LIMNOLOGY
and
OCEANOGRAPHY: METHODS

Limnol. Oceanogr.: Methods 2025

doi: 10.1002/lom3.70002

COMPARATIVE AND INTERCALIBRATION STUDIES

Comparison of open cell and single-step total alkalinity titration methods and implications for organic alkalinity

Ryan J. Woosley,[1]* **Jessica A. Bruno**,[1] **Daina Neithardt**,[1] **Zhaohui Aleck Wang**,[2] **Nagisa Fujiki**,[3] **Masahito Shigemitsu**,[4] **Akihiko Murata**[4]

[1]Center for Sustainability Science and Strategy Department of Earth Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, Massachusetts, USA; [2]Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts, USA; [3]Department of Marine and Earth Sciences, Marine Works Japan LTD., Yokosuka, Japan; [4]Research Institute for Global Change, Japan Agency for Marine-Earth Science and Technology, Yokosuka, Japan

Abstract

An open question in marine carbon chemistry is if organic alkalinity (or some other unidentified species) is present in non-negligible quantities in the open ocean. If organic alkalinity is indeed present, different methods for total alkalinity (TA) analysis with different titration endpoints could titrate different amounts depending on the dissociation constants ($\mathrm{pK_a}$) of the acids present, resulting in meaningful differences or offsets between methods. Two commonly used methods, open-cell titration with non-linear least squares fitting and single-step titration with spectrophotometric endpoint detection, might titrate different amounts of organic alkalinity, if present, depending on their $\mathrm{pK_a}$. We test this hypothesis using paired samples collected on two cruises, one in the northwest Pacific and one in the western Arctic, and analyze the TA using both methods. We found the differences to be statistically indistinguishable ($\Delta \mathrm{TA}_{[\text{Open-Cell}-\text{Single-Step}]} = 0.5 \pm 3.9\ \mu\mathrm{mol\ kg^{-1}}_{\mathrm{sw}}$ mean and standard deviation $N = 206$). Adjustment of the single-step TA to certified reference material could be obscuring a difference in the methods. The good agreement between methods indicated that the analytical method is not the cause of offsets in Pacific TA identified by the Global Ocean Data Analysis Project version 2. From these results, the presence of organic alkalinity in open ocean waters remains inconclusive but suggests that if present, the concentration is either very low or both methods titrate similar amounts.

Precise and accurate measurements of the marine carbon system are crucial for monitoring the carbon cycle, quantifying the uptake of carbon dioxide ($\mathrm{CO_2}$) from the atmosphere, rates of ocean acidification, and increasingly, determining impacts of potential geoengineering strategies such as ocean alkalinity enhancements (Oschlies et al. 2023). Of the four commonly measured inorganic carbon system parameters (dissolved inorganic carbon (DIC), $\mathrm{pH_T}$ (on the total scale), total alkalinity (TA), and fugacity of $\mathrm{CO_2}$ ($f\mathrm{CO_2}$), accurate measurement of TA presents unique challenges. The marine chemistry community typically uses the titration alkalinity definition as laid out by Dickson (1981):

$$\begin{aligned}\mathrm{TA} = {} & \left[\mathrm{HCO_3^-}\right] + 2\left[\mathrm{CO_3^{2-}}\right] + \left[\mathrm{B(OH)_4^-}\right] + \left[\mathrm{OH^-}\right] + \left[\mathrm{HPO_4^{2-}}\right] \\ & + 2\left[\mathrm{PO_4^{3-}}\right] + \left[\mathrm{SiO(OH)_3^-}\right] + [\mathrm{NH_3}] + [\mathrm{HS^-}] \cdots - \left[\mathrm{H^+}\right]_\mathrm{F} \\ & - \left[\mathrm{HSO_4^-}\right] - [\mathrm{HF}] - [\mathrm{H_3PO_4}] - \cdots \end{aligned} \tag{1}$$

Brackets denote total ion concentrations, $[\mathrm{H^+}]_\mathrm{F}$ is the free hydrogen ion concentration, and ellipses denote either unidentified or negligible acids or bases. Conventional wisdom has long held that for open ocean seawater, the concentrations of acids or bases not explicitly accounted for in Eq. 1 were either zero or so low as to be negligible for most purposes. Although the presence of organic acids/bases has long

---

*Correspondence: rwoosley@mit.edu

Associate editor: Hayley Schiebel

been known to be significant in many coastal waters (Cai et al. 1998; Hammer et al. 2017; Hunt 2021; Hunt et al. 2024; Kerr et al. 2021; Song et al. 2020; Wang and Cai 2025).

Several studies have hypothesized that organic alkalinity may be present in open ocean seawater at low (∼ 4–8 μmol $kg^{-1}{}_{sw}$), but non-negligible concentrations (Fong and Dickson 2019; C. H. Lee et al. 2024; Lueker et al. 2000; Millero et al. 2002) and should therefore be explicitly accounted for in Eq. 1. However, attempts to test this hypothesis are often inconclusive (Álvarez et al. 2020; Sharp and Byrne 2021, 2020; Woosley and Moon 2023). The three main reasons testing this hypothesis is difficult are that organic alkalinity is a class of chemicals with a spectrum of properties rather than a single acid/base system, uncertainties in the concentration of boron present in seawater manifest in a similar manner to an unidentified species (Fong and Dickson 2019; K. Lee et al. 2010; Woosley and Moon 2023), and concentrations are near detection limits. Existing methodologies allow for techniques that can directly determine the concentration of organic (or unidentified) alkalinity (Cai et al. 1998; C. H. Lee et al. 2024; Song et al. 2020) in a sample, but they are extremely time-consuming to perform and require special setups that are not commonly available. The technique also relies on knowing the concentration of other non-CO_2 acid/base systems accurately (Sharp and Byrne 2021). The choice of which of the two commonly used values for the boron to salinity relationship (K. Lee et al. 2010; Uppström 1974) introduces a potential uncertainty of around 5 μmol $kg^{-1}{}_{sw}$ near a practical salinity (S_p) of 35, a value comparable to the amount of organic alkalinity that may be present in open ocean water.

There are two potential practical impacts if organic or other acid/base species are present but not accounted for. The importance of such impacts will vary depending on the purpose of a given study. If the analytical methods used are able to fully titrate the organic alkalinity (i.e., the TA is accurate) calculations of carbonate alkalinity will be overestimated. In such a scenario, calculations of other carbon system parameters (e.g., fCO_2, carbonate) as well as derived values such as saturation state and CO_2 fluxes will be inaccurate despite an accurate value of TA. If the analytical methods are not capable of detecting organic alkalinity, then the TA measured would be inaccurate, but inorganic carbon system calculations would not be adversely affected. Calculated pH_T is an exception as the impacts for either scenario would be more complicated and condition specific. Recent work has shown that the type of titration employed and the endpoint detection method can indeed impact the accuracy of TA when organic alkalinity is present (Hunt 2021; Sharp and Byrne 2020; Song et al. 2023). The cause, as well as how significant the inaccuracies are, depends on the specific properties and amounts of the organic matter present. Specifically, errors in accuracy will be higher when the organic acids have a low dissociation constant ($pK_a < \sim 6$; Sharp and Byrne 2020), and methods that employ a lower endpoint pH for fitting will better (although not necessarily completely) titrate organic alkalinity.

The main reason different methods could produce different values of TA in the presence of organic alkalinity is differences in the endpoint pH of the titration. For an open-cell titration with nonlinear least squares fitting (NLSF) titration data from a pH_T range of ∼ 3.0–3.5 is used (Dickson et al. 2003). In a single-step titration with purging of CO_2 an approximate final pH_T value of ∼ 4.2 is obtained (Yao and Byrne 1998) although the exact value will vary. Such differences in endpoints do not impact titrations of inorganic alkalinity because in the definition of Dickson (1981) proton donors and proton acceptors are separated by three orders of magnitude, resulting in an unambiguous separation of acids and bases. However, for organic acids/bases, some functional groups with dissociation constants near the conventionally assigned proton condition ($pK_a \leq 4.5$ at 25°C, zero ionic strength, and atmospheric pressure) defined by Dickson (1981) make their role as proton donors or acceptors ambiguous. In the single-step method, the higher pH of the endpoint (i.e., earlier termination of the titration) would cause less low pK_a organic matter to be titrated, resulting in a lower measured TA if the pK_a were $< \sim 6$ (Sharp and Byrne 2020). For organic matter with high pK_a values, the two methods would produce nearly identical TA values. The methods and theory underlying the ambiguous and complicated contribution of organic acids and bases are discussed extensively in Sharp and Byrne (2020) and references therein.

The implications of a method-dependent quantification of organic alkalinity pose a significant challenge for detecting long-term changes in TA or when comparing measurements made by different laboratories. Although different analytical techniques could potentially produce slightly different values for TA, the data reported are often treated and analyzed without regard to method. The Global Ocean Data Analysis Project (GLODAP) version 2 (Olsen et al. 2016) noted a ∼ 6 μmol $kg^{-1}{}_{sw}$ offset in the TA in the north Pacific Ocean between several cruises led by Japanese laboratories and United States laboratories, although the offset has been less clear in recent updates (Olsen et al. 2020, 2019). The cause of this offset could not be identified, but one hypothesis is the presence of organic alkalinity and differences in analytical methodology. In addition, other differences such as the use (or not) of certified reference materials (CRMs) could also explain the results. Even though the GLODAPv2 covers many decades and methods, and laboratories and methods likely changed over time, in general U.S. laboratories use a Gran titration with either a modified Gran function or NLSF for end-point detection (Dickson et al. 2003), while Japanese laboratories tend to use the single-step titration method with spectrophotometric endpoint detection (Yao and Byrne 1998). If organic acids with pK_a values less than ~ 6 are present in the northwest Pacific, an offset between the two countries laboratories could occur and explain at least part of the offset. Modeling of different titration methods and fitting procedures indicate that the open-cell NLSF titrations will titrate more organic alkalinity than single-step titrations when the $\mathrm{pK_a}$ is less than ~ 6 (Sharp and Byrne 2020) which could lead to a lower measured TA when using the single-step method. However, crossover and inversion analyses such as that done by GLODAP provide no information on the causes of any offsets found between cruises. The best way to test for methodological differences is a direct intercomparison.

Materials and procedure

Sample locations and collection

In order to test if differences in methods lead to offsets in open water TA measurements, samples were collected on two research cruises aboard the *R/V Mirai* in 2023, and MR23-07 (EXPOCODE 49NZ20231006; WOCE/CLIVAR P14 Line) and MR23-06C (EXPOCODE 49NZ20230825; Arctic Challenge for Sustainability II) in the western Arctic Ocean (Watanabe et al. 2025). For simplicity, the northwest Pacific cruise will be referred to as P14 and the Arctic cruise will be referred to as Arctic. The location of the cruises allows for testing of a wide range of TA (1800–2400 $\mu\mathrm{mol\ kg^{-1}}_{\mathrm{sw}}$) and (potentially) organic alkalinity.

At selected stations (Fig. 1) and depths, 207 pairs of samples were collected for TA, DIC, and $\mathrm{pH_T}$ analysis onboard by the Japan Agency for Marine-Earth Science and Technology (JAMSTEC) and analysis in the laboratory onshore at the Massachusetts Institute of Technology (MIT), Cambridge, Massachusetts, USA. Samples for inorganic carbon parameter analysis were collected in standard borosilicate glass bottles, except for $\mathrm{pH_T}$ onboard during P14 where samples were collected in 100-mL aluminum bottles (Mini Bottle Can, Daiwa Can Company). The $\mathrm{pH_T}$ was not measured onboard for the Arctic. For P14, 17–28 paired bottles were collected at 6 stations, allowing for a full depth profile and a wide range of TA values. For the Arctic, 3–12 paired bottles were collected at 14 stations.

The borosilicate glass bottles were filled following standard operating procedures (Dickson et al. 2007). A precise ~ 1% headspace was created by using a pipette to remove an exact volume after the bottle was filled to overflowing. Bottles were sealed using Apiezon L vacuum grease, and stoppers were kept in place by a rubber band and plastic hose clamp. All samples to be analyzed on land and the DIC and TA samples analyzed on board for the Arctic had 120 μL of saturated $\mathrm{HgCl_2}$ added, resulting in a total concentration of 0.04% (vol.) $\mathrm{HgCl_2}$. Samples collected for ship-based TA analysis for P14 were not poisoned. All samples were stored in the dark until analysis. Ship-analyzed samples were stored in the refrigerator (4°C) until analysis, and land-analyzed samples were stored at room temperature.

On P14, samples for shipboard $\mathrm{pH_T}$ at 25°C were rinsed three times and filled by allowing approximately twice the volume to overflow and then closed without a headspace. Samples were stored refrigerated (4°C) until analysis, which occurred within 12 h of sampling.

The land-based measurements of DIC and $\mathrm{pH_T}$ were used for internal consistency calculations and to verify that any differences found between samples could not be attributed to changes during storage. The different types of samples collected and methods used are summarized in Table 1. Full analytical methods are described in the following sections.

Total alkalinity analysis

Single-step titration (TA_{SS})

Samples for TA were measured on board using the single-step titration method (Yao and Byrne 1998). These samples will be denoted as TA single step ($\mathrm{TA_{ss}}$). Measurement of TA was made based on spectrophotometry with a single acid addition procedure using a custom-made system (Nippon ANS, Inc.). The system comprised a water dispensing unit, an autosyringe (Hamilton) for hydrochloric acid, a spectrophotometer (TM-UV/VIS C10082CAH, Hamamatsu Photonics), and a light source (Mikropack), which were automatically controlled by a computer. The water dispensing unit had a water-jacketed pipette (~ 40 mL at 25°C) and a titration cell, which was also controlled to 25°C ± 0.1°C.

A seawater sample of approximately 40 mL was transferred from a sample bottle (DURAN® glass bottle, 100 mL) into the pipette by pressurizing the sample bottle (nitrogen gas) and was introduced into the titration cell. The seawater was used to rinse the titration cell. Then, Milli-Q water was introduced into the titration cell, also as a rinse. Approximately 40 mL of sample was dispensed again by the pipette and transferred into the titration cell. Then, absorbances were measured at three wavelengths (730, 616, and 444 nm) as a seawater blank. After the blank measurement, an acid titrant with bromocresol green indicator dye was added into the titration cell. The volume of the acid titrant added varied between ~1.6 and ~ 2.1 mL according to estimated values of TA. The seawater plus acid titrant solution was stirred for over 9 min with bubbling by nitrogen gas in the titration cell to drive off evolved $\mathrm{CO_2}$ gas. Then, absorbances at the three wavelengths were measured. Calculation of TA in $\mu\mathrm{mol\ L^{-1}}$ was made by the following equation:

$$\mathrm{TA} = \left(-\left[\mathrm{H^+}\right]_{\mathrm{T}} V_{\mathrm{SA}} + M_{\mathrm{A}} V_{\mathrm{A}}\right)/V_{\mathrm{S}} \tag{2}$$

where M_{A} is the molarity of the acid titrant added to the seawater sample, $[\mathrm{H^+}]_{\mathrm{T}}$ is the final total hydrogen ion concentration in the seawater plus titrant, and V_{S}, V_{A}, and V_{SA} are the initial seawater volume, the added acid titrant volume, and the combined seawater plus acid titrant volume, respectively. $[\mathrm{H^+}]_{\mathrm{T}}$ is calculated from the measured absorbances based on the following equation (Yao and Byrne 1998):

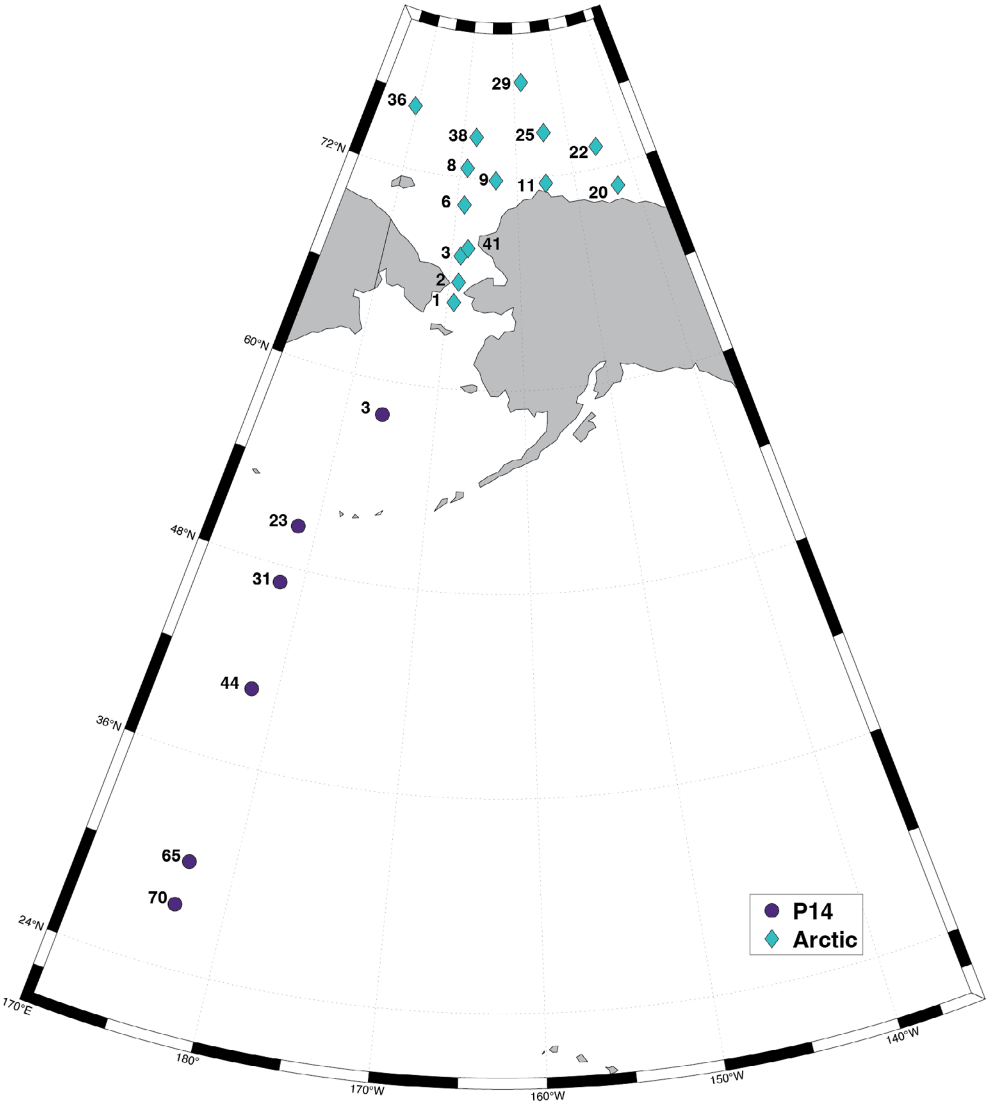

Fig. 1. Location of stations where samples were collected with their respective cruise station numbers. Purple circles are from P14 and teal diamonds are from the Arctic.

$$\mathrm{pH_T} = 4.2699 + 0.002578(35 - S_\mathrm{P}) + \log((R - 0.00131)/(2.3148 - 0.1299 * R)) - \log(1 - 0.001005 * S_\mathrm{P}) \tag{3}$$

where R is the absorbance ratio calculated as:

$$R = (A_{616} - A_{730})/(A_{444} - A_{730}) \tag{4}$$

where A_i is the absorbance at wavelength i nm. The final $\mathrm{pH_T}$ ranged from 3.5–4.1, with all but one sample in the range 3.8–4.1. The TA was converted to units of μmol $\mathrm{kg^{-1}}_{\mathrm{sw}}$ using density determined from S_P and pipette temperature.

The repeatability calculated from replicate seawater samples was 0.7 ± 0.6 μmol $\mathrm{kg^{-1}}_{\mathrm{sw}}$ ($N = 76$). The acid was prepared by JAMSTEC through dilution of 0.5 mol $\mathrm{L^{-1}}$ HCl of known concentration to 0.05 mol $\mathrm{L^{-1}}$ in a 5-L volumetric flask with a background concentration of 0.65 mol $\mathrm{L^{-1}}$ NaCl and 38 μmol $\mathrm{L^{-1}}$ bromocresol indicator. The concentration was calculated from the dilution factor. HCl acid titrant batches 230620-1 and 230620-2 were used for P14 and 230615-1 for the Arctic. Batch numbers are assigned by JAMSTEC when preparing the acid. Certified reference materials from batch 209 provided by Andrew G. Dickson (University of California, San Diego) were used as a standard and were measured at every other station. The difference between the measured and certified value (ΔCRM = Measured − Certified) was −7.0 ± 1.8 ($N = 24$), and –9.7 ± 1.5 μmol $\mathrm{kg^{-1}}_{\mathrm{sw}}$ ($N = 10$) for P14, and –2.7 ± 3.5 ($N = 21$) μmol $\mathrm{kg^{-1}}_{\mathrm{sw}}$ for the Arctic. Measured sample $\mathrm{TA_{SS}}$ was adjusted at the end of the cruise using the ratio of the mean measured CRM value and the certified value for

Table 1. Sampling and methodological details of the different carbon system analysis performed.

Measurand	Abbreviation	Cruises collected	Analysis location	Analysis laboratory	Collection bottle	$HgCl_2$ added	Storage until analysis	Storage time before analysis	Analysis method	CRM adjustment	Endpoint pH_T
TA	TA_{SS}	P14	Ship	JAMSTEC	100-mL borosilicate glass (DURAN®)	No	4°C, dark	< 24 h	Single-step titration	Yes	3.5–4.1
		Arctic	Ship	JAMSTEC	250-mL Brosilicate glass[*]	Yes	4°C, dark	< 60 d (in port at end of cruise)	Single-step titration	Yes	3.5–4.1
	TA_{OC}	P14, Arctic	Lab	MIT	250-mL borosilicate glass (corning)[†]	Yes	Room temp, dark	∼ 15–16 months	Open-cell NLSF	No	3.0–3.5
DIC	DIC_{Ship}	P14	Ship	JAMSTEC	250-mL borosilicate glass (DURAN®) with inner cap	Yes	4°C, dark	< 24 h	Coulometric	Yes	—
		Arctic	Ship	JAMSTEC	250-mL borosilicate glass[*]	Yes	4°C, dark	< 60 d(in port at end of cruise)	Coulometric	Yes	—
	DIC_{Lab}	P14, Arctic	Lab	MIT	250-mL borosilicate glass (corning)[†]	Yes	Room temp, dark	∼ 15–16 months	Coulometric	Yes	—
pH_T at 25°C	pH_{TShip}	P14	Ship	JAMSTEC	100-mL aluminum bottle	No	4°C, dark	< 12 h	Potentiometric	—	—
pH_T at 20°C	pH_{TLab}	P14, Arctic	Lab	MIT	250-mL borosilicate glass (corning)[†]	Yes	Room temp, dark	∼ 15–16 months	Spectrophotometric with meta-cresol purple indicator	—	—

[*] TA and DIC were analyzed from the same bottle.

[†] TA, DIC, and pH_T were analyzed from the same bottle.

each batch of acid. The ratio was 0.99683315 and 0.99561165 for P14 and 0.99828085 for the Arctic. Samples for P14 were analyzed within 24 h of collection, and samples for the Arctic were analyzed in port at the end of the cruise (within 60 d of collection).

Open-cell titration (TA_{OC})

Total alkalinity samples for land-based analysis were carried out in the laboratory based at MIT at 20°C ± 0.1°C approximately 15–16 months after collection. Samples were analyzed using a custom-built open-cell titrator designed and built by the laboratory of Andrew G. Dickson (University of California, San Diego) and described in Dickson et al. (2007, 2003). These samples will be referred to as open-cell TA (TA_{OC}). The instrument used an open-cell Gran titration with a NLSF approach that accounts for reactions with sulfate and fluoride ions. The acid titrant was ~ 0.1 mol kg^{-1} HCl in ~ 0.6 mol kg^{-1} NaCl. The exact concentration of the acid was calibrated by borax titration with methyl red indicator (Klothoff, 1926). Certified reference materials from batch 216 provided by Andrew Dickson (University of California, San Diego) were analyzed at the beginning and end of each day. The mean ΔCRM and standard deviation were 0.71 ± 0.88 ($N = 28$). No adjustment was made to samples based on the ΔCRM value because all components of the instrument are independently calibrated and the measured value is within the 95% confidence interval of the certified value. Analysis of replicate samples was not possible due to water budget limitation preventing an estimate of repeatability.

Dissolved inorganic carbon

Ship-board DIC (DIC_{Ship})

The DIC was measured onboard using an automated TCO_2 analyzer (Nippon ANS, Inc.) with coulometric detection and will be denoted as DIC_{Ship}. Samples were analyzed at 20°C ± 0.1°C. Approximately 15 mL of sample is dispensed via a six-port autosampler into a stripping chamber where DIC is converted to $CO_{2(g)}$ by adding 10% (v/v) phosphoric acid solution. Pure nitrogen gas (99.9999%) is used as a carrier gas to pass the evolved $CO_{2(g)}$ through an electric dehumidifier and chemical desiccant ($Mg(ClO_4)_2$) and finally to a coulometric detector. An in-house made JAMSTEC DIC reference material was used to account for coulometer drift as well as CRMs provided by Andrew Dickson (University of California, San Diego). The repeatability of DIC_{Ship} analysis determined from replicate samples was $0.7 \pm 0.6\,\mu$mol kg$^{-1}{}_{sw}$ ($N = 78$) and 1.5 ± 1.3 ($N = 52$) for P14 and Arctic, respectively.

Lab-based DIC (DIC_{Lab})

The DIC was measured on land by a custom DICE analyzer built by the National Oceanic and Atmospheric Administration Pacific Marine Environmental Laboratory (Seattle, Washington), which is a modern version of the original Single-Operator Multiparameter Metabolic Analyzer system (Johnson 1992). These samples will be denoted as DIC_{Lab}. The procedure is very similar to DIC_{Ship}. A calibrated pipette thermostated to 20°C ± 0.1°C is used to measure approximately 25 mL of sample, which is released into a stripping chamber containing ~ 1 mL of 8.5% (v/v) phosphoric acid, converting all DIC to $CO_{2(g)}$. A pure nitrogen (99.999%) carrier gas is then used to flow the evolved $CO_{2(g)}$ through a 5°C condensing chamber followed by a $Mg(ClO_4)_2$ desiccant and an Orbo53® (Millipore Sigma) silica gel before flowing into the coulometer detection cell. CO_2 is determined coulometrically using a CM5017-O coulometer (UIC., Inc.). Two pure CO_2 (99.999%) gas loops are used to calibrate the coulometer. Certified reference materials from batch 216 were measured for laboratory DIC with a mean $\Delta_{\text{Measured-Certified}}$ and standard deviation of -2.36 ± 1.21 ($N = 16$). Sample values were adjusted to the CRM value analyzed on the same day using a constant offset from the certified value. Replicate samples were not collected for land-based analysis due to water budget limitations.

pH_T

Ship pH_T (pH_{TShip})

The pH_T (on the total scale) at 25°C was measured onboard during the P14 cruise by potentiometer using a pH meter (model F-72 Horiba; serial number A23C0014) with a long glass electrode (Model number 9680S, Horiba; serial number 9Z3A0104) following standard operating procedure 6a from (Dickson et al. 2007). Samples were thermostated to 25°C ± 0.1°C during analysis, and voltages were corrected to exactly 25°C based on the temperature dependence of the buffers. The electrode was calibrated daily using 2-aminophyridine and 2-amino-2-hydrox-1,3-propanediol (TRIS) buffers and multiparametric standard seawater (Uchida et al. 2025, 2020). Due to large uncertainties in the TRIS measurements, only 2-aminophyridine and multiparametric standard seawater were used for electrode calibration. Additionally, Dickson CRMs were measured for comparison. Uncertainty is estimated to be ± 0.0028 based on buffer measurements and repeatability ± 0.0009 ($N = 66$) based on duplicate measurements.

Lab pH_T (pH_{TLab})

The pH_T at 20°C was measured on land using purified meta-cresol purple (Woosley Lab batch 4) and a custom-designed spectrophotometric pH system similar to Carter et al. (2013) which used an Agilent 8454 UV/Vis spectrophotometer. The indicator perturbation was found to be insignificant ($R^2 = 0.17$), and no adjustment was applied. Ignoring the indicator perturbation does increase the uncertainty in the pH_T accuracy but is not significant enough to impact the results, particularly given the good internal consistency, as discussed below. Temperature was controlled to 20°C ± 0.1°C. The pH_T was calculated using the equations of Liu et al. (2011). The accuracy was assessed using TRIS buffers prepared in the laboratory according to Paulsen and Dickson (2020). Four bottles from Woosley Lab TRIS batch 5 were used and had a mean and standard deviation of 8.2412 ± 0.0021 ($N = 12$). The expected TRIS pH_T at 20°C is 8.2517 (DelValls and Dickson 1998).

Internal consistency calculations

Internal consistency calculations were conducted as a quality control check. Calculations were done using CO2sys (Van Heuven et al. 2011) MATLAB version 3.01 (Sharp et al. 2020) with the carbonate dissociation constants of Lueker et al. (2000), bisulfate constant of Dickson (1990), fluoride constant of Perez and Fraga (1987), and total Boron of K. Lee et al. (2010). The internal consistency of the TA_{SS} was $\Delta TA_{(Measured-Calculated)} = 3.3 \pm 3.2\ \mu mol\ kg^{-1}{}_{sw}$ ($N = 124$) and for TA_{OC} was $4.2 \pm 3.8\ \mu mol\ kg^{-1}{}_{sw}$ ($N = 186$), where $TA_{Calculated}$ is calculated from DIC and pH_T. The smaller N for TA_{SS} is due to pH_T only being measured onboard on P14. A positive $\Delta TA_{(Measured-Calculated)}$ could be due to the presence of organic alkalinity but could also be due to other uncertainties in the calculations. Cross comparisons of internal consistency between laboratory and ship analysis were used to confirm a loss/gain of DIC for some samples between collection and analysis in the laboratory.

Data analysis

The difference between the two TA measurements was calculated as:

$$\Delta TA_{(OC-SS)} = TA_{OC} - TA_{SS} \tag{5}$$

A positive value would suggest the presence of unidentified acid/base species with a low pK_a, likely organic acids, that are detected by the TA_{OC} but not by TA_{SS}. Estimating uncertainty in $\Delta TA_{(OC-SS)}$ is difficult since replicate samples could not be analyzed for TA_{OC}. Random uncertainties in TA and DIC in all data in the GLODAP database was recently assessed to be $\sim 2.4\ \mu mol\ kg^{-1}{}_{sw}$ (Carter et al. 2024). As this value is a more robust uncertainty estimate than could be determined from these experiments, it is used here as the overall uncertainty. Using this value as the overall uncertainty in the measurements, we designate any sample with a $|\Delta TA|$ or $|\Delta DIC| > 4.8\ \mu mol\ kg^{-1}{}_{sw}$ to be significantly different with 95% confidence. It is important to note that, if present, both methods would detect some amount of organic alkalinity (Sharp and Byrne 2020); thus, the lack of a statistically significant difference between the two methods does not prove that organic alkalinity is not present. Conversely, a statistically significant difference would be a conservative estimate of the total amount of organic alkalinity that may be present.

Assessment

The mean and standard deviation for $\Delta TA_{(OC-SS)}$ was $0.5 \pm 3.9\ \mu mol\ kg^{-1}{}_{sw}$ ($n = 206$) and for $\Delta DIC_{(Lab-Ship)}$ was $-0.0 \pm 4.8\ \mu mol\ kg^{-1}{}_{sw}$ ($n = 206$). One sample was lost due to analytical instrument error. Neither is statistically different from zero using a single-pair *t*-test (*p*-values 0.0926 and 0.9803 for $\Delta TA_{(OC-SS)}$ and $\Delta DIC_{(Lab-Ship)}$ respectively). Although, in general, there was no significant difference in DIC (Fig. 2), some samples measured in the lab had lower (higher) DIC suggesting loss (gain) of CO_2 either during sample collection, storage, or analysis. Such loss or gain of CO_2 would not impact the TA (Millero 2007). Internal consistency comparisons and station profile plots were used to confirm a loss/gain of CO_2 for most samples with significantly different DIC. The overall good agreement with DIC indicates the samples as a whole were stable and did not change during storage, with some exceptions. Although 23 samples did have statistically different DIC, no correlation was found between ΔDIC and ΔTA (Fig. 2). Only 42 samples had statistically different TA, and only 8 of those also had statistically different DIC. The lack of corresponding changes in DIC and TA indicated $CaCO_3$ precipitation/dissolution or biological activity did not occur during sample storage.

$\Delta TA_{(OC-SS)}$ vs. TA_{SS} (Fig. 3) and depth (Fig. 4) show generally excellent agreement both with TA and depth and no significant trend. There is more scatter in the surface where dissolved organic matter (DOM) is higher and organic alkalinity is hypothesized to be larger. There are also a few samples with high TA (deep depths) with significantly positive values. Some work has suggested that deep water dissolved organic matter has more carboxyl groups (Hertkorn et al. 2006) which typically have pK_as around 4.5. Some samples had significantly negative $\Delta TA_{(OC-SS)}$, which are difficult to explain under the organic alkalinity hypothesis.

Considering only samples deeper than 1500 dbar, which is the cutoff GLODAP generally used for crossover analysis (Olsen et al. 2016), the $\Delta TA_{(OC-SS)}$ was $1.0 \pm 3.5\ \mu mol\ kg^{-1}{}_{sw}$ ($n = 70$). This is statistically significant (*p*-value = 0.0169), but

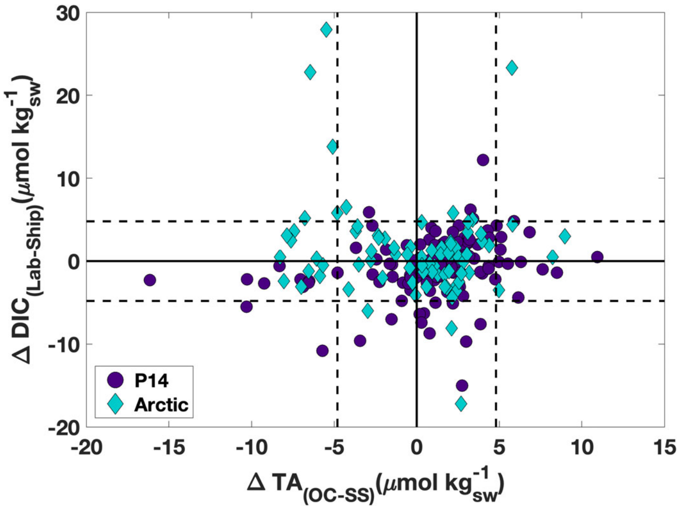

FIG. 2. Comparison of $\Delta TA_{(OC-SS)}$ with $\Delta DIC_{(Lab-Ship)}$ both in units of $\mu mol\ kg^{-1}{}_{sw}$. Purple circles are P14, and teal diamonds are the Arctic.

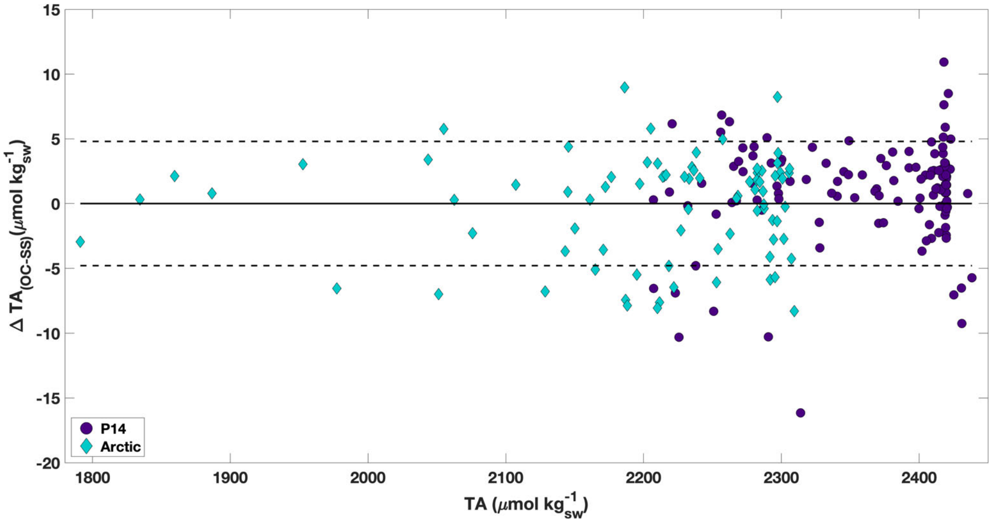

FIG. 3. Measured $\mathrm{TA_{SS}}$ versus $\Delta\mathrm{TA_{(OC–SS)}}$ both in μmol $\mathrm{kg^{-1}}_{\mathrm{sw}}$. Purple circles are P14, and teal diamonds are the Arctic. Solid horizontal line represents zero, and dashed lines represent the ~ 95% confidence interval (4.8 μmol $\mathrm{kg^{-1}}_{\mathrm{sw}}$).

notably less than the offset suggested in GLODAPv2 between Japanese and United States cruises, and within the analytical uncertainty. Care should be taken in interpreting *t*-test results for such a small offset as they only consider the standard deviation of the measurements and do not indicate practical significance.

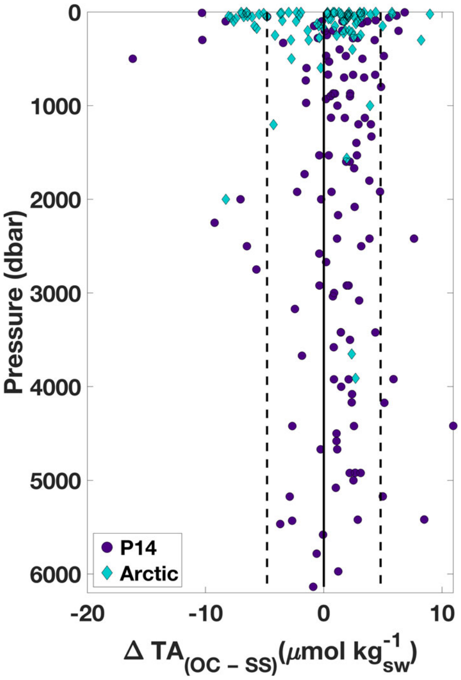

FIG. 4. $\Delta\mathrm{TA_{(OC–SS)}}$ in μmol $\mathrm{kg^{-1}}_{\mathrm{sw}}$ versus pressure (dbar). Purple circles are P14, and teal diamonds are the Arctic. Solid vertical line represents zero, and dashed lines represent the ~ 95% confidence interval (4.8 μmol $\mathrm{kg^{-1}}_{\mathrm{sw}}$).

There were 42 samples (~ 20% of the total) that had significant $\Delta\mathrm{TA_{OC–SS}}$ values (> |4.8| μmol $\mathrm{kg^{-1}}_{\mathrm{sw}}$); 22 from P14 and 20 from the Arctic. Of the 22 from P14, 11 were from station 3, which was located in the Bering Sea (Fig. 1). With only one station in the Bering Sea, it is hard to draw any firm conclusions on whether the Bering Sea has unique chemical characteristics or if there was an issue with the collection, storage, or analysis of these samples. However, all but one of those samples had negative $\Delta\mathrm{TA_{OC–SS}}$. Modeling of organic alkalinity (Sharp and Byrne 2020) indicates that regardless of the $\mathrm{p}K_{\mathrm{a}}$, $\Delta\mathrm{TA_{OC–SS}}$ would only result in positive values. Most explanations for a loss of alkalinity, such as precipitation of $\mathrm{CaCO_3}$ or biological activity, would result in a proportional change in DIC, which did not occur (Fig. 2).

Of the other 31 samples with high $|\Delta\mathrm{TA_{OC–SS}}|$ that were not located in the Bering Sea, they were roughly evenly split between positive and negative values. The majority of samples were within the analytical uncertainty, with 61% falling within 2 μmol $\mathrm{kg^{-1}}_{\mathrm{sw}}$ of zero (Fig. 5). The distributions of all $\Delta\mathrm{TA_{OC–SS}}$ for the two cruises are very similar with the Arctic tending to be skewed slightly more negative. However, given the low number of samples, the differences are not statistically significant.

Discussion

On average, the mean delta of the two methods agrees remarkably well ($\Delta\mathrm{TA_{OC–SS}} = 0.5 \pm 3.9$ μmol $\mathrm{kg^{-1}}_{\mathrm{sw}}$ [$n = 206$]) not only within our globally defined uncertainty of ± 4.8 μmol $\mathrm{kg^{-1}}_{\mathrm{sw}}$, but within the typical analytical random uncertainty of ~ 2 μmol $\mathrm{kg^{-1}}_{\mathrm{sw}}$. Even when considering only samples below 1500 db, or excluding outliers, the means are all less than 2 μmol $\mathrm{kg^{-1}}_{\mathrm{sw}}$. The histogram (Fig. 5) suggests a small positive systematic offset, which could be indicative of

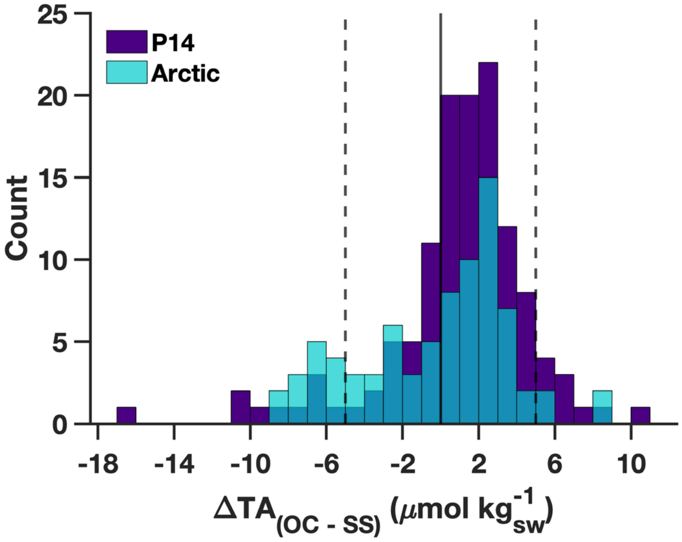

FIG. 5. Histogram of $\Delta TA_{(OC–SS)}$ in μmol $kg^{-1}{}_{sw}$ in 1 μmol $kg^{-1}{}_{sw}$ bins separated by cruise (P14 in purple and Arctic in teal). Solid vertical line represents zero and dashed lines are ~ 95% confidence intervals.

organic alkalinity. Any systematic offset between the methods appears to be on the order of 1–1.5 μmol $kg^{-1}{}_{sw}$ based on the distribution of $\Delta TA_{(OC–SS)}$ (Fig. 5) and deep waters (> 1500 dbar) which had a statistically significant 1.0 μmol $kg^{-1}{}_{sw}$ offset (*t*-test, *p*-value 0.0169). The positive offset could be due to organic alkalinity, but it could also be due to other small uncertainties. The TA_{OC} values were not adjusted to the certified CRM because all components were independently calibrated, and the method is identical to that used to certify the CRMs. The ΔCRM for TA_{OC} (0.7 ± 0.9 μmol $kg^{-1}{}_{sw}$) was also within the ~ 95% confidence interval of the certified value (defined as two times the standard deviation of the certified value of 0.67 μmol $kg^{-1}{}_{sw}$ [obtained from the batch certificate] or ± 1.34 μmol $kg^{-1}{}_{sw}$). Such a small offset in the $\Delta TA_{OC–SS}$ could be caused by small systematic uncertainties in the analysis such as in the concentration of the HCl, the mass of sample titrated, or the amount of HCl added. This small offset is within the estimated accuracy of TA measurements (Dickson et al. 2003). Applying an adjustment to TA_{OC} as was done with TA_{SS} would shift the distribution closer to zero. However, given the way the TA_{OC} instrument was calibrated, such an adjustment is not metrologically justified. As such, the small positive skew in the data distribution could be indicative of a systematic offset between the methods, which could be due to organic alkalinity or some other systematic uncertainty. The results demonstrate that different titration methods are not large enough to explain the offsets between Japanese and US cruises found by GLODAPv2 (Olsen et al. 2016), although more recent cruises have already suggested that the offset is not present in cruises from approximately 2010 onward (Olsen et al. 2020). Other potential causes, such as method calibration or how/when CRM adjustments are applied, should be investigated. The results indicate that any methodological offset between TA_{OC} and TA_{SS} is less than 2 μmol $kg^{-1}{}_{sw}$, and likely on the order of ~ 1 μmol $kg^{-1}{}_{sw}$ if these samples are representative of the global open ocean.

As mentioned in the introduction, the main reason the different methods might produce different values for TA is because of differences in the endpoint pH_T of the titration leading to different amounts of organic matter being titrated. In practice, the endpoint pH_T of TA_{SS} varies with each sample, which could result in the $\Delta TA_{(OC–SS)}$ varying in relation to the endpoint pH_T of the TA_{SS} and indicate that differences are due to organic alkalinity rather than some other source of uncertainty. We found no such correlation ($R^2 = 0.006$, *p*-value = 0.268). The modeling work of (Sharp and Byrne 2020) used endpoints of 3.0–3.5 for TA_{OC} and 4.2 for TA_{SS}. For the experiments here, the actual endpoint pH_T of the TA_{SS} ranged from 3.5 to 4.1 (mean = 4.0), which is closer to our TA_{OC} endpoint (~ 3.0–3.5) and would result in smaller differences between the two methods than if TA_{SS} endpoint pH_T was closer to 4.2. Adjusting the endpoint pH_T in the code provided by (Sharp and Byrne 2020) does indeed reduce, but not eliminate the differences between the two methods.

For P14, the measured dissolved organic carbon (DOC) and the TITRATE.m MATLAB) code of Sharp and Byrne (2020) were used to estimate the potential impact of organic alkalinity on the two methods. The amount of a hypothetical organic acid was estimated as DOC * 0.14 (Kuliński et al. 2014), which results in total organic acid concentrations of 4.8–10.8 μmol $kg^{-1}{}_{sw}$, with a mean value of 5.8 μmol $kg^{-1}{}_{sw}$. Assuming a pK_a of 4.5, the mean predicted difference between the methods, $\Delta TA_{OC–SS} = 3.0$ μmol $kg^{-1}{}_{sw}$, with a maximum of 4.9 μmol $kg^{-1}{}_{sw}$. The mean value is three times larger than the measured $\Delta TA_{OC–SS}$ of 1.0 μmol $kg^{-1}{}_{sw}$ for samples > 1500 dbar. Adjusting the endpoint pH_T of the TA_{SS} to 4.0 (the mean value for the TA_{SS} measurements) would reduce the mean predicted offset to 1.2 μmol $kg^{-1}{}_{sw}$. However, while this is similar to the mean value for deep samples, it is also similar to the ΔCRM of the TA_{OC}, and therefore the cause is inconclusive. Dissolved organic carbon was not measured on the Arctic cruise preventing similar comparisons; however, the DOC in the Arctic surface is significantly higher (Millero et al. 2011) and would therefore produce larger predicted $\Delta TA_{OC–SS}$, which is not found in these measurements (Fig. 5) where the value was lower on average for the Arctic vs. P14.

An explanation for the negative values is hard to come up with and warrants further study. If samples with significantly negative (> −4.8 μmol $kg^{-1}{}_{sw}$) $\Delta TA_{(OC–SS)}$ are considered contaminated and excluded, the mean and standard deviation become 1.5 ± 2.6 ($N = 181$) μmol $kg^{-1}{}_{sw}$ and is statistically significant (*t*-test, *p*-value $\ll 0.05$). The most plausible causes would be precipitation of $CaCO_3$ or biological activity in the sample during storage. However, comparisons to $\Delta DIC_{(Lab–Ship)}$ (Fig. 2) do not support such a loss of alkalinity during storage (i.e., no proportional change in DIC). One hypothesis is that the Arctic and Bering Sea stations occurred near the typical seasonal timing of a phytoplankton bloom (Murata 2006) and the samples may have contained particles which were unstable during storage leading to small changes in TA. Another possibility could be loss of labile dissolved organic matter during storage. Testing these hypotheses would be difficult, but measuring duplicate samples with both methods simultaneously shipboard, perhaps using the same batch of acid would likely reduce uncertainties and minimize other potential sources of variability. Although quality control checks indicate no significant change in the samples during storage, a small undetectable change is still possible, leading to increased noise.

The results demonstrate that organic alkalinity is either not present in significant quantities in the northwest Pacific and western Arctic, or that the two methods detect comparable amounts of organic alkalinity (within $\sim$ 1–1.5 μmol kg$^{-1}{}_{\text{sw}}$). One potential complicating factor in interpreting the results for organic alkalinity is that the single-step method adjusts values for differences between the measured and certified TA values of CRMs. Such adjustments are a common method of instrument calibration but are not universally applied. Some work has shown that CRMs may contain organic alkalinity (C. H. Lee et al. 2024; Sharp and Byrne 2021). If that is indeed the case, then adjusting any measured TA values to the CRM would be correcting the measured single-step values towards the open-cell values because open-cell with NLSF fitting is how the CRM values are determined (Dickson et al. 2003). If the amount of organic alkalinity in a given sample is approximately the same as that in the CRM, then it would remove (at least partially) any methodological artifact and could explain the excellent agreement found here. However, it is highly unlikely that organic alkalinity is roughly constant in the open ocean, which could make adjusting measured values to the CRM problematic. Differences may have also been smaller than predicted because the actual endpoint pH$_{\text{T}}$ for TA$_{\text{SS}}$ was closer to that of the TA$_{\text{OC}}$ than the value used in modeling titrations Sharp and Byrne (2020). The Arctic cruise was chosen for this comparison in part because the high riverine input to the Arctic (Dittmar and Kattner 2003) would make it a hot spot for organic alkalinity if it were significant. Many of those stations are also quite coastal (Fig. 1) and are areas of potentially high organic alkalinity. The results from the Arctic suggest otherwise, because the lowest TA samples would be expected to have the most riverine input and the highest organic alkalinity, thus the largest $+\Delta$TA$_{\text{(OC–SS)}}$. However, nearly the opposite was the case (Fig. 3). This result could potentially be explained by the composition of organic alkalinity in the region. Arctic rivers are known to be high in humic compounds (Dittmar and Kattner 2003) which have a higher pK$_{\text{a}}$ and would therefore be titrated similarly for both methods. Additionally, sea ice melt could contribute to low TA and dilute the organic alkalinity signal. Splitting the Arctic samples into subgroups of shelf and open ocean did not show any patterns, and the number of samples became too small for robust comparisons.

The ΔCRM for the TA$_{\text{SS}}$ was negative (i.e., low) for both cruises, which could be indicative of organic alkalinity in the CRM (Sharp and Byrne 2021), but despite being from the same batch of CRMs, the deltas were significantly different between P14 and the Arctic. The ΔCRM of the TA$_{\text{SS}}$ varied with the batch of acid used, indicating that differences in ΔCRM for TA$_{\text{SS}}$ were mainly due to uncertainties in the acid concentration and, therefore, cannot be used to infer organic alkalinity in the CRMs, if present. Although it is possible that some of the TA$_{\text{SS}}$ ΔCRM is due to organic alkalinity, and the adjustment is compensating for it. An independent calibration of the acid titrant or use of the same batch of acid to measure the same batch of CRM using single-step and open-cell titrations could provide insight into the presence of organic alkalinity in CRMs. Varying the endpoint of TA$_{\text{SS}}$ on the same sample could also provide further insight. A direct measurement of organic alkalinity could provide more insights, but such measurements are difficult to make (Cai et al. 1998; C. H. Lee et al. 2024; Song et al. 2020) particularly for the low concentrations expected. If adjusting measured values to the CRM does in fact correct for organic alkalinity in the CRM, doing so could be potentially problematic if the sample does not contain similar amounts and types of organic alkalinity as the CRM. Such a possibility warrants further research.

If organic alkalinity were present, ΔTA$_{\text{(OC–SS)}}$ would likely correlate with other biogeochemical parameters, particularly DOC. No such correlation was found with any co-measured parameters (DOC, florescent dissolved organic matter, nutrients, temperature, salinity, oxygen, or apparent oxygen utilization). Although given such a small mean offset, any correlation could be obscured by noise. At best, the presence of meaningful amounts of organic alkalinity in the open ocean remains inconclusive. Systematic differences between the two methods were not found to be significant, although a statistically significant difference of 1.0–1.5 μmol kg$^{-1}{}_{\text{sw}}$ was found for a subset of samples. We therefore contend that any methodical differences resulted in a maximum offset of < 2 μmol kg$^{-1}{}_{\text{sw}}$.

Conclusions and recommendations

A direct comparison of TA titration methods was undertaken on two cruises in the northwest Pacific and western Arctic Ocean in 2023. The single-step method conducted on board was compared to paired samples using the open-cell method with the NLSF method conducted in the laboratory. Agreement between the two methods was found to be excellent on average and within the uncertainty of the measurements. Although about 20% of samples did have statistically significant different TA, the differences appear to be random and no correlation with other biogeochemical parameters could be determined. There was a very small but statistically significant offset of $\sim 1\,\mu\text{mol kg}^{-1}{}_{\text{sw}}$ for deep samples (> 1500 dbar) but it is within the accuracy of the methods. The results indicate no meaningful systematic offsets between the two methods, and current methodological differences cannot explain apparent offsets between United States and Japanese led cruises found in GLODAPv2 (Olsen et al. 2016). These results should add confidence that the two methods produce comparable results in the open ocean (within $\sim 2\,\mu\text{mol kg}^{-1}{}_{\text{sw}}$), although differences may still occur in coastal systems, and a small systematic offset less than the analytical random uncertainties may exist. One important caveat is that an adjustment was applied to TA_{ss} for offsets in the measured CRM values. We attribute most of this offset to uncertainties in the acid concentration, although it is possible some of the offset is due to organic alkalinity. Additionally, the lower endpoint pH_{T} for the TA_{SS} in these samples may have lessened the impact of organic alkalinity on $\Delta\text{TA}_{\text{OC–SS}}$. Further investigation into differences in measurements of CRMs using the two methods and how CRM adjustments impact the results (including development of recommendations for when and how to make such adjustments), and how to calibrate acid concentrations is warranted.

Presence of detectable amounts of organic alkalinity in the open ocean remains inconclusive. Non-negligible amounts of organic alkalinity could not be inferred from the $\Delta\text{TA}_{(\text{OC–SS})}$ and even in the small number of samples where deltas were statistically different, about half of them were negative and thus not indicative of organic alkalinity. No satisfactory explanation could be found, but we hypothesize it could be related to particles being unstable or changes in labile organic matter during storage. Further investigation is needed to explain these negative values. These results should add confidence that these two different methods for TA analysis produce values that are comparable within the typical analytical uncertainty ($2\,\mu\text{mol kg}^{-1}{}_{\text{sw}}$). Such good agreement indicates GLODAP may not need to consider analytical TA methods in their interconsistency determinations, although comparisons of more regions and different method protocols are warranted. Finally, some questions still remain. Further comparisons that reduce other potential sources of uncertainty (calibration, storage time, use of CRMs) should be carried out. Additionally, the importance of the exact endpoint pH_{T} used for TA_{SS} should be evaluated.

Author Contributions

Ryan J. Woosley: conceptualization, data curation, formal analysis, funding acquisition, investigation, methodology, resources, supervision, visualization, writing – original draft, writing – review and editing. Jessica A. Bruno: data curation, investigation, writing – review and editing. DN: investigation, visualization, writing – review and editing. Zhaohui Aleck Wang: resources, writing – review and editing. Nagisa Fujiki: investigation, writing – review and editing. Masahito Shigemitsu: investigation, resources, writing – review and editing. Akihiko Murata: investigation, resources, supervision, writing – review and editing.

Acknowledgments

The authors thank the crew and scientists of the R/V Mirai for making this study possible. They also thank Jiyoung Moon for coordinating getting the laboratory sample bottles to and from the ship. Ryan J. Woosley, Jessica A. Bruno, and Daina Neithardt were supported by the National Science Foundation (awards OCE-2148468 and OCE-2342986). Daina Neithardt was also supported by the MIT office of Undergraduate Research Opportunities Program and the MIT Center for Sustainability Science and Strategy. The onboard pH measurements were supported in part by Japan Society for the Promotion of Science KAKENHI Grants 20H04349 and 21H01165.

Conflicts of Interest

None declared.

Data Availability Statement

All data are publicly available. Laboratory TA, DIC, and pH_{T} at 20°C can be found on BCO-DMO (project #890561; https://www.bco-dmo.org/dataset/957527). Shipboard analysis can be found at CCHDO—Hydrographic Cruise: 49NZ20231006 (https://cchdo.ucsd.edu/cruise/49NZ20231006) and KIWA—ADS (https://ads.nipr.ac.jp/data/meta/A20241108-002/) for P14 and Arctic, respectively.

References

Álvarez, M., N. M. Fajar, B. R. Carter, et al. 2020. "Global Ocean Spectrophotometric pH Assessment: Consistent Inconsistencies." *Environmental Science & Technology* 54: acs.est.9b06932. https://doi.org/10.1021/acs.est.9b06932.

Cai, W., Y. Wang, and R. E. Hodson. 1998. "Acid-Base Properties of Dissolved Organic Matter in the Estuarine Waters of Georgia, USA." *Geochimica et Cosmochimica Acta* 62: 473–483. https://doi.org/10.1016/S0016-7037(97)00363-3.

Carter, B. R., J. A. Radich, H. L. Doyle, and A. G. Dickson. 2013. "An Automated System for Spectrophotometric Seawater pH Measurements." *Limnology and Oceanography: Methods* 11: 16–27. https://doi.org/10.4319/lom.2013.11.16.

Carter, B. R., J. D. Sharp, M. I. García-Ibáñez, et al. 2024. "Random and Systematic Uncertainty in Ship-Based Seawater Carbonate Chemistry Observations." *Limnology and Oceanography* 69, no. 10: 1–2488. https://doi.org/10.1002/lno.12674.

DelValls, T. A., and A. G. Dickson. 1998. “The pH of Buffers Based on 2-Amino-2-Hydroxymethyl-1,3-Propanediol (‘Tris’) in Synthetic Sea Water.” *Deep Sea Research, Part I: Oceanographic Research Papers* 45: 1541–1554. https://doi.org/10.1016/S0967-0637(98)00019-3.

Dickson, A. G. 1981. “An Exact Definition of Total Alkalinity and a Procedure for the Estimation of Alkalinity and Total Inorganic Carbon from Titration Data.” *Deep-Sea Research Part A: Oceanographic Research Papers* 28: 609–623. https://doi.org/10.1016/0198-0149(81)90121-7.

Dickson, A. G. 1990. “Standard Potential of the Reaction: $AgCl(S) + 12H_2(g) = Ag(s) + HCl(Aq)$, and the Standard Acidity Constant of the Ion HSO_4^- in Synthetic Sea Water from 273.15 to 318.15 K.” *Journal of Chemical Thermodynamics* 22: 113–127. https://doi.org/10.1016/0021-9614(90)90074-Z.

Dickson, A. G., J. D. Afghan, and G. C. Anderson. 2003. “Reference Materials for Oceanic CO_2 Analysis: A Method for the Certification of Total Alkalinity.” *Marine Chemistry* 80: 185–197. https://doi.org/10.1016/S0304-4203(02)00133-0.

Dickson, A. G., C. L. Sabine, and J. R. Christian. 2007. Guide to Best Practices for Ocean CO_2Measurements. PICES Special Publication. https://doi.org/10.25607/OBP-1342.

Dittmar, T., and G. Kattner. 2003. “The Biogeochemistry of the River and Shelf Ecosystem of the Arctic Ocean: A Review.” *Marine Chemistry* 83: 103–120. https://doi.org/10.1016/S0304-4203(03)00105-1.

Fong, M. B., and A. G. Dickson. 2019. “Insights from GO-SHIP Hydrography Data into the Thermodynamic Consistency of CO_2 System Measurements in Seawater.” *Marine Chemistry* 211: 52–63. https://doi.org/10.1016/J.MARCHEM.2019.03.006.

Hammer, K., B. Schneider, K. Kuliński, and D. E. Schulz-Bull. 2017. “Acid-Base Properties of Baltic Sea Dissolved Organic Matter.” *Journal of Marine Systems* 173: 114–121. https://doi.org/10.1016/j.jmarsys.2017.04.007.

Hertkorn, N., R. Benner, M. Frommberger, et al. 2006. “Characterization of a Major Refractory Component of Marine Dissolved Organic Matter.” *Geochimica et Cosmochimica Acta* 70: 2990–3010. https://doi.org/10.1016/j.gca.2006.03.021.

Hunt, C. W. 2021. Alkalinity and Buffering in Estuarine, Costal, and Shelf Waters. University of New Hampshire.

Hunt, C. W., J. E. Salisbury, X. Liu, and R. H. Byrne. 2024. “Organic Alkalinity Distributions, Characteristics, and Application to Carbonate System Calculations in Estuarine and Coastal Systems.” *Limnology and Oceanography* 70: 1–333. https://doi.org/10.1002/lno.12761.

Johnson, K. M. 1992. Single-Operator Multiparameter Metabolic Analyzer (SOMMA) for Total Carbon Dioxide (CT) with Coulometric Detection. Operator’s manual. Brookhaven National Laboratory. https://doi.org/10.2172/10194787.

Kerr, D. E., P. J. Brown, A. Grey, and B. P. Kelleher. 2021. “The Influence of Organic Alkalinity on the Carbonate System in Coastal Waters.” *Marine Chemistry* 237: 104050. https://doi.org/10.1016/j.marchem.2021.104050.

Klothoff, I. M. 1926. “The Standardization of Hydrochloric Acid with Potassium Iodate as Compared With Borax and Sodium Carboante as Standard Substances.” *Journal of the American Chemical Society* 48: 1447–1780. https://doi.org/10.1021/ja01417a0011926.

Kuliński, K., B. Schneider, K. Hammer, U. Machulik, and D. Schulz-Bull. 2014. “The Influence of Dissolved Organic Matter on the Acid-Base System of the Baltic Sea.” *Journal of Marine Systems* 132: 106–115. https://doi.org/10.1016/j.jmarsys.2014.01.011.

Lee, C. H., K. Lee, J. S. Lee, K. Y. Jeong, and Y. H. Ko. 2024. “Persistent Organic Alkalinity in the Ocean.” *Geochimica et Cosmochimica Acta* 387: 53–62. https://doi.org/10.1016/j.gca.2024.06.010.

Lee, K., T.-W. Kim, R. H. Byrne, F. J. Millero, R. A. Feely, and Y.-M. Liu. 2010. “The Universal Ratio of Boron to Chlorinity for the North Pacific and North Atlantic Oceans.” *Geochimica et Cosmochimica Acta* 74: 1801–1811. https://doi.org/10.1016/j.gca.2009.12.027.

Liu, X., M. C. Patsavas, and R. H. Byrne. 2011. “Purification and Characterization of Meta-Cresol Purple for Spectrophotometric Seawater pH Measurements.” *Environmental Science & Technology* 45: 4862–4868. https://doi.org/10.1021/es200665d.

Lueker, T. J., A. G. Dickson, and C. D. Keeling. 2000. “Ocean pCO_2 Calculated from Dissolved Inorganic Carbon, Alkalinity, and Equations for K_1 and K_2: Validation Based on Laboratory Measurements of CO_2 in Gas and Seawater at Equilibrium.” *Marine Chemistry* 70: 105–119. https://doi.org/10.1016/S0304-4203(00)00022-0.

Millero, F. J. 2007. “The Marine Inorganic Carbon Cycle.” *Chemical Reviews* 107: 308–341. https://doi.org/10.1021/cr0503557.

Millero, F. J., F. Huang, R. J. Woosley, R. T. Letscher, and D. A. Hansell. 2011. “Effect of Dissolved Organic Carbon and Alkalinity on the Density of Arctic Ocean Waters.” *Aquatic Geochemistry* 17: 311–326. https://doi.org/10.1007/s10498-010-9111-2.

Millero, F. J., D. Pierrot, K. Lee, et al. 2002. “Dissociation Constants for Carbonic Acid Determined from Field Measurements.” *Deep Sea Research, Part I: Oceanographic Research Papers* 49: 1705–1723. https://doi.org/10.1016/S0967-0637(02)00093-6.

Murata, A. 2006. “Increased Surface Seawater pCO_2 in the Eastern Bering Sea Shelf: An Effect of Blooms of Coccolithophorid Emiliania Huxleyi?” *Global Biogeochemical Cycles* 20: 1–9. https://doi.org/10.1029/2005GB002615.

Olsen, A., R. M. Key, S. van Heuven, et al. 2016. “The Global Ocean Data Analysis Project Version 2 (GLODAPv2) – An Internally Consistent Data Product for the World Ocean.” *Earth System Science Data* 8: 297–323. https://doi.org/10.5194/essd-8-297-2016.

Olsen, A., N. Lange, R. M. Key, et al. 2019. "GLODAPv2.2019 – an Update of GLODAPv2." *Earth System Science Data* 11: 1437–1461. https://doi.org/10.5194/essd-11-1437-2019.

Olsen, A., N. Lange, R. M. Key, et al. 2020. "GLODAPv2.2020 – The Second Update of GLODAPv2." *Earth System Science Data* 12: 3653–3678. https://doi.org/10.5194/essd-2020-165.

Oschlies, A., A. Stevenson, L. T. Bach, et al. 2023. Guide to Best Practices in Ocean Alkalinity Enhancement Research. State of the Planet Discussion. https://doi.org/10.5194/sp-2-oae2023.

Paulsen, M., and A. G. Dickson. 2020. "Preparation of 2-Amino-2-Hydroxymethyl-1,3-Propanediol (TRIS) pH $_T$ Buffers in Synthetic Seawater." *Limnology and Oceanography: Methods* 18: 504–515. https://doi.org/10.1002/lom3.10383.

Perez, F. F., and F. Fraga. 1987. "Association Constant of Fluoride and Hydrogen Ions in Seawater." *Marine Chemistry* 21: 161–168. https://doi.org/10.1016/0304-4203(87)90036-3.

Sharp, J. D., and R. H. Byrne. 2020. "Interpreting Measurements of Total Alkalinity in Marine and Estuarine Waters in the Presence of Proton-Binding Organic Matter." *Deep-Sea Research. Part I, Oceanographic Research Papers* 165: 103338. https://doi.org/10.1016/j.dsr.2020.103338.

Sharp, J. D., and R. H. Byrne. 2021. "Technical Note: Excess Alkalinity in Carbonate System Reference Materials." *Marine Chemistry* 233: 103965. https://doi.org/10.1016/j.marchem.2021.103965.

Sharp, J. D., D. Pierrot, M. P. Humphreys, et al. 2020. CO2SYSv3 for MATLAB (v3.1). Zenodo. https://doi.org/10.5281/ZENODO.4023039.

Song, S., Z. Aleck Wang, M. Eagle Gonneea, et al. 2020. "An Important Biogeochemical Link between Organic and Inorganic Carbon Cycling: Effects of Organic Alkalinity on Carbonate Chemistry in Coastal Waters Influenced by Intertidal Salt Marshes." *Geochimica et Cosmochimica Acta* 275: 123–139. https://doi.org/10.1016/J.GCA.2020.02.013.

Song, S., R. G. J. Bellerby, Z. A. Wang, E. Wurgaft, and D. Li. 2023. "Organic Alkalinity as an Important Constituent of Total Alkalinity and the Buffering System in River-to-Coast Transition Zones." *Journal of Geophysical Research: Oceans* 128: 1–15. https://doi.org/10.1029/2022JC019270.

Uchida, H., T. Kawano, T. Nakano, M. Wakita, T. Tanaka, and S. Tanihara. 2020. "An Expanded Batch-to-Batch Correction for IAPSO Standard Seawater." *Journal of Atmospheric and Oceanic Technology* 37: 1507–1520. https://doi.org/10.1175/JTECH-D-19-0184.1.

Uchida, H., A. Murata, M. Wakita, et al. 2025. "Development of Multiparametric Standard Seawater (MSSW) for CO_2 Parameters, Dissolved Oxygen, and Density of Seawater." In Chemical Reference Materials for Oceanography: History, Production, and Certification, edited by M. Aoyama, C. Cheong, and A. Murata, 203–235. Singapore: Springer Nature Singapore. https://doi.org/10.1007/978-981-96-2520-8_12.

Uppström, L. R. 1974. "The Boron/Chlorinity Ratio of Deep-Sea Water from the Pacific Ocean." *Deep Sea Research and Oceanographic Abstracts* 21: 161–162. https://doi.org/10.1016/0011-7471(74)90074-6.

Van Heuven, S., D. Pierrot, E. R. Lewis, and D. W. R. Wallace. 2011. MATLAB Program Developed for CO_2 System Calculations ORNL/CDIAC-105b.

Wang, Z. A., and W.-J. Cai. 2025. "The Inorganic Carbon System across the Land-to-Ocean Continuum." In Treatise on Geochemistry, edited by A. D. Anbar and D. Weis, 111–144. Elsevier. https://doi.org/10.1016/b978-0-323-99762-1.00032-2.

Watanabe, E., H. Ueno, T. Kodaira, et al. 2025. "Arctic Marine Environments Regulated by Ocean Transport and Air–Sea–Land Interaction: Findings from the ArCS II Ocean Research Program." *Polar Science*: 101205. https://doi.org/10.1016/j.polar.2025.101205.

Woosley, R. J., and J. Y. Moon. 2023. "Re-Evaluation of Carbonic Acid Dissociation Constants across Conditions and the Implications for Ocean Acidification." *Marine Chemistry* 250: 104247. https://doi.org/10.1016/j.marchem.2023.104247.

Yao, W., and R. H. Byrne. 1998. "Simplified Seawater Alkalinity Analysis." *Deep Sea Research, Part I: Oceanographic Research Papers* 45: 1383–1392. https://doi.org/10.1016/S0967-0637(98)00018-1.

Submitted 21 April 2025
Revised 04 September 2025
Accepted 08 September 2025