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Interpreting measurements of total alkalinity in marine and estuarine waters in the presence of proton-binding organic matter

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ABSTRACT

Total alkalinity (A_T) is one of four measurable cornerstone parameters for characterizing the marine carbonate system, yet its measurement by standard titration methods is subject to systematic misinterpretations in the presence of uncharacterized dissolved organic molecules in ocean and estuarine waters. A consequence of these misinterpretations may be the lack of thermodynamic consistency that is routinely observed among measured and calculated parameters of the carbonate system. In this work, a numerical model is used to illustrate (a) how proton-binding dissolved organic molecules influence the reported results of total alkalinity titrations in marine and estuarine settings and (b) how errors in interpretations of reported A_T values can then propagate through carbonate system calculations, thus distorting biogeochemical interpretations of calculated parameters. We examine five distinct approaches for alkalinity measurement by titration. Ideally, the difference between the measured (reported) A_T and the conventional (thermodynamic) definition of inorganic alkalinity (A_{inorg}) would be zero. However, in the presence of titratable organic matter, our model results show consistent non-zero differences that vary with the chemical properties of the organic matter. For all five titration approaches, the differences between reported A_T and A_{inorg} are greatest when the negative logarithm of the organic acid dissociation constant (pK_{org}) is between approximately 5 and 7. The differences between reported A_T and A_{inorg} also display previously undescribed variation among measurement approaches, most significantly when pK_{org} is between approximately 3 and 6 (typical of carboxylic acid groups). The measurement approaches that are most effective at limiting the unfavorable influence of these relatively low-pK organic acids on A_T are closed-cell titrations and single-step titrations that are terminated at a relatively high pH. For calculated carbonate system parameters relevant to in situ conditions (e.g., pH, pCO_2, calcium carbonate mineral saturation states), errors resulting from the presence of proton-binding organics are largest when calculations are based on the input pair of directly measured dissolved inorganic carbon (C_T) and directly measured A_T, and can vary in magnitude depending on the titration approach that is used to obtain A_T. The modeling results presented in this work emphasize the importance of (a) determining A_T in a manner that accounts for the ubiquity of organic alkalinity in marine and estuarine waters and (b) working toward a clearer understanding of the phenomena underlying the routine lack of internal consistency between measured versus calculated carbonate system parameters. Total alkalinity measurements should begin to incorporate either implicit or explicit evaluations of the titration characteristics of the natural organic carbon present in each sample. To that end, we recommend use of secondary titrations to directly measure organic alkalinity (sample-by-sample), characterization of relationships between total dissolved organic carbon concentrations and organic alkalinity (on local to regional scales), and/or exploration of novel curve-fitting procedures to infer the behavior of organic functional groups from titration data.

1. Introduction

Total alkalinity (A_T) is one of the most important measured parameters pertaining to the chemistry of natural waters. When defined in terms of moles or charge equivalents per kilogram of solution, A_T is not influenced by changes in temperature or pressure, nor is it altered by the exchange of carbon dioxide (CO_2) gas with the atmosphere. As a result, A_T is a carbonate system parameter that mixes conservatively and is

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relatively well-correlated with salinity in marine waters (Broecker and Peng, 1982; Millero et al., 1998). A_T does exhibit minor variations associated with biogeochemical processes such as primary production, organic matter respiration, and the formation or dissolution of calcium carbonate (Brewer et al., 1975; Brewer and Goldman, 1976; Goldman and Brewer, 1980; Sarmiento and Gruber, 2006; Zeebe and Wolf-Gladrow, 2001).

Due to its stable and conservative nature, A_T is useful in estimating other (unmeasured) carbonate system parameters and in characterizing complex biogeochemical processes. In natural waters, measured A_T can be paired with another measured carbonate system parameter — total dissolved inorganic carbon (C_T), pH, or the partial pressure of CO_2 (pCO_2) — to estimate unmeasured parameters. For example, A_T has been used with C_T (Bates, 2007) and pH (Williams et al., 2017) to calculate pCO_2 for quantifications of CO_2 exchange across the air–sea interface. Oceanic distributions of A_T can also be used directly to detect changes in biological calcification or the export of calcium carbonate ($CaCO_3$) from the surface ocean (Carter et al., 2016; Ilyina et al., 2009). Study of these processes is important for determining how carbon is transformed and transported between various global reservoirs. This information is especially critical now, as anthropogenic CO_2 is being continuously released to the Earth system in large quantities (Friedlingstein et al., 2019), fueling global warming (IPCC, 2013) and ocean acidification (Caldeira and Wickett, 2003; Feely et al., 2004; Orr et al., 2005).

In natural waters, A_T is defined by Dickson (1981) as the number of moles of protons equivalent to the excess of proton acceptors over proton donors in 1 kg of solution. Proton acceptors are bases formed from weak acids with dissociation constants (K_A) less than or equal to $10^{-4.5}$ at zero ionic strength, 25 °C, and atmospheric pressure; proton donors are acids with dissociation constants greater than $10^{-4.5}$ under those same conditions. These environmental conditions are indicated by the superscript naught on the dissociation constant: K_A^0. The specification of $K_A^0 = 10^{-4.5}$ as the cutoff between proton acceptors and donors designates the set of chemical species that represent the "zero level of protons" (*ZLP*) (Dickson, 1981; Wolf-Gladrow et al., 2007).

By treating the main inorganic chemical constituents found in natural waters according to Dickson's (1981) definition, an expression is obtained that represents the inorganic alkalinity (A_{inorg}) of natural waters:

$$A_{inorg} = \left[HCO_3^-\right] + 2\left[CO_3^{2-}\right] + \left[B(OH)_4^-\right] + \left[OH^-\right] + \left[HPO_4^{2-}\right] + 2\left[PO_4^{3-}\right] + \left[SiO(OH)_3^-\right] + \left[HS^-\right] + 2\left[S^{2-}\right] + \left[NH_3^0\right] - \left[H^+\right]_f - \left[HSO_4^-\right] - \left[HF^0\right] - \left[H_3PO_4^0\right] \quad (1)$$

Each term in Eq. (1) is a total ionic concentration that encompasses both free and complexed ions, except for $[H^+]_f$, which represents only the free proton concentration. The expression for A_{inorg} given by Eq. (1) is especially robust for practical purposes due to the specification of the *ZLP* at $K_A^0 = 10^{-4.5}$, which separates proton donors and acceptors by more than three orders of magnitude in terms of their K_A^0 values (Wolf-Gladrow et al., 2007). When defined using this *ZLP*, Eq. (1) can be expressed simply as an excess of inorganic proton acceptors ($A_{A,inorg}$) over inorganic proton donors ($A_{D,inorg}$):

$$A_{inorg} = A_{A,inorg} - A_{D,inorg} \quad (2)$$

In natural waters with acid–base systems that are exclusively controlled by well-characterized inorganic species, the mathematical definition of A_{inorg} given in Eq. (1) exactly describes A_T (i.e., $A_T = A_{inorg}$). In this scenario, proper techniques for measuring alkalinity by titration are unambiguous and robust (e.g., Dickson, 1981; Hansson and Jagner, 1973; Millero et al., 1993). In most natural environments, however, dissolved organic molecules with poorly defined proton-exchange properties are present at some concentration, thus complicating interpretations of alkalinity titrations (Bradshaw and Brewer, 1988; Brewer et al., 1986; Cantrell et al., 1990).

Alkalinity is typically determined by titrating a sample with a strong acid of known concentration. Titration proceeds from the sample's initial pH (e.g., approximately 8.1 for surface seawater) to a pH lower than the sample's second equivalence point (e.g., approximately 3.0). Thus, not all organics present in a sample are significant in the context of an alkalinity titration; only those organics with pK_A values within or near to the pH range of the titration will affect the alkalinity determination. In this paper, "titratable organics" refers to those organic chemical species that exchange protons in a quantitatively significant way during an alkalinity titration. Significant concentrations of titratable organics can make the concept of A_T quantitatively ambiguous, because chemical species that are not included in the rigorously defined A_{inorg} of Eq. (1) can contribute to measured A_T. Quantitative ambiguity in A_T can affect not only qualitative interpretations of alkalinity measurements but also calculations of carbonate system parameters.

To account explicitly for the influence of titratable organics, A_T could ideally be written as the sum of inorganic alkalinity (A_{inorg}) plus organic alkalinity (A_{org}). This sum represents the excess of both inorganic proton acceptors (positive terms in Eq. (1)) and organic proton acceptors ($A_{A,org}$) over both inorganic proton donors (negative terms in Eq. (1)) and organic proton donors ($A_{D,org}$):

$$A_T = A_{inorg} + A_{org} = (A_{A,inorg} - A_{D,inorg}) + (A_{A,org} - A_{D,org}) \quad (3)$$

Direct measurements to quantitatively characterize the proton-exchange properties of all organic molecules in a sample would be highly desirable and would allow for the separation of organic proton acceptors and donors using a strict *ZLP* cutoff of $K_A^0 = 10^{-4.5}$ (Dickson, 1981). However, current analytical constraints make this kind of precise characterization impractical (Byrne, 2014; Kuliński et al., 2014).

Assemblages of organic molecules commonly found in natural waters are heterogenous in terms of their chemical composition (Carlson and Hansell, 2015; Repeta, 2015) and their proton-exchange properties (Altmann and Buffle, 1988; Perdue et al., 1984; Perdue and Lytle, 1983; Tipping and Hurley, 1992). An additional complication is that some of the more common functional groups of dissolved organic molecules are carboxyl groups, which exhibit acid dissociation behavior very near to the *ZLP* (Oliver et al., 1983; Ritchie and Perdue, 2003). Therefore, even if the proton-exchange properties of these organic molecules were to be estimated, their role as proton acceptors or donors in the context of an A_T titration would remain ambiguous. Consequently, due to the impracticality of quantifying the A_{org} term in Eq. (3), A_T in systems with titratable organics cannot be rigorously defined.

Measurements of A_T rely on (a) operationally well-defined acidimetric titrations and (b) careful analysis of titration data. Over time, a number of approaches for this two-step process have been developed (see section 2.2). Each approach produces a distinct measured titration alkalinity ($A_{T(meas)}$), which is in actuality an A_T "best estimate" that is linked implicitly to the measurement approach (i.e., the titration technique in combination with the method of data analysis). With this important subtlety in mind, Eq. (3) can be recast in the framework of $A_{T(meas)}$:

$$A_{T(meas)} = A_{inorg} + A_{org(meas)} \quad (4)$$

Here, $A_{T(meas)}$ is the quantity reported as the outcome of an alkalinity titration, A_{inorg} is as defined in Eq. (1), and $A_{org(meas)}$ represents the concentration of all protons that bind to organic molecules during the titration. This $A_{org(meas)}$ term is not defined explicitly as an excess of proton acceptors over donors because, due to the structural heterogeneity and behavioral ambiguity of naturally occurring organic molecules, standard models for acid–base behavior in natural waters do not contain explicit terms for organics. Any organic species that binds protons during an alkalinity titration, no matter the K_A^0 value of the species, will contribute positively to $A_{org(meas)}$ and therefore to $A_{T(meas)}$.

Typically, $A_{org(meas)}$ is assumed to be negligible. In other words, A_T

$_{(\mathrm{meas})}$ (or A_T estimated from regression equations fitted to a dataset of $A_{T(\mathrm{meas})}$ values (e.g., Carter et al., 2018)) is implicitly equated with A_{inorg}. The quantity $A_{T(\mathrm{meas})}$ is often then used as if it were A_{inorg} — e.g., to perform calculations of C_T, pH, pCO$_2$, and other carbonate system parameters. The result can be a set of calculated parameters that are poorly defined.

Significant differences between $A_{T(\mathrm{meas})}$ and A_{inorg} have been demonstrated in certain natural environments (rivers, estuaries, and coastal oceans) and in phytoplankton cultures — all systems reasonably expected to be influenced by titratable organics (Cai et al., 1998; Hernández-Ayón et al., 2007; Hu et al., 2015; Kim and Lee, 2009; Tishchenko et al., 2006). These differences can be practically represented as ΔA_T ($A_{T(\mathrm{meas})} - A_{\mathrm{inorg}}$), and have often been attributed to non-negligible $A_{\mathrm{org(meas)}}$ (see Eq. (4)). ΔA_T values appear to increase in magnitude with increasing concentrations of dissolved organics (Kim and Lee, 2009; Kuliński et al., 2014) and can cause significant errors in calculated carbonate system parameters (Abril et al., 2015; Hoppe et al., 2012; Ko et al., 2016; Koeve and Oschlies, 2012; Tishchenko et al., 2006).

Less obvious, but perhaps more troubling than the expected issues in high-organic environments, is the fact that internal consistency analyses in environments thought to be negligibly influenced by titratable organics (e.g., oligotrophic open-ocean systems) have also proven to be problematic. Studies of over-determined carbonate system datasets have consistently failed to resolve differences between certain measured and calculated carbonate system parameters. A notable example is the repeatedly observed difference between pH measured spectrophotometrically versus pH calculated from paired measurements of $A_{T(\mathrm{meas})}$ and C_T (Carter et al., 2013, 2018; McElligott et al., 1998; Williams et al., 2017). This and other internal consistency issues have led some investigators to propose that, even in the open ocean, $A_{\mathrm{org(meas)}}$ may represent a non-negligible component of $A_{T(\mathrm{meas})}$ (Fong and Dickson, 2019; Patsavas et al., 2015; Salt et al., 2016; Yang et al., 2015).

The aim of the work reported in this paper is to illustrate, through numerical modeling, the quantitative consequences that titratable organics have on $A_{T(\mathrm{meas})}$ determined by titration. The consequences are represented as ΔA_T, or the difference between $A_{T(\mathrm{meas})}$ and the well-defined A_{inorg}. This work examines (1) the implications of choosing one titration technique (and associated data analysis method) over another (2) the importance of the protonation behavior (i.e., p*K*), of the organic matter itself, and (3) the propagation of errors in interpretations of $A_{T(\mathrm{meas})}$ to calculations of other carbonate system parameters. The overarching goal is to help inform the choices of investigators working on carbonate system dynamics in potentially high-organic environments and to stimulate discussions within the marine chemistry community regarding how to manage uncertainties associated with the influence of organic matter on alkalinity titrations.

2. Background

2.1. Quantitative description of A_T

Dickson's (1981) definition of total alkalinity (see section 1) is based on a "proton condition" rather than a purely empirical titration endpoint (see also Johansson and Wedborg, 1982). A proton condition is defined by the group of chemical species that dominate at the *ZLP*. To quantitatively assess any natural-water alkalinity titration according to a proton condition, an accurate model for the acid–base reactions that occur in the sample is critical. As an example, the proton condition relevant to inorganic species in oxygenated seawater (Fig. 1) can be easily surmised from the quantitative information in Table 1 and Dickson's designation of $K_A^0 = 10^{-4.5}$ as the defining value of the *ZLP*:

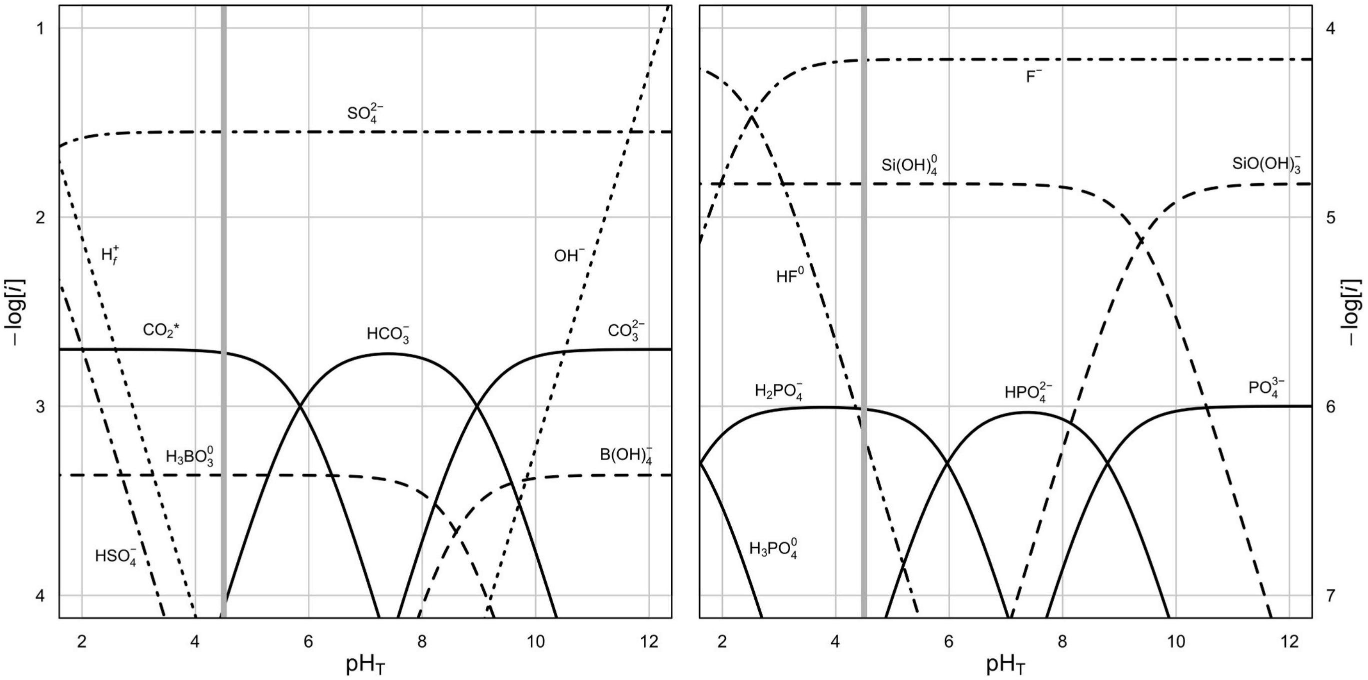

Fig. 1. Bjerrum plots displaying concentrations [*i*] of the major acid–base species in oxygenated seawater with $C_T = 2000$ μmol kg^{-1}, total phosphate (P_T) = 1.0 μmol kg^{-1}, total silica (Si_T) = 15.0 μmol kg^{-1}, salinity (S) = 35, temperature (t) = 25 °C, and pressure (P) = 1 atm. The K_A^0 cutoff of Dickson (1981) that defines the zero level of protons is shown by the thick vertical grey line. The left panel displays species formed from chemical constituents with total concentrations greater than 10^{-4} mol kg^{-1}, whereas the right panel displays species formed from chemical constituents with total concentrations less than 10^{-4} mol kg^{-1}.

$$[\mathrm{H}^+]_f + [\mathrm{HSO}_4^-] + [\mathrm{HF}^0] + [\mathrm{H}_3\mathrm{PO}_4^0] = [\mathrm{HCO}_3^-] + 2[\mathrm{CO}_3^{2-}] + [\mathrm{B(OH)}_4^-] + [\mathrm{OH}^-] + [\mathrm{SiO(OH)}_3^-] + [\mathrm{HPO}_4^{2-}] + 2[\mathrm{PO}_4^{3-}] \tag{5}$$

All symbols included in Eq. (5) and the following discussion are defined in detail in Table A1 in the appendix.

Eq. (5) excludes some terms included in the full definition of A_{inorg} (Eq. (1)) because this discussion focuses on simple, oxygenated seawater. However, additional species formed from inorganic acids (e.g., ammonium and hydrogen sulfide) or organic acids (e.g., carboxyl and phenol groups) could in concept be included as well.

Because A_T represents the excess of proton acceptors over donors, it can be described in the context of this discussion by rearranging Eq. (5) to yield:

$$A_T = [\mathrm{HCO}_3^-] + 2[\mathrm{CO}_3^{2-}] + [\mathrm{B(OH)}_4^-] + [\mathrm{OH}^-] + [\mathrm{SiO(OH)}_3^-] + [\mathrm{HPO}_4^{2-}] + 2[\mathrm{PO}_4^{3-}] - [\mathrm{H}^+]_f - [\mathrm{HSO}_4^-] - [\mathrm{HF}^0] - [\mathrm{H}_3\mathrm{PO}_4^0] \tag{6}$$

Defining A_T in this way (i.e., according to a proton condition) allows for expression of an acidimetric titration of M_0 kilograms of natural water with M_A kilograms of acid of concentration C_A as

$$M_0A_T = M_AC_A + M_T\{[\mathrm{HCO}_3^-] + 2[\mathrm{CO}_3^{2-}] + [\mathrm{B(OH)}_4^-] + [\mathrm{OH}^-] + [\mathrm{SiO(OH)}_3^-] + [\mathrm{HPO}_4^{2-}] + 2[\mathrm{PO}_4^{3-}] - [\mathrm{H}^+]_f - [\mathrm{HSO}_4^-] - [\mathrm{HF}^0] - [\mathrm{H}_3\mathrm{PO}_4^0]\} \tag{7}$$

where M_T is the sum of M_0 and M_A. Using dissociation constant relationships and dilution corrections, Eq. (7) can alternatively be expressed as

$$\begin{aligned} M_0A_T = M_AC_A + M_0 \Bigg\{ & \frac{C_T}{1+\frac{[\mathrm{H}^+]_T}{K_1}+\frac{K_2}{[\mathrm{H}^+]_T}} + \frac{2\cdot C_T}{1+\frac{[\mathrm{H}^+]_T}{K_2}+\frac{[\mathrm{H}^+]_T^2}{K_1K_2}} + \frac{B_T}{1+\frac{[\mathrm{H}^+]_T}{K_B}} + \frac{Si_T}{1+\frac{[\mathrm{H}^+]_T}{K_{Si}}} \\ & + \frac{P_T}{1+\frac{[\mathrm{H}^+]_T}{K_{P2}}+\frac{[\mathrm{H}^+]_T^2}{K_{P1}K_{P2}}+\frac{K_{P3}}{[\mathrm{H}^+]_T}} + \frac{2\cdot P_T}{1+\frac{[\mathrm{H}^+]_T}{K_{P3}}+\frac{[\mathrm{H}^+]_T^2}{K_{P2}K_{P3}}+\frac{[\mathrm{H}^+]_T^3}{K_{P1}K_{P2}K_{P3}}} - \frac{S_T}{1+\frac{K_S}{[\mathrm{H}^+]_f}} \\ & - \frac{F_T}{1+\frac{K_F}{[\mathrm{H}^+]_T}} - \frac{P_T}{1+\frac{K_{P1}}{[\mathrm{H}^+]_T}+\frac{K_{P1}K_{P2}}{[\mathrm{H}^+]_T^2}+\frac{K_{P1}K_{P2}K_{P3}}{[\mathrm{H}^+]_T^3}} \Bigg\} - M_T\left\{[\mathrm{H}^+]_f - \frac{K_W}{[\mathrm{H}^+]_T}\right\} \end{aligned} \tag{8}$$

Dissociation constant relationships (Table A1) are mostly defined in terms of hydrogen ion concentrations on the total scale ($[\mathrm{H}^+]_T$):

$$[\mathrm{H}^+]_T = [\mathrm{H}^+]_f + [\mathrm{HSO}_4^-] = [\mathrm{H}^+]_f + \frac{S_T}{1+\frac{K_S}{[\mathrm{H}^+]_f}} \tag{9}$$

Common terms in Eq. (8) (e.g., phosphate terms with P_T in the numerator) could be combined for mathematical simplicity but here are kept separate to emphasize the individual chemical species described by each term. Eqs. (5)–(8) are the basis for the discussions of alkalinity measurement approaches presented in section 2.2.

2.2. *Measurement approaches for A_T*

As stated in section 1, A_T is generally evaluated by titrating a sample solution with a strong acid of known concentration. A simulated titration curve is shown in Fig. 2. One of two acidimetric titration approaches is typically employed: (1) titration in a stepwise manner, with measurements of electrical potential at each step (a "multi-step titration") or (2) titration to a pre-determined endpoint, followed by CO_2 purging and a measurement of pH (a "single-step titration").

Multi-step titration, the traditional method for measuring A_T in natural waters, is recognized explicitly as the best-practice method for measurements in seawater (Dickson et al., 2007). A multi-step titration is typically monitored by a glass electrode/reference electrode pH cell. Electrical potential is recorded manually or automatically at each titration step. Electrical potential values are related to hydrogen ion concentrations by the Nernst equation:

$$E = E^0 + \left(\frac{RT}{F}\right)\ln[\mathrm{H}^+]_f \tag{10}$$

where E is the electrical potential developed by the pH cell, E^0 is the standard electrode potential, R is the ideal gas constant, T is the absolute temperature in K, and F is the Faraday constant. The Nernst equation can be applied to any pH scale, so long as the electrodes in use are properly calibrated on that scale.

Single-step A_T titration (Breland and Byrne, 1993; Liu et al., 2015; Yao and Byrne, 1998) has become more widely used in recent years due to the precision in total scale pH (pH_T) measurements offered by sulfonephthalein indicators (Byrne and Breland, 1989; Clayton and Byrne, 1993). Single-step titrations are appealing because of their speed (one addition of acid rather than a series of incremental additions) and

Table 1
Inorganic equilibria relevant to the definition of natural-water A_T. Values of pK_A^0 are used to define proton acceptors versus donors, with acceptors having $pK_A^0 \geq 4.5$ and donors having $pK_A^0 < 4.5$ (Dickson, 1981). The values of pK_A and the constituent concentrations ([*i*]) are for oxygenated seawater with $pH_T = 8.1$, $C_T = 2000$ μmol kg^{-1}, $P_T = 1.0$ μmol kg^{-1}, $Si_T = 15.0$ μmol kg^{-1}, $S = 35$, $t = 25$ °C, and $P = 1$ atm.

Equilibrium (bold species contributes to A_T)	Equilibrium Constant	pK_A^0	pK_A	[*i*] (bold species, μmol kg^{-1})	Reference
$\mathrm{H_2O} \rightarrow \mathbf{OH^-} + \mathrm{H^+}$	K_W	13.995	13.220	7.58	Millero (1995)
$\mathrm{Si(OH)_4^0} \rightarrow \mathbf{SiO(OH)_3^-} + \mathrm{H^+}$	K_{Si}	9.825	9.387	0.74	Yao and Millero (1995)
$\mathrm{NH_4^+} \rightarrow \mathbf{NH_3^0} + \mathrm{H^+}$ (anoxic)	K_{NH4}	9.245	9.266	0.00	Yao and Millero (1995)
$\mathrm{HCO_3^-} \rightarrow \mathbf{CO_3^{2-}} + \mathrm{H^+}$	K_2	10.330[a]	8.966	238.51	Lueker et al. (2000)
$\mathrm{HPO_4^{2-}} \rightarrow \mathbf{PO_4^{3-}} + \mathrm{H^+}$	K_{P3}	12.345	8.792	0.17	Yao and Millero (1995)
$\mathrm{B(OH)_3} + \mathrm{H_2O} \rightarrow \mathbf{B(OH)_4^-} + \mathrm{H^+}$	K_B	9.236	8.597	104.39[b]	Dickson (1990a)
$\mathrm{H_2S^0} \rightarrow \mathbf{HS^-} + \mathrm{H^+}$ (anoxic)	K_{S1}	6.980	6.520	0.00	Millero et al. (1988)
$\mathrm{H_2PO_4^-} \rightarrow \mathbf{HPO_4^{2-}} + \mathrm{H^+}$	K_{P2}	7.200	5.965	0.83	Yao and Millero (1995)
$\mathrm{CO_{2(aq)}} + \mathrm{H_2O} \rightarrow \mathbf{HCO_3^-} + \mathrm{H^+}$	K_1	6.351[a]	5.847	1751.70	Lueker et al. (2000)
$\mathbf{HF^0} \rightarrow \mathrm{F^-} + \mathrm{H^+}$	K_F	3.174	2.626	0.00[b]	Dickson and Riley (1979)
$\mathbf{H_3PO_4^0} \rightarrow \mathrm{H_2PO_4^-} + \mathrm{H^+}$	K_{P1}	2.149	1.615	0.00	Yao and Millero (1995)
$\mathbf{HSO_4^-} \rightarrow \mathrm{SO_4^{2-}} + \mathrm{H^+}$	K_{HSO4}	1.993	0.999	0.00[b]	Dickson (1990b)

[a] Values of pK_1^0 and pK_2^0 are from Millero (1979) because the salinity range given by Lueker et al. (2000) is 19–43.

[b] Conservative constituent ratios with respect to salinity for total boron, fluoride, and sulfate are given by Lee et al. (2010), Riley (1965), and Morris and Riley (1966), respectively.

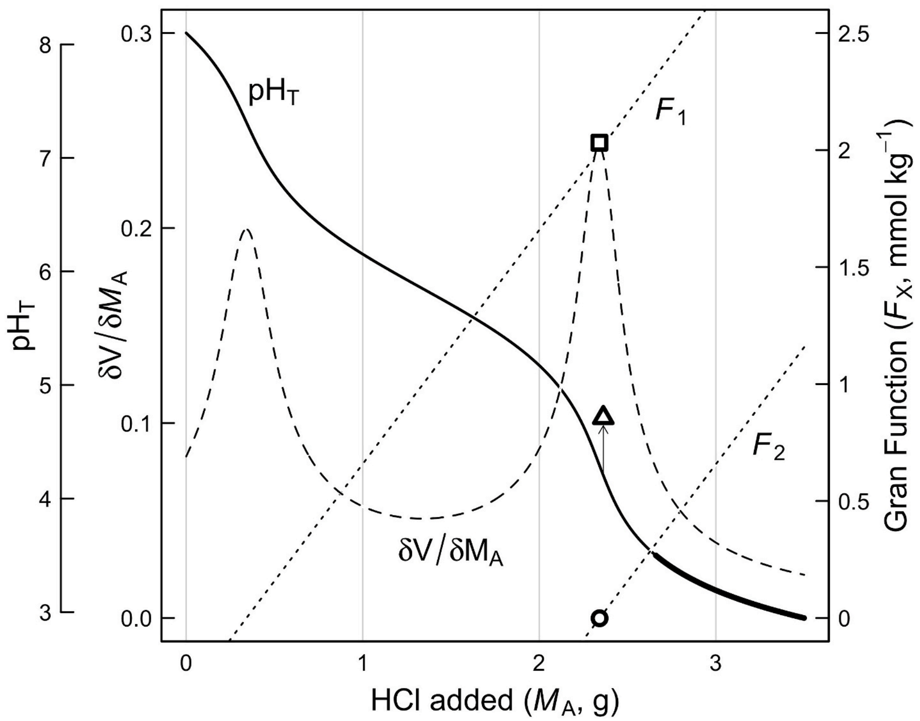

Fig. 2. Simulated titration of a 200 g sample of oxygenated seawater with initial $pH_T = 8.1$, $C_T = 2000\ \mu mol\ kg^{-1}$, $P_T = 1.0\ \mu mol\ kg^{-1}$, $Si_T = 15.0\ \mu mol\ kg^{-1}$, $S = 35$, $t = 25\ ^\circ C$, and $p = 1$ atm. The titrant is 0.2 M HCl. The solid black line is the simulated titration curve — i.e., the pH_T over the course of a typical multi-step titration. The other lines and symbols illustrate the various methods by which $A_{T(meas)}$ can be determined from the titration curve. The dotted lines display the first and second Gran functions, F_1 and F_2 (Eq. (11)), and the circle shows the point at which the second Gran function is equal to zero. The dashed line displays the difference derivative of electrical potential in volts (V), and the square shows the second peak of the difference derivative function. The triangle shows the solution pH_T obtained after terminating a single-step titration at a pH_T of 4.20 and then purging CO_2 (arrow) from the sample solution. The thicker portion of the titration curve shows the pH_T range over which multi-step open-cell titrations are evaluated ($3.5 > pH_T > 3.0$).

Table 2
A_T measurement approaches discussed in this work. The descriptions in column two represent how data analysis is performed by the 'TITRATE.m' model, discussed later in this work.

Measurement approach	Description
Modified Gran function (MGF), open-cell titration data	Standard electrode potential, E^0, is iteratively refined using data from a multi-step titration of a CO_2-purged sample (see Dickson et al., 2003) to calculate values of the second Gran function (F_2; Eq. (12)). F_2 values are fit against M_A by linear least squares analysis from $pH_T = 3.5$ to 3.0 (Hansson and Jagner, 1973) to determine A_T.
Nonlinear least squares fit (NLSF), closed-cell titration data	The full titration curve (Eq. (13)) for a multi-step closed-cell titration is fit using nonlinear least squares analysis. A multiplier f is used with hydrogen ion concentration estimates calculated from measured E values and estimated E^0. Adjustable parameters in the fit are f, A_T, and C_T (Dickson, 1981; Johansson and Wedborg, 1982).
Nonlinear least squares fit (NLSF), open-cell titration data	The titration curve from $pH_T = 3.5$ to 3.0 (Eq. (14)) for a multi-step open-cell titration is fit using nonlinear least squares analysis. A multiplier f is used with hydrogen ion concentration estimates calculated from measured E values and estimated E^0. Adjustable parameters in the fit are f and A_T (Dickson et al., 2003).
Difference derivative (DD) analysis, closed-cell titration data	Difference derivatives (DDs, calculated using Eq. (15)) at each step of a multi-step closed-cell titration are fit against M_A to a cubic spline interpolation. The second peak of the cubic function is located by taking the derivative of the cubic function (Hernández-Ayón et al., 1999).
Single-step titration, open-cell	The final pH_T of the purged solution (after termination of a single-step titration at $pH_T \approx 4.20$) is used with M_A to determine A_T (calculated using Eq. (16)) (Liu et al., 2015; Yao and Byrne, 1998).

simplicity.

This work focuses on five A_T measurement approaches that are widely used today: four involve analysis of multi-step titration data (subsections 2.2.1–2.2.4) and one involves analysis of single-step titration data (subsection 2.2.5). Each approach is summarized in Table 2. Fig. 2 illustrates the corresponding mathematical functions used to determine $A_{T(meas)}$ from the titration curve.

2.2.1. Modified gran function (MGF) analysis of open-cell titration data

Dyrssen (1965) was the first to use the mathematical method of Gran (1950, 1952) to estimate the A_T of natural waters from multi-step titration data. Gran's method transforms nonlinear plots of the electrical potential of a solution versus the amount of added acid into plots ("Gran plots") of linear functions that converge at the titration equivalence point. Dyrssen's (1965) method was further described by Dyrssen and Sillén (1967). Advancements in theory and methodology by Hansson and Jagner (1973) led to the use of modified Gran functions (MGFs), which account for minor acid–base species (i.e., those other than bicarbonate, carbonate, and borate) in A_T determinations. Much subsequent work in the field has been based on the use of MGFs to analyze alkalinity titrations (Almgren et al., 1977; Bradshaw et al., 1981; Bradshaw and Brewer, 1980; Gieskes, 1973).

The MGF pertaining to the second equivalence point of a natural water sample (F_2) describes chiefly the titration of bicarbonate to carbonic acid (Dickson, 1981; Hansson and Jagner, 1973):

$$F_2 = M_T\{[H^+]_f + [HSO_4^-] + [HF^0] + [H_3PO_4^0] - [HCO_3^-]\} \qquad (11)$$

Chemical species that are negligible in concentration across the pH range near the second equivalence point have been dropped from Eq. (11).

MGFs are used most commonly today to evaluate data from open-cell titrations (e.g., Winn et al., 1998), during which CO_2 is allowed to outgas after an initial acid addition before the titration is continued to low pH (as in Dickson et al., 2003). To determine A_T from open-cell titration data using an MGF approach, Eq. (11) is first adjusted to define species concentrations using dissociation constant relationships and to reflect the outgassing of CO_2:

$$F_2 = M_{\mathrm{T}}[\mathrm{H}^+]_f + M_0\left\{\frac{S_{\mathrm{T}}}{1+\frac{K_{\mathrm{S}}}{[\mathrm{H}^+]_f}} + \frac{F_{\mathrm{T}}}{1+\frac{K_{\mathrm{F}}}{[\mathrm{H}^+]_{\mathrm{T}}}} + \frac{P_{\mathrm{T}}}{1+\frac{K_{\mathrm{P1}}}{[\mathrm{H}^+]_{\mathrm{T}}}+\frac{K_{\mathrm{P1}}K_{\mathrm{P2}}}{[\mathrm{H}^+]_{\mathrm{T}}^2}+\frac{K_{\mathrm{P1}}K_{\mathrm{P2}}K_{\mathrm{P3}}}{[\mathrm{H}^+]_{\mathrm{T}}^3}}\right\} \tag{12}$$

After an initial guess is made for E^0, $[\mathrm{H}^+]$ values ($[\mathrm{H}^+]_f$ and $[\mathrm{H}^+]_{\mathrm{T}}$) at each titration step are calculated using Eqs. (9) and (10). An estimate for F_2 is calculated using these $[\mathrm{H}^+]$ values and Eq. (12). Then, a linear least squares regression is performed for the F_2 vs. M_{A} data across the specified pH range to obtain an estimate for A_{T}. An adjustment is made to E^0, and the process is repeated iteratively until the change in A_{T} is below a specified threshold.

The open-cell MGF method is used to determine A_{T} at Station ALOHA in the Pacific Ocean, as part of the Hawaii Ocean Time-series program (Winn et al., 1991).

2.2.2. *Nonlinear least squares fitting (NLSF) of closed-cell titration data*

In the 1980s, nonlinear least squares fitting of the titration curve itself emerged as a method estimating A_{T} and C_{T} from a multi-step titration in a closed cell (Dickson, 1981; Johansson and Wedborg, 1982; Millero et al., 1993). For the nonlinear least squares fit (NLSF) approach, all the terms in Eq. (8) are set to zero (Dickson, 1981; Johansson and Wedborg, 1982):

$$\begin{aligned} M_0A_{\mathrm{T}} - M_{\mathrm{A}}C_{\mathrm{A}} - M_0\Bigg\{ & \frac{C_{\mathrm{T}}}{1+\frac{[\mathrm{H}^+]_{\mathrm{T}}}{K_1}+\frac{K_2}{[\mathrm{H}^+]_{\mathrm{T}}}} + \frac{2\cdot C_{\mathrm{T}}}{1+\frac{[\mathrm{H}^+]_{\mathrm{T}}}{K_2}+\frac{[\mathrm{H}^+]_{\mathrm{T}}^2}{K_1K_2}} + \frac{B_{\mathrm{T}}}{1+\frac{[\mathrm{H}^+]_{\mathrm{T}}}{K_{\mathrm{B}}}} + \frac{Si_{\mathrm{T}}}{1+\frac{[\mathrm{H}^+]_{\mathrm{T}}}{K_{\mathrm{Si}}}} + \frac{P_{\mathrm{T}}}{1+\frac{[\mathrm{H}^+]_{\mathrm{T}}}{K_{\mathrm{P2}}}+\frac{[\mathrm{H}^+]_{\mathrm{T}}^2}{K_{\mathrm{P1}}K_{\mathrm{P2}}}+\frac{K_{\mathrm{P3}}}{[\mathrm{H}^+]_{\mathrm{T}}}} + \frac{2\cdot P_{\mathrm{T}}}{1+\frac{[\mathrm{H}^+]_{\mathrm{T}}}{K_{\mathrm{P3}}}+\frac{[\mathrm{H}^+]_{\mathrm{T}}^2}{K_{\mathrm{P2}}K_{\mathrm{P3}}}+\frac{[\mathrm{H}^+]_{\mathrm{T}}^3}{K_{\mathrm{P1}}K_{\mathrm{P2}}K_{\mathrm{P3}}}} - \frac{S_{\mathrm{T}}}{1+\frac{K_{\mathrm{S}}}{[\mathrm{H}^+]_f}} \\ & - \frac{F_{\mathrm{T}}}{1+\frac{K_{\mathrm{F}}}{[\mathrm{H}^+]_{\mathrm{T}}}} - \frac{P_{\mathrm{T}}}{1+\frac{K_{\mathrm{P1}}}{[\mathrm{H}^+]_{\mathrm{T}}}+\frac{K_{\mathrm{P1}}K_{\mathrm{P2}}}{[\mathrm{H}^+]_{\mathrm{T}}^2}+\frac{K_{\mathrm{P1}}K_{\mathrm{P2}}K_{\mathrm{P3}}}{[\mathrm{H}^+]_{\mathrm{T}}^3}}\Bigg\} + M_{\mathrm{T}}\left\{[\mathrm{H}^+]_f - \frac{K_{\mathrm{W}}}{[\mathrm{H}^+]_{\mathrm{T}}}\right\} = 0 \end{aligned} \tag{13}$$

Using a Gran-type approximation, initial estimates for E^0, A_{T}, and C_{T} are obtained. The estimated E^0 is used with measured E values to calculate estimated hydrogen ion concentrations ($[\mathrm{H}^+]'$) at each titration step. A multiplier f is defined to calculate $[\mathrm{H}^+]_{\mathrm{T}}$ values at each step (Dickson et al., 2007): $[\mathrm{H}^+]_{\mathrm{T}} = f\,[\mathrm{H}^+]'$. Then, values of M_{A} and $[\mathrm{H}^+]'$ are used with a least squares routine (typically a Levenberg–Marquardt algorithm) and Eqs. (10) and (13) to simultaneously compute f, A_{T}, and C_{T}. The multiplier f is used to calculate $[\mathrm{H}^+]_{\mathrm{T}}$ values and E^0.

Barron et al. (1983) demonstrated that there is little difference between A_{T} determined from closed-cell titration data using the MGF approach versus the NLSF approach. The closed-cell NLSF approach has been used on recent repeat hydrography cruises across the globe as part of the US GO-SHIP program (e.g., Baringer et al., 2016; Volkov et al., 2019). Overall, however, the closed-cell titration technique has become somewhat less prevalent in recent years due to the development (Johnson et al., 1985) and refinement of the more reliable coulometric technique for determining C_{T} and also difficulties associated with calibrating the volume of closed-cell systems (Dickson et al., 2003).

2.2.3. *Nonlinear least squares fitting (NLSF) of open-cell titration data*

A method for analyzing A_{T} titrations in open cells (after allowing CO_2 to escape) by least squares fitting of a lower portion of the titration curve (e.g., $3.5 > \mathrm{pH} > 3.0$) was described by Dickson et al. (2003). For this method, inorganic carbon terms and terms that are negligible across a low pH range are dropped from Eq. (13):

$$\begin{aligned} M_0A_{\mathrm{T}} - M_{\mathrm{A}}C_{\mathrm{A}} + M_0\left\{\frac{S_{\mathrm{T}}}{1+\frac{K_{\mathrm{S}}}{[\mathrm{H}^+]_f}} + \frac{F_{\mathrm{T}}}{1+\frac{K_{\mathrm{F}}}{[\mathrm{H}^+]_{\mathrm{T}}}} + \frac{P_{\mathrm{T}}}{1+\frac{K_{\mathrm{P1}}}{[\mathrm{H}^+]_{\mathrm{T}}}+\frac{K_{\mathrm{P1}}K_{\mathrm{P2}}}{[\mathrm{H}^+]_{\mathrm{T}}^2}+\frac{K_{\mathrm{P1}}K_{\mathrm{P2}}K_{\mathrm{P3}}}{[\mathrm{H}^+]_{\mathrm{T}}^3}}\right\} \\ + M_{\mathrm{T}}[\mathrm{H}^+]_f = 0 \end{aligned} \tag{14}$$

Using a Gran-type approximation, initial estimates are obtained for E^0 and A_{T}. The estimated E^0 is used with measured E values to calculate $[\mathrm{H}^+]'$ at each titration step and a multiplier f is again defined: $[\mathrm{H}^+]_{\mathrm{T}} = f\,[\mathrm{H}^+]'$. Then, values of M_{A} and $[\mathrm{H}^+]'$ are used with a NLSF routine and Eqs. (10) and (14) to simultaneously compute f and A_{T}.

The open-cell NLSF method is used to determine the A_{T} of Certified Reference Material (CRM) from Scripps Institution of Oceanography (Dickson et al., 2003). This method, like the closed-cell NLSF method, has also been used on recent repeat hydrography cruises across the globe as part of the US GO-SHIP program (e.g., Cross et al., 2017; Speer et al., 2018).

2.2.4. *Difference derivative (DD) analysis of closed-cell titration data*

Hernández-Ayón et al. (1999) described a method involving the use of difference derivatives (DDs) to directly determine A_{T} from closed-cell multi-step titration data. This approach, which does not depend on a pre-defined acid–base model (e.g., Eq. (1)), allows for the detection of dissolved titratable organics by also providing measurements of initial pH and C_{T}. In this approach, DDs of electrical potential measurements in volts (V) with respect to added acid mass (M_{A}) are computed at each step (n) during a titration:

$$\delta \mathrm{V} \,/\, \delta M_{\mathrm{A}} = (\mathrm{V}_{n+1} - \mathrm{V}_n) \,/\, (M_{\mathrm{A}(n+1)} - M_{\mathrm{A}(n)}) \tag{15}$$

The DDs are plotted as a function of M_{A} and then fit to a cubic spline interpolation. The second peak of the spline function corresponds to the second equivalence point, which is used to determine A_{T}. Hernández-Ayón et al. (1999) demonstrated that this technique is independent of any errors in dissociation constants or conservative constituent ratios.

The DD analysis method has been used for studies of organic alkalinity (Hernández-Ayón et al., 2007; Muller and Bleie, 2008), biological calcification (Steller et al., 2007), and general carbonate system studies (Álvarez et al., 2014; Cantoni et al., 2012).

2.2.5. *Single-step titration in an open cell*

A fundamentally different approach was advanced by Breland and Byrne (1993) with their description of a method for determining A_{T} by using a single addition of HCl (rather than incremental stepwise additions) and spectrophotometric measurement of excess acid after complete purging of CO_2 from the sample solution. This method was based somewhat on the work of Culberson et al. (1970), who described a single-step approach that used electrometric measurement of excess acid. Yao and Byrne (1998) introduced continuous pH monitoring to the Breland and Byrne (1993) approach to minimize the excess acid term, and Liu et al. (2015) automated the process.

In this method, an indicator dye (bromocresol purple or bromocresol green) is added to the sample, which allows the titration to be monitored continuously by a spectrophotometer. This approach permits titrant acid to be added quickly at first, then slowly until the sample reaches a predetermined endpoint (e.g., $pH_T = 4.20$) at which (1) the excess acid exceeds the residual bicarbonate and (2) only free H^+, HSO_4^-, HF^0, and HCO_3^- contribute appreciably to the proton balance.

After CO_2 is purged from the sample using a dry gas stream (e.g., high-purity N_2), HCO_3^- no longer contributes to the proton balance and A_T can be calculated using a modified version of Eq. (8):

$$A_T = \left(M_A C_A - M_T[H^+]_T - M_0 \left\{ \frac{F_T}{1 + \frac{K_F}{[H^+]_T}} \right\} \right) \cdot M_0^{-1} \tag{16}$$

Notice that hydrogen ion concentration here is expressed on the total scale (Eq. (9)), accounting for both $[H+]_f$ and $[HSO_4^-]$; a term (with F_T in the numerator) is therefore included in Eq. (16) to account for HF^0. Alternatively, hydrogen ion concentration could be expressed on the seawater scale (Breland and Byrne, 1993; Yao and Byrne, 1998):

$$[H^+]_{SWS} = [H^+]_f + [HSO_4^-] + [HF^0] \tag{17}$$

and the HF^0 term omitted. The single-step method is appealing because the amount of excess acid remaining after the purging of CO_2 can be kept relatively low (<30 μmol kg^{-1}), meaning that any error in the final pH_T measurement contributes minimally to measured A_T (±0.01 in pH_T translates to about ±0.5 μmol kg^{-1} in $A_{T(meas)}$).

The single-step method has been used to measure alkalinity for studies of $CaCO_3$ dissolution (Naviaux et al., 2019), organic alkalinity (Yang et al., 2015), and cephalopod metabolism (Birk et al., 2018).

Table 3

Summary of selected studies that examined the acid–base properties of dissolved organic matter in terms of p*K* values. The numbered p*K* values (pK_1, pK_2, and pK_3) correspond to explicit fits of titration curves, whereas the “bulk” p*K* values correspond to fits obtained using dissolved organic carbon concentrations and organic alkalinity estimates according to Eq. (4) in Kuliński et al. (2014).

Reference	Location	pK_1	pK_2	pK_3
Paxeus and Wedborg (1985) [a]	Göta River, Sweden	2.66	4.21	5.35
	Göta River, Sweden	6.65	8.11	9.54
Cai et al. (1998)	Satilla River, GA, USA	4.46	6.64	8.94
De Souza Sierra et al. (2001)	Santa Catarina Is., Brazil	5.51–5.99	9.09–9.85	
Hruška et al. (2003)	Czech Republic stream	2.50	4.42	6.70
	Sweden stream	3.04	4.51	6.46
Muller and Bleie (2008)	Norwegian fjord	4.10	9.16	
Yang et al. (2015)	Coquina Key, FL, USA	5.31	7.05	
	Bayboro Harbor, FL, USA	5.45	7.32	
Ko et al. (2016)	Coastal Korea	4.4	6.1	
	Culture species	**pK_1**	**pK_2**	**pK_3**
Fein et al. (1997)	*Bacillus subtilis*	4.82	6.9	9.4
Ko et al. (2016)	*Prorocentrum minimum*	4.9	6.9	
	Emiliania huxleyi	4.8	6.9	
	Skeletonema costatum	4.9	6.8	
	Location	**Bulk p*K***		
Kuliński et al. (2014)	Baltic Sea	7.53		
Ulfsbo et al. (2015)	Baltic Sea	7.34		

[a] Paxeus and Wedborg (1985) described six separate groups of charge sites for a single sample, displayed here across two lines of the table.

3. Introducing additional species to the A_T equation

In section 2.1, it was indicated that additional chemical species (e.g., organic acids) can be added to the proton condition given in Eq. (5), and therefore to the A_T definition given in Eq. (6). To rigorously account for these species, their total concentrations and dissociation behaviors (K_A values) would have to be known. In a system with a non-negligible concentration of total ammonia ($NH3_T$), for example, the influence of ammonia (NH_3^0, defined as a proton acceptor) would be accounted for in Eq. (8) by adding a positive term of the form $M_0(NH3_T/(1 + [H^+]_T/K_{NH4}))$, where K_{NH4} is the dissociation constant of the ammonium ion.

Similarly, a titratable organic base (X^-) formed from a weak acid (HX^0) with a total concentration X_T and a pure water dissociation constant $pK_X^0 \geq 4.5$ at 25 °C would be included in Eq. (8) by adding a positive term of the form $M_0(X_T/(1 + [H^+]_T/K_X))$. A titratable organic acid (HY^0) with a total concentration of Y_T and a pure water dissociation constant $pK_Y^0 < 4.5$ at 25 °C would be included by adding a negative term of the form $-M_0(Y_T/(1 + K_Y/[H^+]_T))$.

Much recent work has focused on qualitatively characterizing organic molecules in natural waters (e.g., Arakawa et al., 2017; Ben Ali Daoud and Tremblay, 2019; Broek et al., 2020; Hertkorn et al., 2006, 2013; Longnecker and Kujawinski, 2017). These studies and others have identified a wide variety of organic molecular functional groups and structures. The continuous spectrum on which these molecular properties occur results in a continuous distribution of proton-exchange behavior (Fukushima et al., 1995; Perdue et al., 1984).

Table 3 displays the results of several studies that have examined the proton-exchange properties of organics found in natural waters or culture experiments. These studies identified approximate centers of distribution for organic acid p*K* values. Some of these studies also reported effective concentrations for each functional group, but those values are not displayed in Table 3 because they are highly variable and hold little value when obtained from phytoplankton cultures or pre-concentrated natural organic matter.

Table 3 illustrates that estimates of organic acid p*K* values can be quite heterogenous; in other words, there is not a clear “typical” set of organic p*K* values that can be applied to natural organic matter. The bulk p*K* values do show some promise for practical application, but more work is needed to determine whether the Baltic Sea material is universally representative of marine and estuarine dissolved organic matter. Due to the pervasive lack of essential p*K* information, organic acids are almost always excluded from the chemical models used to evaluate A_T.

As noted in section 1, any chemical species that binds protons during the course of an acidimetric titration will contribute quantitatively to $A_{T(meas)}$ in the form of $A_{org(meas)}$ (Eq. (4)). These species can certainly include those that are not explicitly accounted for in the acid–base models that defines A_{inorg} (e.g., Eq. (1); Dickson, 1981). The extent to which $A_{T(meas)}$ deviates from A_{inorg} (i.e., ΔA_T) in the presence of unidentified titratable organics is a function of the concentrations and proton-exchange properties of the organic molecules, the inorganic chemistry of the natural water sample, the pH range over which titration

Table 4

Adjustable input parameters for ‘TITRATE.m’.

Parameter	Default value	Unit
Salinity (*S*)	35	none
Temperature (*T*)	25	°C
Total dissolved inorganic carbon (C_T)	2000	μmol kg^{-1}
pH_T	8.1	none
Total phosphate concentration (P_T)	1	μmol kg^{-1}
Total silicate concentration (Si_T)	15	μmol kg^{-1}
Total ammonium concentration (NH_4^+)	0	μmol kg^{-1}
Total hydrogen sulfide concentration (H_2S)	0	μmol kg^{-1}
Sample mass (M_0)	200	g
Titrant molality (C_A)	0.2	mol kg^{-1}
Total organic acid concentration (ORG_T)	0	μmol kg^{-1}
Dissociation constant of organic acid (pK_{org})	0	mol kg^{-1}

data are analyzed, and the method of that data analysis. The effects of these different factors on the results of total alkalinity titrations will be discussed in this paper.

4. Methods

To model A_T measurements in the presence of dissolved organic matter, a program ('TITRATE.m', hereafter referred to as "the model") was written for MATLAB (MathWorks®); this code is available on GitHub at https://github.com/jonathansharp/AlkTitrationModel. The model generates simulated titration data, then analyzes those data using the five independent A_T measurement approaches described in section 2.2, and provides an $A_{T(meas)}$ value that would be obtained by each method. The adjustable input parameters for the model are listed in Table 4, along with the default values for surface seawater without organics.

Conservative constituent ratios and dissociation constants in the model are determined according to the references given in Table 1. At $0 < S < 20$, K_1 and K_2 are determined using the formulation of Waters et al. (2014), which essentially corrects pH scale inconsistencies associated with the K_1 and K_2 formulations given by Millero (2010).

The model simulates an alkalinity titration by first calculating the concentrations of all acid–base species at the initial conditions specified by the input parameters. Then, HCl is incrementally added in a step-wise manner. The total mass of HCl used for the simulated titration ($M_{A(tot)}$) is calculated by the equation given in Dickson et al. (2007): $M_{A(tot)} = 0.0035 \cdot M_0/C_A$. The mass of HCl added at each titration step is $M_{A(tot)}/1000$, meaning the model simulates 1000 steps.

At each step, hydrogen ion concentration is determined using an iterative procedure, both using the initial C_T value (to simulate retention of inorganic carbon for closed-cell titrations) and using $C_T = 0$ (to simulate purging of inorganic carbon for open-cell titrations). Eq. (10) is used to convert hydrogen ion concentrations to E values.

Once the simulated titration is complete, data analysis is performed in five different ways according to the summary of measurement approaches provided in Table 2. For the single-step titration, the closed-cell titration curve is fit to a spline function. The M_A value at which the pH_T estimated from the closed-cell spline function is equal to 4.2 (before purging of inorganic carbon) is used to determine the corresponding open-cell $[H^+]_T$ value (to simulate CO_2 purging). These M_A and $[H^+]_T$ values are used as inputs to Eq. (16). Reported $A_{T(meas)}$ values obtained by each of the five measurement approaches can be compared for a range of assumed organic molecular characteristics.

The model was first used to simulate alkalinity titrations of solutions without any organics (section 5.1); this provided a baseline to assess consistency in $A_{T(meas)}$ among the five measurement approaches. Then, a simple organic acid was added to the model to determine how its presence influenced $A_{T(meas)}$ (and ΔA_T) determined by each approach (sections 5.2 and 5.3). Carbonate system parameters were calculated by treating $A_{T(meas)}$ values as A_{inorg} (section 5.4). Calculations were performed using CO2SYS (Lewis and Wallace, 1998) for MATLAB (Van Heuven et al., 2011), with all other input parameters (besides alkalinity) as defined precisely by the 'TITRATE.m' model inputs. Finally, practical methods for measuring or estimating organic alkalinity are discussed (section 5.5) and the possibility of organic alkalinity in the open ocean is explored (section 5.6).

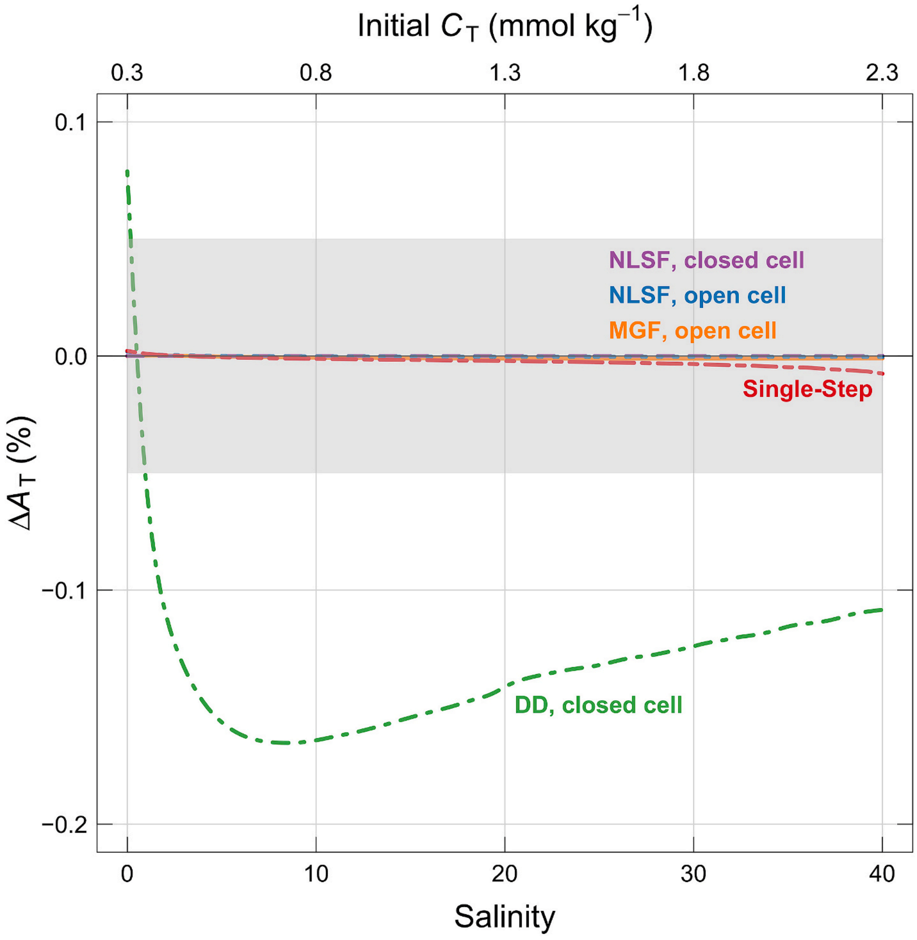

Fig. 3. Modeled differences (%) between $A_{T(meas)}$ and A_{inorg} in a purely inorganic system, for the five data analysis procedures outlined in Table 2: $\Delta A_T = A_{T(meas)} - A_{inorg}$. The shaded region represents a typically estimated measurement precision for A_T (±0.05%). The sample solution is oxygenated natural water with $pH_T = 8.1$, $P_T = 1.0$ μmol kg^{-1}, $Si_T = 15.0$ μmol kg^{-1}, $t = 25$ °C, $p = 1$ atm, and $ORG_T = 0$ μmol kg^{-1}. Results are shown as functions of S and C_T. Values of C_T were determined by assuming a functional relationship with S: $C_T = 50\ S + 300$.

5. Results and discussion

5.1. Validation of ‘TITRATE.m’ model in the absence of titratable organics

5.1.1. Comparison of model results to test dataset

To validate that the data analysis routines embedded in the model provide accurate calculations of $A_{T(meas)}$, two steps were taken. First, open-cell titration data from the example calculation given in section 7.4 of SOP 3b in Dickson et al. (2007) were analyzed using the model’s open-cell NLSF routine. This routine gave an $A_{T(meas)}$ of 2260.09 μmol kg^{-1} and an E^0 of 0.394395 V, nearly identical to the $A_{T(meas)}$ of 2260.06 μmol kg^{-1} and E^0 of 0.394401 V given by the NLSF performed by Dickson et al. (2007). This close agreement confirms that the open-cell NLSF routine embedded in the model is performing as it should.

5.1.2. Comparison among measurement approaches

Next, to validate the other data analysis routines, data generated by the model from simulated titrations of natural water with no organic acids (default conditions given in Table 4) were analyzed by each routine. The resulting $A_{T(meas)}$ values were compared to A_{inorg} as defined precisely by the model inputs according to Eq. (1). Fig. 3 shows relative values of ΔA_T (i.e., $A_{T(meas)} - A_{inorg}$) for these simulated titrations as a function of salinity and corresponding C_T. As detailed in section 1, ΔA_T is conceptually analagous to the $A_{org(meas)}$ quantity presented in Eq. (4); however the two are not identical, as misestimates of A_{inorg} that are unrelated to dissolved organics will also manifest in ΔA_T. The C_T range in Fig. 3 was determined by assuming a functional relationship with salinity: $C_T = S \cdot 50 + 300$. Because no organics were included, $A_{inorg} = A_T$ by definition. So, in a perfectly characterized system, $A_{T(meas)}$ and A_{inorg} will be exactly equal and ΔA_T will be zero.

Fig. 3 shows that most measurement approaches provide $A_{T(meas)}$ values that are virtually identical to A_{inorg}. One noticeable deviation is the single-step method’s slight overestimate of A_T at very low salinities (at most by 0.002%) and underestimate at most other salinities (at most by 0.008%). These minor errors can be explained by small contributions from borate and phosphate species at the final pH, which are not explicitly accounted for by Eq. (16). These errors could be eliminated by the addition of small corrective terms to that equation. However, these corrections are not made here because the errors are well within state-of-the-art measurement precision for total alkalinity, which is typically reported as ±0.05% at best (the shaded region of Fig. 3), and often higher.

The most conspicuous result displayed in Fig. 3, though, is the difference between ΔA_T determined by the DD method versus ΔA_T determined by the other four methods. This result is not entirely surprising (c.f. Rigobello-Masini and Masini, 2001) because the DD method is the only one of the five that is not explicitly based on a proton condition defined rigorously by a thermodynamic acid–base model. So, unlike the methods that rely on a proton condition, the DD method provides a value for $A_{T(meas)}$ that is not necessarily exactly consistent with A_T as defined by Dickson (1981). Still, $A_{T(meas)}$ determined by the DD method remains within 0.2% (less than 3 μmol kg^{-1}) of A_T across the range of salinities and C_T values in Fig. 3, and any inconsistencies can be assessed by comparing measurements of CRMs (Dickson et al., 2003).

The analysis described here validates that (1) the ‘TITRATE.m’ model successfully simulates and analyzes alkalinity titrations and (2) despite the caveat associated with the DD method, the five independent data analysis methods produce $A_{T(meas)}$ values that sufficiently estimate A_T under “normal” conditions (i.e., no organic species).

5.2. Modeled $A_{T(meas)}$ in the presence of titratable organics

5.2.1. Effect of measurement approach

To highlight the effect that titratable organics have on $A_{T(meas)}$, an organic acid with a total concentration equal to 20 μmol kg^{-1} (ORG_T) was added to the model at the inorganic conditions given in Table 4. The value of $ORG_T = 20$ μmol kg^{-1} was chosen because coastal and estuarine waters often have titratable organic concentrations that are near or well above this level (e.g., Cai et al., 1998; Kuliński et al., 2014; Yang et al., 2015), whereas observations in open ocean surface waters suggest that it may be logical to expect concentrations of titratable organic acids of as

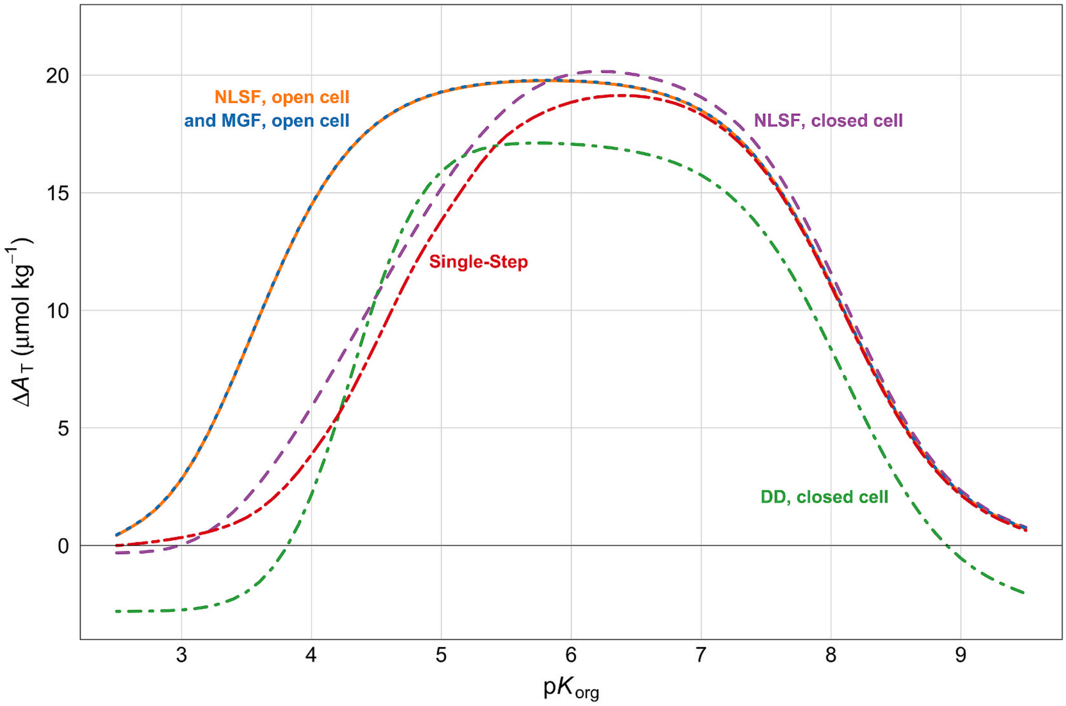

Fig. 4. Modeled differences between $A_{T(meas)}$ and A_{inorg} in a system that includes titratable organics, as a function of pK_{org} (2.5–9.5): $\Delta A_T = A_{T(meas)} - A_{inorg}$. The sample solution is oxygenated seawater with $pH_T = 8.1$, $C_T = 2000$ μmol kg^{-1}, $P_T = 1.0$ μmol kg^{-1}, $Si_T = 15.0$ μmol kg^{-1}, $t = 25$ °C, $S = 35$, $p = 1$ atm, and $ORG_T = 20$ μmol kg^{-1}.

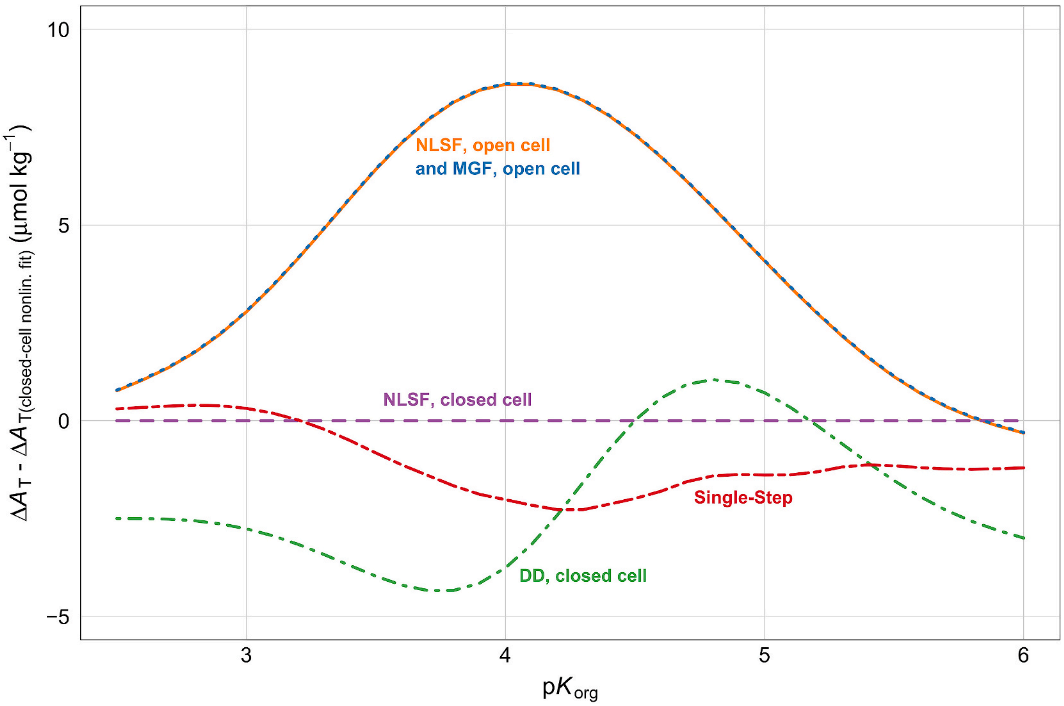

Fig. 5. Differences between ΔA_T for the closed-cell NLSF method versus ΔA_T for the other four methods, as a function of pK_{org} (2.5–6.0). The composition of the sample solution is identical to that used for Fig. 4. Note that the scales of the x- and y-axes differ from those of Fig. 4.

much as 10 µmol kg^{-1}, even in areas where organic alkalinity is traditionally neglected (see section 5.6). So, ORG_T = 20 µmol kg^{-1} is an intermediate value to these two extremes, and is convenient for illustrative purposes.

Across a range of pK_{org} (2.5–9.5), values of ΔA_T were computed for each measurement approach (Fig. 4; Table A2). These ΔA_T values represent the difference between measured total alkalinity ($A_{T(meas)}$, determined using the five discrete data analysis methods) and inorganic alkalinity (A_{inorg}, defined precisely by the model inputs according to Eq. (1)). Again, any difference will be mainly due to the effect of $A_{org(meas)}$ (Eq. (4)). Table A3 similarly contains ΔA_T values across a range of initial sample pH$_T$ and C_T with fixed pK_{org} values.

Fig. 4 shows that the largest ΔA_T values (up to 100% of ORG_T) are seen in the pK_{org} range of about 5.0–7.0. This result is reasonable because, given this pK_{org} range, the organic acid is almost fully dissociated at the initial sample pH and the conjugate base becomes almost

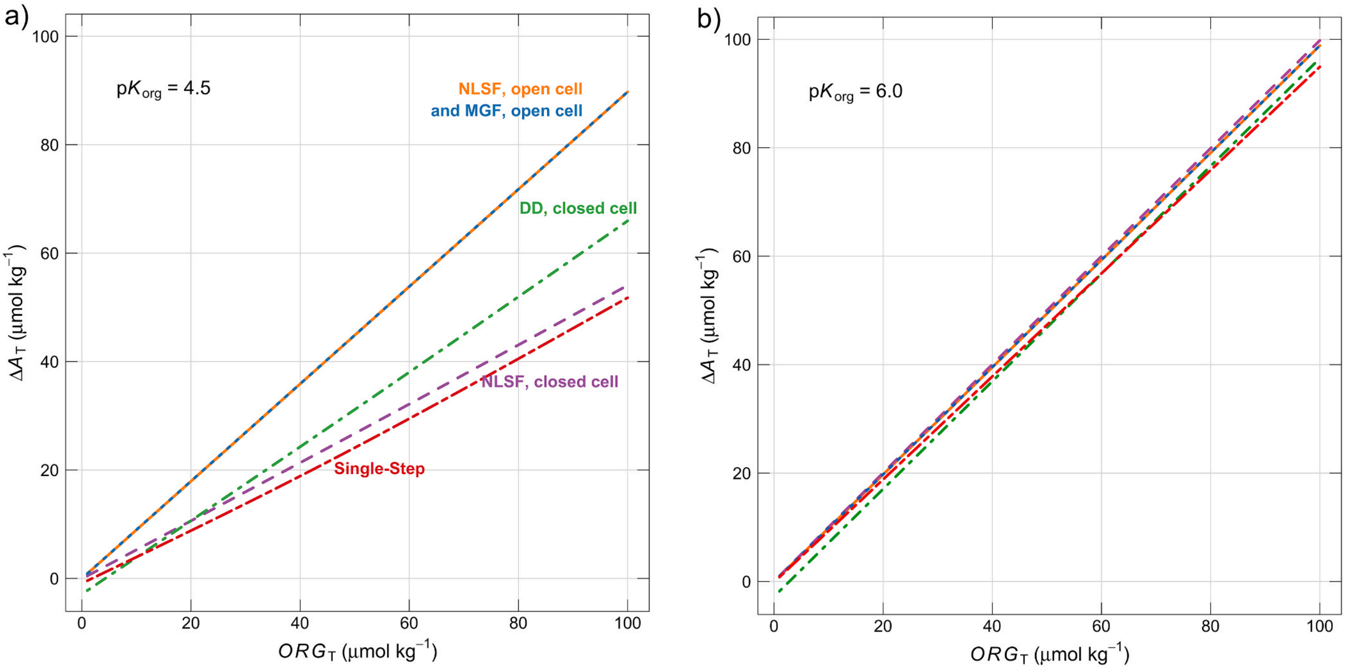

Fig. 6. Modeled differences between $A_{T(meas)}$ and A_{inorg} as a function of total organic content (ORG_T = 0–100 µmol kg^{-1}). The sample solutions are oxygenated seawater with pH$_T$ = 8.1, C_T = 2000 µmol kg^{-1}, P_T = 1.0 µmol kg^{-1}, Si_T = 15.0 µmol kg^{-1}, t = 25 °C, S = 35, and p = 1 atm. The results for two pK_{org} values are shown here: (a) pK_{org} = 4.5 and (b) pK_{org} = 6.0.

fully protonated during the course of each titration.

Aside from the systematic offset of the DD method (Fig. 3), the ΔA_T values are relatively consistent among the different data analysis methods for high pK_{org} values (6.0–9.5). However, the ΔA_T values begin to diverge more significantly for p$K_{org} < 6.0$. To emphasize the divergence among methodologies at low pK_{org} (i.e., <6.0), Fig. 5 shows ΔA_T values within this range relative to ΔA_T obtained from the closed-cell NLSF approach, which tends to provide values intermediate to the other approaches.

The largest ΔA_T values at low pK_{org} are associated with the two multi-step open-cell titration methods, which show nearly identical results. For these two methods, low-pK organic acids exert a relatively strong influence across the low pH range over which the titration data are analyzed.

The NLSF of the full titration curve using closed-cell titration data shows slightly greater ΔA_T values than the other methods at pK_{org} values from about 6 to 8 and lower values than the multi-step open-cell methods at pK_{org} values less than 6 (Fig. 4). The inclusion of titration data spanning a wide range of pH for the closed-cell NLSF minimizes the effect of low-pK organics on $A_{T(meas)}$ compared to the open-cell NLSF.

The DD method produces ΔA_T values in the low pK_{org} range that are offset from the closed-cell NLSF ΔA_T values by an average of about −2.5 μmol kg^{-1} (Fig. 5). This offset varies in magnitude, however, near pK_{org} = 4.3. This variation is due to the approximate location of the second titration equivalence point near pH = 4.3, which is therefore where the DD function peaks. The offset itself is due largely to the systematic offset that is observed between $A_{T(meas)}$ obtained via the DD method versus $A_{T(meas)}$ obtained via the other measurement approaches (Fig. 3).

The single-step method produces ΔA_T values in the low-pK_{org} range that are mostly smaller than the closed-cell NLSF method (Fig. 5). This result is likely due to the relatively high pH (~4.20) at which the titration is terminated. This early termination limits the amount of low-pK organic matter that is titrated, thus limiting the amount detected in the calculation of $A_{T(meas)}$.

5.2.2. Effect of dissolved organic content

Values of ΔA_T scale proportionally with dissolved organic content. This linear scaling has been described in previous studies using measurements of dissolved organic carbon concentration ([DOC]) (Kim and Lee, 2009; Koeve and Oschlies, 2012; Kuliński et al., 2014) and is confirmed by our modeling work using a range of ORG_T.

Fig. 6 shows ΔA_T values that increase linearly as a function of ORG_T (0–100 μmol kg^{-1}). The slope of each line is a function of measurement approach and pK_{org}. For example, with a pK_{org} of 6.0 (Fig. 6b), each measurement approach produces a line with a slope very near to one. However, with a pK_{org} of 4.5 (Fig. 6a), the slopes vary widely by measurement approach and in some cases are much smaller than one.

5.3. Implications of differing $A_{T(meas)}$ results

Differences in the values of ΔA_T among various measurement approaches are significant because, as discussed in section 2.2, different approaches are used by different investigators across the oceanographic community to produce $A_{T(meas)}$ values. However, in the presence of titratable organic molecules, the different approaches don't all generate identical values. Nevertheless, $A_{T(meas)}$ values are treated identically once reported as A_T, and little consideration is given to the potential systematic uncertainties that might vary in magnitude as a function of measurement approach. Going a step further, small variations in how each measurement approach is applied (e.g., fitting an open-cell titration curve across the pH range of 3.7–3.2 rather than 3.5–3.0) can also produce differences in ΔA_T, and thus, differences in reported $A_{T(meas)}$.

In the presence of low-pK organic acids (i.e., p$K_{org} < 6.0$), the difference between $A_{T(meas)}$ and A_{inorg} is relatively small for the closed-cell titration and single-step methods compared to the multi-step open-cell titration methods (Figs. 4 and 5). This pK_{org} range is notable because low-pK carboxyl groups represent a significant portion of dissolved organic matter in natural waters (Hertkorn et al., 2006; Milne et al., 2001; Ritchie and Perdue, 2003; Tipping, 1998). Therefore, a good option for limiting systematic overestimates of A_{inorg} in organic-rich environments may be to employ either the closed-cell NLSF method or the single-step method. Alternatively, multi-step open-cell methods might benefit from evaluations at somewhat higher pH, which can obviate the unwanted influence of low-pK organics while maintaining a relatively simple chemical system. Overall, the potential benefits of modifying specific aspects of commonly employed titration methods or experimenting with new methods must be balanced against the advantages of current best practices.

For many applications, such as using A_T to detect the effects of ocean acidification on marine calcification (Ilyina et al., 2009; Carter et al., 2016), consistency in A_T measurements is most critical. Studies like these that rely on detecting small changes in A_T over time have been made possible by the distribution of CRMs (Dickson, 2010) and the development of best practices (Dickson et al., 2007). For other applications, such as calculating air–sea CO_2 flux using A_T (e.g., Williams et al., 2017), accuracy in determining carbonate alkalinity from total alkalinity is most critical. In this case, carefully obviating or accounting for organic alkalinity may be more important than obtaining historically consistent results.

Finally, the ΔA_T values discussed in this paper assume perfect execution of an alkalinity titration with respect to sample preparation, measurement procedure, and data analysis. However, additional influences on measurement precision and accuracy outside of organic alkalinity should also be considered. For example, closed-cell titrations can suffer uncertainties related to volume calibration (which can introduce major errors in reported alkalinity) and the presence of bicarbonate (which makes equivalence point determinations less reliable) (Dickson et al., 2003). Though certain open-cell titration methods leave the door open for potential systematic errors introduced by titratable organics, they benefit from removal of bicarbonate and, sometimes, gravimetric sample measurement (Dickson et al., 2003).

5.4. Calculated carbonate system parameters in the presence of titratable organics

One of the more impactful consequences of titratable organic matter is its effect on carbonate system calculations performed using measured alkalinity as an input parameter (Hoppe et al., 2012; Ko et al., 2016; Koeve and Oschlies, 2012). Titratable organics have been shown to cause misinterpretations of alkalinity titrations when attempting to estimate A_{inorg} (see section 5.2). These misinterpretations propagate to carbonate system parameters calculated from erroneous A_{inorg} values, thus distorting subsequent calculations of air–sea CO_2 flux, degrees of $CaCO_3$ saturation, budgets and fluxes of inorganic carbon, and more. In other words, titratable organic matter can adversely influence interpretations of a wide array of biogeochemical data.

In the following sections, $\Delta X_{(A_T,Y)}$ refers to the difference between (a) parameter X calculated from $A_{T(meas)}$ and parameter Y (i.e., $X_{(A_T,Y)}$) versus (b) parameter X as defined by the model (i.e., $X_{(model)}$), which can be thought of as a perfectly measured or perfectly calculated parameter X: $\Delta X_{(A_T,Y)} = X_{(A_T,Y)} - X_{(model)}$.

Tables A4 and A5 provide comprehensive sets of errors (due exclusively to organic alkalinity) in carbonate system parameters calculated using different A_T-containing input pairs, measurement approaches, and ranges of pK_{org} values (Tables A4) and initial carbonate chemistries (Tables A5). Subsections 5.4.1–5.4.3 provide illustrative figures and interpretations of these calculation errors.

Results are shown for calculations made at 25 °C and atmospheric pressure, but the interpretations generally hold true for calculations made at conditions relevant to in situ marine and estuarine environments. However, it is important to note that calculations of in situ parameters will still be in error without knowledge of the proton-exchange

Table 5
Summary of methods that can be used to account for organic alkalinity.

Method	Citations	Measurements needed	Pros	Cons
Empirical parameterization	Kuliński et al. (2014) Ulfsbo et al. (2015)	[DOC], two additional carbonate system parameters	Can be applied to a full dataset within a given region	Overdetermination of carbonate system necessary, only applicable when $A_{org} > \sim 8$ μmol kg^{-1}
Proton-binding model	Koopal et al. (2005) Tipping et al. (2011)	[DOC]	Can be applied to a full dataset within a given region	Proton binding models are available only for freshwater organic matter
Secondary titration	Cai et al. (1998) Yang et al. (2015)	Back-titration with NaOH	Provides a direct measurement of excess alkalinity	Potential issues with incomplete removal of dissolved CO_2 and addition of excess CO_2 from NaOH
Advanced curve fitting	Asuero and Michałowski (2011) Michałowski and Asuero (2012)	None	No additional measurements needed	Not yet extensively tested or utilized in the marine chemistry community

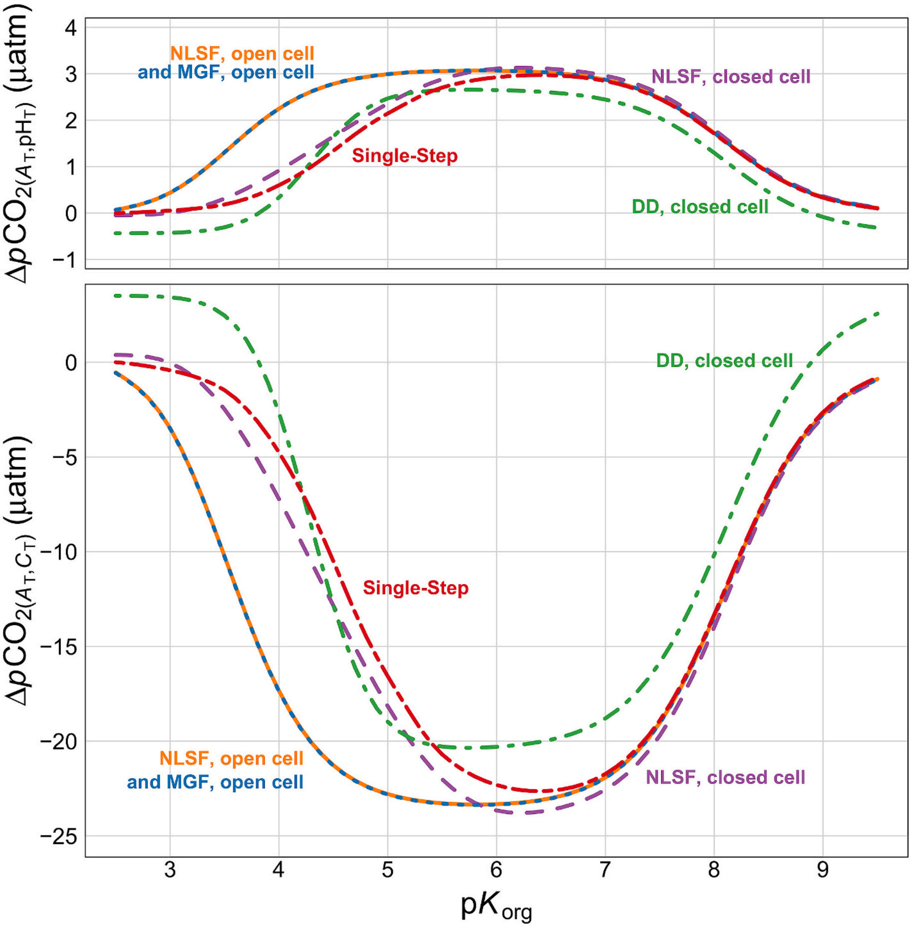

Fig. 7. Modeled difference between pCO_2 calculated from $A_{T(meas)}$ paired with another parameter (pH_T or C_T) versus true $pCO_{2(model)}$, as a function of pK_{org} (2.5–9.5). The composition of the sample solution is identical to that used for Figs. 4 and 5. The scale of top panel is expanded by a factor of about 2.5 relative to the bottom panel.

properties of all acid–base species in a sample, even if the input parameters are perfectly measured at laboratory conditions and even if neither of those measured parameters is A_T. This is because A_T is an intermediary step for all laboratory to in situ conversions. This subtlety, which can be easily overlooked, highlights the importance of developing accurate in situ measurement technologies (Byrne, 2014).

5.4.1. Calculated pCO_2

Fig. 7 shows $\Delta pCO_{2(AT,pHT)}$ and $\Delta pCO_{2(AT,CT)}$ (at 25 °C) as a function of pK_{org} (2.5–9.5) for an ORG_T of 20 μmol kg^{-1} and the inorganic chemical conditions given in Table 4. Additional results for $\Delta pCO_{2(AT,Y)}$ are given in Tables A4 and A5.

The results demonstrate patterns similar to those of the ΔA_T results (Fig. 4), with maximum $\Delta pCO_{2(AT,Y)}$ values near the center of the pK_{org} range and higher variability among measurement approaches in the low-pK_{org} range. Differences in $\Delta pCO_{2(AT,CT)}$ between approaches can be as much as 15 μatm with an input of $ORG_T = 20$ μmol kg^{-1}.

Values of $\Delta pCO_{2(AT,pH)}$ are positive and relatively small, whereas values of $\Delta pCO_{2(AT,CT)}$ are negative and of greater magnitude. This difference is the result of the input-error sensitivity of the iterative process that uses A_T and C_T to determine pH, which is then used to calculate pCO_2 (Koeve and Oschlies, 2012). This difference in the magnitude of pCO_2 calculation errors arising from different input parameters in high-organic environments has been highlighted before (Kim and Lee, 2009; Hoppe et al., 2012; Koeve and Oschlies, 2012; Yang et al., 2015), and it has implications for the design of certain investigations — e.g., phytoplankton culture experiments or coastal/estuarine examinations of CO_2 flux.

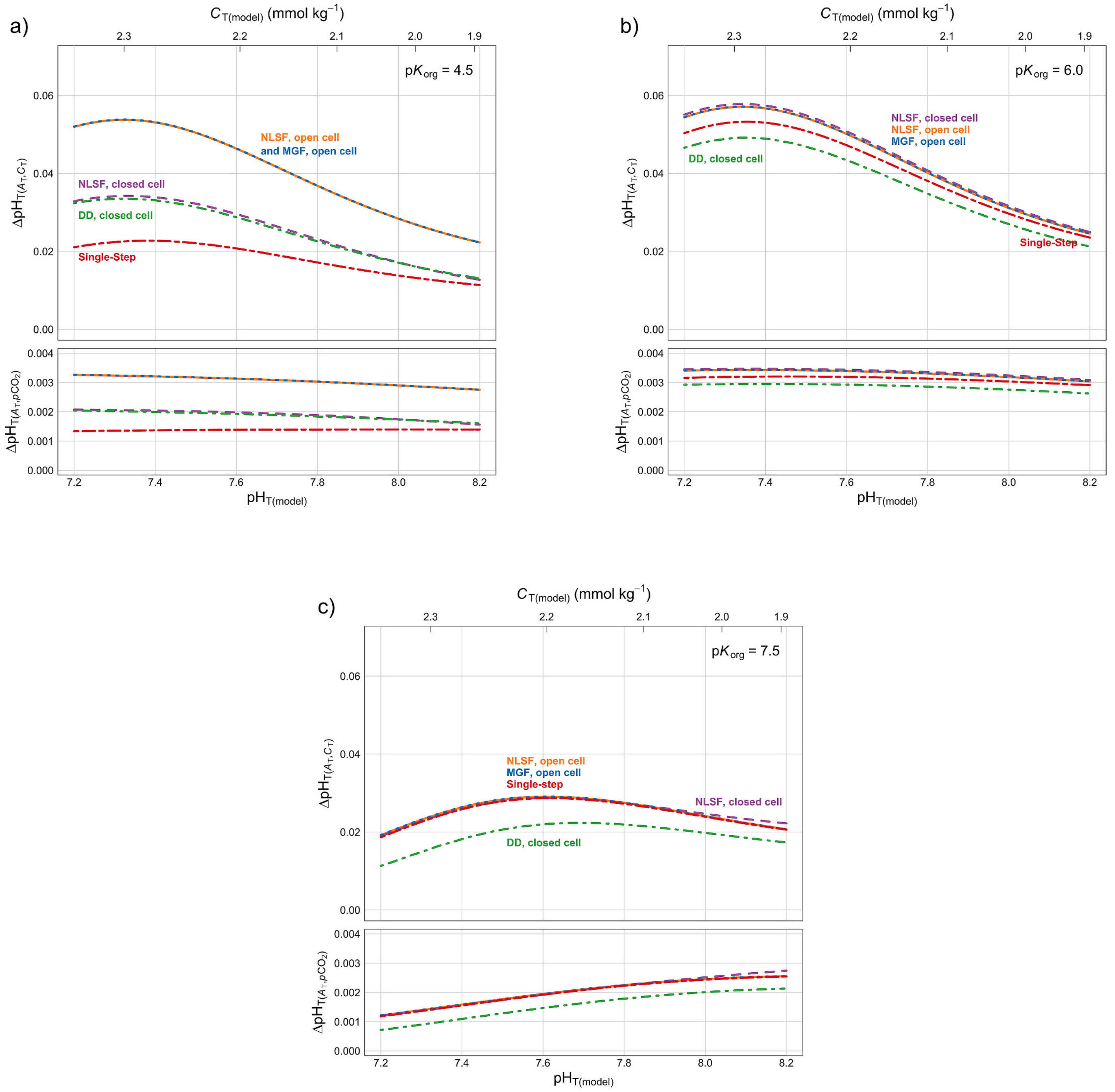

Fig. 8. Modeled differences between pH_T calculated from $A_{T(meas)}$ and another parameter (C_T or pCO_2) versus true $pH_{T(model)}$, as a function of $pH_{T(model)}$ and $C_{T(model)}$. The $C_{T(model)}$ range was determined by calculation with $pH_{T(model)}$ values and a constant A_{inorg} of 2300 μmol kg^{-1}. The sample solutions are oxygenated seawater with $P_T = 1.0$ μmol kg^{-1}, $Si_T = 15.0$ μmol kg^{-1}, $t = 25$ °C, $S = 35$, $p = 1$ atm, and $ORG_T = 20$ μmol kg^{-1}. The results for three pK_{org} values are shown here: (a) pK_{org} = 4.5, (b) pK_{org} = 6.0, and (c) pK_{org} = 7.5. The scale of the bottom panel in each figure is expanded by a factor of about 7 relative to the top panel.

Errors in pCO_2 consistent with those that can arise from calculations based on $A_{T(meas)}$ in organic-influenced environments can predictably lead to CO_2 flux estimates that are significantly in error. However, the results displayed in Fig. 7 demonstrate that those errors can be partially mitigated by choosing to pair $A_{T(meas)}$ with measured pH_T rather than C_T, and can be even further reduced in the presence of low-pK organics by choosing closed-cell titration approaches or the single-step approach rather than multi-step open-cell titrations.

5.4.2. Calculated pH_T

Values of $\Delta pH_{T(AT,Y)}$ were calculated in a similar manner as $\Delta pCO_{2(AT,Y)}$. To illustrate the effect of initial carbonate chemistry on the propagation of nonzero ΔA_T values to calculations of pH_T, Fig. 8 shows $\Delta pH_{T(AT,CT)}$ and $\Delta pH_{T(AT,pCO2)}$ (at 25 °C) as a function of initial pH_T ($pH_{T(model)}$ = 7.2 to 8.2) and corresponding C_T ($C_{T(model)}$ = 2341 to 1895 μmol kg^{-1}) with three fixed pK_{org} values. Inorganic chemical conditions besides pH_T and C_T are given in Table 4. The C_T range was determined by calculation with input pH_T values and a constant A_{inorg} of 2300 μmol kg^{-1}. Additional results for $\Delta pH_{T(AT,Y)}$ are given in Tables A4 and A5.

In this exercise, the effects of organic acids with pK values of 4.5, 6.0, and 7.5 were examined separately. The acid with a pK_{org} of 4.5 (Fig. 8a) can be viewed as a traditional carboxyl-type group, the acid with a pK_{org}

of 6.0 (Fig. 8b) can be viewed as a more basic carboxyl-type group (Ritchie and Perdue, 2003; Tipping, 1998; Tipping and Hurley, 1992), and the acid with a pK_{org} of 7.5 (Fig. 8c) represents the bulk organic pK values (discussed more in section 5.5.1) determined from Baltic Sea data (Kuliński et al., 2014; Ulfsbo et al., 2015). Phenolic-type organics with higher pK values are not included because their high pK values result in minimal contribution to $A_{T(meas)}$.

Fig. 8 shows that $\Delta pH_{T(AT,CT)}$ values are consistently much larger than $\Delta pH_{T(AT,pCO2)}$ values in the presence of titratable organics. This discrepancy between input parameter pairs is due to the aforementioned input-error sensitivity of the iterative procedure to determine pH from A_T and C_T.

In addition to differences in $\Delta pH_{T(AT,Y)}$ based on input parameter pair, different conditions (i.e., pK_{org} value and measurement approach) can produce subtlety different patterns in $\Delta pH_{T(AT,Y)}$ as a function of $pH_{T(model)}$. With pK_{org} values of 4.5 and 6.0, ΔA_T values — which essentially amount to errors in input A_T for calculations of $pH_{T(AT,CT)}$ and $pH_{T(AT,pCO2)}$ — are nearly constant regardless of $pH_{T(model)}$ for a given measurement approach (Table A3). However, the calculation to obtain pH_T from A_T and C_T exhibits greater sensitivity to ΔA_T at low pH_T. So, the slopes in $\Delta pH_{T(AT,CT)}$ as functions of $pH_{T(model)}$ in the top panels of Fig. 8a and b are mainly due to this calculation sensitivity rather than any pattern in ΔA_T as a function of $pH_{T(model)}$. The $pH_{T(AT,pCO2)}$ calculation is more linearly influenced by ΔA_T, so the slopes in the bottom panels of Fig. 8a and b are close to zero. With a pK_{org} value of 7.5, ΔA_T values change as a function of $pH_{T(model)}$ for each measurement approach (Table A3); specifically, ΔA_T increases with higher initial pH_T. However, the $pH_{T(AT,CT)}$ calculation exhibits greater sensitivity to ΔA_T at low pH_T. So, the patterns in $\Delta pH_{T(AT,CT)}$ values as functions of $pH_{T(model)}$ in the top panel of Fig. 8c are results of these two dueling influences. The $pH_{T(AT,pCO2)}$ calculation is more linearly influenced by ΔA_T, so the slopes in the bottom panel of Fig. 8c are modestly positive.

The slopes of $\Delta pH_{T(AT,CT)}$ versus $pH_{T(model)}$ for all approaches except the single-step titration in Fig. 8a ($pK_{org} = 4.5$) and for all approaches in Fig. 8b ($pK_{org} = 6.0$) are between −0.022 and −0.034. These slopes are similar, in terms of sign and magnitude, to those observed in analogous comparisons of pH_T measured spectrophotometrically versus pH_T calculated from open-ocean measurements of A_T and C_T (Carter et al., 2013, 2018; Fong and Dickson, 2019; Williams et al., 2017). This similarity is expected based on the sensitivity of the $\Delta pH_{T(AT,CT)}$ calculation, but emphasizes the possibility explored by Fong and Dickson (2019) that "excess alkalinity" (A_X) from organic bases could be a real complicating factor in internal consistency analyses of marine carbonate system measurements, even in the open ocean. This potential problem of open-ocean organic alkalinity is discussed in more detail in section 5.6.

5.4.3. *Calculated Ω_{ca}*

Calcite saturation state (Ω_{ca}) and aragonite saturation state (Ω_{ar}) are important parameters for modeling ocean geochemistry and for studying the physiology of ocean calcifiers. Here, values of $\Delta\Omega_{ca(AT,Y)}$ were calculated using the same input conditions as were used to calculate $\Delta pH_{T(AT,Y)}$. Fig. 9 shows $\Delta\Omega_{ca(AT,CT)}$, $\Delta\Omega_{ca(AT,pHT)}$, and $\Delta\Omega_{ca(AT,pCO2)}$ as a function of $\Omega_{ca(model)}$. Values of $\Delta\Omega_{ca(AT,Y)}$ are displayed as relative quantities (i.e., percentages of $\Omega_{ca(model)}$) due to the large range of Ω_{ca} (~1–6.5). Additional results for $\Delta\Omega_{ca(AT,Y)}$ are given in Tables A4 and A5.

Similar calculations were performed for the case of aragonite. Relative $\Delta\Omega_{ar(AT,Y)}$ values (not shown) display similar patterns to $\Delta\Omega_{ca(AT,Y)}$. However, because aragonite is more soluble than calcite, the absolute values of $\Delta\Omega_{ar(AT,Y)}$ are smaller in magnitude than those of $\Delta\Omega_{ca(AT,Y)}$.

Fig. 9 shows that $\Delta\Omega_{ca(AT,CT)}$ values are about an order of magnitude larger than both $\Delta\Omega_{ca(AT,pH)}$ and $\Delta\Omega_{ca(AT,pCO2)}$. These large differences, as in the case of calculated pCO_2, are a result of the input-error sensitivity of the iterative process that uses A_T and C_T to determine pH, which is used to calculate $[CO_3^{2-}]$ and, finally, Ω. The differences again highlight the troubling errors that can occur when using the A_T–C_T pair to perform carbonate system calculations for a marine system that contains titratable organics. The relative values of $\Delta\Omega_{ca(AT,CT)}$ can be particularly large at near-saturation conditions (i.e., $\Omega \approx 1$). Like other calculated parameters, $\Delta\Omega_{ca(AT,Y)}$ values are larger for multi-step open-cell methods when pK_{org} is near 4.5.

Errors in calculated Ω, especially under near-saturation conditions, can bring about mischaracterizations of conceptually important geochemical benchmarks. Errors in Ω can lead to the misidentification of saturation horizon depths by hundreds of meters (Naviaux et al., 2019; Patsavas et al., 2015). Further, such errors can lead to misinterpretations of $CaCO_3$ dissolution data. These misinterpretations can encourage the proposal of dissolution suppressors or enhancers, such as soluble reactive phosphate (Berner and Morse, 1974; Walter and Burton, 1986), organic coatings (Honjo and Erez, 1978; Keir, 1980; Naviaux et al., 2019; Subhas et al., 2018), or metabolic processes (Archer, 1991; Emerson and Bender, 1981; Hales, 2003), that may not be active or as significantly active as implied by the misinterpreted data. Accurate description of $CaCO_3$ dissolution behavior is critical in constructing ocean models to reliably predict changes in carbonate chemistry and carbon cycling that will occur in the future as ocean acidification progresses.

Orr et al. (2018) report similar uncertainties in Ω calculations for all input pairs except pH_T-pCO_2. These similarities are primarily due to the high degree of influence that solubility product uncertainty exerts on Ω uncertainty. So, most parameter pairs are equally adequate for calculating Ω in low-organic ocean environments. However, when titratable organics are likely present in solution, the A_T–C_T pair especially should be avoided due to the high degree of Ω uncertainty that can result from that parameter pair (Fig. 9).

5.5. *Practical methods of accounting for organic alkalinity*

As the prevalence of organic alkalinity (A_{org}) in marine and estuarine settings has become more apparent, investigators have examined several different ways to parameterize or directly measure A_{org}. The following subsections review those methods, which are summarized in Table 5.

5.5.1. *Parameterization using [DOC]*

One way to estimate the effect of dissolved organics on alkalinity titrations is to use measurements of [DOC] paired with empirical characterizations of organic protonation behavior. Kuliński et al. (2014), working in the organic-rich Baltic Sea, parameterized a bulk dissociation constant for dissolved organics in a given dataset (K_{DOM}), along with the fraction (f) of [DOC] that carries weakly acidic groups that are protonated during an alkalinity titration by using the equation:

$$K_{DOM} = \frac{[H^+]A_{org}}{(f \cdot [DOC]) - A_{org}} \tag{18}$$

A_{org} values were determined by subtracting A_{inorg} calculated from pH_T and C_T from $A_{T(meas)}$ obtained by titration (i.e., $A_{org} = A_{T(meas)} - A_{inorg}$). Then, K_{DOM} and f were parameterized by a nonlinear least squares fit using Eq. (18) with estimates of A_{org} and measurements of $[H^+]$ and [DOC].

It should be noted that, with an approach like this, all uncertainties in equilibrium constants and thermodynamic inconsistencies in carbonate system measurements are incorporated into the A_{org} term. Yang et al. (2015) calculated that A_{org} values determined based on differences between measured and calculated A_T could be reasonably attributed to an organic influence only if they were greater than about 8 μmol kg^{-1}. The authors used this conclusion to advocate for direct measurements of organic alkalinity in coastal environments, with uncertainties much smaller than 8 μmol kg^{-1}.

Another way to estimate the effect of dissolved organics on alkalinity titrations is to use a humic acid proton-binding model such as the

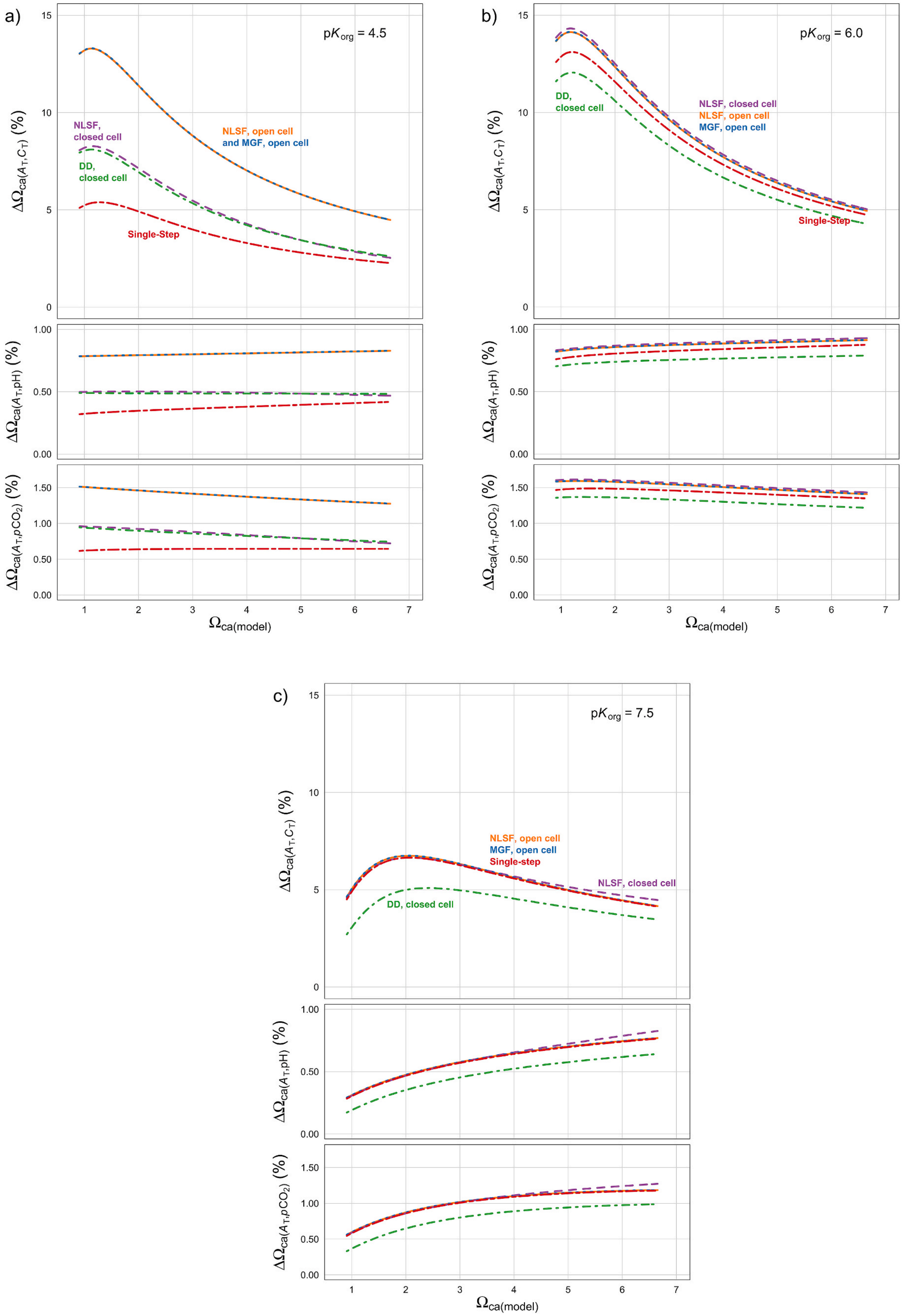

Fig. 9. Modeled relative differences between Ω_{ca} calculated from $A_{T(meas)}$ and another parameter (C_T, pH_T, or pCO_2) versus $\Omega_{ca(model)}$, as a function of $\Omega_{ca(model)}$. The compositions of the sample solutions are identical to those used for Fig. 8. Three pK_{org} values are modeled: (a) $pK_{org} = 4.5$, (b) $pK_{org} = 6.0$, and (c) $pK_{org} = 7.5$. In each figure, the scale of the panels is different.

Windermere Humic Aqueous Model (WHAM) (Tipping et al., 2011), which uses a continuous distribution of pK values to represent the proton-exchange properties of humic substances. This can be useful in coastal waters or inland seas — like the Baltic — that are highly influenced by the input of terrestrial organics. Ulfsbo et al. (2015) obtained pK_{DOM} and f values for a corrected version of the Kuliński et al. (2014) Baltic sea dataset; they compared their f value ($f = 0.12$) to that which would be predicted by WHAM ($f = 0.125$), and obtained impressive agreement.

Whether using bulk K_{DOM} values or a humic acid model like WHAM to account for organic alkalinity, the results are necessarily informed by ancillary measurements of [DOC] and overdeterminations of the carbonate system. Though these ancillary measurements add complexity to alkalinity analyses, they also provide more realistic representations of acid–base behavior (by including a term for organics in the A_{T} equation) and can reduce errors in carbonate system calculations (by allowing more accurate estimates of A_{inorg}). Methods like these should be tested more extensively in a wide array of marine and estuarine environments to assess the universality or regionality of certain bulk pK_{DOM} values and organic acid proton-binding models.

5.5.2. *Secondary titrations*

A more rigorous option for assessing organic alkalinity on a sample-by-sample basis is to augment traditional alkalinity titrations with secondary titrations after removal of dissolved CO_2. Secondary titrations were used by many of the references in Table 3 to estimate the pK values of natural organics.

As an example, Yang et al. (2015) described a fast spectrophotometric secondary titration procedure that builds upon the open-cell single-step titration approach of measuring A_{T}. After the initial open-cell alkalinity titration and removal of CO_2, NaOH is added to raise sample pH. Then a secondary acidimetric titration is performed using bromocresol purple as an indicator (to cover pH 6–4.5). This process is then repeated using cresol red as an indicator for the secondary titration (to cover pH 8–6). These secondary titrations provide an explicit measurement of A_{org}, which can then be subtracted from $A_{\mathrm{T(meas)}}$ (obtained from the initial titration) to determine A_{inorg}. This method benefits from the precision offered by spectrophotometric pH indicators; it is also relatively fast and does not require a separate [DOC] measurement.

The work of Yang et al. (2015) provides a valuable framework for the continued development of alkalinity titration procedures that explicitly account for organic influence. Consistency in titration procedure and data analysis methodology is important here. The initial acidimetric titration should be terminated at a pH that provides a reliable measurement of A_{T} (e.g., pH = 4.20) and is able to be repeated with precision so that the same organic functional groups are titrated during each A_{org} measurement.

5.5.3. *Novel curve-fitting methods*

Novel titration curve-fitting methods should also be explored as a way to incorporate organics into A_{T} determinations. Asuero and Michałowski (2011) and Michałowski and Asuero (2012) have described computational procedures flexible enough to analyze titration curves for complex systems such as natural waters. Unlike traditional alkalinity titration data analysis methods that pre-suppose a particular acid–base model, these curve-fitting methods emphasize the description of constituents with undefined compositions and proton-exchange properties (e.g., fulvic acids).

5.6. *Organic alkalinity in the open ocean?*

It has generally been postulated that titratable dissolved organics have little to no effect on $A_{\mathrm{T(meas)}}$ values obtained from open-ocean alkalinity titrations. However, consider typical open ocean surface DOC concentrations (Hansell et al., 2009) of about 70–80 μmol kg^{-1}. If, as in Ulfsbo et al. (2015), it is assumed that this DOC is composed entirely of WHAM fulvic acid, then we can use $f = 0.125$ as an estimate of the fraction of weakly acidic groups of DOC that will be protonated across the pH range of an alkalinity titration. Multiplying 70–80 μmol kg^{-1} of DOC by 0.125 results in about 8.8–10.0 μmol kg^{-1} of titratable organic matter in open ocean surface waters. Assigning this organic matter a functional pK of 7.34 (Ulfsbo et al., 2015) results in up to about 8.5 μmol kg^{-1} of measured excess alkalinity.

Admittedly, the assumption that all marine DOC consists of WHAM terrestrial fulvic acid is an oversimplification (Tipping et al., 1991). Additionally, the pH distribution of fulvic acid ionizable sites would be somewhat different for open ocean seawater ($S \approx 35$, $C_{\mathrm{T}} \approx 2000$) than for the Baltic Sea water ($S = 6.15$, $C_{\mathrm{T}} = 1470$) studied by Ulfsbo et al. (2015).

Still, many of the fundamental molecular structures in terrestrially-derived organics also occur in marine dissolved organic matter (e.g., Arakawa et al., 2017) and terrestrial organic matter can be transported to the deep ocean by ocean circulation (Medeiros et al., 2016). Further, phytoplankton culture studies have shown that autochthonous marine dissolved organic molecules do contain ionizable sites, some of which participate in proton exchange across the range of a typical alkalinity titration. Kim and Lee (2009), for example, demonstrated a species-specific relationship between ΔA_{T} and [DOC] in marine phytoplankton cultures; Ko et al. (2016) assigned numerical pK values to DOC produced by marine phytoplankton (see Table 3). The slopes reported by these authors for ΔA_{T}–[DOC] relationships actually suggest much larger f values than predicted by the WHAM model, so it is reasonable to expect dissolved organics to influence alkalinity titrations, even in open ocean waters.

This expectation is supported by evidence from carbonate system internal consistency analyses. Repeatedly observed disagreements between certain measured and calculated parameters can be remedied by the introduction of excess alkalinity terms, and many authors have suggested organics as a source of this excess. Millero et al. (2002) assumed some amount of excess alkalinity on two WOCE Pacific Ocean cruises to bring measured versus calculated CO_2 fugacity values into agreement. Patsavas et al. (2015) subtracted 0.18% (~4 μmol kg^{-1}) of measured A_{T} from shelf samples ($S \leq 35$) on two coastal ocean cruises to bring measured versus calculated A_{T} values into agreement. Fong and Dickson (2019) subtracted between 3.5 and 6.6 μmol kg^{-1} from measured A_{T} values on four separate GO-SHIP cruises to bring measured versus calculated pH$_{\mathrm{T}}$ values into agreement.

Realistic representations of excess alkalinity from organics would not, however, be wholesale corrections to datasets, but would include protonation characteristics (i.e., pK_{org} values) and concentrations that vary with location, depth, and time. Hertkorn et al. (2013) emphasized the change in dissolved organic matter composition as a function of depth in the ocean; specifically, they showed that the fraction of carboxylic acids in the dissolved organic matter pool increases with depth. This or any other change in composition would influence the way the dissolved organics in a sample respond to an alkalinity titration, thus changing the appropriate value of A_{X}.

To account for likely spatial variations in A_{X} values, studies can be undertaken to constrain the protonation characteristics of the dissolved organic matter pool in different ocean regions. Perhaps future GO-SHIP cruises could incorporate back-titrations for a subset of A_{T} measurements to investigate these characteristics. Alternatively, alkalinity anomalies could be paired with [DOC] data to infer organic protonation characteristics. Acquisition of these data would surely be a substantial undertaking, but would allow for future evaluations of marine A_{T} with realistic representations of organic alkalinity — including geographic- and depth-dependent estimates of pK values. This more complete thermodynamic model of seawater acid–base behavior should help to resolve inconsistencies between measured and calculated pH values (see section 5.4.2), along with other carbonate system parameters.

6. Conclusions

Most modern alkalinity titration data analysis methods that are used throughout the marine chemistry community produce $A_{T(meas)}$ values that accurately describe A_T (and A_{inorg}) when performed on carefully collected titration data from systems where alkalinity is controlled exclusively by inorganic chemical species (i.e., where $A_T = A_{inorg}$; Fig. 3). However, when titratable organics with pK values between about 2.5 and 9.5 are present in solution (Fig. 4), potentially significant differences (ΔA_T) between reported $A_{T(meas)}$ and A_{inorg} occur, no matter the data analysis method. Those differences are largest for organic molecules with pK values between about 5 and 7.

When low-pK titratable organics (i.e., $2.5 < pK_{org} < 6.0$) are present, quantitative differences occur among the ΔA_T values resulting from the five A_T measurement approaches studied in this work (Figs. 4 and 5). The largest ΔA_T values in this low-pK_{org} range are associated with multi-step open-cell titrations that are analyzed by either MGFs or NLSFs. These low-pK results are especially important because a common class of organic functional groups found in natural waters — carboxyl groups — exhibit pK values in this problematic range. If alkalinity measurements are being made in a system expected to have a high concentration of low-pK organics, and accurate A_{inorg} values are critical for a research goal, this outsized influence on multi-step open-cell titrations should be kept in mind. If, however, consistency in alkalinity titration results over time is critical, the current A_T measurement practices should certainly be retained.

Non-zero values of ΔA_T can lead to significant systematic errors in carbonate system parameters calculated from $A_{T(meas)}$ in organic-influenced environments (i.e., when $A_{T(meas)}$ is presumed equal to A_{inorg}). These errors, like values of ΔA_T, exhibit differences among measurement methods, especially in the presence of low-pK titratable organics. Errors in calculated $p\text{CO}_2$ (Fig. 7), pH_T (Fig. 8), and Ω (Fig. 9) incurred by incorrectly equating $A_{T(meas)}$ with A_{inorg} are each significantly greater for the A_T–C_T input pair than for any other input pair. Errors in calculated $p\text{CO}_2$ can yield air–sea CO_2 flux estimates with particularly large errors (either too low a CO_2 flux out of the ocean or too great a CO_2 flux in). Errors in calculated pH_T may contribute to the internal inconsistencies often observed in over-determined marine carbonate system datasets. Errors in calculated Ω are often greatest in terms of percentages under conditions of near-saturation and may therefore skew efforts to identify saturation horizon depths and interpret $CaCO_3$ dissolution data.

An important point to emphasize is that when organic acids with pK_{org} values near the *ZLP* ($pK_A^0 = 4.5$) are present, $A_{T(meas)}$ becomes an ambiguous representation of A_T. Dickson's (1981) cutoff between proton acceptors and donors was designed to describe alkalinity associated with inorganic chemical species that have the following properties in natural waters: (1) all have well-defined and discrete pK_A^0 values and (2) none have a pK_A^0 value close to 4.5. Organic functional groups found in natural waters, however, do not exhibit these properties. Instead, they (1) exhibit a continuous spectrum of pK_A^0 values and (2) appear to be characterized by a major functional class that exhibits dissociation behavior very near $pK_A^0 = 4.5$ (carboxyl groups). This functional behavior of dissolved organics results in ambiguity as to how to treat them in the context of defining and measuring A_T.

Several characteristics of organics in natural waters suggest that the way total alkalinity is measured, particularly in coastal and estuarine environments, should be re-evaluated: the ubiquity and heterogeneity of titratable organics, the inability of traditional alkalinity titration methods to obviate the influence of organics on carbonate system calculations, and the ambiguity of $A_{T(meas)}$ values in the presence of low-pK organics. Section 5.5 suggests some practices that can be implemented to account for organic alkalinity. In implementing any changes, a major focus should be on optimizing new or revised analytical procedures for precision, accuracy, simplicity, and speed, while keeping in mind the continuous spectrum of pK values displayed by natural dissolved organic matter.

Finally, it must be recognized that the organic alkalinity problem may exist not only in coastal areas but the open ocean as well. Overall, recent indications of significant contributions by organic matter to alkalinity titrations in a wide array of environments should motivate a critical evaluation of how A_T is determined in marine and estuarine waters around the globe.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.dsr.2020.103338.

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