculations is the first to incorporate pH measurements obtained using a purified spectrophotometric indicator for improved pH accuracy (Liu et al., 2011) and is unique in encompassing both coastal and pelagic conditions to depths >4000 m. Our data include recent state-of-the-art  $\text{CO}_2$  system measurements from two extensive coastal cruises, one of which obtained measurements of all four carbon system parameters. This overdetermination allows for unique comparisons that are not possible when fewer parameters are measured.

## 2. Methods

### 2.1. WCOA2011 cruise (2011)

The West Coast Ocean Acidification cruise (WCOA2011) was a 28-day NOAA Ocean Acidification Program cruise conducted in August–September 2011 aboard the *R/V Wecoma* (Fig. 1). DIC, TA, and pH were measured;  $f\text{CO}_2$  was not. Conductivity–temperature–depth (CTD) and nutrient data were also collected. The number of WCOA2011 samples is 1005.

### 2.2. GOMECC-2 cruise (2012)

The Gulf of Mexico and East Coast Carbon-2 cruise (GOMECC-2) was a 24-day NOAA Ocean Acidification Program cruise conducted in July–August 2012 aboard the *R/V Ronald H. Brown* (Fig. 2). All four carbon system parameters (DIC, TA, pH, and  $f\text{CO}_2$ ) were measured throughout the water column. CTD and nutrient data were also collected. The number of seawater samples with the full suite of inorganic carbon system, nutrient, and CTD data is 885.

### 2.3. $\text{CO}_2$ system calculations

We used the  $\text{CO}_2$  system analytical methods and quantitative relationships described in Dickson et al. (2007). The at-sea pH method was modified to incorporate the use of purified (as opposed to off-the-shelf) meta cresol purple (mCP) (Patsavas et al., 2013) and the updated pH equations of Liu et al. (2011).

Thermodynamic system calculations were performed using the Excel macro  $\text{CO}_2\text{SYS}$ , version 2.1 (Pierrot et al., 2006). Because pH was determined on the total hydrogen ion concentration scale, the dissociation constants ( $K_1'$  and  $K_2'$ ) of Lueker et al. (2000) were used for all routine calculations. These constants are based on the original data of Mehrbach et al. (1973), in which  $K_1'$  was estimated from potentiometric titrations of natural seawater and  $K_2'$  was determined from measurements of the product of  $K_1'$  and  $K_2'$ . The procedures used by Lueker et al. (2000) to calculate  $K_1'$  and  $K_2'$  from the original data of Mehrbach et al. (1973) are very similar to the calculation procedures of Dickson and Millero (1987). For one set of comparative calculations, we also used other constants: Millero et al. (2002), Mojica Prieto and Millero (2002), Millero et al. (2006), Dickson and Millero

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