

Unveiling carbonate dissolution in coastal sediments and its influence on seawater buffering capacity with $\delta^{13}\text{C}_{\text{DIC}}$ and ^{224}Ra – ^{228}Th disequilibria

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Abstract

Organic carbon mineralization is generally recognized as the primary source of dissolved inorganic carbon (DIC) released from sediments in coastal seas. The CO_2 accumulation or the formation of corrosive microenvironment induced by organic carbon degradation can promote the dissolution of calcium carbonate (CaCO_3) in sediments, complicating the efficiency of carbon burial and total alkalinity (TA) inputs to aquatic environments. However, quantitative assessments of sediment CaCO_3 dissolution and its impacts on the seawater carbonate remain poorly constrained. In this study, we selected typical high-productivity regions, mariculture farms, and applied the ^{224}Ra – ^{228}Th disequilibrium approach to quantify the effluxes of DIC and TA across the sediment-water interface. Stable carbon isotopes of DIC ($\delta^{13}\text{C}_{\text{DIC}}$) were employed to trace DIC sources in porewater. The results showed that CaCO_3 dissolution in sediments accounted for $29 \pm 13\%$ – $55 \pm 10\%$ of the benthic DIC efflux. Notably, a high contribution of CaCO_3 dissolution did not coincide with strong organic carbon degradation across sites, suggesting that dynamic disturbance on sediments, which weakened the metabolic CO_2 accumulation in porewater, was also a crucial factor affecting carbonate dissolution. According to the evaluation of the influence that benthic DIC and TA efflux exerted on the seawater CO_2 content, the TA supplied by the CaCO_3 dissolution was identified to enhance the carbonate buffering capacity of seawater and counteracted the acidification driven by organic matter remineralization. This indicates that CaCO_3 dissolution in sediments should be involved in coastal carbon cycling and assessments on coastal ecosystem resilience under the risk of CO_2 elevation.

Keywords: Sediment CaCO_3 dissolution; DIC- $\delta^{13}\text{C}$; Benthic efflux; ^{224}Ra – ^{228}Th disequilibria

1 Introduction

Over half of atmospheric carbon dioxide (CO_2) is estimated to be fixed by marine primary production and the coastal ocean contributes over 1.0 Pg C y^{-1} (Bauer et al., 2013; Mathis et al., 2024). Consequently, the coastal sediment becomes a crucial carbon reservoir as a result of particulate carbon deposition, particularly in high production regions such as estuaries and seaweed farms (Friedlingstein et al., 2025; Duarte et al., 2025). Some of the buried carbon undergoes early diagenetic processes, e.g., aerobic mineralization, and is transformed into dissolved inorganic carbon (DIC), reducing the long-term carbon burial (Burdige et al., 2016; Silverberg et al., 2000). For instance, approximately 35% of the deposited carbon in the surface sediment was returned to the water column in the Baltic Sea (Wakeham and Canuel, 2006); and studies in China estuaries demonstrated that DIC effluxes from sediments were in the same order of magnitude with those from the riverine or submarine groundwater discharges (Cai et al., 2015; Hong et al., 2017). Meanwhile, the accumulation of DIC may decrease porewater pH, potentially degrading the ecological environment.

In general, the degradation of organic carbon is considered the dominant process to add DIC to sediment porewater in coastal seas (Berner, 1980; Middelburg, 2018). Some studies have demonstrated that carbonate dissolution can be triggered by microbial respiration even in the calcite-oversaturated waters (Cai et al., 2006; Wang et al., 2025). The role of calcium carbonate (CaCO_3) dissolution in absorbing CO_2 and increasing total alkalinity (TA) in marine systems is recognized (Jahnke et al., 1997; Morse et al., 2006). Marine calcifying organisms are widely distributed throughout the ocean so surface sediments above the saturation horizon generally contain abundant CaCO_3 debris (Harikrishnan and Nathan, 2023; Ying et al., 2024), implying that both CaCO_3 dissolution and organic matter degradation likely occur ubiquitously within sediments (Goossens et al., 2026). Some chamber experiments have demonstrated that the CO_2 produced from organic matter degradation drove CaCO_3 dissolution in marginal sea sediments. However, the extent of such CO_2 -induced dissolution varied widely in different regions. As the chamber experiments mostly focus on biochemical influences on CaCO_3 dissolution, the constraints of dynamic processes are still unclear (Jahnke et al., 1994, 1997; Ortega et al., 2005). Moreover, the TA increased by CaCO_3 dissolution is demonstrated to mitigate the risks of water acidification induced by organic matter remineralization (Millero, 2007; Boudreau et al., 2018; LaRowe et al., 2020), but quantitative influence on the carbonate buffering capacity of seawater is also lack of constraint. Therefore, it is crucial to clarify the mechanism on biogeochemical cycling of inorganic carbon at the sediment-water interface, in particular when CaCO_3 dissolution may act as an important regulator maintaining the long-term stability of marine carbonate systems.

Sansha Bay in Fujian Province (China) represents one of major mariculture regions in the world and has undergone rapid expansion of seaweed farming in recent decades (FAO, 2024). Previous studies have

shown that the sediment carbon inventories under the farming zones have been ten times higher than those in non-mariculture seas (Duarte et al., 2025; Zhao, 2023; Wang et al., 2023). Despite such high productivity, the seawater in the bay does not deteriorate into acidification. In addition to active tidal exchange with shelf waters, CaCO_3 dissolution is hypothesized to play a key role in counteracting acidification (Wang et al., 2025). However, the regulating mechanism and quantitative influence on seawater are still unclear. In this study, a natural radionuclide approach (^{224}Ra – ^{228}Th disequilibrium, Cai et al., 2015) was applied to quantify benthic fluxes of DIC and TA in Sansha Bay. By integrating stable carbon isotopic signatures ($\delta^{13}\text{C}$) of sedimentary carbon (Alling et al., 2012), we further identify the relative contributions of organic carbon degradation and CaCO_3 dissolution to benthic DIC release under different benthic environments, delineating the mechanism controlling sediment CaCO_3 dissolution. At last, the processes improving the seawater buffering capacity were recognized by comparing the changes of CO_2 and pH induced by various processes, elucidating the benthic influence on the carbonate system of seawater.

2 Materials and methods

2.1 Study sites and sample collection

Sansha Bay (26.5–26.8°N, 119.5–120.1°E, [abbreviated as SSW](#)) is a semi-enclosed bay located in southeastern China with water depths ranging from several meters to ~50 m. The local currents are dominated by tides and the rates of tidal currents are over 1 m s^{-1} near channel zones (Lin et al., 2019). The seaweed farms are widely distributed throughout Dongwuyang and the tidal zones adjacent to the main channels, and are controlled by regular semi-diurnal tides. Macroalgae-shellfish co-culture is the main practice of farms in Dongwuyang. The dominant macroalgae species are *Saccharina japonica* and *Gracilariopsis lemaneiformis*, and shellfish species are *Haliotis discus hannai* and *Crassostrea* (Wang et al., 2019).

Field work was conducted in 2024 and three stations were selected to represent contrasting mariculture settings (Fig. 1a). Station SSW-A is located within the Dongwuyang seaweed farms, where the sediment contains abundant shell debris and polychaetes fragments (Fig. 1b). SSW-B is located in a sea cucumber culture zone adjacent to the main channel, with comparatively low farming intensity. SSW-C, near the bay mouth and outside the seaweed-farming zone, serves as a reference site for a non-mariculture condition (Fig. 1b). Water depth varied with tides and the specific depths during core collection ranged from 4–9 m. Detailed sampling information was listed in Appendix Table S1. In particular, sediments in the embayment are in [highly](#) heterogeneity due to the mariculture behaviors. Human activities such as channel dredging and seasonal feeding can also change the sediment characters. The sampling sites in this study were mainly considered for the different hydrodynamic environments

100 (inner and outer bay) and anthropogenic influences (with and without mariculture), not for the representative of the whole embayment. Overall, intensive aquaculture activities introduce shell fragments and coarse particles into the sediments so the sediment was mainly characterized by silty clay and clayey silt. Influenced by tidal currents and biological activities, the surface sediment in the bay is generally permeable.

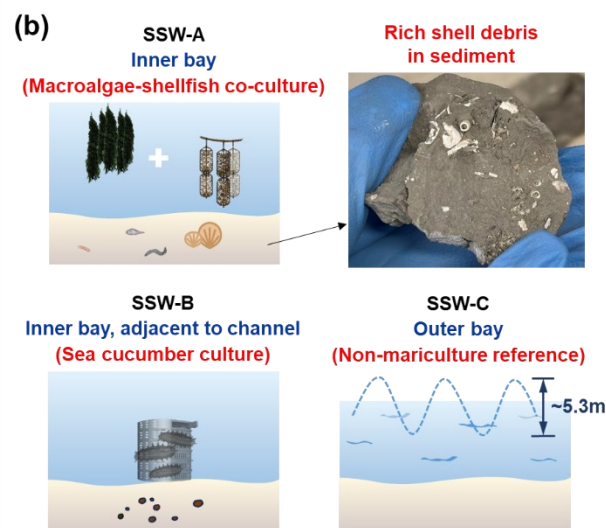
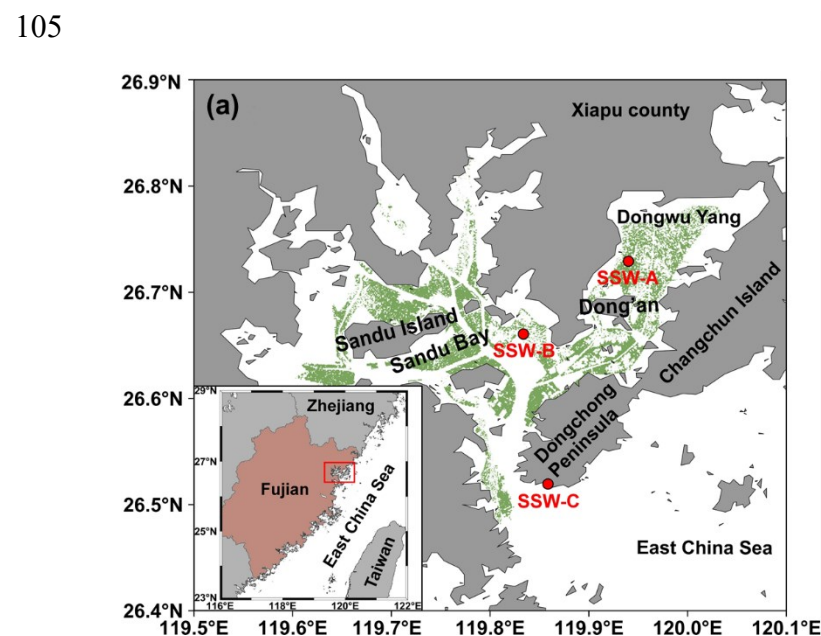


Figure 1: (a) Sampling stations (red circles) in Sansha Bay (Abbr. SSW). The inserted map shows the location of the bay. The green-shaded area within the bay indicates the distribution of mariculture. (b) Schematic diagrams of mariculture types of different sites.

110 Bottom water was collected with a 5-liter Niskin bottle. Samples for carbonate parameters (DIC, TA and $\delta^{13}\text{C}_{\text{DIC}}$) were stored in 250 mL borosilicate glass bottles and ~5 L of water was transferred into a clean cubitainer for ^{224}Ra enrichment. Sediment cores were collected by a single-tube sampler, using polycarbonate tubes (i.d. 65 mm) with pre-drilled holes. After siphoning off the overlying water, sediment porewater was extracted using Rhizon samplers via the holes at 1–2 cm intervals (Seeberg-Elverfeldt et al., 2005). Porewater from two cores was stored for carbonate analysis, ensuring the total volume >10 mL; the same depth porewater from different cores was combined so >30 mL porewater was used for a ^{224}Ra measurement. An intact core longer than 15 cm was sliced at a 1-cm interval for ^{224}Ra – ^{228}Th disequilibria and particle analysis (Cai et al., 2015). Seawater and porewater samples for DIC and TA were killed with saturated HgCl_2 solution by 0.5‰ (vol./vol.). Water samples for dissolved ^{224}Ra (D- ^{224}Ra) were filtered through 142-mm glass fiber filters (GF/F) and stored at room temperature for radium enrichment.

2.2 Sample analysis

2.2.1 ^{224}Ra and ^{228}Th

Each of the sediment slices was transferred into a 250 mL Teflon beaker and mixed with approximately 200 mL of Milli-Q water. The slurry was thoroughly stirred and subjected to ultrasonication for 5–10 minutes to ensure complete dispersion of sediment particles. Subsequently, concentrated ammonia solution was added to the slurry to adjust the pH to 8–9. Thereafter 1.00 mL of KMnO_4 solution (3.0 g L^{-1}) and 1.00 mL of MnCl_2 solution ($8.0 \text{ g L}^{-1} \text{ MnCl}_2 \cdot 4\text{H}_2\text{O}$) were sequentially added to form a MnO_2 suspension that coprecipitated Ra from the slurry. The particles of the slurry were filtered through a 142-mm GF/F filter ($0.7\text{-}\mu\text{m}$ nominal pore size), and the bulk ^{224}Ra activity of the sediment was measured using a radium delayed coincidence counting system (RaDeCC, Scientific Instrument Inc., USA). After ~ 10 days and ~ 25 days, when ^{224}Ra had ingrown to secular equilibrium with its parent ^{228}Th , the second and third measurements were conducted in the same system. The final activities of both ^{224}Ra and ^{228}Th in the sediment were calculated from the first and the average of the last two measurements (Cai et al., 2012). A comparison between the last two runs was performed to check the reproducibility, yielding a mean ratio of 1.018 ± 0.026 ($R^2 = 0.98$, $n = 29$), suggesting that the RaDeCCs' efficiency kept stable during the analysis.

In the enrichment of D- ^{224}Ra , 30–40 mL of porewater was transferred into a 100 mL Teflon beaker and ^{224}Ra was coprecipitated with MnO_2 following the similar procedure to the bulk ^{224}Ra . The precipitates were collected on a 47-mm GF/F filter. For the bottom water ($\sim 5 \text{ L}$), 5 mL of KMnO_4 (3.0 g L^{-1}) and MnCl_2 ($8.0 \text{ g L}^{-1} \text{ MnCl}_2 \cdot 4\text{H}_2\text{O}$) solutions were sequentially added into the sample and mixed for full reaction. The formed MnO_2 coprecipitates were then filtered onto a 142-mm GF/F filter. D- ^{224}Ra activities were determined by counting the filters in RaDeCCs for more than 8 hours (Cai et al., 2015).

The final ^{224}Ra and ^{228}Th activities were corrected with chance coincidences, detector efficiencies and self-decay (Cai et al., 2012), and the uncertainties, propagated from counting statistics, were approximately 5% for total ^{224}Ra - ^{228}Th and 8–10% for D- ^{224}Ra . According to the standard deviation of the activity ratios of ^{224}Ra to ^{228}Th ($^{224}\text{Ra}/^{228}\text{Th}$) in aged sediment samples ($n = 29$), sediment layers with $^{224}\text{Ra}/^{228}\text{Th}$ of 1.00 ± 0.05 were considered to be in secular equilibrium between ^{224}Ra and ^{228}Th .

2.2.2 DIC, $\delta^{13}\text{C}_{\text{DIC}}$ and TA

The DIC concentrations in seawater and porewater were determined with a non-dispersive infrared analyzer (Li-Cor 7000, USA) after acidification with a mixture of 3% H_3PO_4 and 7% NaCl (Sun et al., 2024). The relative standard deviation (RSD) of replicates was well controlled less than 0.2%. The $\delta^{13}\text{C}_{\text{DIC}}$ (‰) was analyzed with an automatic DIC- $\delta^{13}\text{C}$ analyzer with an accuracy (1σ) of $\pm 0.1\%$ (Picarro G2131-i, USA). The TA was measured following the Gran titration (Gran, 1952). Porewater samples were first

diluted with TA-known aged seawater. The titrant was 0.1 mol L⁻¹ HCl and the titration was automatically terminated using a titrator (Apollo AS-ALK3, USA) with an Orion AR1-17304 pH electrode. Each TA sample was measured 2–3 times, yielding the RSD within ±0.5% after volume correction. Both DIC and TA concentrations were calibrated with Scripps Certified Reference Material (CRM, Batch #198) (Dickson et al., 2003).

2.2.3 The $\delta^{13}\text{C}$ isotope of sediment TOC ($\delta^{13}\text{C}_{\text{TOC}}$)

Dried sediment samples were ground and homogenized with a mortar and pestle. Approximate 1 g of each sample was weighed and acidified with 1.2 N HCl (guaranteed reagent, GR). The mixture was subjected to ultrasonication for 1 h, followed by a 5-h water bath at 60°C to completely remove the inorganic carbon. Subsequently, the samples were repeatedly rinsed with Milli-Q water until the pH of the supernatant was neutral. The remaining particles were then dried at 60°C and accurately weighed. The mass loss relative to the dry sediment was assumed as total CaCO₃ in this study. Total inorganic carbon (TIC) was calculated from CaCO₃ and the precision (0.1 mg) was based on that of the weight scale. The TOC content was determined using an elemental analyzer (vario ISOTOPE, Elementar., Germany) and calibrated with an acetanilide standard (Sigma-Aldrich). The $\delta^{13}\text{C}_{\text{TOC}}$ was simultaneously measured with a continuous-flow isotope ratio mass spectrometer and the accuracy (1 σ) was ±0.1‰.

2.3 The influence of benthic effluxes on carbonate system

With the analytical results of the above-mentioned parameters, the total benthic fluxes of DIC and TA were calculated using the radionuclide approach (the ²²⁴Ra–²²⁸Th disequilibrium), and the relative contributions of organic carbon degradation and CaCO₃ dissolution to the benthic DIC flux were quantitatively determined using $\delta^{13}\text{C}_{\text{DIC}}$ values of porewater. Thereby, the impacts of these benthic processes on water-column carbonate system, including CO₂ concentrations, pH, calcite saturation (Ω_{calcite}), were then quantified via the flux proportions and the CO2SYS program (Lewis et al., 1998). A schematic flowchart illustrating the quantitative approach is provided (Fig. 2) and detailed descriptions are presented in the following sections.

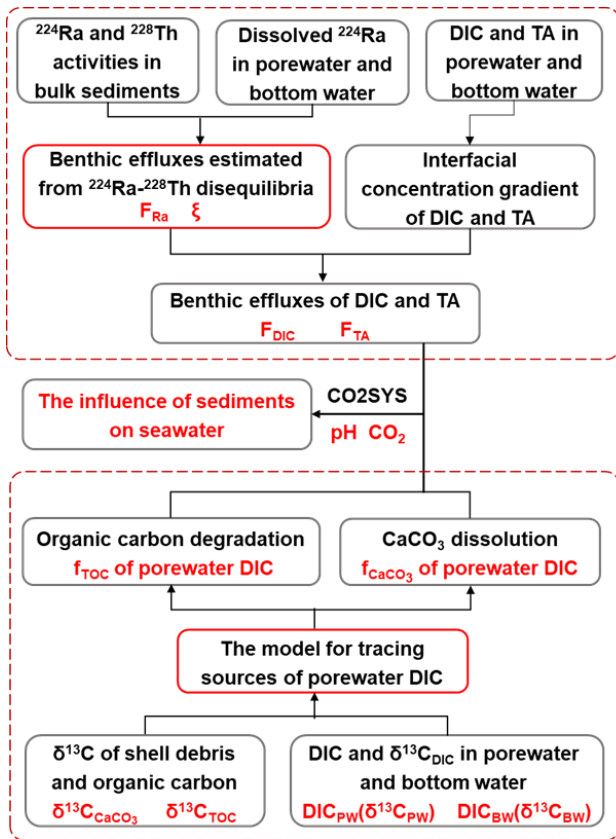


Figure 2: A schematic flowchart of quantitative approaches. The top frame illustrates the approach for benthic effluxes of DIC and TA; the bottom frame illustrates the approach for contribution proportions of organic carbon degradation (TOC) and CaCO₃ dissolution to porewater DIC. The red highlights the key parameters in the assessment of the benthic influence on seawater carbonate system.

2.3.1 Benthic effluxes estimated from ²²⁴Ra–²²⁸Th disequilibria

In a hydrodynamic system like Sansha Bay, the interface between sediment and seawater has been extended by active benthic irrigation so traditional methods such as diffusion or incubation experiments may fail to accurately estimate benthic exchange fluxes (Shi et al., 2018). In contrast, the ²²⁴Ra–²²⁸Th disequilibrium approach has been confirmed as a robust method for capturing complex interfacial processes in most China coastal seas (Shi et al., 2019). In the ²³²Th decay series, ²²⁴Ra is the daughter of ²²⁸Th. Owing to the distinct particle reactivities, ²²⁴Ra can be desorbed from particles in saline waters, whereas ²²⁸Th remains strongly bound on sediment particles. With exchanges between bottom waters and porewaters, total ²²⁴Ra generally presents deficits relative to its parent ²²⁸Th in surface sediments (Cai et al., 2015). Therefore, the ²²⁴Ra efflux (F_{Ra}) across the sediment-water interface can be quantified from

the disequilibria between ^{224}Ra and ^{228}Th (Eq. 1, Cai et al., 2015):

$$F_{\text{Ra}} = \lambda_{\text{Ra}} \int_0^z (A_{\text{Th}} - A_{\text{Ra}}) dz \quad (1)$$

200 where λ_{Ra} represents the decay constant of ^{224}Ra (0.189 d^{-1}), A_{Ra} and A_{Th} represent the ^{224}Ra and ^{228}Th activities in bulk sediments (dpm cm^{-3}) corrected with porosity (Φ), respectively, and z denotes the depth at which ^{224}Ra and ^{228}Th approach secular equilibrium. This efflux reflects the synergistic effect with molecular diffusion, bioturbation and irrigation at the interface so a diffusion model embedding increased surface area can be applied to stand for the exchange:

$$205 \quad F_{\text{Ra}} = \xi \Phi D_s^{\text{Ra}} \frac{\partial A_{\text{DRa}}}{\partial z} \quad (2)$$

where ξ denotes the factor indicating the enhancement of interface area, D_s^{Ra} represents the molecular diffusion coefficient of ^{224}Ra that has been corrected with in-situ temperature and sediment porosity, and $\frac{\partial A_{\text{DRa}}}{\partial z}$ is the ^{224}Ra activity gradient at the sediment-water interface.

Under the same circumstance, the area-enhancement model should be appropriate to other solutes so
210 the benthic fluxes of carbonate parameters (DIC and TA) can be estimated as

$$F_m = \xi \Phi D_s^m \frac{\partial C^m}{\partial z} \quad (3)$$

where F_m refers to the benthic flux of DIC or TA across the sediment-water interface, D_s^m represents the diffusion coefficient of bicarbonate (HCO_3^-), and $\frac{\partial C^m}{\partial z}$ denotes the concentration gradient of DIC or TA at the interface.

215 **2.3.2 The model for tracing sources of porewater DIC**

In marine environments, $\delta^{13}\text{C}_{\text{TOC}}$ is generally around -20‰ (Jahnke et al., 1997; Hu and Burdige, 2007), whereas CaCO_3 in shells exhibits $\delta^{13}\text{C}$ values ($\delta^{13}\text{C}_{\text{CaCO}_3}$) ranging from -7.7‰ to -2.6‰ (Surge et al., 2001; Gillikin et al., 2006; Hadden et al., 2018). Although sediment porewater is derived from bottom seawater, the degradation of organic matter and the dissolution of CaCO_3 in sediments can add lighter
220 carbon to porewater DIC (DIC_{PW}), resulting in the $\delta^{13}\text{C}$ of DIC_{PW} more negative than those of bottom water (DIC_{BW}). Assuming that the differences in DIC concentrations between bottom water and porewater are solely attributed to the two processes (organic carbon degradation and CaCO_3 dissolution), their relative contributions to the porewater DIC can be defined as f_{TOC} and f_{CaCO_3} , namely

$$f_{\text{CaCO}_3} + f_{\text{TOC}} = \frac{\text{DIC}_{\text{PW}} - \text{DIC}_{\text{BW}}}{\text{DIC}_{\text{PW}}} \quad (4)$$

225 The isotopic composition of DIC in porewater ($\delta^{13}\text{C}_{\text{PW}}$) can be expressed as (Alling et al., 2012)

$$\delta^{13}\text{C}_{\text{PW}} \cdot \text{DIC}_{\text{PW}} = \delta^{13}\text{C}_{\text{BW}} \cdot \text{DIC}_{\text{BW}} + \delta^{13}\text{C}_{\text{CaCO}_3} \cdot f_{\text{CaCO}_3} \cdot \text{DIC}_{\text{PW}} + \delta^{13}\text{C}_{\text{TOC}} \cdot f_{\text{TOC}} \cdot \text{DIC}_{\text{PW}} \quad (5)$$

where $\delta^{13}\text{C}_{\text{BW}}$ represents the $\delta^{13}\text{C}$ -DIC in bottom water; and $\delta^{13}\text{C}_{\text{CaCO}_3}$ and $\delta^{13}\text{C}_{\text{TOC}}$ stand for the $\delta^{13}\text{C}$ of shell debris and organic carbon (TOC) in the sediment, respectively. By combining Eq. (4) and Eq. (5),

f_{TOC} and f_{CaCO_3} can be calculated.

230 2.4 Data analysis

Significance tests were performed using R (R Core Team, 2023). The Shapiro–Wilk test (`shapiro.test`) was used to assess the normality of $\delta^{13}\text{C}_{\text{DIC}}$ in porewaters and bottom waters, and a t -test was applied for the value comparison. In Sect. 4.3, a [linear](#) mixed-effects model (from the package 'lme4') was employed to test whether the theoretical $\delta^{13}\text{C}_{\text{DIC}}$ derived solely from TOC degradation matched the measured porewater $\delta^{13}\text{C}_{\text{DIC}}$.

Considering the variabilities of $\delta^{13}\text{C}_{\text{CaCO}_3}$ and $\delta^{13}\text{C}_{\text{TOC}}$ in natural samples, a Monte Carlo simulation, performed with the software Oracle Crystal Ball (Release 11.1.2.4; Oracle Corporation), was used for the estimate of source proportions. In each simulation, $\delta^{13}\text{C}_{\text{CaCO}_3}$ and $\delta^{13}\text{C}_{\text{TOC}}$ were independently sampled from their respective distributions, and then were substituted into the equations (4) and (5) to calculate f_{CaCO_3} and f_{TOC} . For each layer, this procedure was repeated 10000 times. The final results are reported with the average of the simulations, and the standard deviation (1SD) represents the uncertainty.

3 Results

245 3.1 The distributions of ^{224}Ra and ^{228}Th in the sediment

The total ^{224}Ra and ^{228}Th present similar vertical distributions in sediments as ^{224}Ra is derived from the radioactive decay of ^{228}Th (Fig. 3a). At SSW-A and SSW-C, deficits of ^{224}Ra , with the average $^{224}\text{Ra}/^{228}\text{Th}$ of 0.89 ± 0.05 ($n = 14$, 1SD), were observed in the upper 10 cm, whereas equilibrium between ^{224}Ra and ^{228}Th was characterized below 12 cm ($^{224}\text{Ra}/^{228}\text{Th} = 0.98 \pm 0.03$, $n = 4$). For SSW-B, the total ^{224}Ra was nearly in equilibrium with ^{228}Th (Fig. 3b). In the outer-bay sediments (SSW-C), the ^{224}Ra and ^{228}Th activities were in the range of 1.70 ± 0.10 – 4.55 ± 0.29 dpm g^{-1} and 2.01 ± 0.06 – 4.54 ± 0.16 dpm g^{-1} , respectively. In comparison, the sediment in the inner bay (SSW-A and SSW-B) had lower radionuclide activities (1.34 ± 0.09 – 3.00 ± 0.20 dpm g^{-1} for ^{224}Ra and 1.40 ± 0.05 – 3.25 ± 0.10 dpm g^{-1} for ^{228}Th , Table S1 in Appendix).

Vertical profiles of D- ^{224}Ra activities in porewater and bottom water (depth = 0) are presented in Fig. 3c. The activities of D- ^{224}Ra in bottom water, ranging from 0.11 ± 0.01 to 0.39 ± 0.02 dpm L^{-1} , were 1–2 orders of magnitude lower than those in porewaters (Table S2 in Appendix). The differences in porewater D- ^{224}Ra between stations were consistent with the total ^{224}Ra in sediments. Namely, D- ^{224}Ra activities at SSW-C (16.2 ± 1.9 – 52.4 ± 3.1 dpm L^{-1}) were higher than those at inner-bay stations (4.0 ± 0.8 – 25.8 ± 2.4 dpm L^{-1}). At depths where total ^{224}Ra was deficient relative to ^{228}Th , D- ^{224}Ra activities exhibited obvious

variations. Correspondingly, layers where ^{224}Ra – ^{228}Th activities approached equilibria, such as 4–10 cm at SSW-B, coincided with stable distributions of $\text{D-}^{224}\text{Ra}$ (RSD < 7%).

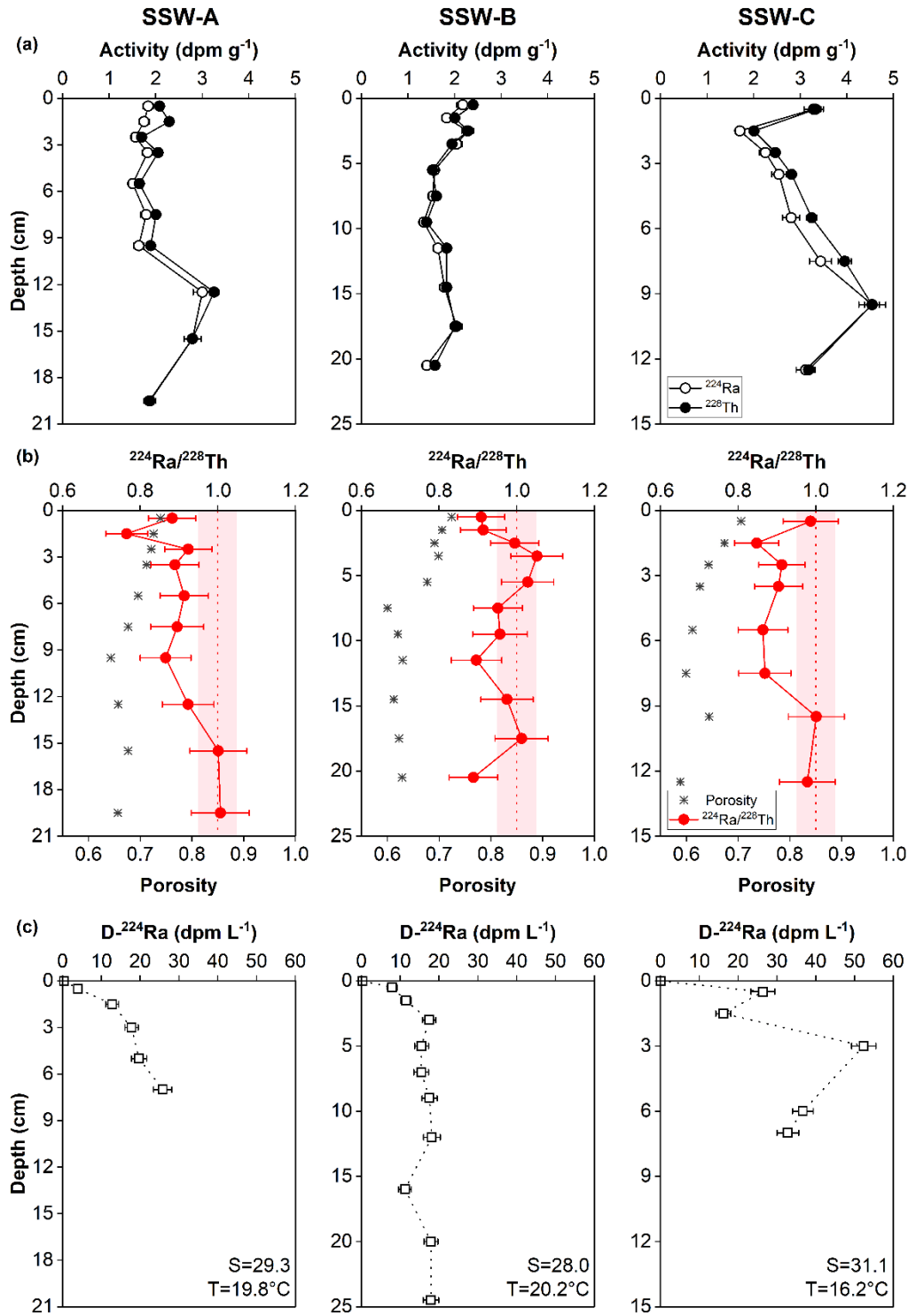


Figure 3: (a) Vertical profiles of bulk ^{224}Ra and ^{228}Th (error = $\pm 1\sigma$) activities in the sediment. (b) **Porosity distributions** and activity ratios of ^{224}Ra to ^{228}Th , with the shaded indicating secular equilibrium between ^{224}Ra and ^{228}Th ($^{224}\text{Ra}/^{228}\text{Th} = 1.0 \pm 0.05$); (c) Vertical profiles of $\text{D-}^{224}\text{Ra}$ (error = $\pm 1\sigma$) in porewater (the symbol at depth = 0 represents the bottom water). Note that the activity ranges and depth ranges differ slightly among stations.

3.2 The distributions of DIC, TA, and $\delta^{13}\text{C}_{\text{DIC}}$ in the porewater

In the bottom water, the DIC and TA concentrations were in the range of 1964–2229 $\mu\text{mol kg}^{-1}$ and 1982–2357 $\mu\text{mol kg}^{-1}$, respectively. The porewater exhibited particularly higher DIC and TA (ranging from 2184 to 3007 $\mu\text{mol kg}^{-1}$, from 2326 to 3081 $\mu\text{mol kg}^{-1}$, respectively) than the bottom water (Table S3 in Appendix). At SSW-A and SSW-C, the DIC and TA concentrations generally increased with depth (Fig. 4). At SSW-B, unexpectedly, both DIC and TA concentrations decreased with depth below 3 cm, and the concentrations of DIC above 15 cm were higher than TA.

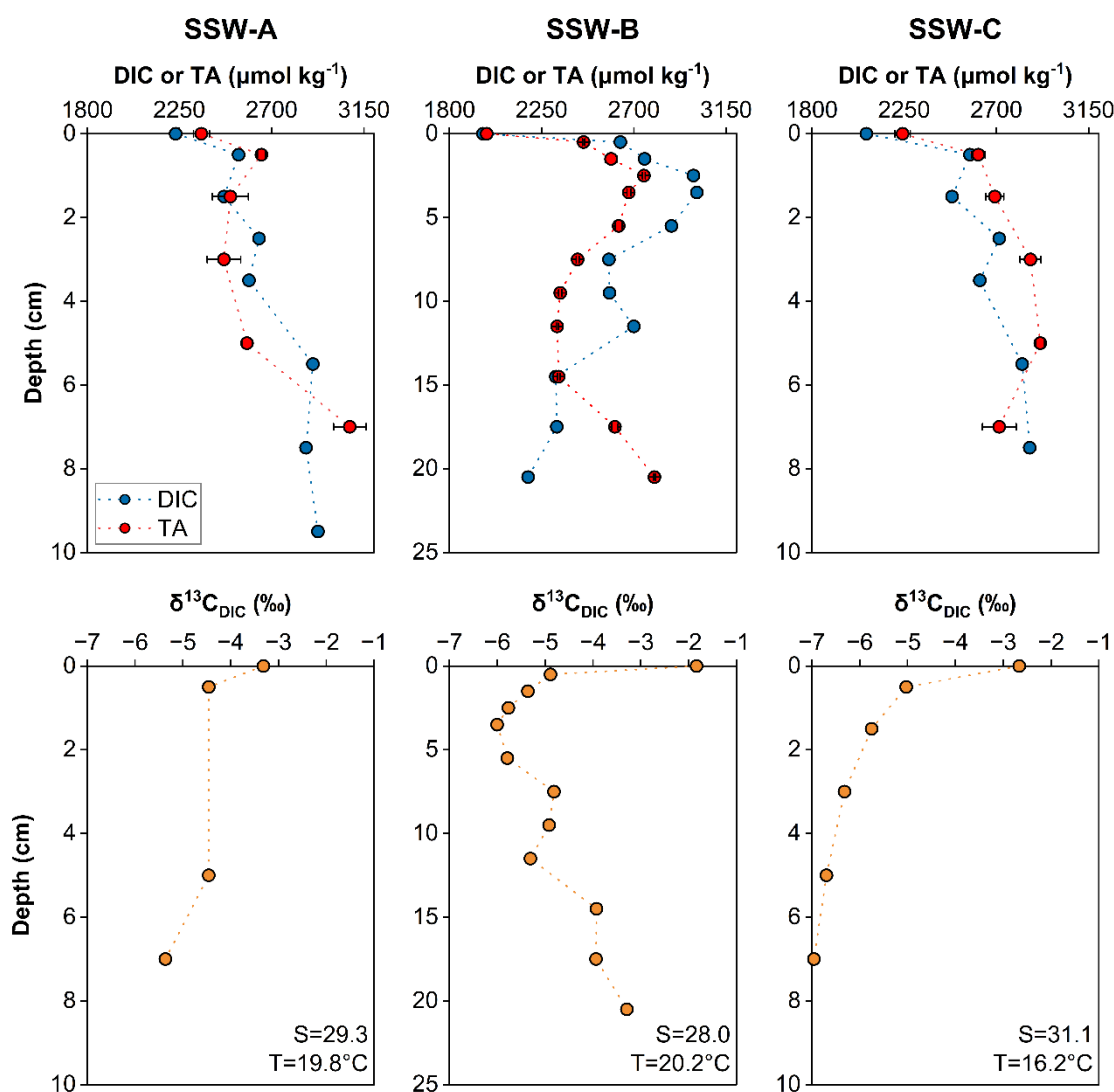


Figure 4: Vertical profiles of DIC, TA (error = $\pm 1\text{SD}$), and $\delta^{13}\text{C}_{\text{DIC}}$ in porewater, where depth = 0 represents the bottom water layer. Note that the depth ranges at Station SSW-B are different from the other stations.

In comparison, the profiles of porewater $\delta^{13}\text{C}_{\text{DIC}}$ and DIC overall exhibited opposite trends although the $\delta^{13}\text{C}_{\text{DIC}}$ values at station SSW-A were discrete due to the restricted number of samples (Fig. 4). The $\delta^{13}\text{C}_{\text{DIC}}$ of the bottom water in our study area ranged from -3.3‰ to -1.8‰, more negative than the values of offshore waters in the East China Sea (-1.2–0.8‰) (Wang et al., 2016). The $\delta^{13}\text{C}_{\text{DIC}}$ values of the porewater varied between -7.0‰ and -3.3‰, significantly lower than those of the bottom water ($p < 0.001$, t -test, Fig. 4). Especially, the porewater $\delta^{13}\text{C}_{\text{DIC}}$ at SSW-A was the heaviest while that at SSW-C contained the lightest $\delta^{13}\text{C}_{\text{DIC}}$ although the DIC concentrations of the two stations were comparable.

3.3 The $\delta^{13}\text{C}$ in shells and sediment TOC

Shells for $\delta^{13}\text{C}_{\text{CaCO}_3}$ were collected from oysters and abalones and the values ranged from -4.5‰ to -3.4‰ ($n = 9$) with a median of -3.8‰ (Fig. 5). The sediment $\delta^{13}\text{C}_{\text{TOC}}$ of all subsamples was in the range of -24.6 to -22.4‰ ($n = 27$), the median of which was -23.3‰. In particular, the TIC contents were highest in the sediment of SSW-A (15.4 to 35.4 mg g^{-1} , Table S1 in Appendix), coincident with the abundant shell debris in the sediment and the relatively positive porewater $\delta^{13}\text{C}_{\text{DIC}}$ at this station (Fig. S1 in Appendix).

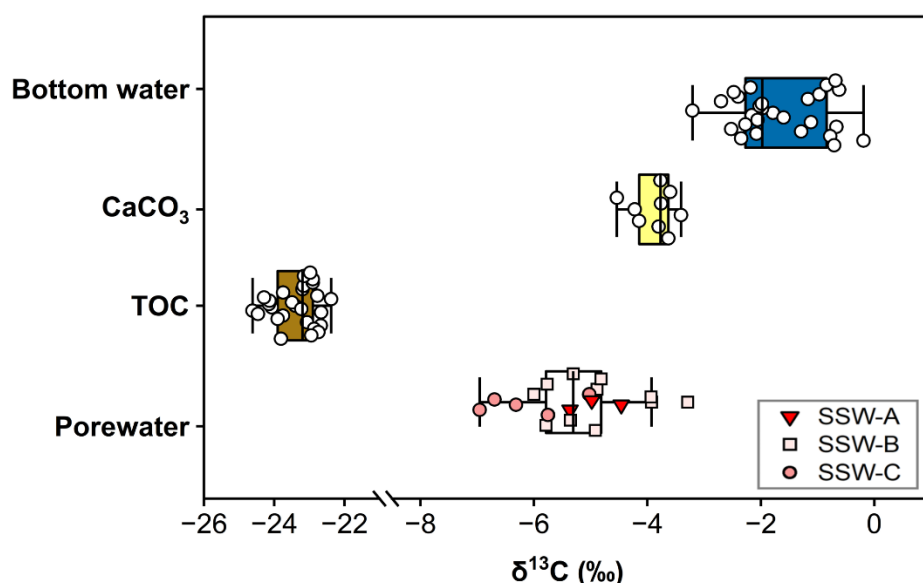


Figure 5: The $\delta^{13}\text{C}$ values in different matrix. CaCO_3 represents shells collected from oysters and abalones. TOC refers to the sediment TOC at our sampling sites.

4 Discussion

4.1 The mechanism of interfacial exchange revealed by the ^{224}Ra – ^{228}Th disequilibria

In comparison of ^{224}Ra profiles, the high D- ^{224}Ra in porewater corresponds to the high bulk ^{224}Ra in sediment (SSW-C). The layers where ^{224}Ra – ^{228}Th activities presented disequilibria coincided with high

305 variations of D-²²⁴Ra (RSD of three adjacent D-²²⁴Ra larger than 10%), indicating that the sediment served as the major source of D-²²⁴Ra. As the ²²⁴Ra–²²⁸Th disequilibria provided a reliable indicator of D-²²⁴Ra transfer, the ²²⁴Ra effluxes (F_{Ra}), as well as the interface area factor (ξ), were calculated with the method in Sect. 2.3 (Eq. 1 and Eq. 2) based on the activity gradients of D-²²⁴Ra at the sediment-water interface (Table 1). The integration depth of SSW-A and SSW-C was set at the first layer where the ²²⁴Ra and ²²⁸Th
310 reached equilibrium. For SSW-B, the full core was integrated as the radionuclides were basically in equilibrium. The gradients were calculated from the D-²²⁴Ra activity differences between 0-1 cm porewater and bottom water.

Although the ²²⁴Ra fluxes at SSW-A and SSW-C were similar, the ξ at SSW-A was 6–7 times higher. Given that SSW-A was located in seaweed farms where dense macrobenthic communities existed (Wang et al., 2019), the sediment contained abundant burrows and tunnels generated by benthic fauna activities, effectively increasing the area of the sediment-water interface and thereby enhancing the ²²⁴Ra flux. In contrast, the ξ values at SSW-B and SSW-C were comparable but the ²²⁴Ra flux at SSW-C was approximately three times higher, implying that processes other than bioturbation stimulated the benthic exchange at SSW-C. As the Dongchong Channel is dominantly affected by semi-diurnal tides, the
320 sediment-water interface at SSW-C nearby is subject to stronger hydrodynamics than SSW-B (Lin et al., 2017). Fine particles were entrained to open waters by tidal currents and the coarser ones were retained so the sediment at SSW-C was of permeability. Therefore, the benthic effluxes were dominated by bioactivities in inner-bay mariculture zones while tidal currents and flow turbulence accounted for the active interfacial exchange in outer-bay zones.

325 **Table 1: The molecular diffusion coefficient of ²²⁴Ra (D_s^{Ra}), the activity gradient of D-²²⁴Ra ($\frac{\partial A^{Ra}}{\partial z}$), the integration depth (z_{int}) used to calculate the benthic flux of ²²⁴Ra, the ²²⁴Ra flux (F_{Ra}) and the interface area enhancement factor (ξ) at each sampling station. Uncertainties for all parameters are reported as $\pm 1\sigma$.**

Station	D_s^{Ra} ($10^{-6} \text{ cm}^2 \text{ s}^{-1}$)	$\frac{\partial A^{Ra}}{\partial z}$ (dpm L ⁻¹ cm ⁻¹)	z_{int} (cm)	F_{Ra} (dpm cm ⁻² d ⁻¹)	ξ
SSW-A	4.5	7.16 ± 1.54	16	0.53 ± 0.11	260.1 ± 78.44
SSW-B	4.4	15.4 ± 2.50	21	0.17 ± 0.08	41.22 ± 19.49
SSW-C	3.8	52.5 ± 6.15	10	0.54 ± 0.13	44.75 ± 11.64

330 Moreover, the ²²⁴Ra effluxes were utilized to quantify the residence time (τ) of the bay water if we assumed that the addition of ²²⁴Ra in the inner bay were all derived from the sediment. According to the

²²⁴Ra activities of water column in Sansha Bay (Wang et al., 2018), we constrained the endmembers in Sandu Bay and selected the ²²⁴Ra activities of mid-salinity tidal water and bay-mouth seawaters to plot the conservative mixing line (Fig. S2a in Appendix). Consequently, low-salinity inputs from rivers or submarine groundwater discharge were not included in this model. Excess ²²⁴Ra above the conservative line (ΔRa) was assumed to be derived from the sediment so τ can be estimated as

$$\tau = \frac{\Delta Ra}{F_{Ra}} h \quad (6)$$

where h denotes the average water depth of the bay, and a value of 14 ± 3 m was assigned in consideration of the tidal ranges and the water depths measured during the field work. Since all of seawater ²²⁴Ra referred to were collected within Sandu Bay (Wang et al., 2018; Fig. S2b in Appendix), we adopted the ²²⁴Ra flux of SSW-B, which is located in the middle of the bay, to represent the average benthic ²²⁴Ra input to the bay (F_{Ra}). It should be noted that the ²²⁴Ra released from the sediment was assumed to be rapidly mixed into seawater due to the influence of semi-diurnal tides, and that the radioactive decay of ²²⁴Ra was not considered due to the frequent water exchange in this model. Therefore, the τ estimated here represents the low limit of the water residence time. By substituting these values into Eq. (6), the seawater residence time based on ΔRa of Sandu Bay ranged from 0.11 to 3.7 days (Fig. S2b), comparable to those of the wet season (0.2–3.0 days) in Sandu Bay estimated by the seawater ²²⁴Ra/²²⁸Ra (Wang et al., 2018).

4.2 Fluxes of DIC and TA across the sediment-water interface

By applying the area-enhancement model to other solutes (Eq. 3 in Sect. 2.3), the benthic fluxes of DIC and TA at each station were estimated (Table 2). The gradients of DIC and TA were calculated from the concentration differences between 0-1 cm porewater and bottom water, and the uncertainties, ranging from 25%–50%, were mainly derived from the fluxes and interfacial gradients of ²²⁴Ra. The largest DIC and TA fluxes, approximately $600 \text{ mmol m}^{-2} \text{ d}^{-1}$, were exhibited in the farming zone (SSW-A) although the porewater DIC and TA concentrations were not the highest. The fluxes at the other two stations ranged from 105 to $207 \text{ mmol m}^{-2} \text{ d}^{-1}$. The magnitude of these DIC fluxes is comparable to the estimates in the intermediate-salinity zones of the nearby Jiulong River estuary with the approach ²²⁴Ra-²²⁸Th disequilibrium ($26\text{--}1000 \text{ mmol m}^{-2} \text{ d}^{-1}$, Hong et al., 2017). In particular, the high benthic DIC and TA fluxes were dominated by the enlarged interface areas (ξ). If only molecular diffusion was considered, benthic DIC flux at SSW-A ($\sim 2.4 \text{ mmol m}^{-2} \text{ d}^{-1}$) fell within the reported range derived from the porewater gradient model ($0.54\text{--}2.65 \text{ mmol m}^{-2} \text{ d}^{-1}$, Jahnke et al., 1997), a method that has been confirmed to underestimate benthic exchanges (Glud et al., 2016). The decoupling between fluxes and concentration gradients (Table 2) indicates that dynamic processes are important in interfacial exchanges and must therefore be involved in the quantification of benthic effluxes.

365 The DIC and TA fluxes estimated from the ^{224}Ra - ^{228}Th disequilibria are generally higher than those from *in-situ* chamber experiments. Ortega et al. (2005) compiled DIC and TA fluxes using benthic chambers in the ranges of $5\text{--}700\text{ mmol m}^{-2}\text{ d}^{-1}$ and $1\text{--}200\text{ mmol m}^{-2}\text{ d}^{-1}$, respectively, but most were less than $100\text{ mmol m}^{-2}\text{ d}^{-1}$. Except for the regional disparity, the relatively low fluxes were attributed to the exclusion of advective transport by chambers. In their studies of three Cantabrian estuaries, despite in-
 370 situ flow rates differing by an order of magnitude, the average of benthic DIC effluxes, 342, 252 and 217 $\text{mmol m}^{-2}\text{ d}^{-1}$, were similar. Although the porewater DIC and TA in Sansha Bay were not particularly high, the fast currents in the bay ($\sim 1\text{ m s}^{-1}$, Lin et al., 2017) strengthened the benthic exchange by irrigating the permeable sediment. Consequently, the DIC effluxes at stations SSW-B and -C were comparable to the chamber results in Cantabrian estuaries where organic carbon oxidation was considerable. Furthermore,
 375 the current influence was amplified when the sediment was also subject to intensive benthos disturbance. As a result, the DIC and TA fluxes in the farming zone (SSW-A) were higher by a factor of 3–5 than others.

In addition, the spatial variations of DIC and TA concentrations in water column can also illustrate the robustness of the flux estimate. The increased DIC and TA derived from the benthic efflux ($\Delta\text{DIC}_{\text{sw}}$ and $\Delta\text{TA}_{\text{sw}}$) can be calculated with the modified Eq. (6). Here the residence time (τ) from Sandu Bay were adopted owing to the similar hydrodynamic conditions (Table 2). As a result, the benthic release at SSW-A contributed the largest amounts of DIC and TA to the water column ($>150\text{ }\mu\text{mol kg}^{-1}$, Table 2). In the meantime, elevated DIC and TA concentrations were observed in Dongwuyang, where the average concentrations of DIC and TA were higher by $122\text{ }\mu\text{mol kg}^{-1}$ and $64\text{ }\mu\text{mol kg}^{-1}$ than those in the main
 385 channel, respectively (Liu et al., 2025; Fig. S3 in Appendix). The elevations were consistent with the magnitudes of $\Delta\text{DIC}_{\text{sw}}$ and $\Delta\text{TA}_{\text{sw}}$, confirming that the sediment served as the dominant source of DIC and TA in the inner bay. In contrast, stations close to channels showed minimal sediment influences on seawater concentrations ($<15\text{ }\mu\text{mol kg}^{-1}$), indicating that tidal exchange was the dominant factor for the variations of DIC and TA in the outer bay. This corresponds to the dynamic mechanism regulating the
 390 interfacial exchange at SSW-C illustrated by the ^{224}Ra - ^{228}Th disequilibria. However, we need to point out that the estimates here only reflect an average efflux over two weeks around sampling time as the time scale of the ^{224}Ra - ^{228}Th disequilibrium approach is constrained by the half-life of ^{224}Ra (3.66 days). Given that there are high spatial and temporal heterogeneity on sediments in Sansha Bay, these effluxes are not suitable for assessments of annual exchange or carbon budget of the whole bay.

395

Table 2: The summary of parameters for flux calculation including the molecular diffusion coefficients of DIC (D_s^{DIC}) and the concentration gradients of DIC and TA at the interface ($\frac{\partial C^{\text{m}}}{\partial z}$), and benthic flux of DIC and TA (F_{m}) at each sampling station. The last three rows represent the

residence time (τ) and increased concentrations of DIC and TA to the water column ($\Delta\text{DIC}_{\text{sw}}$ and $\Delta\text{TA}_{\text{sw}}$) estimated from Fm and τ . Uncertainties for all parameters are reported as $\pm 1\sigma$.

Parameters	Stations		
	SSW-A	SSW-B	SSW-C
$*D_s^{\text{DIC}} (10^{-6} \text{ cm}^2 \text{ s}^{-1})$	6.0	5.9	5.1
$\frac{\partial C^{\text{DIC}}}{\partial z} (\mu\text{mol L}^{-1} \text{ cm}^{-1})$	626.5	1367	1033
$\frac{\partial C^{\text{TA}}}{\partial z} (\mu\text{mol L}^{-1} \text{ cm}^{-1})$	598.2	963.7	754.8
$F_{\text{DIC}} (\text{mmol m}^{-2} \text{ d}^{-1})$	624 ± 188	207 ± 97.4	143 ± 37.3
$F_{\text{TA}} (\text{mmol m}^{-2} \text{ d}^{-1})$	595 ± 180	146 ± 68.7	105 ± 27.3
$F_{\text{TA}}/F_{\text{DIC}}$	0.95 ± 0.40	0.70 ± 0.47	0.73 ± 0.27
$\tau (\text{d})$	3.73 ± 0.38	0.86 ± 0.09	0.24 ± 0.03
$\Delta\text{DIC}_{\text{sw}} (\mu\text{mol kg}^{-1})$	163 ± 62.5	12.6 ± 6.7	2.4 ± 0.9
$\Delta\text{TA}_{\text{sw}} (\mu\text{mol kg}^{-1})$	156 ± 59.6	8.9 ± 4.7	1.8 ± 0.6

* The dominant component of DIC and TA is HCO_3^- so the same diffusion coefficient is used.

In a semi-enclosed embayment, Luoyuan Bay, located close to our study region, the settling fluxes of particulate organic carbon (POC) estimated using sediment traps were reported to range from 92 to 375 $\text{mmol C m}^{-2} \text{ d}^{-1}$, comparable with those on the inner shelf of the East China Sea (60–608 $\text{mmol C m}^{-2} \text{ d}^{-1}$) (Hung et al., 2013; Wang et al., 2018). As the sediment trap was deployed in a shallow aquaculture zone during a macroalgae blooming, we supposed that Sansha Bay exhibited a similar range of POC flux. Correspondingly, the DIC released from sediment were equal or even higher than the deposited POC. This indicates, on one hand, that the sediment was characterized with intense microbial activities, allowing rapid remineralization of the deposited POC. Furthermore, the higher DIC efflux relative to POC flux suggests that organic carbon degradation was not the sole process responsible for DIC increment in the sediment, particularly in the inner bay (SSW-A).

4.3 The contributions of organic carbon degradation and CaCO_3 dissolution to porewater DIC

With the method in Sect. 2.3.2, conservative DIC addition to porewater relative to the bottom water and porewater $\delta^{13}\text{C}_{\text{DIC}}$ variations were used to quantify the contributions of organic carbon degradation and CaCO_3 dissolution. Although the concentrations of DIC and TA have indicated that the bottom water of Sansha Bay during sampling period presents calcite oversaturated ($\Omega_{\text{calcite}} = 1.15\text{--}3.50$ based on

CO2SYS), CaCO₃ dissolution still likely occurs, as microbial remineralization and the oxidation of reduced sulfur species may modify porewater carbonate chemistry and generate localized acidic microenvironments (Ku et al., 1999; Hu and Burdige, 2007; Wang et al., 2025). In order to prove the necessity of including CaCO₃ dissolution in this study, TOC degradation as a sole DIC addition was modelled with the modified Eq. (5), $\delta^{13}\text{C}_{\text{PW}} = \delta^{13}\text{C}_{\text{BW}} \frac{\text{DIC}_{\text{BW}}}{\text{DIC}_{\text{PW}}} + \delta^{13}\text{C}_{\text{TOC}} \frac{\text{DIC}_{\text{PW}} - \text{DIC}_{\text{BW}}}{\text{DIC}_{\text{PW}}}$, where $\delta^{13}\text{C}_{\text{TOC}} = -23.2\text{‰}$ (the median of all subsamples). The theoretical porewater $\delta^{13}\text{C}_{\text{DIC}}$ as a result of TOC degradation solely would range from -9.2‰ to -4.0‰ (red plots in Fig. 6, data in Table S3), significantly different from the measured $\delta^{13}\text{C}_{\text{DIC}}$ in the porewater ($p < 0.001$, linear mixed-effects model; blue plots in Fig. 6). The negative deviation indicates that other source with heavier carbon than TOC, i.e., CaCO₃, collectively influenced the porewater DIC concentrations.

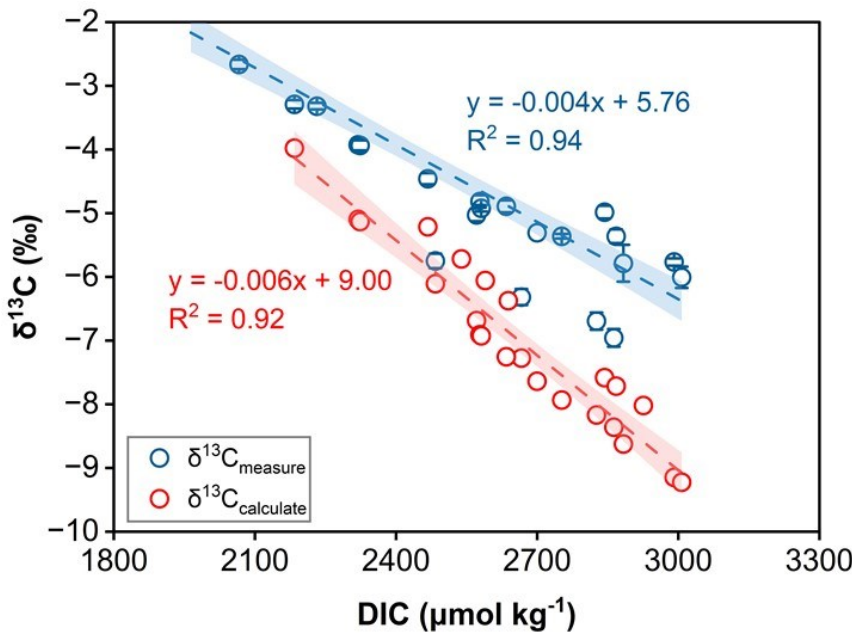


Figure 6: The correlations between $\delta^{13}\text{C}$ and DIC concentrations, where $\delta^{13}\text{C}_{\text{measure}}$ (error = $\pm 1\sigma$) represents the laboratory-measured porewater $\delta^{13}\text{C}_{\text{DIC}}$, and $\delta^{13}\text{C}_{\text{calculate}}$ represents the theoretical $\delta^{13}\text{C}_{\text{DIC}}$ values influenced solely by organic carbon degradation. The shaded areas represent the 95% confidence intervals.

The contributions of TOC degradation (f_{TOC}) and CaCO₃ dissolution (f_{CaCO_3}) were quantified based on $\delta^{13}\text{C}_{\text{CaCO}_3}$ and $\delta^{13}\text{C}_{\text{TOC}}$ values derived from Monte Carlo simulations (see Sect. 2.4). The $\delta^{13}\text{C}_{\text{CaCO}_3}$ values were sampled in a range of -4.54 to -3.41‰, which was defined based on a uniform distribution of the shell-derived CaCO₃ ($n = 9$); and for $\delta^{13}\text{C}_{\text{TOC}}$, a triangular distribution was identified as the best-fitting model based on the measured values ($n = 27$) so the simulations were parameterized from -25.06‰ to -22.15‰ with the likeliest value of -22.86‰. With 10000-time repetition, the uncertainties of the

proportions were under 0.7%. The f_{CaCO_3} and f_{TOC} in each sediment layer are listed in Table S4 (in Appendix) and are depicted in Fig. 7. Overall, bottom water dominated the composition of porewater. The TOC degradation contributed 5.6–20.3% of the porewater DIC and f_{CaCO_3} were in the range of 2.0–17.5%. Meanwhile, the relative contributions between f_{TOC} and f_{CaCO_3} varied between stations. It is evident that CaCO_3 dissolution played a greater role than TOC degradation at SSW-A, consistent with the phenomenon of abundant shell debris and the highest TIC content in the sediment (Table S1 in Appendix). At SSW-B where sea cucumber mariculture existed, f_{TOC} was elevated and the DIC concentrations of the porewater were also higher than others. This enhancement is likely associated with the decomposition of organic matters accumulated from local feeding. In contrast, f_{TOC} was significantly higher than f_{CaCO_3} at SSW-C ($p < 0.005$, t -test) where TIC content was relatively low. It seems that high degradation of organic carbon cannot always lead to a high CaCO_3 dissolution, suggesting that except for the sediment matrix, the bottom hydrodynamics may influence the relative proportions. As SSW-C was located near the bay mouth and the water exchange was active, the oxic environment promoted the organic matter degradation in the surface sediment. But the strong interfacial exchange limited the CO_2 accumulation, consequently weakening the CaCO_3 dissolution in the sediment. By comparison, the DIC was enriched in the sediment porewater at the inner-bay stations so more CaCO_3 dissolution was triggered. The inference is also supported by the vertical variation of SSW-B: the highest f_{CaCO_3} and f_{TOC} were presented in the subsurface sediment where DIC was highest; and meanwhile, the lowering f_{CaCO_3} with depth showed the opposite effect that CaCO_3 dissolution was weakened when the porewater DIC was diluted as a result of seawater irrigation.

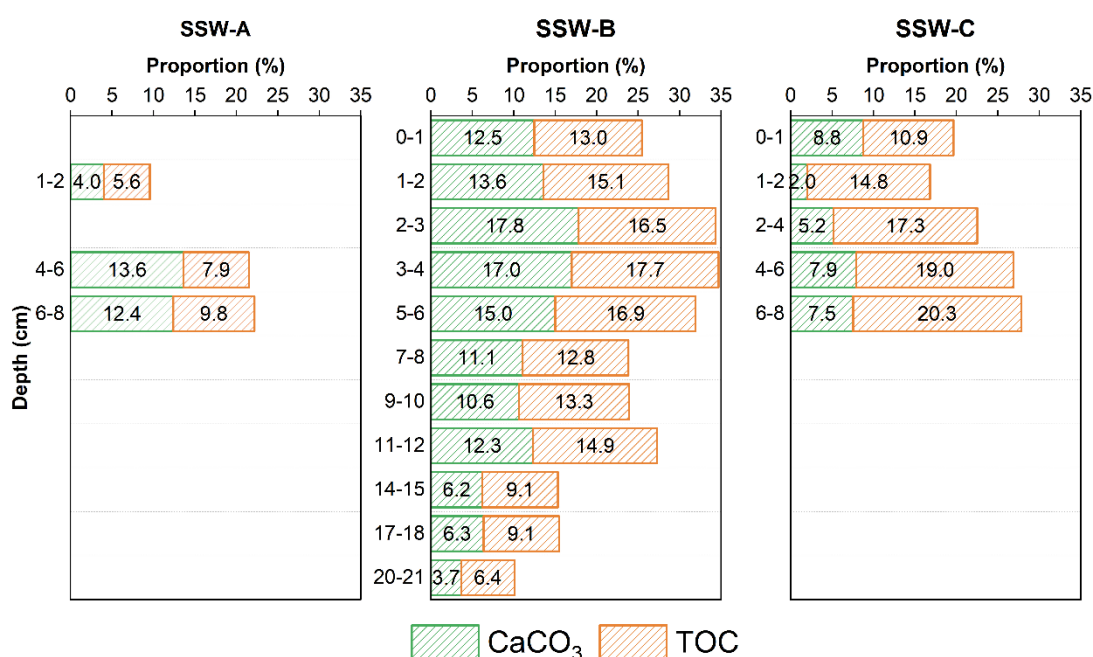


Figure 7: The contribution proportions of organic carbon degradation (f_{TOC} , orange bars) and

CaCO₃ dissolution (f_{CaCO₃}, green bars) to porewater DIC in different sediment layers. Values within bars indicate the respective proportion.

465

In assumption that the benthic DIC efflux was derived solely from two processes in the sediment, i.e., TOC degradation and CaCO₃ dissolution, the specific flux contributed by each process can be quantified with the ratio between f_{CaCO₃} and f_{TOC} (f_{CaCO₃}/f_{TOC}) as

$$F_{\text{DIC-CaCO}_3} = F_{\text{DIC}} \frac{f_{\text{CaCO}_3}}{f_{\text{CaCO}_3} + f_{\text{TOC}}} = F_{\text{DIC}} \frac{\frac{f_{\text{CaCO}_3}}{f_{\text{TOC}}}}{\frac{f_{\text{CaCO}_3}}{f_{\text{TOC}}} + 1}$$

$$F_{\text{DIC-TOC}} = F_{\text{DIC}} \frac{f_{\text{TOC}}}{f_{\text{CaCO}_3} + f_{\text{TOC}}} = F_{\text{DIC}} \frac{1}{\frac{f_{\text{CaCO}_3}}{f_{\text{TOC}}} + 1} \tag{7}$$

In practice, the average of ratios ($\frac{f_{\text{CaCO}_3}}{f_{\text{TOC}}}$) of all layers (Table S4 in Appendix), with the standard deviation (1SD) as the uncertainty, was applied to each site. By substituting the DIC flux derived from ²²⁴Ra-²²⁸Th disequilibria, the DIC effluxes contributed by CaCO₃ dissolution (F_{DIC-CaCO₃}) and TOC degradation (F_{DIC-TOC}) can be calculated (see Table 3). Overall, the DIC efflux contributed by CaCO₃ dissolution at each station was 345 ± 121, 94.5 ± 45.3 and 41.4 ± 21.0 mmol m⁻² d⁻¹, contributing 29–55% of the total DIC efflux. These proportions are in agreement with the results of previous studies that about one third to half of DIC fluxes were derived from CaCO₃ dissolution in benthic chambers experiments (Ortega et al., 2005; Jahnke et al., 1997). Given that the chamber studies well demonstrated that the CO₂ produced by aerobic and anaerobic degradation was vital for CaCO₃ dissolution in sediments, the TOC degradation was likely the trigger mechanism in this study. Furthermore, we introduced the hydrodynamic conditions in explaining the different extents of CaCO₃ dissolution that were hardly simulated in past research: except for the metabolic CO₂, the intensity of interfacial exchange determined whether the CO₂ could be accumulated to produce a microenvironment for continuous dissolution. This study provides a new perspective on the reason why the role of metabolic CO₂ in CaCO₃ dissolution varied regionally in previous studies.

Table 3: The proportion ratios in use and the estimates of specific fluxes contributed by CaCO₃ dissolution (F_{DIC-CaCO₃}) and TOC degradation (F_{DIC-TOC}) at each station. Uncertainties for f_{CaCO₃}/f_{TOC} are the standard deviation of the ratios of sampling layers (Table S4); Uncertainties for fluxes are derived from error propagation.

Parameters	Stations	SSW-A	SSW-B	SSW-C

$\frac{f_{\text{CaCO}_3}}{f_{\text{TOC}}}$	1.24 ± 0.51	0.84 ± 0.15	0.41 ± 0.25
$F_{\text{DIC-CaCO}_3}$ (mmol m ⁻² d ⁻¹)	345 ± 121	94.5 ± 45.3	41.4 ± 21.0
$F_{\text{DIC-TOC}}$ (mmol m ⁻² d ⁻¹)	279 ± 105	113 ± 54	102 ± 32

4.4 Sediment influence on the carbonate buffering capacity of seawater

Based on the benthic addition to the water column estimated in Sect. 4.2, the seawater DIC and TA without sediment influence (DIC₀ and TA₀) can be calculated by deducting $\Delta\text{DIC}_{\text{sw}}$ and $\Delta\text{TA}_{\text{sw}}$ from the measured DIC and TA of seawater (Table 2). Similar with the efflux contributions, the increased DIC concentrations derived from sediment organic matter degradation ($\Delta\text{DIC}_{\text{TOC}}$) can be estimated as $\Delta\text{DIC}_{\text{TOC}} = \Delta\text{DIC}_{\text{sw}} \frac{1}{1 + \frac{f_{\text{CaCO}_3}}{f_{\text{TOC}}}}$. Using the same proportion ratios (see Table 3), TOC degradation can raise DIC concentrations by 71.5, 7.9 and 1.8 $\mu\text{mol kg}^{-1}$ for SSW-A, SSW-B and SSW-C, respectively. If assuming that aerobic mineralization is the dominant pathway of TOC degradation in the sediment, the DIC in seawater would be $\text{DIC}_0 + \Delta\text{DIC}_{\text{TOC}}$ while the change of TA was assumed to be negligible (R1).

$$\text{OC} + \text{O}_2 \rightarrow \text{CO}_2 + \frac{16}{106}\text{NH}_3 + \frac{1}{106}\text{H}_3\text{PO}_4, \frac{\Delta\text{TA}}{\Delta\text{DIC}} = (16/106 - 1/106)/1 = 0.14 \quad (\text{R1})$$

in assumption that the composition of sediment OC follows the Redfield ratio; C:N:P = 106:16:1 (Middelburg et al., 2020). The DIC and TA concentrations we measured in seawater are considered to reflect the combined effects of aerobic mineralization and CaCO₃ dissolution. Therefore, three scenarios can be set up to show the changes in carbonate system of water column: 1) without benthic influence, 2) only sediment TOC degradation, and 3) with all benthic input. The influence of the two processes can be distinguished by pairwise comparison (Table 4).

The CO2SYS program (Lewis et al., 1998) was deployed to calculate CO₂ concentrations and Ω_{calcite} of the seawater DIC and TA in assumed scenarios (Table 4). At SSW-A, the TOC degradation increased CO₂, and lowered pH and Ω_{calcite} by 0.2 and 1.0, respectively; while when additional TA was involved, CO₂ decreased by approximate 30% and Ω_{calcite} was restored. Although the variation in different scenarios was not obvious at SSW-B as the Ω_{calcite} was relatively low, the CO₂ induced by TOC degradation was still slightly lowered by ~3% via adding extra TA. In contrast, the parameters at SSW-C kept consistent in the scenarios, indicating that the water was little influenced by benthic inputs. However, the absolute amount of TA added is not the primary factor in elevating pH. Although the TA level in seawater groups is elevated to a similar extent relative to the other two groups, the pH shows opposite response: the pH of seawater group is higher than that in the DIC-TOC-only group but lower than that in the no-efflux group.

Table 4: The concentrations of TA and DIC in seawater influenced by different processes. The pH and CO₂ were calculated from the DIC and TA ahead using the CO2SYS program[#].

Station	Scenarios	TA ($\mu\text{mol kg}^{-1}$)	DIC ($\mu\text{mol kg}^{-1}$)	pH	CO ₂ ($\mu\text{mol kg}^{-1}$)	Ω_{calcite}	$\frac{\Delta\text{TA}}{\Delta\text{DIC}}$
SSW-A	No benthic input	2201	2066	7.86	21.9	2.73	0.96 ^{\$}
	DIC-TOC only	2201	2137	7.65	37.5	1.76	2.18 [*]
	Seawater	2357	2229	7.83	25.7	2.73	—
SSW-B	No benthic input	1973	1951	7.52	46.8	1.18	0.70 ^{\$}
	DIC-TOC only	1973	1958	7.49	49.9	1.11	1.27 [*]
	Seawater	1982	1964	7.51	48.6	1.15	—
SSW-C	No benthic input	2241	2048	8.03	15.6	3.50	0.73 ^{\$}
	DIC-TOC only	2241	2050	8.03	15.8	3.48	0.99 [*]
	Seawater	2243	2051	8.03	15.7	3.50	—

[#] The carbonic acid dissociation constants (K_1 and K_2) are from Millero et al. (2006), K_{HSO_4} dissociation constants are from Dickson (1990), and total borate-salinity relationship is from Lee et al. (2010). All pH values are reported on the total hydrogen scale (pH_T).

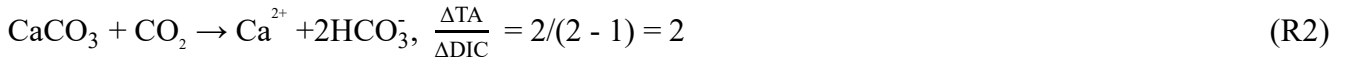
^{\$} The ratio is calculated by comparing "No benthic input" and "Seawater" scenarios.

^{*} The ratio is calculated by comparing "DIC-TOC only" and "Seawater" scenarios.

In general, changes in TA and DIC in a system (i.e., $\Delta\text{TA}/\Delta\text{DIC}$) are used to reflect the developing trend of the carbonate buffering capacity. The threshold for lowering CO₂ release or elevating pH of a seawater system at present-day conditions is $\Delta\text{TA}/\Delta\text{DIC} \approx 1.2$ (Natividad et al., 2026). Accordingly, the sediment of Sansha Bay was overall not a role in promoting the buffering capacity of seawater, as $\Delta\text{TA}/\Delta\text{DIC}$ values between "No benthic input" and "Seawater" scenarios were all less than 1.0 (see the last column of Table 4). Comparing with SSW-C, the inner-bay stations presented lower pH and Ω_{calcite} , which can be accounted for organic carbon degradation. However, the pH at SSW-A was higher than that at SSW-B, although the DIC efflux at SSW-A was three times higher. The $\Delta\text{TA}/\Delta\text{DIC}$ ratios between "Seawater" and "DIC-TOC-only" scenarios show that reactions leading to $\Delta\text{TA}/\Delta\text{DIC} > 1.2$ mitigated the potential acidification caused by R1.

CaCO₃ dissolution produces double TA than DIC by absorbing CO₂ released by organic degradation (R2). Based on the contributions to DIC effluxes in Sect. 4.3 ($F_{\text{DIC-CaCO}_3}$ in Table 3), the TA release via sediment CaCO₃ dissolution was consequently approximately 690 ± 244 , 189 ± 90.6 and 82.8 ± 42.0 mmol m⁻² d⁻¹ at SSW-A, SSW-B and SSW-C, respectively, comparable with the benthic TA fluxes estimated from ²²⁴Ra-²²⁸Th disequilibria (see Table 2). Therefore, CaCO₃ dissolution was likely the

process that enhanced TA and maintained the carbonate buffering system of seawater.



Presently, the available data have suggested that CaCO_3 dissolution commonly occurs in the sediment of Sansha Bay, even that the bottom water is calcite-oversaturated and no mariculture is deployed (i.e., SSW-C). The metabolic CO_2 was considered to trigger the reactions. As TOC degradation is inevitable in coastal zones, CaCO_3 dissolution likely occurs in other coastal sediment while the reaction intensity may vary in different benthic environments (Fig. 8). However, the reaction ratios ($f_{\text{CaCO}_3}/f_{\text{TOC}}$) and the flux results are hardly directly applicable to other environments, as the seafloor dynamics generally exhibit substantial variability. Moreover, there are also limitations in the estimates of the CaCO_3 -promotion TA. Following the average $f_{\text{CaCO}_3}/f_{\text{TOC}}$ ratios (1.24 ± 0.51 , 0.84 ± 0.15 and 0.41 ± 0.25 for SSW-A/B/C) and the stoichiometry of R1 and R2, the theoretical $F_{\text{TA}}/F_{\text{DIC}}$ ratios can be calculated as 1.17 ± 0.19 , 0.99 ± 0.08 and 0.68 ± 0.23 for SSW-A/B/C. In fact, the practical $F_{\text{TA}}/F_{\text{DIC}}$ ratios estimated from ^{224}Ra - ^{228}Th disequilibria for these sites were 0.95 ± 0.40 , 0.70 ± 0.47 , and 0.73 ± 0.27 , respectively (see Table 2). The lower practical $F_{\text{TA}}/F_{\text{DIC}}$ ratios indicate that employing the average $f_{\text{CaCO}_3}/f_{\text{TOC}}$ of the entire core introduced bias when quantifying process influences on benthic TA effluxes. In addition, only aerobic mineralization (R1) was considered in organic carbon degradation, while anaerobic mineralization including denitrification or reduction of Fe and Mn oxides can also change the concentrations of TA and DIC in sediments, even providing a higher $\Delta\text{TA}/\Delta\text{DIC}$ than R1 (Middelburg et al., 2020). This may also lead to the inconsistency of theoretical and practical $F_{\text{TA}}/F_{\text{DIC}}$.

Overall, the benthic effluxes did not act to lower the CO_2 of water column in Sansha Bay. On the contrary, the sediment served as a source of DIC and tended to increase the CO_2 concentrations of the inner-bay seawater. The released DIC, derived from organic carbon degradation, weakened the buffering capacity and thereby potentially posed a risk of acidification in the inner bay. However, CaCO_3 dissolution in the sediment mitigated this risk by absorbing CO_2 and releasing extra TA. In particular, active irrigation in the seafloor promoted this reaction by enhancing the interfacial area, leading to a reduction of ~30% in the CO_2 generated from organic carbon degradation (Fig. 8). In summary, sediment CaCO_3 dissolution was the key process that enhanced TA and regulated the carbonate system, alleviating the acidification induced by organic matter degradation in Sansha Bay. This process was further promoted under conditions of abundant calcified biological debris and active interfacial exchanges. Accordingly, the implementation of a co-culture model involving shellfish as an additional CaCO_3 supply is necessary in maricultural farms, not only for economic benefits but also for the self-regulation on carbonate buffering capacity.

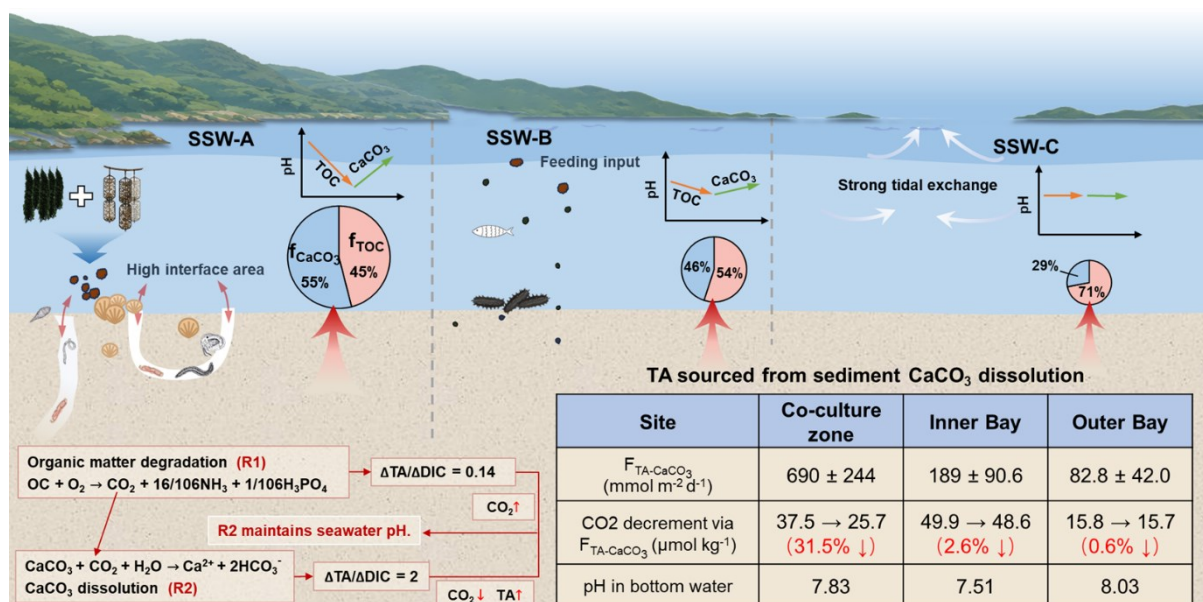


Figure 8: Conceptual diagram illustrating the mechanism of benthic processes regulating the benthic effluxes of DIC and TA in Sansha Bay. The DIC flux is presented with pie charts, of which the size indicates the proportion and the colors show the contributions of different processes (CaCO₃ dissolution in blue and TOC degradation in red). The axial pH graphs indicate the influences of benthic processes on water column. The inserted table specifies the TA contributed by CaCO₃ dissolution ($F_{TA-CaCO_3}$) and its effectiveness in buffering the carbonate system of the bay seawater.

5 Conclusions

This study chose a coastal bay as a high-productivity representative and quantified the benthic processes affecting the carbonate system. Using the ²²⁴Ra–²²⁸Th disequilibrium approach, the highest fluxes of DIC and TA were found in the regions of seaweed farms, demonstrating that the benthic input accounted for the DIC and TA hotspots observed in water columns. Intensive bioturbation in the sediment and the hydrodynamics were confirmed to regulate the exchange across the sediment-water interface in the bay. Based on the $\delta^{13}C_{DIC}$ signatures of different sources, the roles of organic matter degradation and CaCO₃ dissolution in elevating porewater DIC concentrations were quantified. The results illustrated that CaCO₃ dissolution contributed 29 ± 13%–55 ± 10 % of the increased DIC in porewater and dominated the TA release from the sediment, balancing the H⁺ increment induced by aerobic mineralization.

This research sheds light on the self-regulating mechanism of the carbonate system in a high-productivity coastal zone, and for the first time, illustrates the dynamic impact on sediment CaCO₃ dissolution: intensive disturbance affects the accumulation of metabolic CO₂ from organic carbon

degradation, thereby influencing the extent of CaCO₃ dissolution. The benthic TA input from the sediment CaCO₃ dissolution is validated as a key role in maintaining the buffering capacity of seawater, lowering the potential acidification associated with the organic carbon remineralization. As biogenic CaCO₃ commonly exist in sediments, the sediment CaCO₃ dissolution was likely a ubiquitous process in the ocean, even in CaCO₃ supersaturated surroundings. This provides an insight into the carbon cycling of coastal and marginal seas that sediment CaCO₃ dissolution needs to be included in assessing the budget of inorganic carbon.

Appendix

Supporting information in appendix includes Tables S1 to S4 and Figures S1 to S3.

Code and data Availability

The sediment and porewater data, the R codes for statistical testing and the Monte Carlo simulation results are available through Mendeley Data, V2, doi: 10.17632/wd5xyszzjv.3.

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Conflict of Interest

The authors declare there are no conflicts of interest for this manuscript.

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635

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