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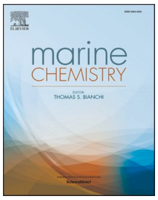

Evaluation of the temperature dependence of dissociation constants for the marine carbon system using pH and certified reference materials

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ABSTRACT

Due to the uptake of anthropogenic carbon dioxide (CO_2) from the atmosphere, and the resulting ocean acidification, long term monitoring of the marine carbon cycle is of utmost importance and requires high precision and accuracy across many laboratories over several decades. Despite this, many uncertainties still remain in carbon system measurements and calculations. Calculations of the carbon system are facilitated by publicly available software, but the large number of options for various constants make data and study inter-comparability challenging. Here, the carbon system is evaluated using internal consistency calculations and spectrophotometric pH measurements on two batches of Certified Reference Material over the full oceanic range of temperatures (−1.7–40 °C). The choice of formulation for the bisulfate dissociation constant is insignificant over at least the salinity range of the CRM ($S = 33.4$–33.8). The choice of formulation of the hydrogen fluoride dissociation constant adds a small amount of uncertainty, but the best option is unclear. The total boron concentration significantly impacts the calculated pH, with the value of Lee et al. (2010) being more internally consistent and, thus, recommended. Of the 8 carbonic acid dissociation constant sets evaluated, nearly all remain internally consistent at near-surface open-ocean salinities (~31–36) within the accuracy of pH measurements. Nevertheless, the values of Mehrbach et al. (1973), as refit by Dickson and Millero (1987), and Lueker et al. (2000) were the most internally consistent and therefore are preferred for current surface ocean studies ($S \approx 31$–36, $T = -1.7$–40 °C, $fCO_2 < 500$ μatm). The pH was more internally consistent at lower temperatures than higher temperatures.

1. Introduction

Studies of the marine carbon cycle are of great importance due to the uptake of anthropogenic carbon dioxide (CO_2) from the atmosphere, resulting in an increase in total dissolved inorganic carbon (DIC) and a decrease in pH (negative logarithm of the hydrogen ion concentration). The marine inorganic carbon system can be characterized by four measurable parameters, DIC, total alkalinity (TA), partial pressure or fugacity of CO_2 (pCO_2 or fCO_2 respectively), and pH. Although pCO_2 is often the measured variable, fCO_2 accounts for the non-ideal behavior of CO_2, making it more appropriate for thermodynamic calculations. Thus, fCO_2 will be used from here on. Direct measurement of a fifth parameter, carbonate ion concentration ($[CO_3^{2-}]$), has recently become possible (Byrne and Yao, 2008; Sharp et al., 2017), but has not yet been widely adopted. All of the measurable parameters are interrelated through a series of reaction constants (Park, 1969). Thus, one needs only measure any two parameters in order to calculate the remaining measurable parameters, or ancillary parameters such as the CO_3^{2-} concentration or the calcium carbonate saturation state. In theory, the choice of which parameters are measured and which are calculated is irrelevant (Dickson and Riley, 1978). In practice, some pairs are better than others (Dickson and Riley, 1978; McLaughlin et al., 2015) due to propagation of uncertainties in both the measurements and in the constants themselves (Orr et al., 2018). The agreement between measured and calculated parameters is called internal consistency. Good internal consistency occurs when a model (calculated values) is in consensus with measured values. Measurements pairs that typically produce the most internally consistent results combine one temperature and pressure independent measurement (DIC or TA) with a temperature and pressure dependent measurement (pH or fCO_2). Irrespective, DIC and TA are the most commonly measured pair in the field.

In the early days of marine carbon research, measurement uncertainties dominated the uncertainty in the calculated parameters, meaning that uncertainties in the constants were generally negligible (Dickson and Millero, 1987). Between the mid–1980s through the 1990s, significant improvements were made in analytical precision and accuracy of all four measurable parameters. When current best practices are followed, the uncertainties due to the constants are of similar magnitude as the uncertainties from the measurements and can no longer be ignored (Orr et al., 2018). With such analytical improvements, many workers have determined the carbonic acid dissociation constants over a wide range of temperatures and salinities. Today, there are at

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least 17 sets of carbonic acid dissociation constants applicable to seawater. Although some are no longer in widespread use, several formulations are commonly used, leading to issues of data intercomparability between studies, and uncertainty in accuracy and precision of results. Despite numerous studies, there remains no recommended set of constants based on a systematic evaluation.

2. Marine inorganic carbon system

When CO_2 gas dissolves in seawater it undergoes a series of equilibrium reactions as follows:

$$CO_{2(g)} \overset{K_0^*}{\rightleftharpoons} CO_{2(aq)} \tag{1}$$

$$CO_{2(aq)} + H_2O_{(l)} \overset{K_H^*}{\rightleftharpoons} H_2CO_{3(aq)} \tag{2}$$

$$H_2CO_{3(aq)} \overset{K_1^*}{\rightleftharpoons} H^+_{(aq)} + HCO^-_{3(aq)} \tag{3}$$

$$HCO^-_{3(aq)} \overset{K_2^*}{\rightleftharpoons} H^+_{(aq)} + CO^{2-}_{3(aq)} \tag{4}$$

where the subscripts g, l, and aq refer to the species state (gas, liquid, and aqueous solutions respectively). Analytically, distinguishing between the $CO_{2(aq)}$ and $H_2CO_{3(aq)}$ species is difficult, and they are therefore summed into a hypothetical species CO_2*. Redefining eqs. 1–3 in terms of CO_2* produces:

$$CO_{2(g)} \overset{K_0^*}{\rightleftharpoons} CO^*_{2(aq)} \tag{5}$$

$$CO^*_{2(aq)} + H_2O_{(l)} \overset{K_1^*}{\rightleftharpoons} H^+_{(aq)} + HCO^-_{3(aq)} \tag{6}$$

From the above equilibria (eq. 5,6, 4, respectively), the stoichiometric dissociation constants (K_i*) are:

$$K_0^* = \frac{[CO_2^*]}{fCO_2} \tag{7}$$

$$K_1^* = \frac{[HCO_3^-]\ [H^+]}{[CO_2^*]} \tag{8}$$

$$K_2^* = \frac{[CO_3^{2-}]\ [H^+]}{[HCO_3^-]} \tag{9}$$

where brackets denote total concentrations. The K_0* equation was determined by Weiss (1974) across a wide range of temperatures and salinities and has become the only formulation commonly in use. The K_1* and K_2* values, however, have been determined and redetermined by a number of studies.

The importance of H^+ (and pH) is evident in the equilibria above. Seawater is a complex ionic medium and the direct determination of hydrogen ion activities is difficult or impossible for most applications, leading to the development of several different conventions or concentration scales for pH (Dickson, 1984; Dickson et al., 2016). Each scale has been promoted as the preferred one at various times or for various uses (Dickson, 1984; Dickson et al., 2016; Dickson and Millero, 1987; Waters and Millero, 2013), but the total scale is currently the most commonly used. The various scales attempt to account for the inability to measure single-ion activities in such a complex electrolyte solution as seawater by including interactions of the proton with the media (*e.g.* HSO_4^- and HF). The free, total, and seawater scales are defined, under the constant ionic medium convention, as:

$$pH_F = -log\left([H^+]_F\right) \tag{10}$$

$$pH_T = -log\left([H^+]_F + [HSO_4^-]_T\right) \tag{11}$$

$$pH_{sws} = -log\left([H^+]_F + [HSO_4^-]_T + [HF]_T\right) \tag{12}$$

where subscripts F, T and SWS on pH refer to free, total, and seawater scales, respectively. The F and T subscripts on the concentrations refer to free and total concentrations of the species. All three scales can be quantitatively converted among each other by knowing the concentrations and dissociation constants of bisulfate and hydrogen fluoride. A fourth scale, the National Bureau of Standards (NBS), now National Institute of Standards and Technology, is only defined under the infinite dilution convention (ionic strength $<\sim 0.1$) and cannot be quantitatively converted without knowing the apparent hydrogen ion activity coefficient (γ_H). Partly because the γ_H is related to the unique liquid junction potential of the electrode used in the measurement, it is irreproducible between electrodes, and therefore must be determined for each study. Conversion between scales is simple (Dickson et al., 2007) and can be carried out by publicly available software (*e.g.* Van Heuven et al., 2011b). All of the constants used in this study were determined on the seawater scale aside from two that were determined on the total scale (Lueker et al., 2000; Papadimitriou et al., 2018). The spectrophotometric pH method was calibrated using TRIS buffers without F^- and therefore used the total scale. All pH values used in this study are on the total scale.

A hydrogen electrode is the most accurate method of measuring pH but due to interferences from some natural components of seawater it cannot be used in natural seawater (Dickson et al., 2016). TRIS (2-hydroxymethyl-1,3-propanediol) buffers made in artificial seawater are used to minimize the liquid junction potential of glass electrodes and to relate hydrogen electrode measurements to direct seawater measurements made using other methods. Uncertainties due to differences in ionic interactions between the TRIS buffers and natural seawater lead to a large uncertainty in the accuracy of pH (~0.02; McLaughlin et al., 2015). As a result, the uncertainty in the accuracy of direct pH measurements is much greater than the precision. The disparity between accuracy and precision make it challenging to evaluate the accuracy of carbon system calculations, therefore, internal consistency is used instead. Consequently, the marine carbon system may be internally consistent, but inaccurate. Inaccuracies in DIC and TA measurements may also contribute to the problem, but to a much smaller degree than pH.

3. History of carbonic acid dissociation constants

Several determinations of K_1* and K_2* were made between 1932 and 1968, but even after correcting for differences in definitions of the carbonic acid dissociation constants and H^+ activities, agreement among studies was poor (Hansson, 1973), particularly for K_2* (Mehrbach et al., 1973). The first reasonably reliable values for seawater came in the early 1970s from Hansson (1973) and Mehrbach et al. (1973). Dickson and Millero (1987) refit the data of both Hansson (1973) and Mehrbach et al. (1973) after converting them to a common basis and presented the results on the seawater scale. Hansson (1973) used artificial seawater that lacked fluoride (F^-), and the concentration of sulfate (SO_4^{2-}) varied from that of real seawater, requiring corrections. Dickson and Millero (1987) provided three different fits of the results, refitting the two studies individually and then together. They noted an offset between the refits of Mehrbach et al. (1973) and Hansson (1973), but given that the bias was within the uncertainty of the constants and there was a larger uncertainty in the parameter measurements at that time, this was ignored.

Continued discrepancies in internal consistency calculations and among investigators resulted in several studies aiming to re-determine the dissociation constants with new measurements. Goyet and Poisson (1989) and Roy et al. (1993) made independent re-determinations of the constants over a broader range of temperatures and salinities using artificial seawater. Both studies used artificial seawater without boron (B), but Goyet and Poisson (1989) used solutions containing F^- while

Roy et al. (1993) did not. Roy et al. (1993) used a hydrogen electrode rather than a glass electrode, improving accuracy. Although more accurate, a hydrogen electrode cannot be used in natural seawater due to interferences from F^-. Millero (1995) combined the two datasets to provide one fit for each constant, but the equations never came into widespread use. Cai and Wang (1998) combined several older studies to provide a set of constants applicable from fresh estuarine waters to the salty open ocean. Due to the measurements used in the fit, these equations have a larger uncertainty than other constants, are typically not used in open ocean studies, and will not be considered further.

With many options available and no systematic determination of which was "best", numerous internal consistency studies were carried out, each finding a different set of constants to be the most internally consistent for their given dataset (Byrne et al., 1999; Clayton et al., 1995; Lee et al., 2000; Lee and Millero, 1997, 1995; McElligott et al., 1998; Wanninkhof et al., 1999). A generalized summary of these studies is that calculations involving $f\mathrm{CO_2}$, TA, and DIC show better internal consistency with Mehrbach et al. (1973) refit by Dickson and Millero (1987), but studies involving pH, TA, and DIC show better internal consistency with Goyet and Poisson (1989) or Roy et al. (1993). A $f\mathrm{CO_2}$ dependent offset that increased with increasing $f\mathrm{CO_2}$ was commonly observed (Millero, 1995; Wanninkhof et al., 1999). Another confounding factor in these studies is that DelValls and Dickson (1998) redetermined the pH values assigned to TRIS buffers used in calibrating pH measurements, resulting in a correction of +0.0047. Impurities in the indicator can also cause biases in pH (Liu et al., 2011). Both biases make it difficult to apply results of pre-2011 internal consistency studies to modern results.

Given the conflicting results of the many internal consistency studies, further research was conducted to redetermine and reevaluate the constants (Lueker et al., 2000; Millero et al., 2006, 2002; Mojica Prieto and Millero, 2002). Most studies used similar methods to earlier work, but with improvements in technique and precision. Millero et al. (2002) took a different approach by using field measurements, where all four parameters were measured, to back calculate the constants. All of these studies used natural seawater. Mojica Prieto and Millero (2002) also did several experiments with artificial seawater and demonstrated that the offsets between natural and artificial seawater noted in many previous studies was caused by lack of borate in artificial seawater. There is still some debate about the exact nature of the ionic interactions causing the offset. As a result, constants determined in artificial seawater (Goyet and Poisson, 1989; Hansson, 1973; Roy et al., 1993; Tishchenko et al., 2013) should not be applied to natural seawater, yet some studies still use values determined from artificial seawater.

Lueker et al. (2000) repeated the exercise of Dickson and Millero (1987) and refit the values of Mehrbach et al. (1973), but now on the total pH scale. Lueker et al. (2000) also determined that there was a significant decrease in internal consistency at $f\mathrm{CO_2}$ values above ~500 μatm. Such offsets seen in other studies were hypothesized to be caused by an unknown contribution of organic alkalinity in deep waters (Lueker et al., 2000), but only surface seawater that had been UV irradiated to remove organics was used in these experiments, implying that another factor must be important; although the UV irradiation may not completely remove organic material (Andrew Dickson, personal communication). One potential cause could be errors in K_0*, which were evaluated by Lueker (1998). A small but significant offset between those measurements and those of Weiss (1974) was found at 25 °C. Recent work in NaCl solutions also indicates possible errors in K_0* (Bailey et al., 2018) at low temperatures. As K_0* is not used in calculations involving pH, TA, and DIC, it will not be discussed further here, but a reevaluation of K_0* is warranted. As Lueker et al. (2000) discussed, the recommendation of Mehrbach et al. (1973) refits only applies to calculations involving $f\mathrm{CO_2}$, TA, and DIC at near surface conditions ($f\mathrm{CO_2} < \sim 500$ μatm). Such qualification impedes any explicit recommendation of a set of constants in the best practices manual (Dickson et al., 2007). Dickson and Millero (1987) and Lueker et al. (2000) converted Mehrbach et al. (1973) values to different pH scales, but had slightly different fitting procedures. As a result, the two should be nearly identical over salinities of 20–40 and temperatures of 2–35 °C but likely vary somewhat near the low salinity range.

Millero et al. (2002) used field measurements to back calculate the constants. Very few cruises exist where all four parameters were measured, and many that do, measured pH by the less precise potentiometric method. Both pH and $f\mathrm{CO_2}$ are highly temperature dependent, but due to practical constraints, discrete measurements must be made at a set temperature (typically 20 or 25 °C), thus requiring a conversion back to *in-situ* temperature. There are constant-independent methods to convert $f\mathrm{CO_2}$ to *in-situ* temperature (Takahashi et al., 1993), but there are no reliable constant-independent conversions for pH (Woosley et al., 2017). These data limitations add uncertainty to the temperature dependence of these constants.

Millero (2010) combined the results of several prior studies using natural seawater (Mehrbach et al., 1973; Millero et al., 2006; Mojica Prieto and Millero, 2002) to develop one set of constants applicable to the full range of oceanographic conditions, including estuarine waters. Due to the sheer number of measurements by Millero et al. (2006), accounting for ~85% of the total measurements, the combined formulation is very similar to that reported by Millero et al. (2006).

Several newer formulations exist but have not gained widespread use, or inclusion into CO2sys or similar programs (Papadimitriou et al., 2018; Tishchenko et al., 2013; Waters et al., 2014; Waters and Millero, 2013). Waters and Millero (2013) refit the same data as Millero (2010) using a Pitzer model to reevaluate the carbonic acid dissociation constants as well as the dissociation constant of bisulfate (K_{HSO4^-}*,). They determined a new K_{HSO4^-}*, which agreed well with Dickson (1990a) at S = 35, but varied for waters with both high salinities (> 35) and low temperatures (< 25 °C). Papadimitriou et al. (2018) determined the carbonic acid dissociation constants in sea ice derived brines (S = 33–100) at low temperatures (≤ 25 °C), and will be evaluated here. Tishchenko et al. (2013) used artificial seawater without borate and found similar offsets as earlier studies compared to natural seawater and will not be evaluated.

More recent internal consistency calculations tend to be used as a quality control measure rather than an evaluation of the constants (*e.g.* Millero et al., 2016), or an *a priori* set of constants is used to evaluate uncertainties in the marine carbon system (Álvarez et al., 2020; Carter et al., 2017; Fong and Dickson, 2019; Sulpis et al., 2020). Given that the last comprehensive evaluation of the various sets of constants in order to identify a recommended "best" set was carried out 20 years ago (Lee et al., 2000), that there have been significant improvements in measurement techniques, particularly for pH (Carter et al., 2013; Liu et al., 2011; Takeshita et al., 2020), and the number of constant choices has swelled, it is time for a reevaluation. Such a study allows for a systematic evaluation of the currently available constants, allowing for explicit recommendations based on the current state of the science, or identification of areas for future research.

Table 1
Certified and ancillary data for the two batches of CRM used in this study.

Batch	179	189
Salinity	33.841	33.494
DIC	1941.92 ± 0.68	2009.48 ± 0.74
TA	2219.26 ± 0.86	2205.26 ± 0.31
Soluble reactive phosphate	0.45	0.45
Si	7.3	2.1
NO_2^-	0.03	0.01
NO_3^-	2.6	6.2

Salinity is practical salinity and all other values are in units of $\mu mol \cdot kg^{-1}$ of seawater

4. Methods

The approach taken here varies significantly from prior studies. Laboratory measurements of pH were made on two different batches (179 and 189) of certified reference material (CRM) obtained from Andrew Dickson (University of California, San Diego) to evaluate the internal consistency of the carbonic acid dissociation constants using pH, TA, and DIC. The certified values and ancillary data for the two batches are given in Table 1. The advantage to using CRMs is that the values of DIC and TA are as accurate and precise as currently available, and since they are produced in large batches, a large number of measurements can be made at different temperatures with the same water. The disadvantage is that a CRM only provides one salinity and pH (fCO$_2$) value, limiting the applicability of the results to near-surface open-ocean regions. Despite this limitation, this study still covers the vast majority of ocean surface conditions where anthropogenic CO$_2$ uptake and storage is most significant. As pH and the carbonic acid dissociation constants are only a secondary function of salinity (Millero, 1995), the results presented here likely apply to a salinity range of ~31–36, temperatures -1.7–40 °C, and an fCO$_2$ < 500 μatm (Lueker, 1998; Lueker et al., 2000). Coastal areas which may fall within these ranges can have large concentrations of organic alkalinity and cannot be evaluated with the experiments here. These conditions have been termed near-surface open-ocean here and throughout. Pressure is also an important factor which cannot be evaluated here as all measurements were done at atmospheric pressure.

5. pH measurements

A custom designed, automated spectrophotometric pH system similar to that of Carter et al. (2013) was used. Briefly, a Kloehn v6 syringe pump (Noragen Inc., Las Vegas, NV) with a 10 mL syringe is used to draw water from the sample bottle and fill a 10-cm quartz micro-volume spectrophotometric cell (Starna Cells, Inc., Atascadero, CA). The Kloehn pump is used to rinse the cell and add/mix the meta-cresol purple (mCp) indicator dye contained in a labtainer (Thermo-Fischer Scientific, USA) bag to minimize oxidation. A single batch of ~2 millimolar purified dye (provided by Dr. Robert H. Byrne, University of South Florida) prepared in ~0.7 M NaCl was used. An Agilent 8454 UV–Vis spectrophotometer (Agilent Technologies, Inc. Santa Clara, CA) with factory calibration was used to measure the absorbance (A_i) of the sample at four wavelengths (where subscript i refers to wavelength 434, 578, 730 nm or the isosbestic (iso) point). The absorbance ratio (R) is determined from the two absorbance peaks of mCp ($R = (A_{578}\text{-}A_{730})/(A_{434}\text{-}A_{730})$). The isosbestic point wavelength is temperature dependent, but is found at approximately 488 nm (Liu et al., 2011). The equations of Liu et al. (2011) were used to calculate pH on the total scale and can be found in the **supplemental information**.

The sample bottle and spectrophotometer cell were thermostated throughout the measurement using a Versacool recirculating water bath (Thermo-Fischer Scientific, USA). The spectrophotometer cell is too small to measure the temperature of the sample directly. Instead, the temperature is measured from a platinum resistance thermometer located adjacent to the cell in a custom designed aluminum cell holder. A micro thermistor, calibrated with the platinum thermometer, was used to determine the temperature differential between the cell and the cell holder; it was <0.1 °C. For each set of measurements at a given temperature, the water bath was adjusted to maintain a stable temperature within ~0.1 °C of the desired value as measured by the thermometer in the spectrophotometer cell holder. The temperature equilibration was carried out for a minimum of 45 min to ensure all samples reached the desired temperature (determined empirically). An additional 30 min was allotted for temperatures below 5 °C. The equilibration time before taking a blank or absorbance spectra was also determined empirically for each temperature using TRIS buffers that are twice as temperature sensitive as seawater. The equilibration times ranged from 80 to 150 s. The TRIS buffers were prepared according to Dickson et al. (2007).

Each CRM bottle was measured four times, twice with a low amount of dye, and twice with a high amount of dye ensuring that absorbance values were within the linear range of the spectrophotometer (~0.3–1.2). A_{iso} was used as a proxy for the amount of dye added. The dye amount was alternated between samples and bottles to ensure differences were due to the dye perturbation and not gas exchange between measurements. The time that a bottle can be open before the pH is measurably altered due to gas exchange was found to be ~25 min if a Kimwipe is inserted into the neck of the bottle to restrict airflow, while preventing a vacuum from forming, and the sample is drawn from the bottom of the bottle. Depending on the equilibration time, a bottle was open between 14 and 22 min during analysis. Precision of individual bottle pH was generally <0.0010, but for a majority of bottles was ≤ 0.0005. Five CRM bottles were measured at each temperature for a total of 20 measurements per CRM batch per temperature. Seven measurements were determined to have not reached temperature and were excluded from analysis (4 measurements from bottle 536, 1 measurement from bottle 847, and 2 measurements from bottle 1151).

The dye perturbation is particularly challenging for these specific measurements. Typically, the impact of adding the dye (an acid/base pair itself) on the pH is determined empirically for each batch of dye by measuring the pH of many samples from a wide range of pH with differing amounts of dye and then fitting a line to determine the change in R relative to the change in the isosbestic point absorbance ($\Delta R/\Delta A_{iso}$, Carter et al., 2013) or volume of dye added (Clayton and Byrne, 1993). Without a range of pH values at each temperature, two options were considered. A range of pH values (~7.8–8.4) was created by varying the temperature so the Carter et al. (2013) method could be used by combining all measurements. It is unknown how the perturbation varies with temperature given that there is a small variation in the isosbestic point with temperature (Liu et al., 2011). Another option is to make multiple measurements on the same sample with different amounts of dye. There is a linear relationship between the measured R of the same sample with the amount of dye added (Clayton and Byrne, 1993). In a linear fit of either R or pH *versus* A_{iso}, the intercept is the R or pH without the addition of dye. For each CRM batch at each temperature, all 20 measurements, each with slightly different amounts of dye, were fit to obtain a single ensemble pH value per temperature. The Matlab® fitlm function was used with "robust" on and default tuning parameters to minimize the influence of outliers. Using either R or pH in the fitting procedure produced identical results to within 0.0001. The results using the extrapolation to zero dye and fitting all measurements at all temperatures agreed within 0.0010 pH units. The extrapolation of pH to zero indicator added for each temperature was used to determine the final measured pH values. The standard error was taken to be the standard error in the intercept. The mean standard error was 0.0021, with a range of 0.0007–0.0055. The 0.0055 is for 40 °C batch 189 and is thought to be a result of poor temperature control because some of the CRM bottles would not fit completely into the water-jacketed bottle holder. Excluding that value, the maximum standard error is 0.0034. The standard error reflects both instrument precision and bottle to bottle variability. Although the different methods of determining the dye perturbation produced similar results, it is still a significant source of uncertainty in the accuracy of these measurements. The extrapolated pH values are provided in **supplemental table 1** and the raw unadjusted absorbances and R values are archived at the biological and chemical oceanography data management office (Woosley, 2020a, 2020b).

6. Internal consistency calculations

Calculations of pH were carried out using the Matlab® version of CO2sys (Lewis and Wallace, 1998; Van Heuven et al., 2011b) modified to add options for the dissociation constant of HF, K_F*, of Perez and Fraga (1987), the K_{HSO_4}*, K$_1$*, and K$_2$* of Waters and Millero (2013) with corrections (Waters et al., 2014) and K$_1$*, and K$_2$* of Papadimitriou

Table 2
References, type, applicable ranges, and abbreviations for constants used or evaluated in this study.

Reference	Abbreviation	Salinity Range	Temp. Range (°C)	Original Data/Refit[a]	Media
Carbonic Acid Dissociation Constants (K^*_1 and K^*_2, eqs. 8 and 9)					
Mehrbach et al. (1973) refit by Dickson and Millero (1987)	DM87	19–35	2–35	R	Natural seawater
Lueker et al. (2000)	L00	19–35	2–35	R	Natural seawater
Mojica Prieto and Millero (2002)	MPM02	12–45	5–45	O	Natural seawater
Millero et al. (2002)	M02	33–37	−1.6–38	O	Natural seawater
Millero et al. (2006)	M06	0.1–50	1–50	O	Natural seawater
Millero (2010)	M10	0.1–50	1–50	R	Natural seawater
Waters and Millero (2013) (with Corrigendum Waters et al., 2014)	WM13	0.1–50	1–50	R	Natural seawater
Total Boron Concentration ($[B]_T$)					
Uppström (1974)	U74				Natural seawater
Lee et al. (2010)	L10				Natural seawater
Bisulfate Dissociation Constant ($K_{HSO_4}{}^*$)					
Khoo et al. (1977)	K77	20–45	5–40	O	Artificial Seawater
Dickson, 1990a	D90	5–45	0–45	O	Artificial Seawater
Waters and Millero (2013)	WM13	5–45	0–45	R	Artificial Seawater
Hydrogen Fluoride Dissociation Constant ($K_F{}^*$)					
Dickson and Riley (1979)[b]	DR79	26.7–34.6	25	R	Natural seawater
Perez and Fraga (1987)	PF87	10–40	9–33	O	Natural seawater
meta-Cresol Purple Indicator (mCp)					
Liu et al. (2011)		20–40	5–35	O	TRIS Buffers

[a] O = Original Data, R = Refit.
[b] Original data at 2 salinities and 25 °C, extended using enthalpy and infinite dilution data, but not stated over what range equations are applicable. Natural seawater is assumed, though not explicitly stated.

et al. (2018). Carbonic acid dissociation constants determined in artificial seawater are known to be biased and were excluded, as were the constants of Cai and Wang (1998) as previously stated. Two other options, GEOSECS and Peng, only remain in CO2sys to maintain back compatibility with old GEOSECS data and are not intended for modern measurements. Therefore, of the 17 options for the carbonic acid dissociation constants, 8 were used ((Mehrbach et al., 1973) as refit by Dickson and Millero (1987), (Lueker et al., 2000; Millero, 2010; Millero et al., 2006, 2002; Mojica Prieto and Millero, 2002; Papadimitriou et al., 2018; Waters and Millero, 2013)). These will henceforth be abbreviated by the author(s)' initials and year. The abbreviations and details of the constants are given in Table 2. Although Dickson and Millero (1987) provided three different fits, only the refit of Mehrbach et al. (1973) is used, and will therefore be abbreviated DM87.

Aside from the carbonic acid dissociation constants, other constants and concentrations are important in seawater measurements due to the complex chemical nature of this aqueous solution. For seawater, the main non-CO_2 component of TA is boric acid, with smaller contributions from sulfate, fluoride, silicic and phosphoric acids and ammonia. As major constituents of seawater, the concentrations of boron (B), SO_4^{2-}, and F^- can be estimated from salinity. Phosphate and silicate must be measured for each sample but are generally low, particularly for surface waters. Ammonia only accumulates substantially in sulfidic waters and is generally considered negligible for open ocean carbon system research (Xu et al., 2017). The dissociation constants for each of these seawater constituents are necessary for accurate calculations, but due to their minor contribution, their accuracy is less important than for the CO_2 constants. In CO2sys, the silicate and phosphate dissociation constants are from Yao and Millero (1995). As the contribution of these constituents is small, the uncertainty in these constants is considered negligible. For the borate dissociation constant only the value of Dickson (1990b) is used. For $K_{HSO4^-}{}^*$, there are three options (Dickson, 1990a; Khoo et al., 1977; Waters and Millero, 2013), abbreviated D90, K77, and WM13 respectively. There are two options for $K_F{}^*$ (Dickson and Riley, 1979; Perez and Fraga, 1987), abbreviated DR79 and PF87 respectively, and two options for total boron concentration (Lee et al., 2010; Uppström, 1974), abbreviated L10 and U74 respectively.

The definition of TA does leave open the possibility of other, currently unrecognized, acids or bases (Dickson, 1981) which could contribute to inaccuracies in TA. The existence of an organic alkalinity component has been debated over the years (Fong and Dickson, 2019; Kim and Lee, 2009; Lueker et al., 2000; Millero, 1995), but aside from estuarine (Song et al., 2020), pore-water (Lukawska-Matuszewska, 2016), and some coastal environments (Yang et al., 2015), has only been hypothesized and never been proven significant in the open ocean (Álvarez et al., 2020). The water used to prepare CRMs is filtered and UV irradiated (Dickson, 2010) although these treatments may not be enough to completely remove organic alkalinity if present (Andrew Dickson, personal communication). The existence and importance of organic alkalinity in open-ocean waters is highly debated (Álvarez et al., 2020; Fong and Dickson, 2019). If present, the calculations done here would be biased as carbonate alkalinity would be overestimated. Uncertainty due to organic alkalinity is not considered here because accounting for it requires not only knowledge of the concentration, but also of the pK of the organic matter (Sharp and Byrne, 2020). If organic alkalinity is found to be significant in CRMs, the results may need to be revisited.

7. Internal consistency comparisons

The difference between the measured and calculated pH ($\Delta pH = pH_{meas} - pH_{calc}$) is a measure of the internal consistency, or agreement between the model and the measurements. A positive (or negative) value indicates the calculation under- (or over-) estimated the measured value. A fully internally consistent system has a ΔpH of 0 ± the precision of the measurements. For the marine CO_2 system, the pH has a higher precision than the uncertainty in the calculation that is propagated from the constants. The Orr et al. (2018) add-on package was used for error propagation in CO2sys where appropriate. There is also a significant uncertainty in the accuracy of pH (Dickson et al., 2016). The disparity between the measurement and calculated uncertainty, accuracy of pH, and the lack of a certified pH standard means that the smaller the ΔpH, the more internally consistent the system is, but that does not mean it is the most accurate. There are also inaccuracies in DIC and TA that contribute to uncertainties in the marine carbon system although their contribution to the overall uncertainty is much smaller than that of pH.

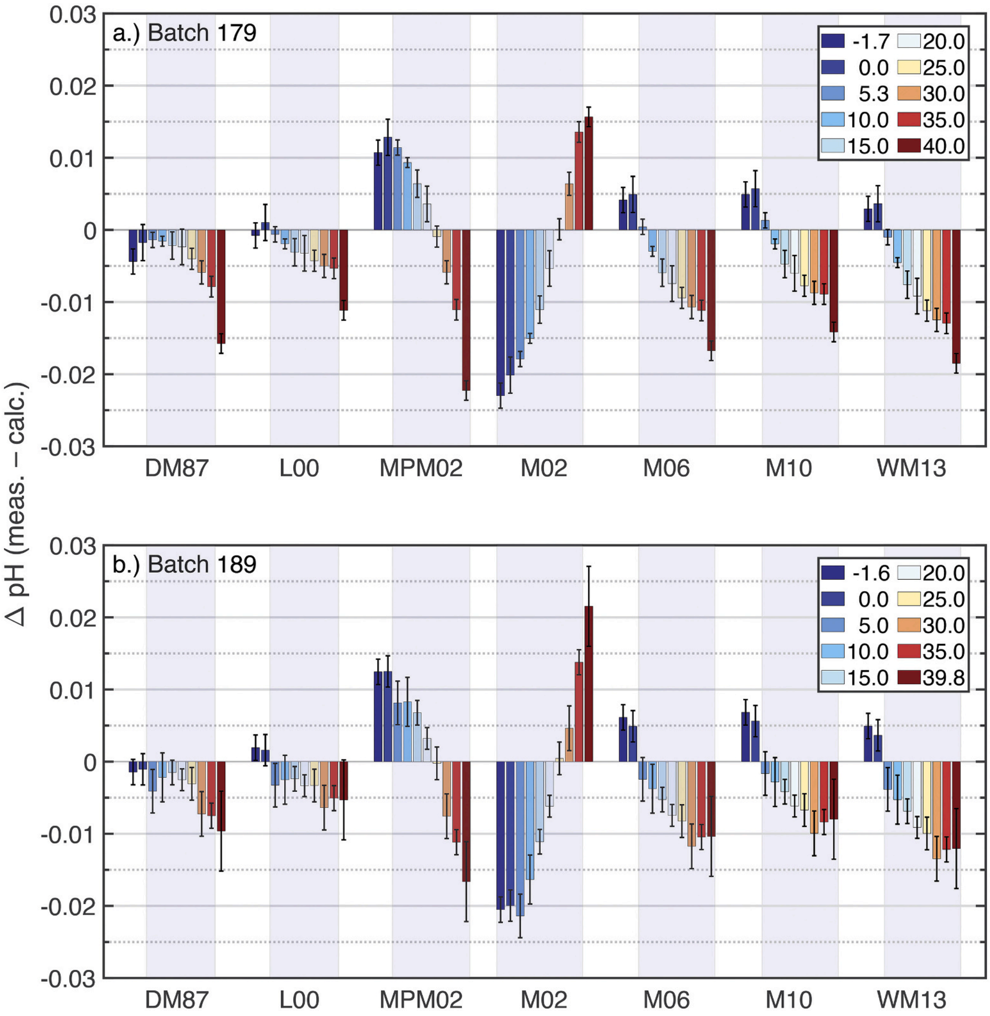

Fig. 1. Internal consistency ($\Delta pH = pH_{meas.} - pH_{calc}$) for a.) batch 179 and b.) batch 189 using the $K_{HSO_4}{}^*$ of D90, $K_F{}^*$ of PF87, and total boron of L10. See Table 2 for list of abbreviations. Colors represent measurement temperature, and error bars are the standard error of the measurements. Light gray shading indicates temperature range over which the carbonic acid dissociation constants were determined.

8. Results and discussion

The results, comparing the ΔpH of the different constants at each temperature (Figs. 1**–2, and Supplemental Figs. S1 – S10**) for CRM batches 179 and 189 (Table 1), show interesting patterns. P18 had very poor internal consistency (generally >0.05) over their valid temperature range (< 25 °C), and given that P18 was intended for sea-ice derived brines, and the poor internal consistency, they are not shown in the figures or discussed further. With a few exceptions, the calculated pH values overestimate the measured value. With the exception of M02, the constants are generally more internally consistent at lower temperatures (<20 °C). The reason for the different trend in M02 can only be speculated on but may have to do with the way in which the temperature dependence was determined (see History of Carbonic Acid dissociation Constants). Surprisingly, the most internally consistent results are not found at 25 °C, again with the exception of M02 and MPM02. Across all temperatures, DM87 and L00 tended to be the most internally consistent. Calculations using $[B]_T$ of L10 are more internally consistent than U74. There is good general agreement between the two batches of CRMs. Before looking further into the differences between the different carbonic acid dissociation constants, the non-CO_2 options will be evaluated.

9. Choice of Total boron concentration

Recently, L10 found the total boron concentration in seawater to be ~4% larger than previously thought. This small difference impacts the calculation of carbonate alkalinity from TA. Calculations using the value of U74 will overestimate carbonate alkalinity relative to calculations using L10 and therefore overestimate pH. Yet, there is some debate over which to use. Orr et al. (2015) recommended U74 because it was the value used in determining all sets of constants evaluated here and using L10 for calculations could add additional uncertainty. The maximum error that could be added to the pKs themselves by using U74 for their determination is ~0.001, which is below the uncertainty of the measurements (~ 0.015, Orr et al. (2018)), but the methods used to determine the constants likely reduce the uncertainty below 0.001. For example, whereas borate alkalinity is included in the fitting procedure for K_1* (Mehrbach et al., 1973), within the pH range (~5–6) over which the data are fitted the borate alkalinity (< 2 μmol·kg^{-1}) is negligible because most of the borate has been converted to boric acid. The difference in borate alkalinity between the two $[B]_T$ in that pH range is <0.15 μmol·kg^{-1} (**Supplemental Fig. S11**). For K_2* measurements using the equilibrium pH method of Mehrbach et al. (1973), borate alkalinity is not part of the calculation and does not contribute to the uncertainty. Nevertheless, studies that fit titration data to determine K_2* (*e.g.* M06), or that back calculate the constants (*e.g.* M02) likely have a small added uncertainty from using U74.

If the $[B]_T$ used to determine the constants is an important source of error in carbon system calculations one would expect M02 to have better internal consistency when U74 is used, but the opposite is true (Figs. 1

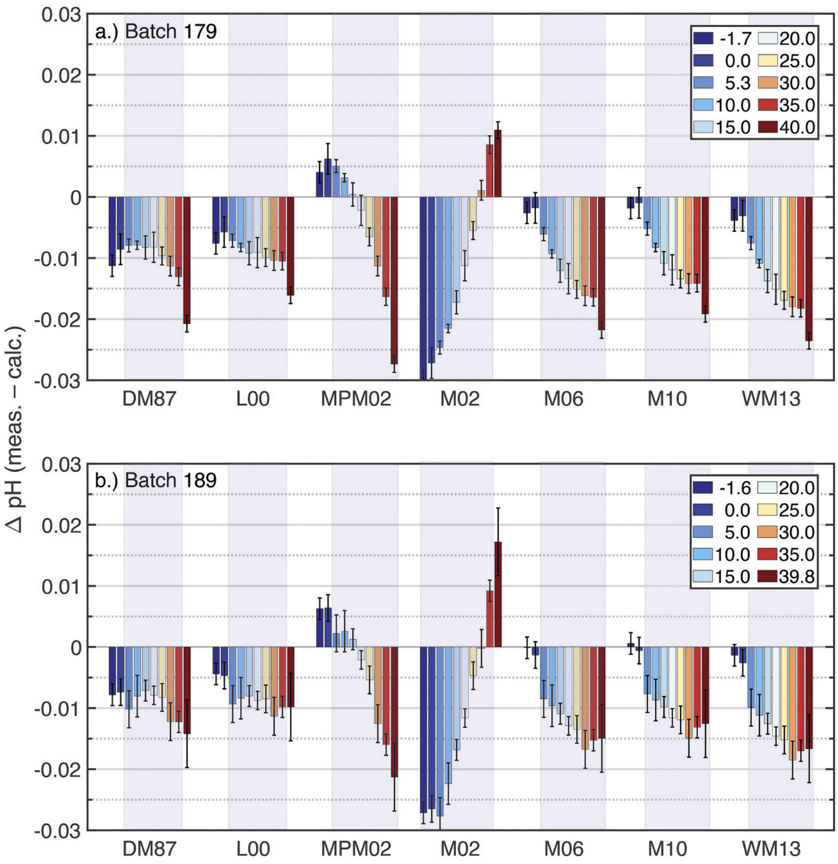

Fig. 2. Internal consistency ($\Delta pH = pH_{meas.} - pH_{calc}$) for a.) Batch 179 and b.) Batch 189 using the $K_{HSO_4^-}$* of D90, K_F* of PF87, and total boron of U74. See Table 2 for list of abbreviations. Colors represent measurement temperature, and error bars are the standard error of the measurements. Light gray shading indicates temperature range over which the carbonic acid dissociation constants were determined.

and 2). In fact, M02 has the best internal consistency of all options at 25 °C. These results further support the idea that $[B]_T$ is a small source of error in the carbonic acid dissociation constants themselves but is a large source of error for calculating the carbon system parameters.

The choice of total boron concentration makes an enormous difference in the internal consistency. For all choices of carbonic acid dissociation constants, using the total boron concentration of L10 (Fig. 1) is more internally consistent than using U74 (Fig. 2), in agreement with the internal consistency check carried out in L10. The use of U74 overestimates measured pH significantly more so than L10 for both CRM batches. At all temperatures and for all constants, the pH using U74 is ~0.005–0.007 pH units higher. Using the default 2% uncertainty of Orr et al. (2018), the uncertainty from $[B]_T$ alone is ~0.0015–0.0050, if 4% is used (the difference between U74 and L10) the uncertainty is doubled, but this estimated uncertainty still underestimates the differences at low temperatures. It is reasonable to assume that L10 is more accurate because they used ~15 times more samples across a broader geographic region with an improved method, and the value has been confirmed by at least one follow up study (Olafsson et al., 2020). Thus, the actual uncertainty in the boron/salinity relationship would be ~0.3%, which translates to <0.0005 pH units using Orr et al. (2018). Unless it is shown that L10 is less accurate than U74, the use of U74 for CO_2 system calculations under near-surface open-ocean conditions should be avoided. If U74 continues to be used, the $[B]_T$ uncertainty used in Orr et al. (2018) should be increased to at least 4%.

10. Choice of HSO_4^- dissociation constant

Although only the bisulfate dissociation constant of D90 is in common use, two other formulations exist (K77 and WM13) and deserve evaluation. Since D90 tends to be the preferred choice, the other two options are compared relative to it. The results were found to be nearly identical within the measurement precision of pH. When comparing D90 (Figs. 1–2 **and Supplemental figs. S1–S2**) to K77 (**Supplemental figs. S3–S6**), the largest difference was 0.00036. Despite K77 being known to be less reliable (Millero, 1995), its contribution to uncertainty is small. Nevertheless, this relatively small error should not encourage use of K77. When comparing D90 to WM13 (**Supplemental Figs. S7–S10**), the maximum difference was 0.00015. Good agreement is expected for waters of salinities near 35 across all temperatures. WM13 found the biggest differences between their value and D90 for waters having both high salinities (> 35) and low temperatures (< 25 °C). The two values should be evaluated under such conditions but, based on the results presented in this study, the choice of K_{HSO4^-}* contributes little uncertainty to CO_2 system calculations at near-surface, open-ocean conditions. D90 will likely remain the preferred value unless WM13 is shown to be more accurate or internally consistent at other salinities or entirely new values are determined. Regardless of the value chosen, it should always be clearly stated.

11. Choice of HF dissociation constant

There are two options for K_F*, DR79 (**Supplemental Figs. S1, S2, S5, S6, S9, S10**) and PF87 (Figs. 1, 2 **and Supplemental Figs. S3, S4, S7, S8**). DR79 is used more often because the Matlab version 1.1 of CO2sys (van Heuven et al., 2011a) does not include the PF87 option, although it has been added in a recently released version (Sharp et al., 2020). DR79 did not actually determine K_F* but combined two very limited studies at infinite dilution (Broene et al., 1947) and salinities of 26.7 and 34.6 at 25 °C (Culberson et al., 1970), with ΔH data (Hepler

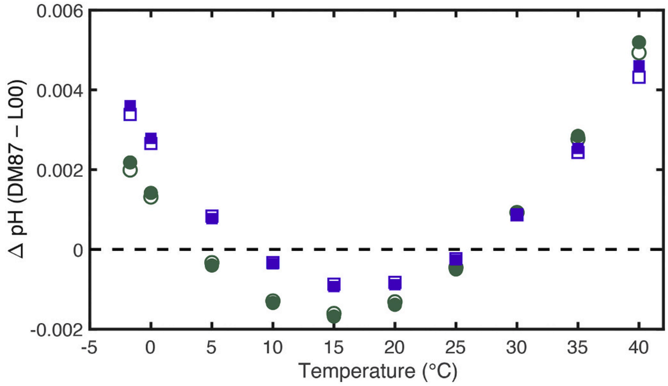

Fig. 3. The difference between calculations using the carbonic acid dissociation constants of DM87 and L00 (ΔpH = DM87 – L00). Green circles used the K_F* of DR79 and blue squares used the value of PF87. All calculations used the $K_{HSO_4^-}$* of D90 and $[B]_T$ of L10. Closed symbols are from CRM batch 179 and open symbols are from batch 189. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

et al., 1953) used to expand the temperature range. The valid temperature range is not stated. PF87 determined the constant over salinities of 10–40 and temperatures of 9–33 °C. Internal consistency differences between the two options are generally small, with differences decreasing with increasing temperature. Differences in pH ranged from 0.00002–0.0011 (excluding L00). The differences for L00 were much smaller because L00 was determined on the total scale, so knowledge of K_F* is not required when the total scale is used. Since all calculations in CO2sys performed here are reported on the total scale, internal conversions with K_F* cancel out for L00. DM87 and L00 were determined on different pH scales, making K_F* a source of discrepancy between them. The difference between the choice of K_F* for DM87 and L00 (Fig. 3) is <0.0014. Note that DM87 used DR79 to convert Mehrbach et al. (1973) to the seawater scale. Orr et al. (2018) do not consider uncertainty in K_F*, but these results would indicate that comparing studies that used different values for K_F* have a small but significant and unaccounted for bias. Given that PF87 were determined using more modern techniques, and contain a significantly larger number of direct measurements, it would be reasonable to consider them more accurate, but calculations with DR79 done here were slightly more internally consistent (though the difference between PF87 and DR79 is not statistically significant). Such conflicting results indicate that more work should be done to evaluate K_F*, as the selection is more critical than the choice for $K_{HSO_4^-}$*, on the order of the pH precision itself, particularly at low temperatures.

12. Choice of carbonic acid dissociation constants

The choice of carbonic acid dissociation constants has the most significant impact on the internal consistency of pH, with |ΔpH| values ranging from 0.00009–0.00230. Having determined the preferred $K_{HSO_4^-}$* and $[B]_T$ parameterizations, and noted the K_F* values are statistically indistinguishable, I only discuss the calculations that use $K_{HSO_4^-}$* of D90, K_F* of PF87, and $[B]_T$ of L10 (Fig. 1). All other possible combinations can be found in **supplemental figs. S1-S10**, but the conclusions remain the same. In the purest sense of internal consistency, M02 at 25 °C has the smallest ΔpH, but given the large deviation of these constants at other temperatures, their use appears limited. The poor internal consistency at other temperatures is likely due to the limited data available to M02 at other temperatures. MPM02 also has excellent internal consistency at 25 °C, but it increasingly deviates at higher or lower temperatures. The reason is currently uncertain, but could be because they only measured a broad range of salinities at 25 °C and used Mehrbach et al. (1973) to fill in gaps at other temperatures. Over the entire temperature range considered here, DM87 and L00 are the most internally consistent, as has been found in other recent work (Chen et al., 2015; Woosley et al., 2017). As expected, there is no statistical difference between the two over the temperature range that these constants were determined (2–35 °C). The largest differences (Fig. 3) are found at low and high temperatures and may result from differences in their fitting procedures and K_F*. There is better agreement between them when the K_F* of DR78 is used. The difference between the two batches of CRMs was small (*e.g.* Fig. 3) and not statistically significant, except for a few constants at 40 °C. It is important to note that some of these calculations extend beyond the temperature ranges over which the constants were determined. Extending the constants beyond their valid temperature or salinity range is generally ill advised, but for an evaluation study such as this, assessing constants beyond their valid ranges can be useful for determining what future research is most required. The good internal consistency at subzero temperatures for DM87 and L00 indicate small extrapolations do not add significant uncertainty or errors are canceled out by uncertainties in the measured pH. The good internal consistency below 5 °C is encouraging as the mCp indicator was not calibrated for these near freezing temperatures (Liu et al., 2011).

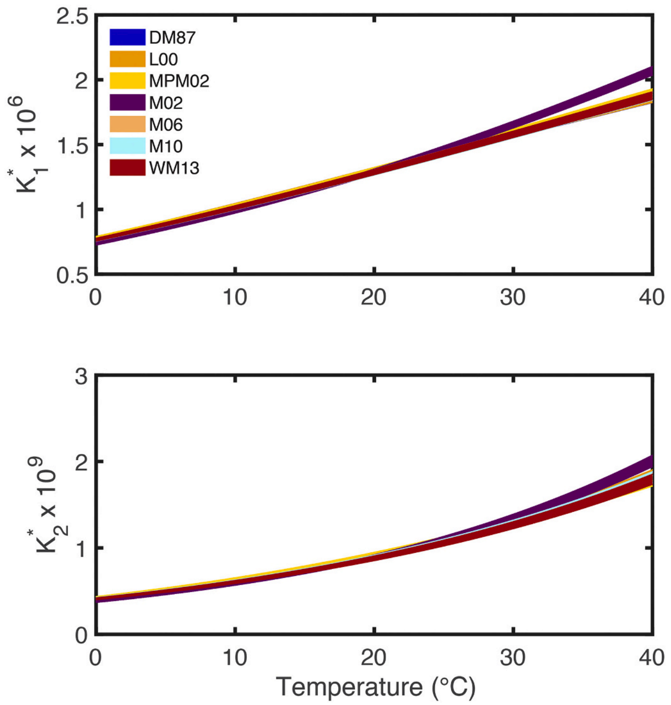

Fig. 4. K_1*and K_2* including the default uncertainty of Orr et al. (2018) *versus* temperature with S = 34. All the constants agree with each other except for M02 at high temperatures. Not all constants were determined over the full temperature range shown, but the values were still calculated to illustrate the agreement between the different constants. Note the lower uncertainty at lower temperatures resulting from the conversion of pK to K. See Table 2 for list of abbreviations and range of temperatures over which each set of constants were determined.

Given the improvements in measurement techniques, the comparatively poor internal consistency for MPM02, M06, M10, and WM13 is intriguing. It is first important to point out that internal consistency does not necessarily translate into accuracy. Given the uncertainty in the accuracy of pH (~0.02 (McLaughlin et al., 2015)), any one of these sets of constants could be the most accurate. The accuracy of pH measurements is largely dependent on the values assigned to the TRIS buffers used for calibration. As demonstrated by Millero (1995), errors in K_1* alone contribute little to errors in pH calculated from TA and DIC. This was confirmed by Orr et al. (2018), where using their default uncertainties, uncertainty in K_1* contributes <0.001 to the uncertainty in calculated pH, whereas uncertainty in K_2* contributes ~0.0025–0.0073

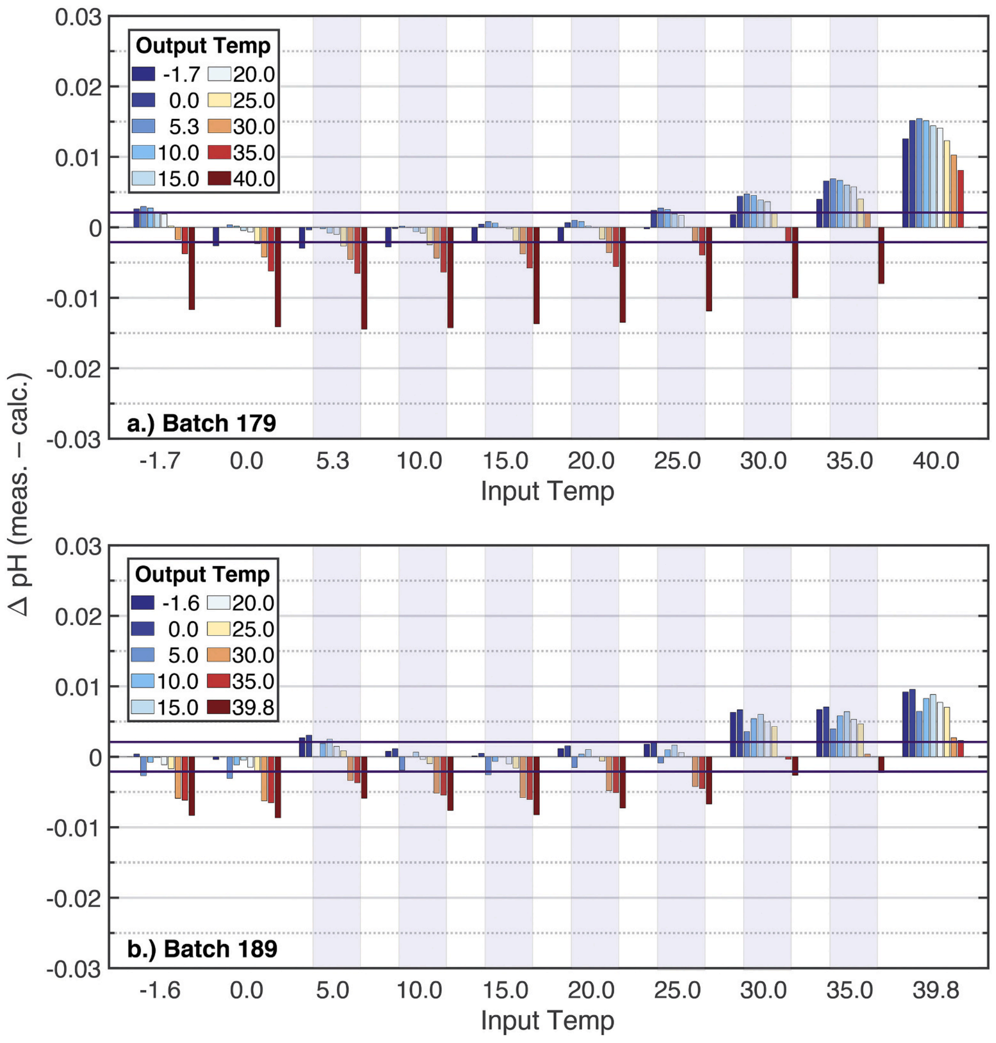

Fig. 5. Conversion of pH from measured temperature to other temperatures using the measured pH at each temperature (input temp), the certified TA, the K_{HSO4^-}* of D90, K_F* of PF87, total boron concentration of L00 and carbonate constants of DM87. See Table 2 for list of abbreviations. Colors represent the output temperature. Purple line represents the mean standard error of the measurements (0.0021) and indicates the bounds at which a calculated value is equivalent to the measured value. Light gray shading indicates temperature range over which the carbonic acid dissociation constants were determined. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

depending on the temperature. Because the calculation also depends on $K_1^* \times K_2^*$ (Park, 1969), the combined uncertainty from the constants to calculated pH is ~0.0045–0.0129. The uncertainty in calculated pH as a result of uncertainty in the carbonic acid dissociation constants is greater than the measurement precision.

For K_1^* and K_2^*, all constants agree with each other at the salinity of the CRMs within the estimated uncertainty of the constants (Fig. 4), except for M02 which are significantly higher than the others at high temperatures. As a result, biases in the measurements or calculations that lead to internally consistent, yet inaccurate results are impossible to detect. This is to say that even though the carbonic acid dissociation constants produce calculated pH values that deviate significantly beyond the measurement precision, the uncertainty in the constants themselves is too large to determine which one is more accurate. While an unsatisfying result, internal consistency, despite being imperfect, is currently our best method of determining which constants to use. Due to the limitations inherent in internal consistency evaluations, further improvements to our understanding of the thermodynamics of the marine carbon system are required to definitively identify any of the constants evaluated here as being inaccurate or less accurate. Based on the results presented in this study, the carbonic acid dissociation constants of DM87 or L00 are the most internally consistent over the temperature range − 1.7–40 °C and salinity of the CRM (33.4–33.8). This result is likely applicable to the near-surface open-ocean ($T = -1.7$–40, S = 31–36, and fCO$_2$ < 500 μatm) conditions, and thus continue to be the preferred values for now. Given that future research could determine that one of the other constants, or a newly determined set, is a better choice, it is important for all marine carbon system studies to clearly document all constants used and make the necessary data available for calculations to be redone in the future. For pH, this includes raw absorbance values or absorbance ratios, temperatures, and details of indicator purity and preparation.

13. *In-situ* pH conversions

Because of the uncertainties in the constants, it would seem that pH should, ideally, always be measured directly rather than calculated. Compared to the other three measurable parameters, the equipment required is relatively cheap and easy to use, even for a non-specialist, making it a much easier parameter to measure. Aside from the uncertain accuracy, the problem inherent with discrete pH measurements is that due to the strong dependence of pH on temperature, temperature must be stable, and known to an accuracy of ~0.1 °C during the measurement. Thus, for practical reasons, it is best to measure pH at a set temperature (typically 25 °C, but sometimes 15 or 20 °C) and then convert the value to *in-situ* temperature. There are empirical equations that can be used for this purpose (Lui and Chen, 2017; Millero, 1995), but their range of applicability is small due to limitations in how they were determined and can lead to internally inconsistent results over large temperature adjustments (Woosley et al., 2017). A more common method is to use another measured parameter and CO2sys or similar program.

The way CO2sys calculates pH at *in-situ* temperature is to first compute TA and DIC, regardless of the input parameters. The reason being that TA and DIC are temperature independent, and therefore the only two that can link the temperature dependent parameters of pH and fCO_2. For example, if the input parameters were pH and TA, the program would first calculate DIC, and then use the measured TA and calculated DIC to derive pH at the *in-situ* temperature. The measured pH at each temperature and certified TA were used to calculate the pH at the other temperatures. Use of DIC instead of TA does not yield statistically different results (not shown). For calculations using the constants of DM87 (Fig. 5), the results are generally internally consistent for temperatures below 25 °C, both as input and outputs. In general, for all constants, the smaller the temperature adjustment, the more internally consistent the *in-situ* pH. It would appear that 25 °C is not the ideal measurement temperature, as temperature adjustments beyond ~10 °C should be avoided. Improved internal consistency is found at lower pH measurement temperatures. For measurement temperatures of 15 or 20 °C, the *in-situ* pH is within the measurement uncertainty for nearly all temperatures between 0 and 25 °C. Given that the uncertainties in the constants decrease with temperature (Fig. 4**,** Orr et al. (2018)), it is not surprising that lower temperatures produce more consistent results. Poor internal consistency for field measurements made at 25 °C and converted to low *in-situ* temperatures is likely a result of errors at lower salinities (Woosley et al., 2017). The average surface ocean temperature is ~17 °C and the average of all ocean water is ~4 °C. Perhaps best practices should be modified to measure pH at 20 °C. Whereas 15 °C might be better still, measuring at 15 °C can be difficult in high humidity environments due to condensation. For study inter-comparability a consistent measurement temperature is desirable and should be agreed upon within the community.

14. Conclusions

There are currently at least 84 possible combinations of constants to use in calculating CO_2 system parameters (excluding options known to be inaccurate). A systematic evaluation of all these options has never been done. Based on the evaluation carried out on certified reference materials, over the full oceanic range of temperatures, several recommendations can be made to improve the consistency of calculations between different studies. Although this study was limited to one salinity and fCO_2, the results are likely applicable to most of the near-surface open-ocean ($T = -1.7$–40 °C, $S = 31$–36, $fCO_2 < \sim500$ μatm) as pH and the carbonic acid dissociation constants are a weak function of salinity (Millero, 1995) and the validation experiments carried out by L00 indicate good agreement for $fCO_2 < \sim500$ μatm. The pressure dependence of the constants was not evaluated.

For the non-carbon related constants under near-surface open-ocean conditions, the $[B]_T$ of L10 should be used whenever possible. The $K_{HSO4^-}{}^*$ of D90 and WM13 can be used almost interchangeably with minimal added uncertainty. Nevertheless, differences at high salinities and low temperatures are possible and still need to be evaluated. There are small, but non-negligible, differences in the $K_F{}^*$ of DR79 and PF87. The value of PF87 covers a wider range of salinities and would be expected to be more accurate, but the limited salinity range covered in this study prevents a more systematic evaluation.

For the carbonic acid dissociation constants, the DM87 and L00 values are statistically interchangeable below 35 °C, and are the most internally consistent over the temperature range of –1.7–35 °C, although other constants are more internally consistent at 25 °C. Despite the better internal consistency for DM87 and L00, all sets of constants evaluated in this study were within the uncertainty in the accuracy of pH. Until the accuracy (or our understanding of the accuracy) of pH can be improved, or the uncertainty in the constants reduced, DM87 and L00 are preferred for near surface conditions ($S \sim 31$–36 and $fCO_2 < \sim500$ μatm). Organic alkalinity is not considered here but may also contribute to uncertainty in the carbon system. Evaluation at other salinities and fCO_2 is needed and currently underway. Due to the practicality of measuring pH at a set temperature and its conversion to *in-situ* temperature, and results presented here, it may be better to measure pH at 15 or 20 °C rather than 25 °C, but consensus within the community is needed.

Declaration of Competing Interest

The author declares no conflicts of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marchem.2020.103914.

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