

Alkalinity distribution in the western North Atlantic Ocean margins

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[1] Total alkalinity (TA) distribution and its relationship with salinity (S) along the western North Atlantic Ocean (wNAO) margins from the Labrador Sea to tropical areas are examined in this study. Based on the observed TA-S patterns, the mixing processes that control alkalinity distribution in these areas can be categorized into a spectrum of patterns that are bracketed by two extreme mixing types, i.e., alongshore current-dominated and river-dominated. Alongshore current-dominated mixing processes exhibit a segmented mixing line with a shared mid-salinity end-member. In such cases (i.e., Labrador Sea, Gulf of Maine, etc.), the y-intercept of the high salinity segment of the mixing line is generally higher than the local river alkalinity values, and it reflects the mixing history of the alongshore current. In contrast, in river-dominated mixing (Amazon River, Caribbean Sea, etc.), good linear relationships between alkalinity and salinity are generally observed, and the zero salinity intercepts of the TA-S regressions roughly match those of the regional river alkalinity values. TA-S mixing lines can be complicated by rapid changes in the river end-member value and by another river nearby with a different TA value (e.g., Mississippi-Atchafalaya/Gulf of Mexico). In the wNAO margins, regression intercepts and river end-members have a clear latitudinal distribution pattern, increasing from a low of $\sim 300 \mu\text{mol kg}^{-1}$ in the Amazon River plume to a high value between ~ 500 – $1100 \mu\text{mol kg}^{-1}$ in the middle and high latitude margins. The highest value of $\sim 2400 \mu\text{mol kg}^{-1}$ is observed in the Mississippi River influenced areas. In addition to mixing control, biological processes such as calcification and benthic alkalinity production may also affect ocean margin alkalinity distribution. Therefore, deriving inorganic carbon system information in coastal oceans using alkalinity-salinity relationships, in particular, those of generic nature, may lead to significant errors.

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1. Introduction

[2] Ocean margins account for $\sim 10\%$ of the global oceanic area but a disproportionately large amount of primary production [Ducklow and McCallister, 2004; Wollast, 1998]. It has been shown that ocean margins may contribute significantly to the oceanic uptake of atmospheric CO_2 [e.g., Borges *et al.*, 2005; Cai *et al.*, 2006; Thomas *et al.*, 2004; Tsunogai *et al.*, 1999] and the export of organic carbon to the pelagic oceans [Vlahos *et al.*, 2002]. Ocean margins are also a continuum for material transport [Liu *et al.*, 2003], for example, moving riverine bicarbonate (weathering products) from continents to the open ocean [Cai *et al.*, 2008]. Furthermore, ocean margins are especially susceptible to climate

changes and anthropogenic influences such as sea level rise and ocean acidification, and they may respond to these changes on a much shorter time scale than the open ocean [e.g., Andersson *et al.*, 2005, 2006]. Therefore, ocean margins constitute an important link in the global carbon cycle. The ocean margin inorganic carbon system is thus crucial to understanding CO_2 dynamics, particularly in regard to continental shelf pump theory [Rippeth *et al.*, 2008; Tsunogai *et al.*, 1999] and concerns about ocean acidification [Feely *et al.*, 2004].

[3] Along with other inorganic carbon parameters such as the concentration of dissolved inorganic carbon (DIC) and partial pressure of CO_2 ($p\text{CO}_2$), total alkalinity (hereafter, TA or alkalinity) is one of the most frequently measured quantities in ocean carbon cycle studies. In the open ocean, alkalinity has been used extensively to address a variety of geochemical questions including global ocean carbonate production and dissolution [Berelson *et al.*, 2007; Chung *et al.*, 2003; Milliman and Droxler, 1996]. However, major questions remain unanswered, for example, the potential carbonate imbalance in the global ocean can be translated

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into an alkalinity imbalance, in which the rate of riverine alkalinity input does not match the rate of oceanic alkalinity removal by net carbonate preservation. At the same time, alkalinity export to the open oceans remains poorly quantified [Berelson *et al.*, 2007; Chen, 2002]. Before we can provide a more accurate global alkalinity budget and unravel its underlying control mechanisms, we must first obtain a better understanding of ocean margin alkalinity in terms of its distribution and transport to the open ocean. This study is the first systematic examination to address large scale alkalinity distribution in ocean margin areas.

[4] Seawater alkalinity in the open ocean is largely controlled by factors such as precipitation, evaporation, water mass mixing, carbonate dissolution, and precipitation. Alkalinity is also affected, although to a lesser extent, by organic matter production (primary production) and remineralization [Brewer *et al.*, 1975]. Nevertheless, alkalinity is often treated as a conservative parameter in seawater chemistry. It exhibits a linear relationship with respect to salinity (S) in the surface waters of the three major oceans. Standard deviations of these TA-S regressions are typically $\sim 10 \mu\text{mol kg}^{-1}$ [Millero *et al.*, 1998b]. If the temperature term is further considered with carefully categorized zones, the predicted alkalinity values can have a root mean square deviation (RMSD, hereafter σ) as low as $4\text{--}6 \mu\text{mol kg}^{-1}$ [Lee *et al.*, 2006]. Therefore, it was hoped that a high resolution characterization of inorganic CO_2 parameters (i.e., concentrations of DIC, carbonate and bicarbonate ions, as well as pH) over large areas of the global ocean can be obtained using predicted alkalinity values in conjunction with underway $p\text{CO}_2$ data [e.g., Lee *et al.*, 2006; Lewis and Wallace, 1998; Millero *et al.*, 1998b]. However, a recent study [McNeil *et al.*, 2007] suggested that the multiparameter linear regression using the temperature term in the work of Lee *et al.* [2006] was subjected to significant temporal variations in its predictive power in the Southern Ocean. Further study is needed to reconcile these variations. Finally, alkalinity predicted from salinity has also been used in conjunction with moored $p\text{CO}_2$ data to study daily to-seasonal CO_2 dynamics [DeGrandpre *et al.*, 1997]. As $p\text{CO}_2$ mooring efforts gain popularity, such needs are expected to increase.

[5] Compared to the relatively simple conditions in the open ocean, ocean margin areas (estuaries, continental shelves, and upper slopes) may involve more complicated processes. In a river-influenced ocean margin, if alkalinity and salinity follow a conservative mixing process of two end-members, a linear equation in the form of

$$\text{TA} = \text{TA}^0 + bS \quad (1)$$

can be used to predict alkalinity over the salinity range where mixing occurs. Here the constant TA^0 , or y-intercept in the regression line, is the river end-member alkalinity value at zero salinity, and b is the slope.

[6] Such an ideal two-end-member mixing scenario is not always observed, however, as other factors also play a role in controlling ocean margin alkalinity distribution. Contributing factors include lateral alongshore current transport, upwelling of deep slope water, which is enriched with alkalinity due to enhanced carbonate mineral dissolution [Millero *et al.*, 1998b], and consumption by biological cal-

cification [Cai, 2003]. Therefore, the TA-S relationship in ocean margins can easily deviate from this simple two-end-member mixing model.

[7] Another much less understood and quantified mechanism is alkalinity production through anaerobic respiration of organic matter in coastal sedimentary environments such as denitrification and sulfate reduction [e.g., Chen, 2002; Chen and Wang, 1999; Wang and Cai, 2004]. A recent coastal ocean carbon cycle modeling paper [Fennel and Wilkin, 2009] demonstrated that alkalinity gain (as a result of benthic denitrification) could influence model-predicted surface water $p\text{CO}_2$.

[8] The objective of this study is to examine alkalinity distribution and its relationship to salinity along the western North Atlantic Ocean (wNAO) margins including the western tropical Atlantic margin. Factors controlling alkalinity distributions and TA-S relationships will also be explored.

2. Methodology

2.1. Data Consideration

[9] Data used in this paper include those gathered from transects of the World Ocean Circulation Experiment (WOCE), U.S. Repeat Hydrography Program for Climate Variability and CO_2 studies (CLIVAR), the Ocean Margins Program (OMP) (for details see DeGrandpre *et al.* [2002] and Vlahos *et al.* [2002]), Repeat Mantra/Pirana studies (MP) [Cooley, 2006; Cooley *et al.*, 2007], Gulf of Mexico East Coast Carbon Program (GOMECC, <http://www.aoml.noaa.gov/ocd/gcc/GOMECC/>), the South Atlantic Bight (SAB) [Jiang *et al.*, 2008], and the northern Gulf of Mexico (nGMx) study (i.e., this study).

[10] The 2007 GOMECC study was an integral part of a collaborative research project that examined previously undersampled North American coastal regions (the east and the Gulf coasts) in terms of understanding their role in air-sea CO_2 exchange, as well as carbon export to the pelagic ocean. Additionally, this study contributed to database development that supported the North American Carbon Program. Over a 26-day cruise, a wide array of hydrographic and chemical parameters were measured along nine offshore transects between Galveston, TX and Boston, MA.

[11] The geographic locations and sampling times for the data sets used in this study are listed in Table 1 and Figure 1. Two types of data selection criteria were used to define our data sets. For large river-dominated areas, data were gathered from the upper 200 m of the water column including slope waters. This criterion was adopted based on the fact that large river plumes often extend beyond continental shelf breaks [e.g., Cooley and Yager, 2006]. For ocean margins, alkalinity data from all nearshore stations with water depths no greater than 250 m were used, although most continental shelf breaks occur at 100–200 m [e.g., de Haas *et al.*, 2002]. In the Gulf of Maine (GoME), however, the entire shelf and basin region reaches a depth of 290 m; thus, all GoME data were used.

2.2. Methods

[12] Alkalinity data from all the cruises considered in this study were collected using potentiometric titration with hydrochloric acid as the titrant. Both open- and closed-cell

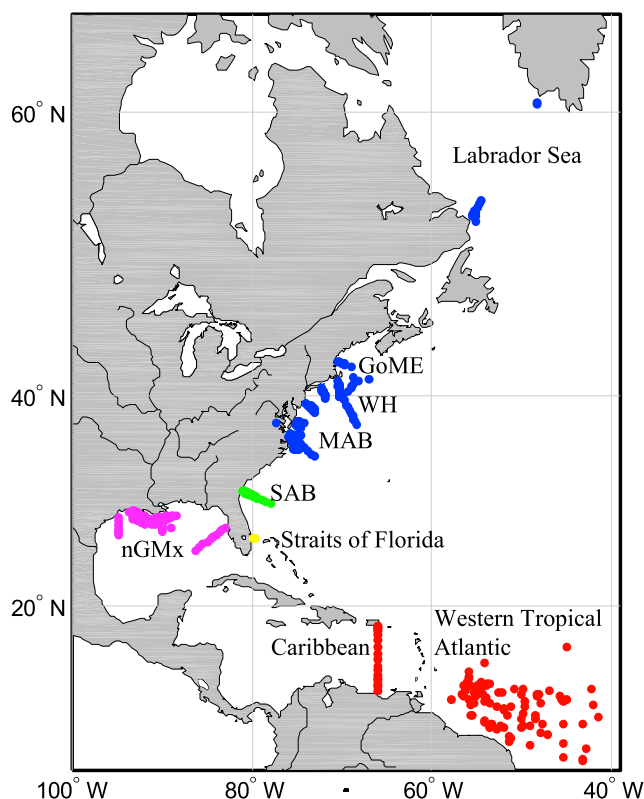


Figure 1. Map of the western North Atlantic Ocean margin. See Table 1 for cruise details.

titration methods were used [Cooley and Yager, 2006; Dickson *et al.*, 2007; Millero *et al.*, 1998a; Wang and Cai, 2004]. Titration sample volumes were about 100 mL except for the GOMECC cruises, and the analytical precision of these different surveys varied only slightly (0.1–0.2%).

[13] Alkalinity samples for the GOMECC study were collected in 10-L Niskin bottles on a rosette and were stored in 250-mL ground-glass bottles following the standard

procedure of Dickson *et al.* [2007] but without HgCl_2 poisoning. All samples were analyzed within 24 h of collection. A 25-mL seawater sample was used for each titration in an open-cell setting [Wang and Cai, 2004]. Variable amounts of 0.06 N HCl were added to the seawater samples until they reached a pH value of 3.8. After a 30-s delay, equal volumes of HCl were added seven or eight times to the titration vessel until a final pH value of <3 was reached. The titration end-point was determined by a linear function, i.e., Gran titration method [Grasshoff *et al.*, 1999]. Water samples, standards, titrants, and titration vessels were all kept at 22.0°C using water jackets. The entire process was automated and completed within 6–8 min. Each sample was titrated at least twice with an overall precision of 0.08% (one standard deviation). CO_2 certified reference material from A. Dickson (SIO, UCSD) was used throughout the cruise to standardize the titrant. Internal data consistency was evaluated using the CO2SYS program [Lewis and Wallace, 1998], along with available DIC and $p\text{CO}_2$ (obtained at 20°C) data from the same samples [Wanninkhof and Thoning, 1993]. Carbonate dissociation constants were from Millero *et al.* [2006]. Calculated $p\text{CO}_2$ values were slightly higher than measured values ($9.2 \mu\text{atm}$) with one standard deviation of $15.4 \mu\text{atm}$.

[14] Alkalinity values for SAB samples were determined using a similar method. However, these water samples were preserved by adding saturated HgCl_2 (40 μL in 125 mL glass bottles). Titration was conducted in our laboratory at the University of Georgia.

3. Results

3.1. General Pattern of the TA-S Relationship at wNAO Margins

[15] The relationship between alkalinity and salinity in the entire wNAO margin database demonstrated a clear regional pattern (Figure 2). Shelf areas in the northern Gulf of Mexico (e.g., nGMx) that were influenced by the Mississippi and Atchafalaya River System had the highest zero-salinity y -intercept ($\text{TA}^0 = \sim 2400 \mu\text{mol kg}^{-1}$), whereas

Table 1. Summary of Cruise Data Sources^a

Cruise	Transect	Geographical Location	Sampling Time
WOCE	A01W	Labrador Sea	Jul–Aug 1994
CLIVAR	AR07W	Labrador Sea	Jun–Jul 1998
WOCE	A20	French Guiana	Aug 1997
CLIVAR Repeat	A20_2003	French Guiana	Oct 2003
WOCE	A22	Massachusetts-Trinidad	Aug–Sept 1997
CLIVAR	A22_2003	Massachusetts-Trinidad	Oct–Nov 2003
WOCE	A06	Offshore French Guiana	Feb 1993
WOCE	A17N	Offshore French Guiana	Mar 1994 ^b
Repeat MP	MP1	Subtropical North Atlantic and off Brazil	Jan–Feb 2001
Repeat MP	MP3	Subtropical North Atlantic and off Brazil	Jul–Aug 2001
Repeat MP	MP8	Offshore Brazil	Apr–May 2003
GOMECC	Florida	Gulf Stream	Jul 2007
GOMECC	Savannah	South Atlantic Bight	Jul 2007
GOMECC	NC	Mid-Atlantic Bight	Jul 2007
GOMECC	Woods Hole	Mid-Atlantic Bight	Aug 2008
GOMECC	GoME	Gulf of Maine	Aug 2008
MAB	see Table S1 in Text S1	Mid-Atlantic Bight	1994–1996
SAB	—	South Atlantic Bight	2005–2006
nGMx	—	Northern Gulf of Mexico	Aug 2007

^aWOCE and MP data were obtained from <http://cdiac.ornl.gov/oceans/datmet.html>.

^bCruise times shown here are the periods during which the indicated areas were surveyed.

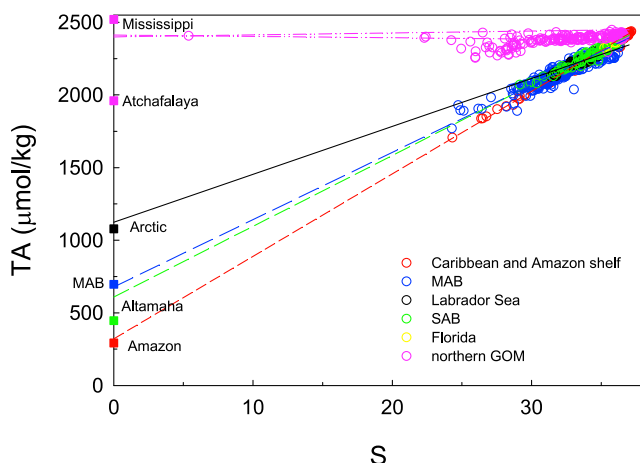


Figure 2. A summary of TA-S relationships across the wNAO margins. The markers on the y axis represent different river alkalinities in this region (see text for details). The lines are the least square linear fit to individual regions under examination. The river alkalinity values are: Mississippi River - $2520 \mu\text{mol kg}^{-1}$ (USGS); Atchafalaya River - $1960 \mu\text{mol kg}^{-1}$ (USGS); composite Arctic rivers - $1100 \mu\text{mol kg}^{-1}$ (PARTNERS program); MAB rivers - $697 \mu\text{mol kg}^{-1}$ (USGS); Altamaha River - $450 \mu\text{mol kg}^{-1}$ (W.-J. Cai, unpublished data, 2010); and Amazon River - $293 \mu\text{mol kg}^{-1}$ [Cooley, 2006].

tropical margins influenced by the Amazon and Orinoco rivers had the lowest TA^0 ($\sim 300 \mu\text{mol kg}^{-1}$). The SAB ($\sim 600 \mu\text{mol kg}^{-1}$), Mid-Atlantic Bight (MAB, $\sim 700 \mu\text{mol kg}^{-1}$), and Labrador Sea ($\sim 1100 \mu\text{mol kg}^{-1}$) were in the middle. These TA^0 values were, in general, similar to the respective regional river alkalinity values (Figure 2). As a related property, the slope of the regression lines decreased from the western tropical North Atlantic margin to the Labrador Sea and to the nGMx margin. The TA-S re-

lationships at each region or transect were examined in the following sections.

3.2. Labrador Sea

[16] The continental shelf of the Labrador Sea is dominated by water with relatively low salinity (<35). Relatively uniform vertical salinity and temperature distributions in the top ~ 50 m of the water along the Labrador coast extending ~ 180 km into the Labrador Sea were observed for both the A01 and AR07W transects. A linear regression line derived from the high salinity ($S = 32.7\text{--}34.8$) portion of the TA-S plot produced a very high TA^0 value of $1124 \mu\text{mol kg}^{-1}$ at zero salinity (Figure 3). The shallowest water samples ($8\text{--}10$ m) that were also the lowest in salinity (<32), however, fell off the regression line. A linear regression that used the average alkalinity and salinity values for the top 10 m of water and subsurface water produced a TA^0 value of $273 \mu\text{mol kg}^{-1}$ (Figure 3).

3.3. Gulf of Maine

[17] A plot of TA-S for the GOMECC GoME data showed two distinct segments of linear curves with different slopes and TA^0 values (Figure 4). Within the low salinity (<31.8) waters of the inner shelf, the regressed TA^0 ($75 \mu\text{mol kg}^{-1}$) was not significantly different from zero ($P = 0.8$). In contrast, in the high salinity offshore waters (>31.8), alkalinity and salinity exhibited a tight linear correlation with an elevated TA^0 of $933 \mu\text{mol kg}^{-1}$, a value only slightly lower than that of the Labrador Sea.

3.4. Woods Hole Transect

[18] In addition to the GOMECC Woods Hole (WH) transect, we included both of the WOCE and CLIVAR/ CO_2 Repeat transects (A22 and A22_2003) from offshore Cape Cod given the similar geographic location of these three transects. Similar to the GoME TA-S plot, two distinct salinity TA-S segments were found in Figure 5. Again, the

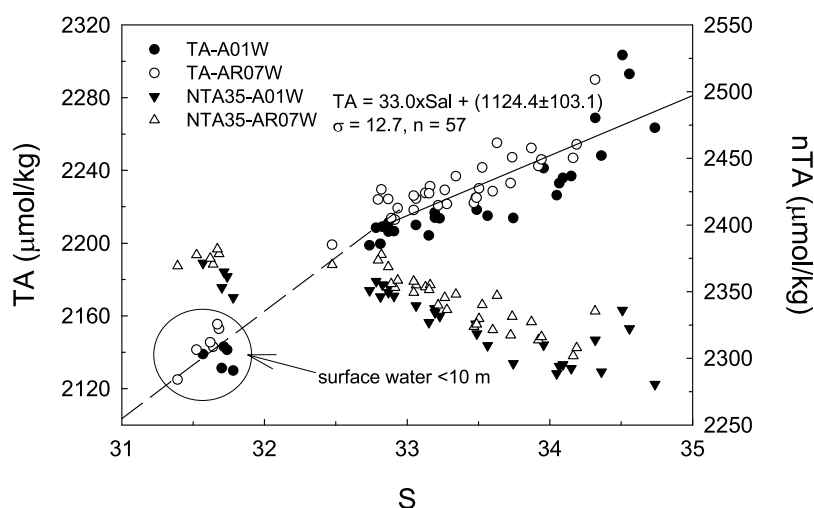


Figure 3. TA-S relationship in the Labrador Sea. The solid circles represent data from the WOCE A01W transect and open circles are from the CLIVAR AR07W transect. The dashed line represents the linear regression between alkalinity and salinity in the top 10 m and subsurface waters. Note that the uncertainty expressed within the parentheses in the equation is the regressed standard error for the regressed TA^0 .

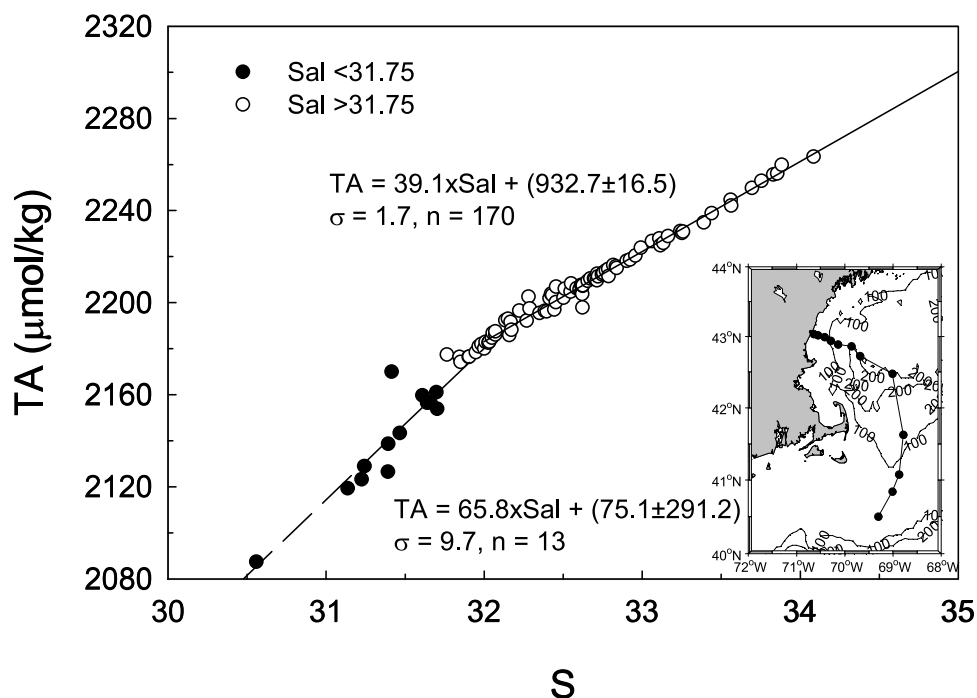


Figure 4. TA-S relationship in the Gulf of Maine. The solid circles represent samples with salinity < 31.75 and open circles represent samples with salinity > 31.75. The insert shows the cruise transect.

high salinity segment had a very high TA^0 value. The low salinity data from the WH transect, however, generated a negative TA^0 . It should be pointed out that this value ($-189 \mu\text{mol kg}^{-1}$) was not statistically significant or different from zero ($P = 0.06$) due to the scatter of data and the limited salinity range.

3.5. Middle Atlantic Bight

[19] The GOMECC NC transect and multiyear OMP cruises (total 32 transects [DeGrandpre *et al.*, 2002]) covered a broad expanse of the MAB area. Although MAB shelf water exhibited statistically significant spatial and

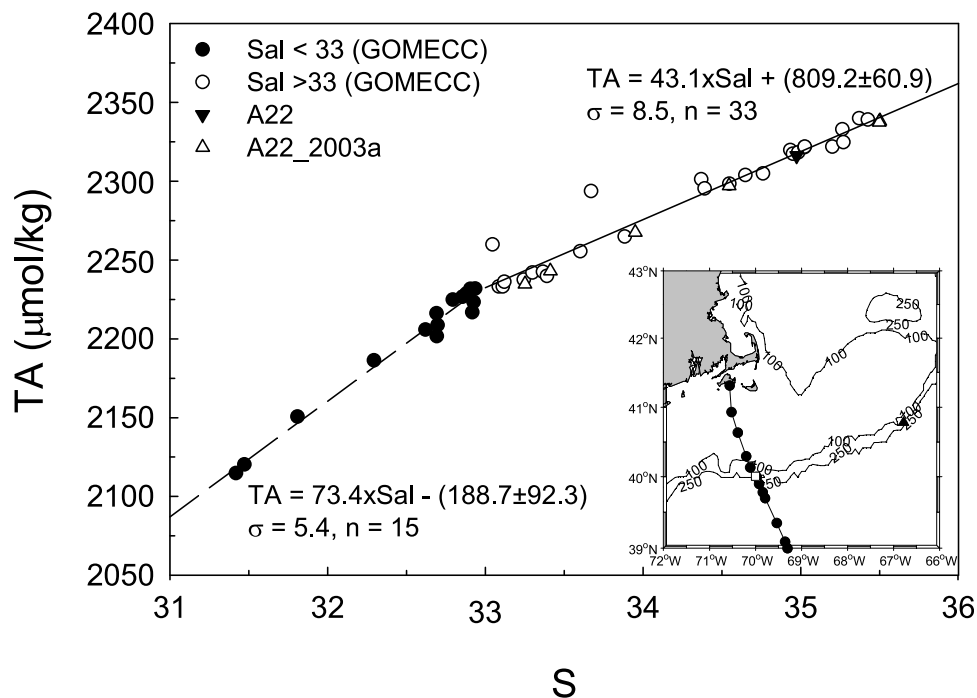


Figure 5. TA-S relationship along the Woods Hole transect during GOMECC. Two additional transects from both WOCE (A22) and CLIVAR (A22_2003) are included. The solid circles represent samples with salinity < 33 and open symbols represent samples with salinity > 33.

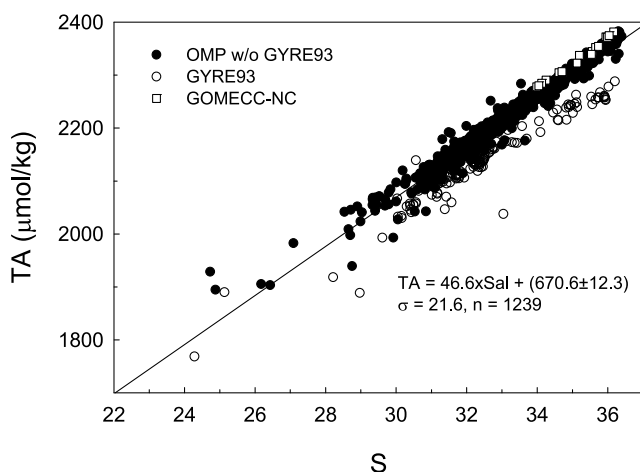


Figure 6. TA-S relationship in the Middle Atlantic Bight. Open circles are data from the GYRE93 cruise and solid circles are from the rest of the OMP data set. The regression line is based on all the data. If the GYRE93 data are excluded, the regressed slope and TA^0 become 46.6 and $676 \pm 8 \mu\text{mol kg}^{-1}$, respectively, and σ decreases to $12 \mu\text{mol kg}^{-1}$.

temporal variations in terms of its TA-S relationship (see section 4 and Table S2 in Text S1), a linear regression of the pooled OMP data showed a relatively good fit (Figure 6). It appears that the GYRE93 data somewhat strayed from the rest of the data set. If the GYRE93 data set was excluded, however, there was little change in terms of the regressed slope and TA^0 (see Figure 6 caption), although r^2 improved (from 0.93 to 0.97).

3.6. South Atlantic Bight

[20] Multiple SAB cruises were conducted in 2005–2006, and a transect (C transect, see Jiang *et al.* [2008] for details) starting from Sapelo Sound and crossing through the SAB shelf into waters with depths greater than 600 m was sampled repeatedly. Data obtained from the GOMECC GA transect that coincided with the C transect stations (but without the innermost ones) were also examined along with the SAB results.

[21] Despite seasonal variations, a linear regression on the pooled 2005–2006 data generated a good fit with a TA^0 ($609 \pm 28 \mu\text{mol kg}^{-1}$, Figure 7) slightly lower than that in the MAB. However, the May 2006 data did not fit the regression as well. Compared to the 2005 data that had a salinity range of 29.2–36.5, the May 2006 survey exhibited a much narrower salinity range (33.3–36.5), although the sampling stations were exactly the same (see section 4.5 for a discussion). If the 2006 data were excluded, the regressed slope and TA^0 changed somewhat (see Figure 7 caption), and r^2 improved only slightly. Furthermore, the regression on the March and July 2005 data produced a TA^0 of $520 \pm 31 \mu\text{mol kg}^{-1}$. Surprisingly, the linear regression on the GOMECC GA data yielded a negative TA^0 (Table S3 in Text S1). However, the salinity range observed in this transect was very narrow (35.5–36.4) due to the more offshore location of the sampling stations and a historically dry year.

[22] The TA^0 values derived from shelf-water data (520 – $609 \mu\text{mol kg}^{-1}$) roughly agreed with the Altamaha River

estuarine alkalinity values [Cai and Wang, 1998]. Furthermore, weekly monitoring of the Altamaha River yielded a discharge weighted average alkalinity of $433 \mu\text{mol kg}^{-1}$ ($n = 24$) at the head of tides for the period of February–July 2005 (W.-J. Cai, unpublished data, 2010). The Altamaha River, which is the largest in the SAB and discharges into an area immediately south of this transect, may serve as a proxy for the freshwater end-member in the study of shelf-water mixing processes in the SAB.

3.7. Straits of Florida

[23] The only TA-S data set available for the Straits of Florida was obtained from the GOMECC Florida transect along the 27°N line between Florida and Little Bahama Bank. Benthic topography along the west side of this transect is very steep, and water depths exceed 250 m only ~ 15 km offshore. Additionally, no rivers exist in this area. Thus, our data set was limited if we only considered shelf waters shallower than 250 m. Despite this, a strong linear relationship between alkalinity and salinity was clearly seen (Figure 8). An examination of the data from the entire transect (maximum depth 650 m) provided even stronger evidence that two-end-member mixing occurred between a less salty but denser deep water wedge ($26.7 < \sigma_\theta \leq 27.3 \text{ kg/m}^3$) and the overlying salty but more buoyant ($\sigma_\theta \leq 26.7 \text{ kg/m}^3$) Gulf Stream water. The bottom water mass had a salinity of 34.9 and a potential temperature of 7.3°C , which were in close agreement with the Antarctic Intermediate Water that flows northward through the Straits of Florida [Atkinson, 1983; Seim *et al.*, 1999].

3.8. Northern Gulf of Mexico and Western Florida Shelf

[24] Data from three GOMECC transects (July 2007) and an additional survey in the Mississippi River plume area immediately after the GOMECC study (Table 1 and Figure 1) were included in our analysis. Since the latter survey covered

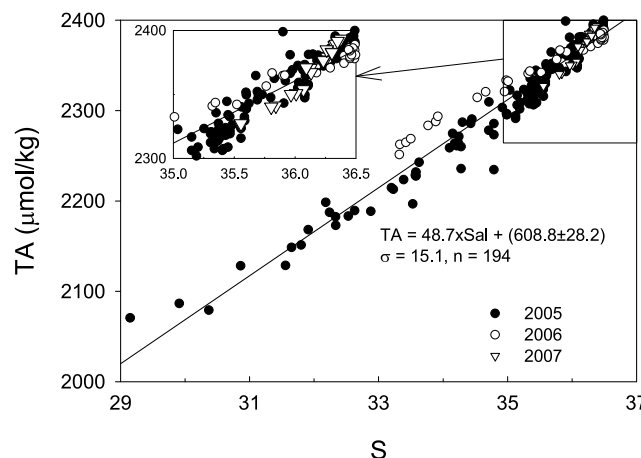


Figure 7. TA-S relationship in the South Atlantic Bight. Solid circles are data collected from 2005 and open circles are data from 2006. The 2007 GOMECC GA transect data are depicted as open triangles (see insert). The regression line is based on the combined 2005 and 2006 data sets. If the May 2006 data are excluded, the slope and TA^0 of the regression change to 49.7 and $569 \pm 30 \mu\text{mol kg}^{-1}$, respectively, although σ is similar ($15 \mu\text{mol kg}^{-1}$).

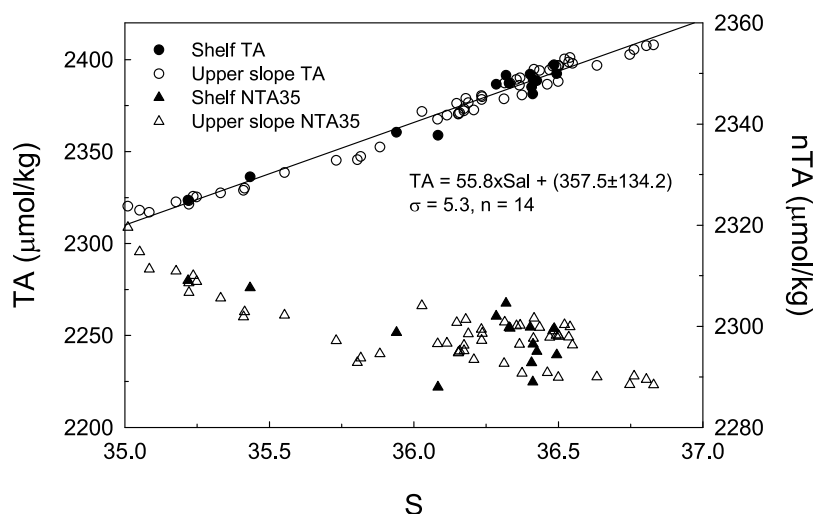


Figure 8. TA-S relationship in the Straits of Florida. The solid symbols represent data from within the 250 m shelf area and open symbols are from outside of the shelf area. The regression was performed on data within the shelf ($n = 14$).

an area with water depths less than 150 m, for consistency we used <150-m data for all three GOMECC transects as well (Figure 9).

[25] Alkalinity values from our surveys in the nGMx and Western Florida Shelf areas were consistently high (ranging between 2250 and 2450 $\mu\text{mol kg}^{-1}$) throughout our observed salinity range (5.4–36.5). Linear regression on the data from the GOMECC Galveston transect produced a lower bound of the regressed TA^0 value ($1997 \pm 32 \mu\text{mol kg}^{-1}$). On the other hand, using the 2007 nGMx data, if we took the two boundary alkalinity values (2447 $\mu\text{mol kg}^{-1}$ at $S = 35.8$ and 2379 $\mu\text{mol kg}^{-1}$ at $S = 36.4$) as the Gulf water end-member and regressed them with the sole low salinity data point ($S = 5.4$, alkalinity = 2407 $\mu\text{mol kg}^{-1}$), the extrapolated TA^0 value had a narrow range (2400–2412 $\mu\text{mol kg}^{-1}$, Figure 9). This was in reasonable agreement with the measured Mississippi River alkalinity value of $2375 \pm 239 \mu\text{mol kg}^{-1}$ ($n = 4$) at the St. Francisville USGS Hydrological Station (upstream of New Orleans, LA) and Atchafalaya River value of $1960 \pm 371 \mu\text{mol kg}^{-1}$ ($n = 4$) at the Melville USGS Hydrological Station during June–August 2007 (USGS “Water Quality Data for the Nation,” <http://nwis.waterdata.usgs.gov/nwis/qw>, hereafter USGS). Clearly the low salinity data points were heavily weighted in this type of regression. Nevertheless, these data sets indicate a very high alkalinity river water end-member in this region, reflecting the dominant influence by the Mississippi–Atchafalaya River System that contains high levels of weathering products [Cai, 2003; Cai and Lohrenz, 2010; Raymond and Cole, 2003].

[26] Shelf water along the Tampa transect on the west Florida Shelf had a narrow salinity range (36.4 ± 0.2 , $n = 27$), and alkalinity also varied very little ($2399 \pm 6 \mu\text{mol kg}^{-1}$, $n = 27$), indicative of low freshwater input in this area. Furthermore, high salinity (>36) shelf waters along the nGMx shelves between Galveston and Tampa appeared to have fairly uniform alkalinity.

3.9. Caribbean Sea

[27] Data from the WOCE A22 and CLIVAR A22_2003 transects conducted within the Caribbean Basin along the

66°W line between Puerto Rico and the northern coast of Venezuela were analyzed (Figure 1). The A22 data set had a narrower salinity range (35.3–37.3) than the A22_2003 data set ($S = 33.5$ –37.3). An ANCOVA (analysis of covariance) test found no significant difference between the two sets of TA-S regressions (see auxiliary material).¹ A linear regression on the pooled data yielded a tight correlation with a low TA^0 value of only 296 $\mu\text{mol kg}^{-1}$ (Figure 10).

3.10. Amazon River Plume and Nearby Areas

[28] In the tropical North Atlantic region influenced by the Amazon River plume, temporal changes in salinity were clearly observed. Salinity values from the WOCE A06, WOCE A17N, and MP1 (winter and early spring seasons) transects were all greater than 35, whereas all other cruises (summer and early fall) covered waters with a much greater salinity range. A regression of data from the individual transects also revealed temporal and spatial variations in the TA-S relationships in this area. A deflection point ($S = 35$) on the TA-S plot, although not apparent in Figure 11, was identified through statistical means for the WOCE A20 and A20_2003 transects (Table S4 in Text S1). Despite all the variations, a regression on the pooled data generated a tight fit (Figure 11), and the resultant TA^0 (321 $\mu\text{mol kg}^{-1}$) agreed reasonably well with the observed alkalinity value (293 $\mu\text{mol kg}^{-1}$) at the Amazon River mouth [Cooley and Yager, 2006; Cooley et al., 2007].

4. Discussion

4.1. Coastal Ocean Mixing Model

[29] To better interpret TA-S relationships in ocean margin waters, we must first briefly review the nature of water mass mixing in coastal oceans and the salinity normalization approach used in the literature. In the case of two-end-member mixing of river water and seawater, the slope and intercept of the mixing line, as defined in equation (1) and

¹Auxiliary materials are available in the HTML. doi:10.1029/2009JC005482.

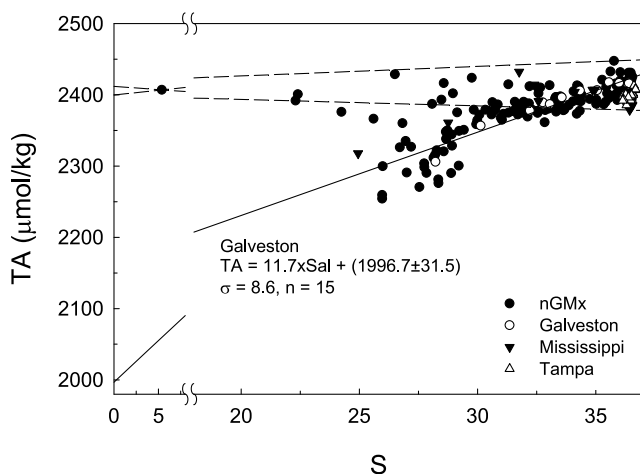


Figure 9. TA-S relationship in the northern Gulf of Mexico continental shelf. The two dashed lines are derived from a linear regression between the lowest salinity data point and the two extreme alkalinity data points at the oceanic salinity (see text for details). The solid regression line is derived using the GOMECC Galveston transect data ($r^2 = 0.92$).

illustrated in Figure 12 (e.g., line AC or DC), largely depends on river water alkalinity, as seawater alkalinity is nearly constant at a specific region. An extreme case is the dotted line denoted in Figure 12 as OC with zero alkalinity in fresh water (i.e., $TA^0 = 0$ in equation (1)). In a three-end-member mixing case, however, the resulting salinity and alkalinity pair is located within a triangle limited by the end-members. For example, triangle DAC represents mixing of two nearby rivers, having end-member values of A and D, with the seawater [Cai *et al.*, 2004]. Moreover, two separated mixing processes with a common mid-salinity end-member may also occur, e.g., lines represented by BD and BC in Figure 12.

[30] In oceanographic literature, the concept of normalized alkalinity, nTA , defined as TA/S multiplied by a reference

salinity of 35 or an average salinity in the study area, has been widely used to correct for alkalinity and salinity changes caused by precipitation and evaporation (see above [also see Friis *et al.*, 2003; Robbins, 2001]). Another related definition, specific alkalinity (i.e., TA/S), has also been used as a tracer to study water mass mixing and carbonate production in the water column [e.g., Morse *et al.*, 1984; Wong, 1988]. In fact, specific alkalinity is the slope of a TA-S line between the seawater end-member and a hypothetical freshwater end-member that has zero alkalinity (Figure 12). If a parcel of seawater is only influenced by precipitation and evaporation, normalized or specific alkalinity does not change since the pair of salinity and alkalinity values only move along this mixing line. An example is the dotted line denoted as OB (or OC) in Figure 12, which has only one slope, and every point on the line has the same nTA value. However, if the river end-member's alkalinity is greater than zero, a series of different slope values (specific alkalinity) or nTA values exists for water masses made of river water and seawater with different mixing ratios, i.e., a group of lines with different slopes can be drawn from various locations on the line AC (or DC) to the origin (O). Furthermore, such nTA values, or the slope of the lines, will become greater as salinity decreases (i.e., the line rotates from OC toward OB with one end anchored at the origin and the other moving along the mixing line BC). This outcome is called “over-correction” [Friis *et al.*, 2003] and is clearly inconsistent with the original purpose of using salinity normalization to correct for the dilution of TA. On the other hand, the nTA value for a specific water mass along line BC becomes its characteristic value if the subsequent process is only a dilution by zero alkalinity freshwater (i.e., mixing along the dotted lines OC or OB). This feature is useful for identifying a mixture of seawater and high alkalinity river water that is subsequently diluted by water from melting ice and/or local rivers with a very low TA.

[31] TA-S distributions in the wNAO reflect different mixing processes, i.e., alongshore current-dominated mixing, river-dominated mixing, and intermediate mixing cases. The river-dominated mixing (Figures 9, 10, and 11) is characterized by a single mixing line, as it is the local

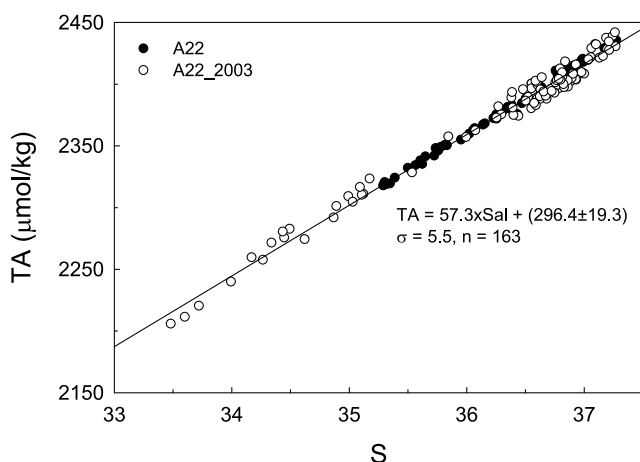


Figure 10. TA-S relationship in the upper Caribbean Sea (≤ 200 m). The solid circles represent data from the WOCE A22 transect and open circles are from the CLIVAR A22_2003 transect.

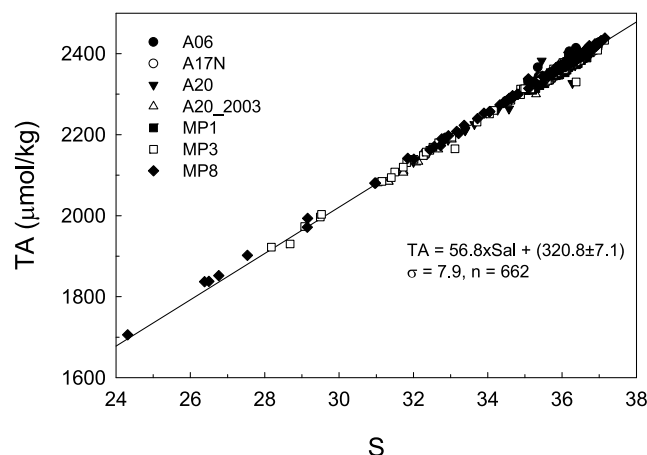


Figure 11. TA-S relationship in the western tropical North Atlantic Ocean margin surrounding the Amazon River plume.

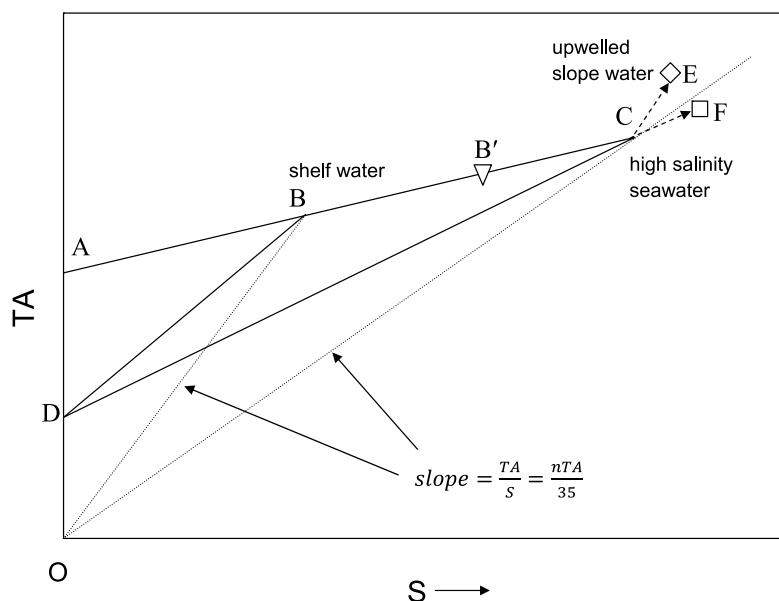


Figure 12. Schematic diagram representing conservative mixing between different water masses. The slopes of the two dotted lines represent the specific alkalinity of the two different water masses. The two solid lines are hypothetical mixing lines between a seawater end-member and a riverine end-member. Points A, D, and O represent three freshwater end-members with high, mid, and low (or zero) alkalinity at zero salinity. B represents shelf water, and C represents the high salinity seawater end-member (see text for details). E represents upwelled slope water. F is the high salinity oceanic end-member, and B' represents modified shelf water along the WH transect (see section 4.2.2 for details).

mixing between two end-members. The alongshore current-dominated mixing is characterized by a shared mid-salinity end-member, coming from outside the region, and a two-segment mixing line (Figures 3, 4, and 5). Admittedly, this categorization is rather empirical and simplistic, but it helps us to analyze and synthesize the nature of observed TA-S relationships in related regions.

[32] Areas controlled by alongshore current-dominated mixing have little local freshwater input. In these margins, coastal currents control much of the TA-S relationship. These areas include the Labrador Sea, GoME, and offshore Woods Hole (section 4.2). In contrast, margins controlled by river-dominated mixing are exemplified by areas influenced by the world's largest rivers, e.g., the Amazon-influenced shelf and slope (i.e., western tropical North Atlantic), Caribbean Sea, and the Mississippi Shelf (section 4.3). Between these two clearly definable classes, there are cases such as the SAB and MAB that are less clearly defined. Finally, biogeochemical processes may also influence the alkalinity distribution in some of these systems (section 4.5).

4.2. TA-S Patterns in Alongshore Current-Dominated Margins

[33] Local freshwater discharges in the Labrador Sea, GoME, and offshore Woods Hole are insignificant when compared to that carried by alongshore currents. For example, river discharge into the GoME is only $35 \text{ km}^3 \text{ yr}^{-1}$ [Brown and Irish, 1993], which is much smaller than the amount of freshwater, $726 \text{ km}^3 \text{ yr}^{-1}$, carried by the alongshore current which has a large volume of $\sim 0.4 \text{ Sv}$ or $1.3 \times 10^4 \text{ km}^3 \text{ yr}^{-1}$ [e.g., Chapman and Beardsley, 1989].

4.2.1. Control by Arctic Ocean Export and Ice Melting: Labrador Sea

[34] Alkalinity distribution in the Arctic Ocean is primarily controlled by terrestrial runoff and sea ice formation/melting, along with predominant Pacific water that is transported through the Bering Strait into the Arctic Basin. According to a recent study, a composite river end-member alkalinity value in the Arctic Ocean was $\sim 1100 \mu\text{mol kg}^{-1}$ (PARTNERS Program, <http://ecosystems.mbl.edu/partners/data.html> [Cooper et al., 2008]). River runoff in the Arctic Ocean enters the North Atlantic Ocean through the Denmark Strait and the Canadian Arctic Archipelago [Anderson et al., 2004]; water transported through the latter primarily contributes to the Labrador Sea. Continental shelf waters at both of the Labrador transects represent a conservative mixing between the Labrador Seawater with higher salinity but lower $n\text{TA}$ (referenced to $S = 35$; same hereafter) and the outflowing freshened Arctic surface waters. The latter have higher $n\text{TA}$ [Frolov et al., 2005] but lower salinity. The TA^0 of the TA-S regression in the $>10\text{-m}$ shelf waters (Figure 3) is consistent with the composite river alkalinity value from the Arctic Ocean. On the other hand, in the stratified water column, the top 10-m layer has a low regressed TA^0 but similar $n\text{TA}$ values ($2368 \pm 11 \mu\text{mol kg}^{-1}$) as those from the subsurface ($\sim 50\text{--}70 \text{ m}$) ($n\text{TA} = 2358 \pm 9 \mu\text{mol kg}^{-1}$) (Figure 3). This suggests that surface water is most likely the result of subsurface water being diluted by ice meltwater.

[35] The TA^0 obtained from low-salinity surface water data ($273 \pm 98 \mu\text{mol kg}^{-1}$, Figure 3) also agrees with sea-ice meltwater alkalinity ($175\text{--}550 \mu\text{mol kg}^{-1}$ at a salinity range of 2.5–9.7) [Jones et al., 2008; Rysgaard et al., 2007]. This

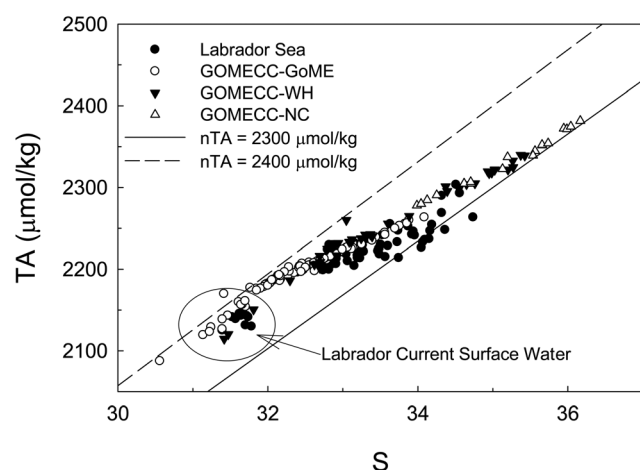


Figure 13. Combined TA-S plots for the northern wNAO margins that are influenced by the Labrador Current. The two linear lines (solid and dashed) represent the slope of the two water masses with an alkalinity of 2300 and 2400 $\mu\text{mol kg}^{-1}$ at salinity 35, respectively.

agreement further supports the conclusion that the low salinity region is a dilution of the subsurface water by ice meltwater.

4.2.2. Control by the Labrador Current-GoME and Offshore Woods Hole

[36] A branch of the Labrador Current that flows through the Scotian Shelf (by mixing with the glacial melt and river runoff) [Chapman and Beardsley, 1989] is believed to affect waters in the GoME and MAB shelves before it finally exits from the southern MAB [Chapman and Beardsley, 1989; Churchill and Berger, 1998]. Thus, the Labrador Current is expected to influence alkalinity variation in the midlatitude wNAO margins as well.

[37] In the GoME data set, the two-segmented TA-S relationship shows two separated mixing regimes sharing a common mid-salinity end-member (Figure 4 and line OBC in Figure 12, see section 4.1). The low salinity segment reflects mixing, which occurs solely in the surface low salinity water between the continental freshwater runoff and the incoming Scotian Shelf Water [e.g., Salisbury *et al.*, 2008] that has a relatively low salinity surface layer. Together, they form the mixing line represented by line OB in Figure 12. The second segment of mixing occurs between the modified surface water and the deep shelf water. The latter comes from the Labrador Slope Water [Brown and Irish, 1993; Ramp *et al.*, 1985] and has a higher alkalinity and salinity but lower $n\text{TA}$ (as represented by the dotted line OC in Figure 12). Therefore, a conservative mixing between these two end-members produces the mixing line represented by line BC in Figure 12.

[38] Farther south, the low salinity (<33) water on the Woods Hole transect represents a continuation of the out-flowing surface current from the GoME as its $n\text{TA}$ value ($2366 \pm 7 \mu\text{mol kg}^{-1}$, $n = 15$) is similar to that of its northern neighbors. Continued mixing between surface low salinity waters and deep shelf and slope waters would, however, modify the “mid-salinity end-member” toward the right along the mixing line BC (Figure 12). Hence, there is an increase in salinity but a decrease in the $n\text{TA}$ or the slope of

the low salinity mixing line (i.e., point B moves toward B' in Figure 12).

[39] At the same time, the high salinity end-member along the Woods Hole transect also exhibits higher alkalinity and salinity (Figure 5) but lower $n\text{TA}$ ($2311 \mu\text{mol kg}^{-1}$) than that in the GoME ($2324 \mu\text{mol kg}^{-1}$ in Figure 4). This phenomenon may be explained in terms of a mixing diagram as point C moves toward F in Figure 12. The mixing line, BC, then tilts slightly counterclockwise. Therefore, we may obtain a lower regressed TA^0 and elevated slope values (line B'F) (i.e., Figure 5 versus Figure 4). Based on this trend, we would expect a continuous “tilting” of this mixing line along the flow path of the Labrador Current as it continues to mix with slope waters, and its influence gradually diminishes. A compilation of the Labrador, GoME, Woods Hole, and NC transects clearly shows this trend in the high salinity zone (Figure 13). At the NC transect, the TA-S deflection point is no longer observed (all $S \geq 34$) (Figure 6).

[40] In summary, in high- to midlatitude ocean margins influenced by alongshore currents, it is unlikely that the extrapolated TA^0 value would agree with the alkalinity for local continental runoff (i.e., intercept A or D in Figure 12). Rather, this TA^0 reflects the collective result of the mixing of multiple sources. Furthermore, in these areas the TA^0 of the high salinity segment ($809\text{--}1124 \mu\text{mol kg}^{-1}$) generally agrees with the high latitude river export, which reflects the origin of the alongshore current.

4.3. TA-S Patterns in Large River-Dominated Margins

[41] Combined freshwater discharge by the Amazon and Orinoco rivers is as high as $7.8 \times 10^3 \text{ km}^3 \text{ yr}^{-1}$, which amounts to 21% of the total global river discharge [Dai and Trenberth, 2002]. In the tropical North Atlantic margins influenced by these rivers, regression lines precisely predict the river end-member alkalinity (Figure 2). This result strongly supports the argument that river-ocean mixing is the dominant process controlling alkalinity distribution in large river impacted ocean margins. Moreover, the combined discharge of the Mississippi-Atchafalaya River System is also high ($580 \text{ km}^3 \text{ yr}^{-1}$). Here, the mixing line is largely controlled by river-ocean mixing. It is of significant interest to point out that the high alkalinity input from the Mississippi River and other large midlatitude and subtropical rivers such as the Huanghe, Changjiang, and Pearl rivers in China exert a strong carbonate buffering effect on river plumes. Such buffering effect is insignificant in low alkalinity tropical rivers like the Amazon River plume [Cai *et al.*, 2004, 2008].

4.3.1. Two-End-Member Mixing in Regions Impacted by the Amazon and Orinoco Rivers

[42] Several studies have investigated the inorganic carbon system in the western tropical North Atlantic region to address carbon cycling problems associated with Amazon River discharge [Cooley and Yager, 2006; Cooley *et al.*, 2007; Subramaniam *et al.*, 2008 and references therein]. Basin-wide net precipitation and thus, river discharge, exhibit a seasonal pattern in the Amazon River drainage basin. The highest discharge occurs in May and the lowest occurs in November. In addition, both measured and modeled alkalinity values show a clear seasonal pattern. The TA^0 of the regressions from all individual cruises (Table S4 in Text S1) agree well with the river end-member alkalinity

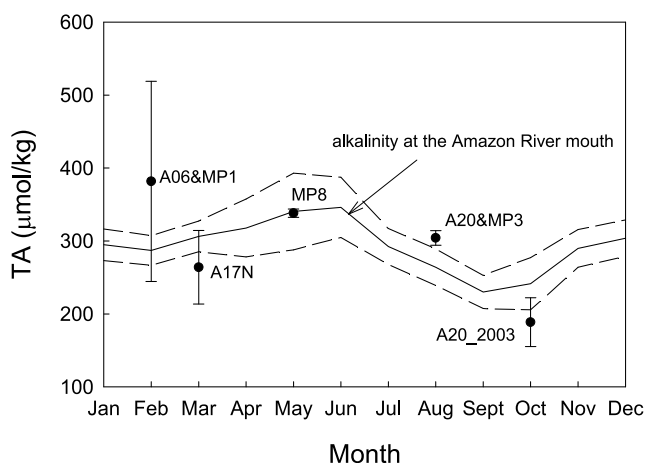


Figure 14. Relationship between the Amazon River end-member alkalinity (solid line) and regressed TA^0 (data points with error bars) from individual western tropical North Atlantic Ocean margin cruises. The solid line is modeled alkalinity reproduced from Cooley *et al.* [2007], and the dashed line represents the 95% confidence interval. Error bars of the data points represent standard errors derived from TA-S linear regressions for each individual data set.

values (Figure 14) [also see Cooley *et al.*, 2007]. This agreement further confirms that conservative mixing between river water and seawater is the dominant process in this area.

[43] The top 200 m of Caribbean seawater along the 66°W line is considered to be a mixture of Caribbean Surface Water and water masses from both the North and South Atlantic oceans. In addition, the Caribbean Surface Water is a mixture of North Atlantic surface waters and river waters (Amazon, Orinoco, and other local rivers [Hernández-Guerra and Joyce, 2000]). In terms of the TA-S variations, however, a simple linear relationship between these two parameters is present despite the possibility of a complex mixing scheme in this region (Figure 10). Temporal variations of salinity in this region can be mostly accounted for by seasonal river discharge rates. For example, the Orinoco River discharge peaks in August and is lowest in the spring [Hernández-Guerra and Joyce, 2000; Hu *et al.*, 2004]. This coincides with the two different salinity ranges observed during the WOCE/CLIVAR transects (i.e., $S = 35.3\text{--}37.3$ from the August 1997 cruise had less river influence compared to $S = 33.5\text{--}37.3$ from the October 2003 cruise, Table 1 and Figure 10). It is also worth noting that differences in the freshwater contribution do not appear to be sufficient to alter the TA-S relationship. The close agreement between the two TA^0 values from the Amazon area and Caribbean Sea (Figures 10 and 11) also suggests common characteristics, i.e., low concentrations of weathering products and low seasonal variability in these two large South American tropical rivers [Cai *et al.* 2008].

4.3.2. Complicated Mixing in the Mississippi-Atchafalaya River-Influenced Area

[44] In the Mississippi River plume and nGMx, the TA-S correlation is not as simple as in the Amazon and Orinoco river-influenced areas. A low alkalinity signal, of up to 100 $\mu\text{mol/kg}$ below the mixing line, if we follow the dashed mixing line (Figure 9), was observed in the mid-

salinity waters (Figure 9), which agreed with an earlier report [Cai, 2003]. We offer three possible explanations. First, river end-member alkalinity could change significantly with river discharge in the Mississippi River [Cai, 2003] and other middle latitude large rivers [Cai *et al.*, 2008]. Such a quick change in end-member alkalinity could create an apparent “alkalinity removal or addition” [Officer, 1979]. Depending on whether river discharge was increasing or decreasing, the river end-member alkalinity value could be decreasing or increasing, i.e., a relatively stable weathering rate being diluted by net precipitation with a certain time lag [Cai *et al.*, 2008]. The Mississippi River end-member alkalinity variability was as large as $\pm 239\text{ kg}^{-1}$ in June–August of 2007 (Figure 15).

[45] Second, the low alkalinity at salinity 25–30 could be a third end-member signal from the Atchafalaya River, which receives source water from both the Mississippi River and local small rivers. We had observed before that alkalinity values from both rivers were very similar (in Aug. 1998 [see Cai and Lohrenz, 2010]). It was thus concluded that the Mississippi River plume was a two-end-member mixing regime [Cai, 2003]. However, the USGS records (Figure 15) and our recent studies indicate that Atchafalaya River alkalinity values could often be much lower than the Mississippi River, depending on the level of contributions from its local water sources. For example, in June and August 2007, alkalinity in the Atchafalaya River was lower than the Mississippi River by as much as 200 to 600 kg^{-1} . Therefore, this interpretation of the low alkalinity signal in mid-salinity plume appears reasonable. In addition, we will offer a third explanation – biological carbonate production to account for this apparent alkalinity loss in section 4.5. Despite these complications, the TA-S relationships in the majority of this region follow a two-end-member mixing pattern between the river water and the seawater.

4.4. Intermediate Mixing Cases

4.4.1. Mixing Dominated by a River and an Ocean End-Member

[46] Despite the existence of a southward Labrador Current in the MAB area [e.g., Chapman and Beardsley, 1989],

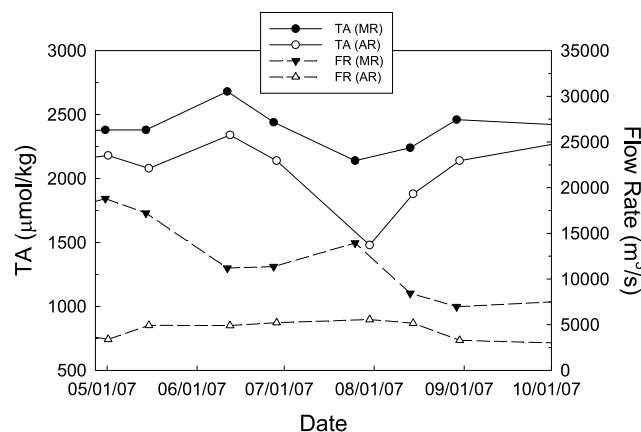


Figure 15. River water alkalinity and flow rates of the Mississippi and Atchafalaya Rivers during May–October, 2007 (USGS). MR and AR represent the Mississippi River and Atchafalaya River, respectively.

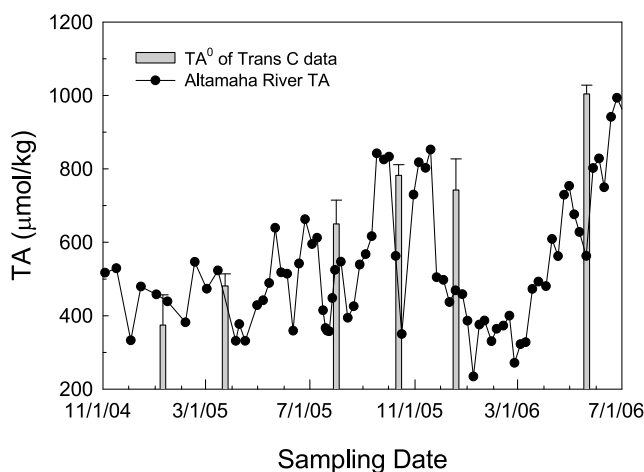


Figure 16. Relationship between the Altamaha River end-member alkalinity (solid line) and the regressed TA^0 (vertical bars) for each cruise. Uncertainties in the vertical bars are standard errors for TA^0 obtained from the linear regressions.

it appears that the third end-member water mass has limited influence on the OMP data set (Figure 6). A salinity break in the TA-S plots similar to that for the GoME and offshore Woods Hole was found in only very few cases. In addition, the distinction between the two segments in each of the three plots was rather small (data not shown). We argue that the combined result of the following two factors may have masked the difference between the two segments. First, local rivers in the MAB have higher alkalinity than those in the GoME area (i.e., O or D moves upward toward A, Figure 12). Second, as the Labrador Current extends south, both salinity and alkalinity increase. Thus, the shelf water end-member B moves closer to or even merges with the slope water end-member C. Despite a relatively coarse sampling resolution in the low salinity range (<30) waters, the TA^0 value (Figure 6) is very close to the discharge weighted average alkalinity ($697 \mu\text{mol kg}^{-1}$, USGS, see Table S5 in Text S1) of several major rivers, including the Susquehanna, Connecticut, and Hudson in the MAB region.

[47] The TA-S relationship in the SAB follows a two-end-member mixing line very well (Figure 7). The TA^0 values derived from the shelf waters ($520\text{--}609 \mu\text{mol kg}^{-1}$, section 3.6) in the SAB are close to the average value of the weekly Altamaha River alkalinity (see section 3.6 and Figure 7) and that within the estuary [Cai and Wang, 1998]. More importantly, seasonal variations of Altamaha River alkalinity appear to match TA^0 values obtained from the five individual SAB cruises (Figure 16). Note that there is a time lag between the riverine alkalinity and the regressed TA^0 values given the approximate one-month residence time of freshwater in the SAB inner shelf [Atkinson, 1985; Menzel, 1993]. The close resemblance between river alkalinity and regressed TA^0 supports conservative mixing mechanisms between freshwater and seawater end-members (e.g., mixing line DC, Figure 12). We interpret the small discrepancy between them as a benthic biogeochemical production of alkalinity (section 4.5).

[48] In summary, despite the existence of alongshore currents, alkalinity and salinity distributions in the MAB and SAB also appear to be controlled largely by the freshwater-

ocean mixing process. However, the influence of both slope water upwelling (section 4.4.2) and nearshore benthic processes (see section 4.5) is present. In both regions, freshwater inputs are significant (150 and $66 \text{ km}^3\text{yr}^{-1}$ respectively). This feature further enables us to associate them with river-dominated margins when discussing river influence on the TA-S relationship.

4.4.2. Mixing Between Shelf and Slope Waters

[49] In the Straits of Florida, local river runoff is minor and is reflected by the narrow salinity range ($35.2\text{--}36.5$). Seawater in this region is characterized by a two-layer structure, i.e., Gulf Stream water on the surface and Antarctic Intermediate Water on the bottom (section 3.7). Fast flow (strong shear) in the western half of the Straits produces nearly parallel isopycnal surfaces relative to the benthic topography. Thus, dominant mixing in this region is between the upwelled bottom water and the salty surface water. The average nTA value is greater in the bottom layer than in the surface layer (Figure 8). The mixing line BC in Figure 12 again explains this mixing scheme: B represents low salinity but high nTA deep water and C represents the upper layer of the Gulf Stream that has high salinity but lower nTA . Thus, the TA^0 obtained does not represent an alkalinity value for an actual freshwater end-member. Therefore, it is difficult to associate the TA-S relationship in the Straits of Florida, controlled by shelf-slope mixing, with either the river-dominated or alongshore current-dominated mixing type.

[50] Exchanges between shelf and deep slope water also appear to affect TA-S distributions in the offshore SAB. For example, the 2007 GOMECC GA transect data set yielded a set of much different regression coefficients when compared to all the other individual C transect data sets (Figure 7 and Table S3 in Text S1). Similarly, we can use Figure 12 to illustrate this TA-S variation. During 2007, the shelf area was dominated by offshore water due to low freshwater discharge at a time of historic drought and a more offshore sampling location. Mixing between the slope water (diamond point E) with a higher salinity and higher nTA (above the line OC) with this shelf water in a very narrow salinity range ($35.5\text{--}36.3$) produced a negative TA^0 (i.e., line B'E). A similar observation in this area was also reported by Wong [1988]. This TA^0 value, however, did not physically reflect the river input, e.g., acidic river water, as the water samples were collected far from shore.

4.5. Biological Modifications of the TA-S Relationship

[51] Biological processes that can alter coastal water alkalinity include carbonate formation/dissolution, benthic alkalinity production and, to a lesser extent, water column photosynthesis/respiration. All of these processes cause TA-S relationships to deviate from linear conservative mixing patterns. We will, however, limit our discussion to river-dominated margins in this paper. Their simple two-end-member mixing scheme allows deviations from ideal behavior to be detected more easily.

[52] A significant decrease in alkalinity (up to $100 \mu\text{mol kg}^{-1}$ from the mixing line) was observed in the middle salinity region ($S \sim 25\text{--}30$) of the Mississippi River plume (Figure 9). In section 4.3.2, we offered two explanations: an influence of a lower alkalinity third end-member and a single but changing river end-member. Another plausible explanation

is calcification [Cai, 2003]. In the mid-salinity zone, due to strong biological CO_2 uptake, we observed a condition of low $p\text{CO}_2$ ($\sim 100 \mu\text{atm}$), high pH (8.5), and high aragonite saturation state (5–8 times), favoring calcification (W.-J. Cai, unpublished data, 2010). Note that DIC deficit relative to the mixing line was greater than the TA deficit [see Cai, 2003; W.-J. Cai, unpublished data, 2010]. Although coccolithophore calcification was observed on filters (W.-J. Cai, unpublished data, 2010), further research is needed to determine quantitatively the contribution of calcification. Such a calcification process, if confirmed by further experiments, would play an important but opposite role (i.e., releasing CO_2) from that of primary production (i.e., taking up CO_2) in the ocean margin carbon cycle.

[53] Benthic alkalinity production may also contribute to water column alkalinity inventory [Fennel and Wilkin, 2009; Thomas et al., 2009]. In the SAB, TA^0 values derived from the TA-S regressions of shelf waters ($520\text{--}609 \mu\text{mol kg}^{-1}$) were greater than the composite riverine alkalinity value ($433 \mu\text{mol kg}^{-1}$). This observation agrees reasonably well with the conclusion of Cai and Wang [1998]. The current study and the earlier work [Cai et al., 2003] also show that alkalinity extrapolated from a linear regression of data from the shelf is higher than the river alkalinity but lower than that found in inshore waters. Cai and Wang [1998] proposed that sedimentary anaerobic respiration (e.g., sulfate reduction and denitrification) was the main cause for such apparent non-conservative mixing behavior. The location of such “excess alkalinity” production may be found in the salt marshes that dominate the SAB coastal sounds and estuaries. This mechanism was substantiated later by field observations in waters around Sapelo Island [Wang and Cai, 2004]. Therefore, in the SAB, the TA^0 obtained from the TA-S regression represents a composite end-member of river, estuarine and nearshore marsh, and sedimentary contributions to alkalinity [Cai et al., 2003]. Shallow water depths in the SAB would allow such benthic signals to be more visible. Longer shelf water residence time during periods of drought may also allow the benthic signal to accumulate in the shelf water (see Table S3 note in Text S1).

4.6. Controls of the Global Scale TA-S Pattern in Ocean Margins

[54] As demonstrated in this paper, the TA^0 values obtained from the TA-S regressions performed on ocean margin areas are largely controlled by the river end-member TA. River water alkalinity, however, exhibits both spatial and temporal variations as a result of CaCO_3 mineral content and precipitation rate in river basins [Cai et al., 2008]. Alkalinity in the world's major rivers exhibits a latitudinal distribution pattern. Low latitude ($<23^\circ$) rivers generally have the lowest alkalinity due to very low carbonate mineral content and high precipitation (hence discharge) rates in their drainage basins. High latitude ($>60^\circ$) rivers are more enriched with alkalinity than low latitude rivers. Midlatitude ($23\text{--}60^\circ$) rivers have the highest alkalinity, largely due to high carbonate mineral content in their drainage basins (see Cai et al. [2008] for a detailed discussion). Although the alkalinity of a river end-member is not necessarily represented by the exact zero-salinity value of the ocean margin TA-S regression, Figure 2 does show a general dependence of these TA^0 values on latitude that agrees reasonably well

with river-water alkalinity adjacent to the margins examined here, as well as general river alkalinity distribution globally [Cai et al., 2008].

5. Summary and Conclusions

[55] The controls on TA-S relationships for the western North Atlantic Ocean margins (including the western tropical Atlantic margin) can be categorized by a spectrum of patterns that are bracketed by two extreme mixing cases, namely, river-dominated and alongshore current-dominated. In the river-dominated mixing case, the TA^0 values of the TA-S regressions follow those of the river alkalinity values, which show a latitudinal pattern due to carbonate mineral content and precipitation in their respective drainage basins. Such an agreement implies that conservative mixing is often the dominant process in these ocean margins. The extent of river-ocean mixing control relies on the strength of the river discharge and the absence of a strong coastal alongshore current. This is clearly demonstrated by the perfect mixing lines in the area influenced by the Amazon and Orinoco rivers. Such simple mixing scenarios are complicated in the Mississippi-Atchafalaya River plume area as the two river end-member values differ and vary with discharge. In contrast, a segmented mixing line with a shared mid-salinity end-member is common in the mid- to high-latitude areas linked by a strong alongshore current (i.e., Labrador Sea, GoME, and Woods Hole). In these areas, local riverine freshwater export is often relatively insignificant compared to the magnitude of non-local freshwater carried by the alongshore current. Accordingly, alkalinity distribution is mainly controlled by the alongshore currents. TA-S relationships in the MAB and SAB indicate mixing processes between these two extreme cases but can be associated more closely with the river-dominated mixing process. Finally, in the Straits of Florida, mixing occurs between the shelf and the upwelled slope waters.

[56] Meanwhile, biological activities that may consume alkalinity (e.g., calcification) or produce alkalinity through anaerobic processes from nearshore regions may also affect water column alkalinity inventory. However, further studies on both processes are needed to explore the underlying mechanisms and quantify their significance.

[57] As a conservative parameter in ocean water mixing, TA-S relationships in ocean margin areas provide important information on water mixing, along with traditionally measured hydrographic parameters. As HCO_3^- is the dominant component in both alkalinity and DIC, alkalinity variations provide a particularly powerful tool for studying the biological alteration of DIC. Therefore, applications that link alkalinity distribution with water mixing will be very useful in studying the ocean margin carbon cycle.

[58] On the other hand, despite recent efforts to promote ocean margin research, ocean margins still remain greatly undersampled in terms of inorganic carbon dynamics (including alkalinity). This is primarily due to the complexity and high heterogeneity caused by land-ocean interactions. Hence at the present stage using salinity derived alkalinity in calculating the inorganic carbon system will inevitably lead to significant errors, depending on the “tightness” of the TA-S fits. For example, uncertainties associated with calculated DIC concentrations are $\sim 19 \mu\text{mol kg}^{-1}$ in the MAB

and $\sim 13 \mu\text{mol kg}^{-1}$ in the SAB, if we use the regressed alkalinity–salinity relationship and measured $p\text{CO}_2$ data assuming an uncertainty of $\pm 3 \mu\text{atm}$ in $p\text{CO}_2$. These uncertainties are likely to be amplified due to seasonal changes that affect TA–S relationships. Therefore, before we can begin using simpler and more easily obtained hydrographic proxy data (e.g., salinity), more detailed direct measurements of carbonate parameters such as TA, DIC, and $p\text{CO}_2$ are clearly necessary.

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