Distribution of carbon and nitrogen as indictors of environmental significance in coastal sediments of Weizhou Island, Beibu Gulf

Zhiyi Tang[2,4], Chao Cao[1,3]*, Kunxian Tang[1,3], Hongshuai Qi[1,3], Yuanmin Sun[1,3], Jiangbo Yang[4] and Xinong Xie[2,4]

1 Third Institute of Oceanography, Ministry of Natural Resources, Xiamen 361005, China

2 Hubei Key Laboratory of Marine Geological Resources, China University of Geosciences, Wuhan 430074, China

3 Fujian Provincial Key Laboratory of Marine Ecological Conservation and Restoration, Xiamen 361005, China

4 College of Marine Science and Technology, China University of Geosciences, Wuhan 430074, China

* Correspondence: caochao@tio.org.cn; Tel: +86-592-2195306

Abstract: Carbon and nitrogen contents and their isotopic components and AMS radiocarbon dating ages were measured for 57 coastal sediments from Weizhou Island to analyze the distribution of total inorganic carbon (TIC) and its carbon and oxygen isotopic components ($\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$), total organic carbon (TOC) and total nitrogen (TN) contents and their stable isotopic components ($\delta^{13}C_{TOC}$ and $\delta^{15}N_{TN}$) and environmental significance. The results showed that the oldest age of coastal sediments on Weizhou Island was 2750 cal. a BP, and the average TIC contents of A1, A2, B1, C1, and D1 in the intertidal zone were all greater than 5%, where $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ were enriched, while the TIC contents in A3, C2, and D2 of the supra-tidal zone were low, where $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ were depleted. Moreover, TIC decreased sharply from the estuary to upstream region in the C1-C2 section. The average C/N ratio was 7.02, and $\delta^{13}C_{TOC}$ and $\delta^{15}N_{TN}$ were between -14.96‰~-27.26‰ and -14.38‰~4.12‰, respectively. These measurements indicated that the TIC in coastal sediments mainly came from seawater. A1, A2, and B1 in the northern intertidal zone

exhibited organic terrestrial signals because of C_3 and C_4 plant inputs, which proved that the important source of the northern coast of Weizhou Island came from the island. The lacustrine facies deposits were mainly distributed in the upper reaches of the river, the northern coastline was rapidly advancing toward the sea, and part of the southwestern coastal sediments rapidly accumulated to the shore under the influence of a storm surge. The relative sea level of the Weizhou Island area has continuously declined at a rate of approximately 2.07 mm/a, using beach rock as a marker, since the Holocene.

Key words: Inorganic carbon; organic carbon and nitrogen; carbon and nitrogen isotopes; coastal sediments; environmental significance

1 Introduction

The continental margin sediments contain more than 90% of the carbon buried in the ocean, and the estuary coastal zone, as a sensitive exchange zone for sea-land carbon pools, effectively indicates the global carbon cycle process is driven by sea level changes [1,2]. However, as an open system, the biogeochemical signals of coasts are complex due to the influence of multiple natural factors (such as global coastline and paleoclimate changes) and the interference of human activities [3-7].

The most important form of inorganic carbon in marine sediments is carbonate, whose precipitation or dissolution is controlled by the overlying water and pore water ion concentration, pH, temperature, CO_2 diffusion rate, and biological disturbance [8, 9]. As total inorganic carbon (TIC) mainly comes from water evaporation, lighter ^{12}C and ^{16}O are preferentially gathered in the reactants under the isotope dynamic fractionation mechanism. With the diffusion of CO_2 into the atmosphere, only heavier ^{13}C and ^{18}O remain [10]. Although coastal organic matter is complex due to its origin of marine organic matter and terrestrial plant detritus [11], the ratio of total organic carbon to total nitrogen (TOC to TN) and their stable isotope components ($\delta^{13}C_{TOC}$ and $\delta^{15}N_{TN}$) under different sources can distinguish the sources of organic matter, which is helpful for reconstructing the evolution of the environment and the process of human activities [12-17]. Therefore, TIC, organic carbon and nitrogen and their stable isotopic components are not only the main components of biogeochemistry in coastal sediments but also the main response indicators of environmental evolution

[18]. Gao et al. (2012) [19] noted that the contribution rate of terrestrial organic matter could be obtained by calculating the $\delta^{13}C_{TOC}$ component; Bejugam and Nayak (2017) [20] believed that calcium carbonate was related to the particle size of sediments and the concentration of carbonate ions in seawater, and the C/N ratio was associated with the source of organic matter in rivers, such as the Mahanadi River. Zhan et al. (2012) [21] inferred that the decrease in C/N and the increase in $\delta^{13}C_{TOC}$ in the sediments of the Yangtze River Estuary at 9 cal. Ka BP were related to the decrease in terrestrial source input caused by abrupt sea level rise.

Weizhou Island is located in the central part of the Beibu Gulf in the South China Sea (Figure 1) and has a tropical monsoon climate zone with an average annual temperature of 22.6°C and rainfall of 1380.2 mm. Under the control of the monsoon, the south and southwest winds and waves are strong, resulting in strong erosion in the south and west regions of Weizhou Island, while the wave-shadow areas in the northern part of the island accumulate under the favorable coastal currents and coral reef unloading. This process results in the transgression of the southern coastline but the regression of the northern coastline [22, 23].

Previous studies on carbon, nitrogen and their related isotopes have been used successfully in coastal zones and estuaries, but the application of land-sea interaction units on islands is relatively rare. As a young island that originated from a volcanic eruption, Weizhou Island has experienced sea level decline, weathering and erosion since the Holocene [24]. Compared with the densely populated coastal zone, the environment has a lower degree of disturbance from human activities. The sediment deposition has a weak diagenesis and shorter history, which well preserved the environmental evolution information of Weizhou Island, which has been exposed to air since the Holocene. In this paper, inorganic carbon and its carbon and oxygen isotope analysis and organic carbon and nitrogen and their isotope tracing technology were used to understand the geochemical characteristics of the coastal area of Weizhou Island since the formation in the Holocene. That is, we explored the material provenance of Weizhou Island under the change in sediment chemical composition to speculate on the environmental evolution process since the Holocene and confirmed the applicability of geochemical elemental characteristics in environmental changes.

2 Materials and methods

2.1 Sample collection

For the distribution of inorganic carbon content and its isotope and the organic carbon and nitrogen contents and their isotope components in the coastal sediments of Weizhou Island, a total of 57 sediments were collected from 9 typical sedimentary profiles in multiple directions on Weizhou Island. WZ-35 is located on the laterite platform on the island, while A1, A2, B1, C1, and D1 are located in the intertidal zone, and A3, C2 and D2 are located in the supra-tidal zone. Among them, there are obvious coral clastic interlayers in A1, B1, and D1, but C1 contains beach rock. After sampling, the sediment and coral debris were packaged and marked separately, and all samples were bagged, brought back to the laboratory, and stored in a refrigerator at -4°C to prevent oxidation. The specific sampling profile location, core information and measurement items are shown in Figure 1 and Table 1.

2.2 Sample analysis

The samples were classified and processed before the inorganic carbon and its carbon and oxygen isotopes, organic carbon and nitrogen contents and isotopes, and AMS radiocarbon dating were analyzed. The sample was placed in a glass dish before putting it in the freezer for 2 h to pre-freeze the water in the sample into ice; then, the sample was placed in a freeze dryer for vacuum freeze-drying for 24 h, removed and ground to 200 mesh powder with an agate mortar. However, before TOC, TN and their isotope ($\delta^{13}C_{TOC}$ and $\delta^{15}N_{TN}$) measurements, it was necessary to add 6 M hydrochloric acid and allow the sample to soak for 6 h to remove carbonate; then, the sample was washed with deionized water to elute the residual hydrochloric acid until the pH was neutral. Finally, according to the freeze-drying method, 25-50 mg powder was dried and weighed for analysis.

The ground sample was analyzed with a Thermo NE1122 elemental analyzer for total carbon (TC) and total nitrogen (TN) contents, and the error was less than 0.2%. The TOC in the acid-treated sample was measured by a Thermo NE1122 elemental analyzer, and the difference between the two was the TIC, that is, TIC=TC-TOC [25]. According to the repeated measurement results of the standard substance by this instrument, the relative error was within 0.2%. The carbon and oxygen isotopes in the

carbonate of the sediment samples were titrated with phosphoric acid to produce CO_2 gas, and the $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ were measured by a Thermo Delta Plus AD isotope mass spectrometer with an accuracy of ±0.2%. The organic carbon and nitrogen isotopes must be accurately measured. $\delta^{13}C_{TOC}$ and $\delta^{15}N_{TN}$ were, respectively measured by CO_2 and N_2 after the gas was carried into the Thermo Delta Plus AD through the carrier gas (such as high purity He gas), of which the CO_2 and N_2 were obtained by the powder samples burned in the element analyzer with high temperature before oxidation and purification. The results were calculated according to the V-PDB standard ratio [26, 27]. Every 12 samples were calibrated with 2 standard samples to examine the measurement error, which was not more than 0.2%. The sample analysis was carried out on the shared test platform of the Third Institute of Oceanography, Ministry of Natural Resources.

The coral debris samples in the sediments were sent to the American Beta Laboratory for AMS radiocarbon dating, and the age of the coral debris in the coastal sediments of Weizhou Island was dated as the age data of the same sample of the coastal sediments of Weizhou Island to explain its chronological significance.

3 Results

3.1 Inorganic proxies of costal sediments in Weizhou Island

3.1.1 Distribution of TIC in coastal sediments

The results of inorganic carbon in the coastal sediments of Weizhou Island show that the average value of TIC is between 0.02% and 10.52% (mass percentage) and polarized between intertidal and supra-tidal. Compared to the schematic diagram of the coastal sediment sampling station of Weizhou Island in Figure 1, the TIC contents of all samples in profiles A1, A2, B1, C1, and D1 are above 3% and between 5.09%-7.33%, on average; additionally, the TIC content of sample A1-8 is 10.52%, which is close to the 12% value of the calcium carbonate inorganic component. It is significantly higher than that of the supra-tidal profile (A3, C2, and D2), whose average TIC content is generally close to zero, but there is a small amount in the lower profile only in C2. The TIC mostly changes periodically from the surface to the bottom in the intertidal zone.

3.1.2 The distribution of $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ in the coastal sediments

The stable carbon isotopes of carbonates range from -12.67‰ to -0.01‰, and the distribution is proportional to the TIC. The sediment $\delta^{13}C_{carb}$ in the intertidal zone is relatively positive, with most values higher than -3‰, while the supra-tidal is negatively biased, suggesting that TIC shows obvious differences from the coast to offshore areas. However, anomalies appear at the low parts of A3 and C2.

The carbonate oxygen stable isotopes are -20.20‰ to -3.49‰, and the distribution shows a positive correlation with $\delta^{13}C_{carb}$. The intertidal profile $\delta^{18}O_{carb}$ is relatively positive, approximately -5‰, while the continental profile has a significant negative bias. However, the degree of negative bias is weak at low parts of A3 and C2.

3.2 Organic proxies of coastal sediments on Weizhou Island

3.2.1 Distributions of TOC and TN in the coastal sediments

The TOC values of all samples do not exceed 2% and 0.09%-1.25%, on average, and the trend is fluctuating and increasing from the surface to the bottom, except at B1 and D1, which show the opposite trend.

The results of organic nitrogen content in the sediments of Weizhou Island show that the TN contents of sediments in all profiles are between 0.02 and 0.17%, and the TN distribution is nearly consistent with that of TOC.

3.2.2 Sediment $\delta^{13}C_{TOC}$ and $\delta^{15}N_{TN}$ distributions

$\delta^{13}C_{TOC}$ ranges from -14.96‰ to -27.26‰. In the A1-A3 section, $\delta^{13}C_{TOC}$ is relatively positive, and anomalies appear only at the low part of A2. In the supra-tidal zone, the A3, C2 and D2 $\delta^{13}C_{TOC}$ distributions are relatively concentrated; only at low part of D2 is there $\delta^{13}C_{TOC}$ enrichment. A1, B1, C1 and D1 show positive bias trends.

$\delta^{15}N_{TN}$ ranges from -14.38‰ to 4.12‰, with an average value of -1.91‰, which is roughly positively correlated with $\delta^{13}C_{TOC}$. However, there are exceptions at the low parts of A1, A2 and C2. Overall, the distribution of $\delta^{15}N_{TN}$ in the intertidal profile is low, but it is enriched in the supra-tidal zone.

Compared with the laterite platform of profile WZ-35, the coastal sediments of Weizhou Island have significant differences in TIC, $\delta^{13}C_{carb}$, $\delta^{18}O_{carb}$, TOC, TN, $\delta^{13}C_{TOC}$ and $\delta^{15}N_{TN}$, indicating that the coastal sediment is not the basalt weathered soil generated in situ but rather a secondary mixture.

3.3 AMS radiocarbon dating analysis

The coral clastic samples of coastal sediments on Weizhou Island ranged from 450 to 2750 cal. a BP (Table 2), with an average age of 1392 ± 30 cal. a BP. They belong to the late Holocene (Table 2) Q_4^3 sediment. The stratum was deposited in order from the surface to bottom, and the geological age increases with depth. The average deposition rate of A1 is approximately 3 mm/a, that of B1 is approximately 1.37 mm/a, and that of C1 is approximately 0.13 mm/a. There is a relatively stable deposition environment, but the geological age of the sediments on the D1 profile is reversed.

4 Discussion

4.1 Environmental significance of inorganic proxies under evaporation

4.1.1 Source analysis of TIC content

Inorganic carbon is an important part of coastal sediments, and it has always played an important role in tracing the source, deposition, circulation, and decomposition of coastal materials (including biomass and sandy coast). The main source of inorganic carbon in the sandy coast is the input of particulate or dissolved substances brought by the tide; the second is the residual deposits of the dead bodies of beach organisms; the third is the input of marine steam transport and evaporation in the pores of sandy beaches; the fourth is the input of terrestrial debris brought by surface runoff [8, 28].

The coastal sediment TIC of Weizhou Island increases rapidly from the coast to offshore areas, and the TIC content in the supra-tidal zone is close to zero, indicating that marine contribution dominates the carbonate input of coastal sediments. In the ocean-influenced dominated intertidal zone, the carbonates carried by marine vapor and seawater are transported to the sandy coast under the transportation of waves and remain in the pores of the beach. The high-salinity pore water is supersaturated by high-temperature evaporation, forming a micro-water rock environment. The chemical equation is as follows:

$$Ca^{2+} + 2HCO_3^- \Leftrightarrow CaCO_3 + CO_2 + H_2O$$
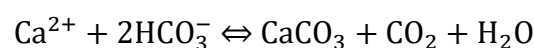
Evaporation increases the carbonate ion concentration and shifts the balance to the

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right, which is conducive to the precipitation of carbonate and preservation resulting in enrichment in the sediment. Meanwhile, in the high-abundance carbonate sedimentary profile dominated by the marine contribution, the surficial sediment TIC of C1 is significantly lower than that in other high-abundance carbonate profiles because the fresh water carried by the Shipan River dilutes the beach pore water, which contributes to a lower salinity and suppresses this progress. The distribution of a small amount of carbonate at the low part of C2 may be due to the intrusion of seawater following the increase in carbonate ions in the pore water to precipitate carbonate. Weizhou Island is an island of volcanic origin covered with basalt-weathered laterite platform deposits and Holocene residues. WZ-35, composed of laterite, has nearly no TIC deposits, indicating that the island is not the source of the soil inorganic carbon. In addition, the abundant surface runoff has a strong desalination and erosion effect on the surface sediments on Weizhou Island, so the TIC in the supra-tidal zone with a limited marine contribution is close to zero. The content of carbonate on sandy beaches can determine the degree and range of marine contributions.

4.1.2 Ocean influence dominated the area of distributions of $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$

In a sedimentary environment dominated by marine contributions, the deposition process of inorganic carbon is closely related to the evaporation and concentration processes of water. Among isotopic kinetic fractionation, lighter isotopes are usually preferentially enriched in the reaction products before the reaction reaches equilibrium. Therefore, ^{12}C is preferentially enriched in the reaction products in evaporation or plant photosynthesis. In addition to the size of the bond energy, carbonate tends to be rich in ^{18}O because O prefers to be bound to the small and high-priced C^{4+} ion [10].

The coastal sediments of Weizhou Island show obvious differences in the distributions of $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$. The intertidal zone carries sufficient seawater evaporation and concentration from tides and waves following a faster diffusion rate of lighter ^{12}C and ^{16}O. This process leads to the abundant accumulation of $^{13}C_{carb}$ and $^{18}O_{carb}$ in carbonate. In the supra-tidal zone, the limited marine contribution affected the lack of sufficient seawater evaporation and concentration and the absorption of inorganic carbon by terrestrial plants, as well as the input of rainwater and surface runoff supporting abundant CO_2, which enriches ^{12}C and ^{16}O from air, leading to a

decrease in the components of $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$.

4.2 Organic matter sources of coastal sediment on Weizhou Island

4.2.1 Source analysis of organic carbon and nitrogen

According to the geochemical signal response for different sources, C/N ratios are often used to distinguish the sources of organic matter [29]. When the C/N ratio is greater than 12, it indicates that the organic matter comes from terrestrial contributions [30]. The C/N ratios of typical marine matter are less than 8 [31], while those between 8-12 are a mixed source of materials from land and sea [18, 29]. The C/N ratios in coastal sediments of Weizhou Island are 0.90-14.42, with an average value of 7.02. Most of the samples have been imported by marine organic matter.

4.2.2 Correlation of $\delta^{13}C_{TOC}$ and $\delta^{15}N_{TN}$ and its environmental significance

Since the process of soil degradation may have a significant impact on C/N and $\delta^{13}C_{TOC}$, choosing a single factor to consider is likely to result in a wrong understanding of the environmental evolution process [21]. Therefore, the C/N attached to the $\delta^{13}C_{TOC}$ relationship diagram is a more effective way to qualitatively analyze the source of organic matter [19, 29, 32, 33]. Generally, when different organisms are carrying out life activities, the application of carbon is different due to inner- or outer conditions, such as enzymes and the existing environment, resulting in the differentiation of organic carbon isotopes of synthetic products [34]. C_3 plants preferentially absorb the ^{12}C component during photosynthesis, resulting in plant organic carbon $\delta^{13}C_{TOC}$ values lower than the $\delta^{13}C_{TOC}$ of CO_2 in the air (-8‰), ranging from -26‰ to -28‰ [35]. Planktonic algae $\delta^{13}C_{TOC}$ is relatively positive, between -19‰ and -22‰ [36]. C_4 plants have vascular bundle sheaths and PEP enzymes resulting in the absorption of CO_2 by photosynthesis, which is different from the former; thus, their $\delta^{13}C_{TOC}$ range is approximately from -17‰ to -8‰ [11, 34, 37].

The organic carbon content of sediments gradually decreases with increasing profile depth, which is consistent with the changes in sediment nitrogen content [34]. In this paper, TN and TOC were significantly positively correlated (R^2=0.9104) in the scatter plots, suggesting that the two had a common source, but Figure 9 shows that the TN axis had an intercept of b=0.0110, indicating that TN contained inorganic nitrogen, which may decrease the C/N. Combining the C/N and $\delta^{13}C_{TOC}$ to distinguish the source of organic matter (Figure 10) in the intertidal zone, terrestrial contributions

of organic matter occurred below the middle of A1. The C/N of A2 decreased from bottom to top, and $\delta^{13}C_{TOC}$ became heavier and approached that of terrestrial C$_3$ plants at low levels; however, the middle $\delta^{13}C_{TOC}$ became lighter, indicating that the composition of C$_3$ plants from organic matter sources in A2 was reduced. B1 was located on the transition zone between phytoplankton and C$_3$ plants, approaching the marine plot, indicating that the overall organic matter was mainly from marine contributions, but it was affected by the input of terrestrial C$_3$ plant detritus. C1 was completely within the range of marine algae. C/N and $\delta^{13}C_{TOC}$ in D1 approached the marine phytoplankton unit. In the supra-tidal zone, the C/N of most samples was low but significantly deviated from the marine phytoplankton interval. Combined with the human geographical history of Weizhou Island, it is speculated that in addition to the mix of inorganic nitrogen, it is likely that the C/N is reduced due to the sowing of nitrogen fertilizer on agricultural land. This result can also be seen in the fluctuating correspondence between $\delta^{15}N_{TN}$ and $\delta^{13}C_{TOC}$ in the supra-tidal zone. The C/N and $\delta^{13}C_{TOC}$ of A3 fall within the range of marine phytoplankton as a whole. All C2 samples are in the transition zone between marine and terrestrial sources. C2-7 indicates the transition zone between marine algae and C$_3$ plants, while the remaining points are in the transition zone between marine algae and C$_4$ plants. It is likely that the replacement of terrestrial organic matter sources between C2-7 and C2-6 represents a succession of plant communities. C/N and $\delta^{13}C_{TOC}$ in D2 are located in the transitional range of sea sources and C$_3$ plants. Combined with the whole profile, the input of organic matter from the marine source at the low part is inferred from storm surge deposition.

Meanwhile, $\delta^{15}N_{TN}$ can indicate the source of organic matter. Phytoplankton $\delta^{15}N_{TN}$ ranges from 4‰ to 10‰, fluvial and terrestrial organic matter $\delta^{15}N_{TN}$ varies greatly, but most are lower than marine organic matter, ranging from -10‰ to 10‰; additionally, the $\delta^{15}N_{TN}$ from human pollutants is usually positive [33, 38]. In this study, the overall growth trend between $\delta^{15}N_{TN}$ and $\delta^{13}C_{TOC}$, except that individual points may be interfered by man-made pollution sources, is roughly the same, indicating that the two are likely to come from the same provenance. In the intertidal zone, $\delta^{15}N_{TN}$ is relatively negative, which confirms the existence of terrestrial organic matter [39, 40].

4.3 The regression of the coastal environment on Weizhou Island

The coral clastic samples of coastal sediments on Weizhou Island are all Holocene sediments, and the deposition rates of A1 and B1 are relatively high (Figure 12). Because A1 and B1 are located in the northwest and northeast wave shadows and the low-lying area of the island, respectively, coupled with the unloading force of the developed coral reef on waves, coastal erosion is weak, and sediments are transported and collected by coastal currents and surface runoff. C1 is located in the southeastern corner of the island, which is affected by the monsoon. Waves cause strong coastal erosion in autumn and summer, and the sedimentation effect is significantly lower than the former.

The TIC, $\delta^{13}C_{carb}$, $\delta^{18}O_{carb}$, C/N, $\delta^{13}C_{TOC}$ and $\delta^{15}N_{TN}$ values of coastal sediments on Weizhou Island and the analysis of the sedimentary characteristics of the island's landform showed that it obviously obtained a supply of sediment from the ocean (Figure 13). The intertidal TIC was positively correlated with $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$, indicating that the ocean played an important role in the intertidal zone. However, the increase in the input of terrestrial organic matter at low parts of A1 and A2, as well as the input of organic matter from the marine source in A3, reflected the obvious regression trend in northern Weizhou Island. The northern coast has advanced approximately 500 m offshore, which proves that the northern coast of Weizhou Island is rapidly accumulating and the coastline is expanding [23]. Xiong et al. (2018) [41] reported that the sea level in the northern part of the South China Sea had not changed much in the past 7000 years, and Yao et al. (2009) [42] suggested that the Middle Holocene had been affected by tectonic movement and sedimentation. Although the sea level has not changed much in the South China Sea, it is mainly regressive, and the land area in the northwest has been expanding. It can be inferred that in the surroundings of Weizhou Island, the relative sea level has been declining since the late Holocene due to tectonic rise. The sediments of B1 were mainly imported from marine sources, and a small amount of C_3 plant debris was mixed in the organic matter; the estuary area of the C1-C2 section was strongly affected by the waves of the open sea, but due to the influence of the river, the TIC was rapidly reduced due to the desalination of the sea. $^{13}C_{carb}$ and $\delta^{18}O_{carb}$ were depleted, and the input of organic matter changed from ocean influence dominated to land-sea mixed sources resulting from the ocean's role in the estuary area being sharply weakened. Following the sediment input from the D1-D2 section enhanced by the reduction of

marine matter input to the shore and the surface runoff from abundant rainfall, the terrestrial contribution of D2 was enhanced, but the input signal of terrestrial organic matter at the low part of D2 was weekended, as well as the reversal age of D1, supporting the disturbance caused by storm surges to coastal sediments.

The C1 coral clastic profile is located on the beach rock of the coastal beach. The beach rock is the petrified sediment of the ancient intertidal zone or the wave splash zone, and its formation represents the location of the ancient sea level [43, 44]. Taking C1-3 as the ancient sea level point and referring to radiocarbon dating age, the average sea level decline rate of Weizhou Island has been approximately 2.07 mm/a in the past 2750 years, which is similar to the value of 1.6~2.1 mm/a estimated by Mo Yongjie (1989) [45]. This is consistent with the holocene sea level decline in the South China Sea [46].

5 Conclusion

The carbon and nitrogen contents and their related isotope measurements of coastal sediments of Weizhou Island showed that the TIC content was between 0.02% and 10.52%, and the ranges of $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ were -12.67‰~-0.01‰ and -20.20‰~-3.49‰, respectively. TIC, $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ were enriched in the intertidal zone. C/N was between 0.90 and 14.42, and the ranges of $\delta^{13}C_{TOC}$ and $\delta^{15}N_{TN}$ were -27.26‰~-14.96‰ and -14.38‰~4.12‰, respectively. The organic matter burial, as well as their isotopes, was different in different profiles, while the isotope fractionation effect was remarkable.

According to the identification of the geochemical information of coastal sediments on Weizhou Island, the main source of TIC was the concentration of water in the intertidal zone, which was dominated by ocean actions such as tides and waves. The decline of terrestrial organic matter in the northern profiles A1, A2, and B1 proved that the important source of the "northern deposition" of Weizhou Island came from the island. The decrease in TIC and the change in organic matter in the C1-C2 section reflected the controlling effect of rivers in the estuary area. The enhanced marine source signal at the low part of D2 was speculated to be evidence of residual organic matter in the marine source swept by the storm surge.

The coast of Weizhou Island is generally regressing, and the source is mainly

from the ocean. The northern coast is an accumulative landform with enhanced terrestrial contribution, but there are weak deposits on the southeastern coast. Based on the dating data of the C1 profile, it is estimated that the average sea level decline rate in the past 2750 years has been approximately 2.07 mm/a.
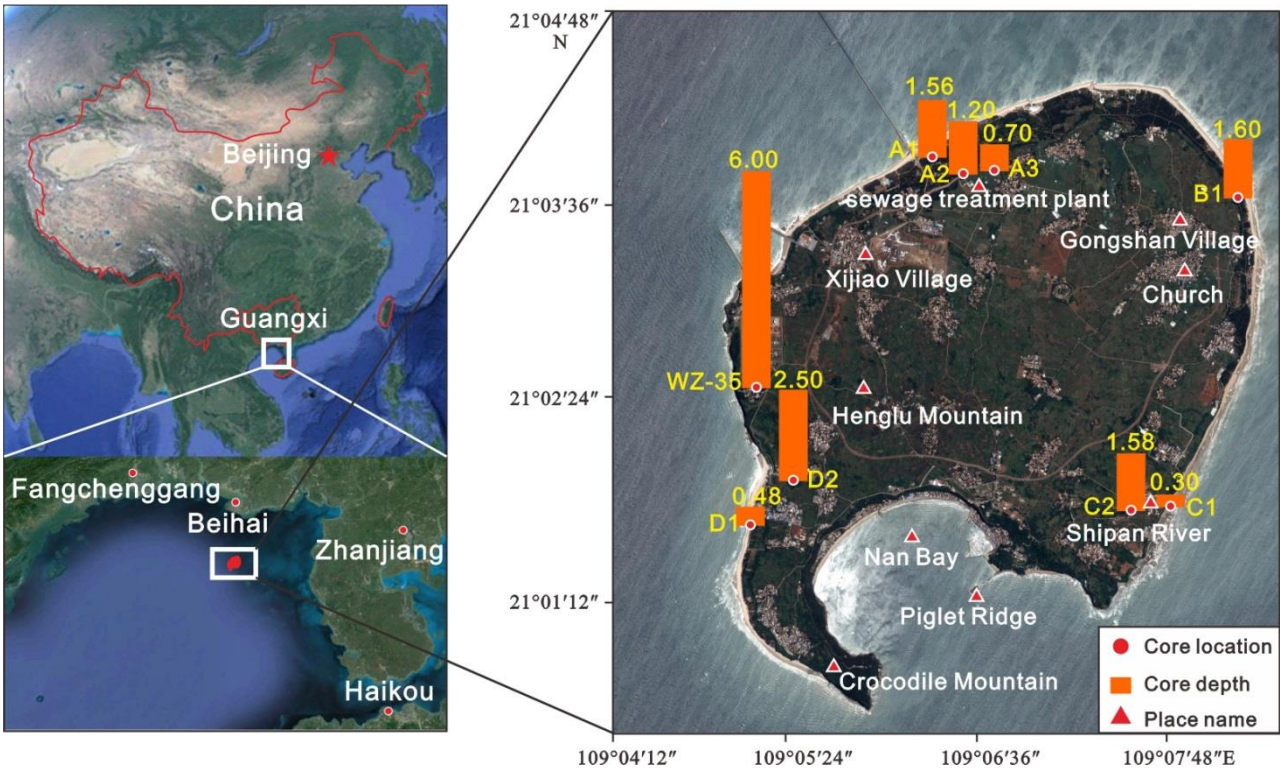
Figure Legends

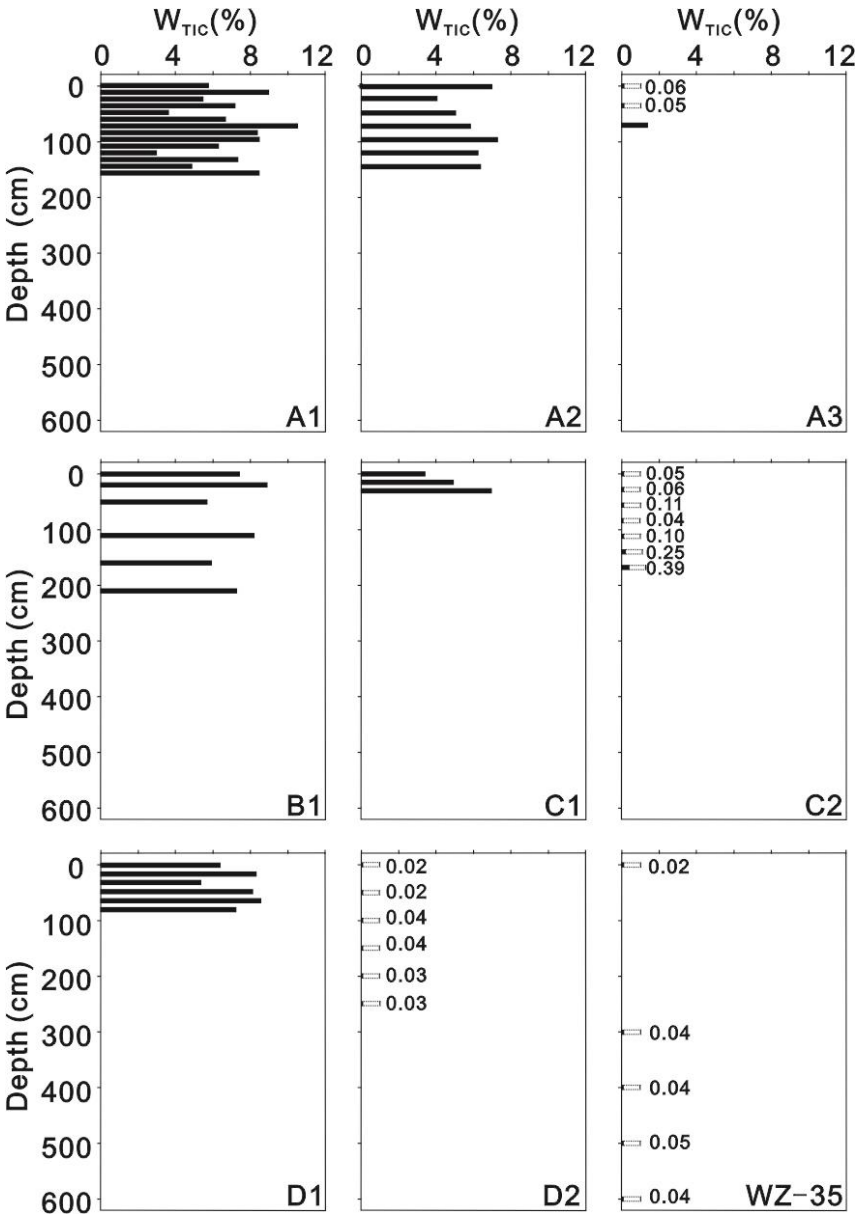**Figure 1.** Map of study area showing the core location on Weizhou Island
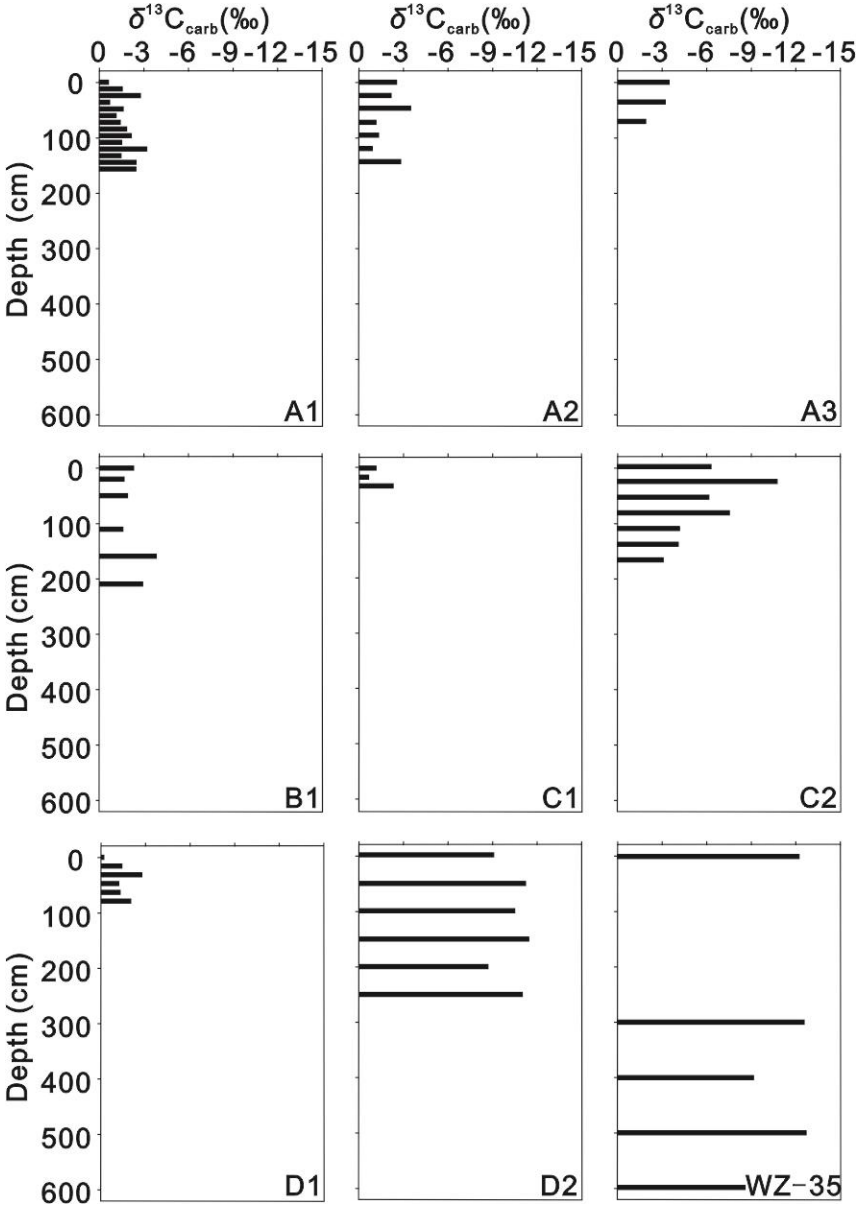
Figure 2. Distribution of TIC of the core sediments

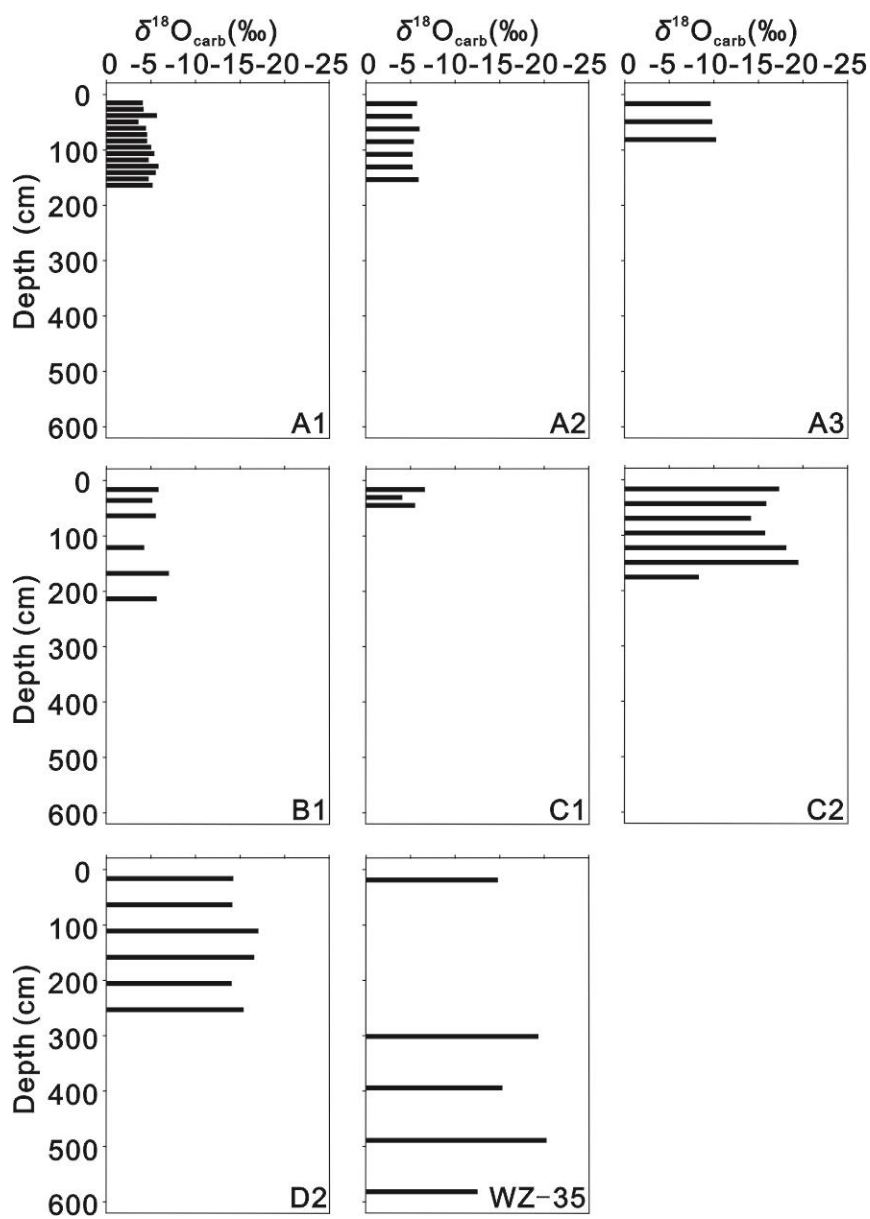**Figure 3.** Distribution of $\delta^{13}C_{carb}$ of the core sediments

Figure 4. Distribution of $\delta^{18}O_{carb}$ of the core sediments
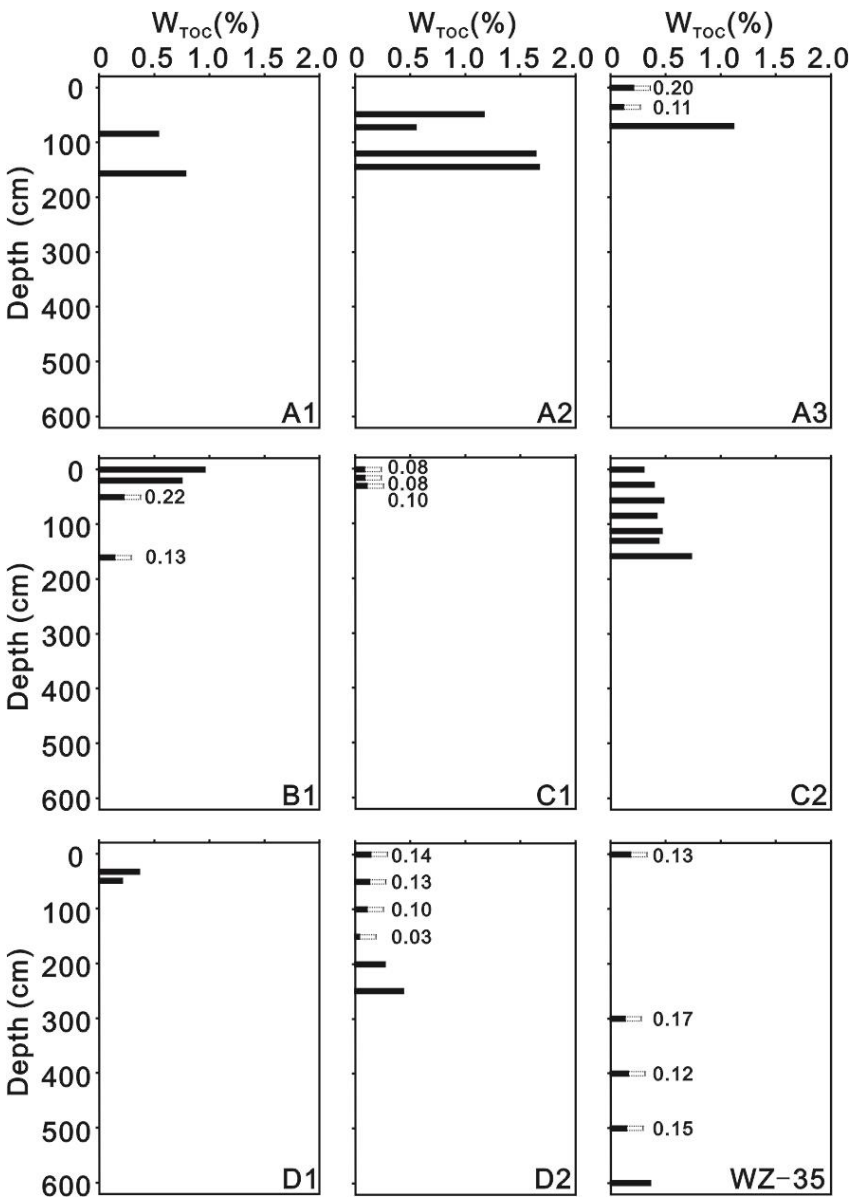
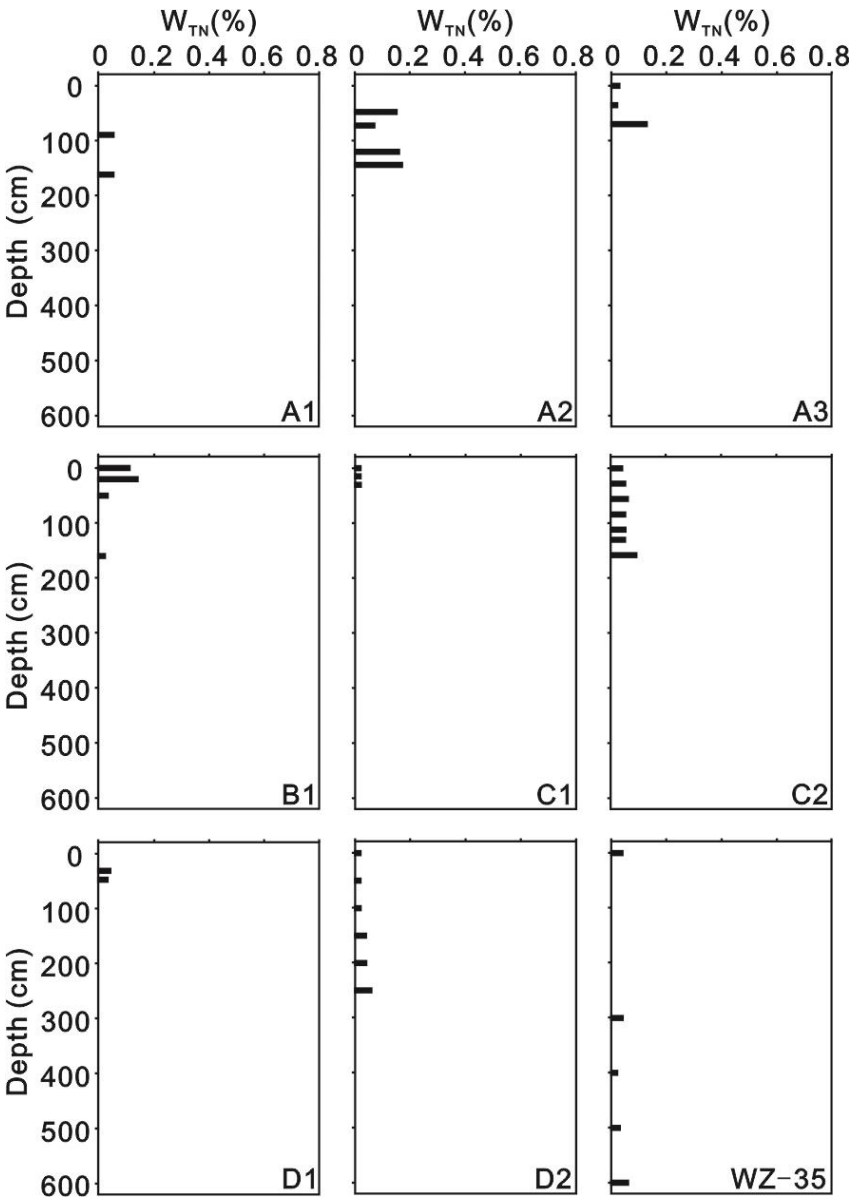**Figure 5.** Distribution of W_{TOC} of the core sediments

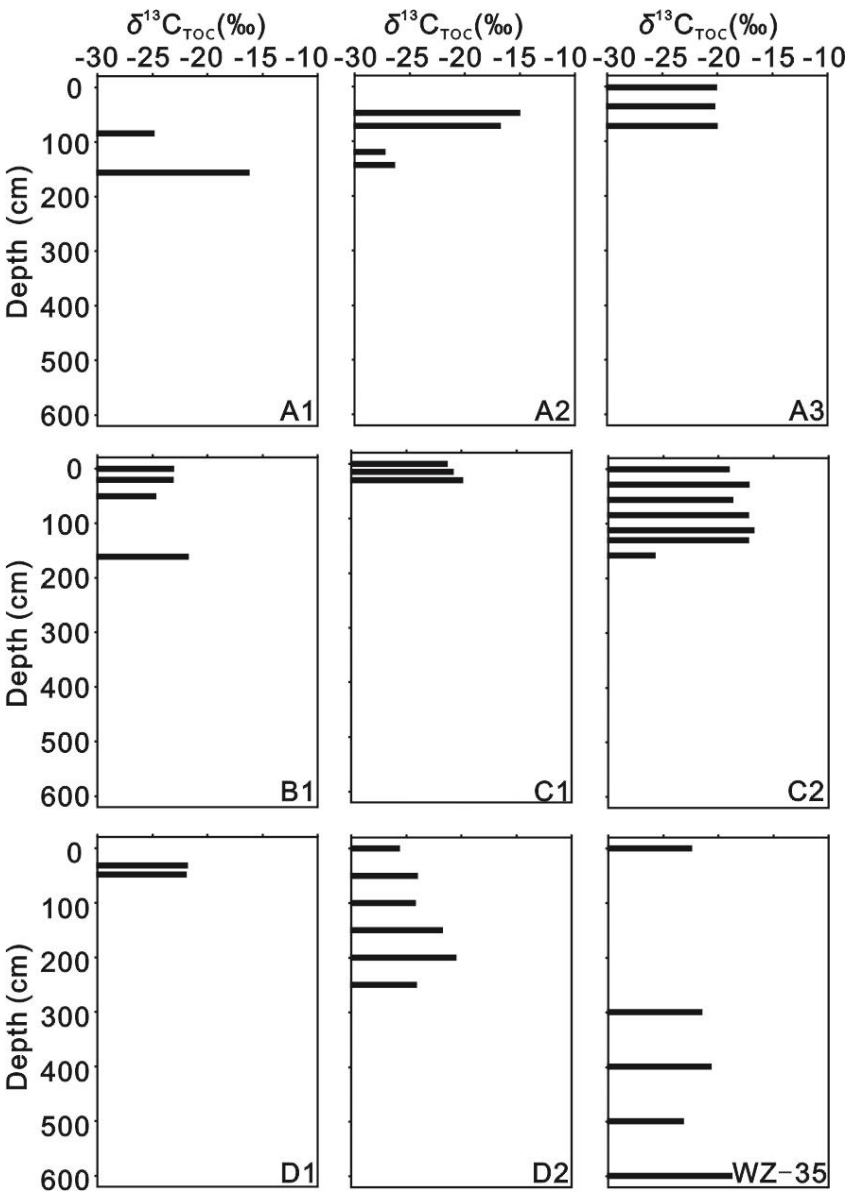**Figure 6.** Distribution of W_{TN} of the core sediments

Figure 7. Distribution of $\delta^{13}C_{TOC}$ of the core sediments

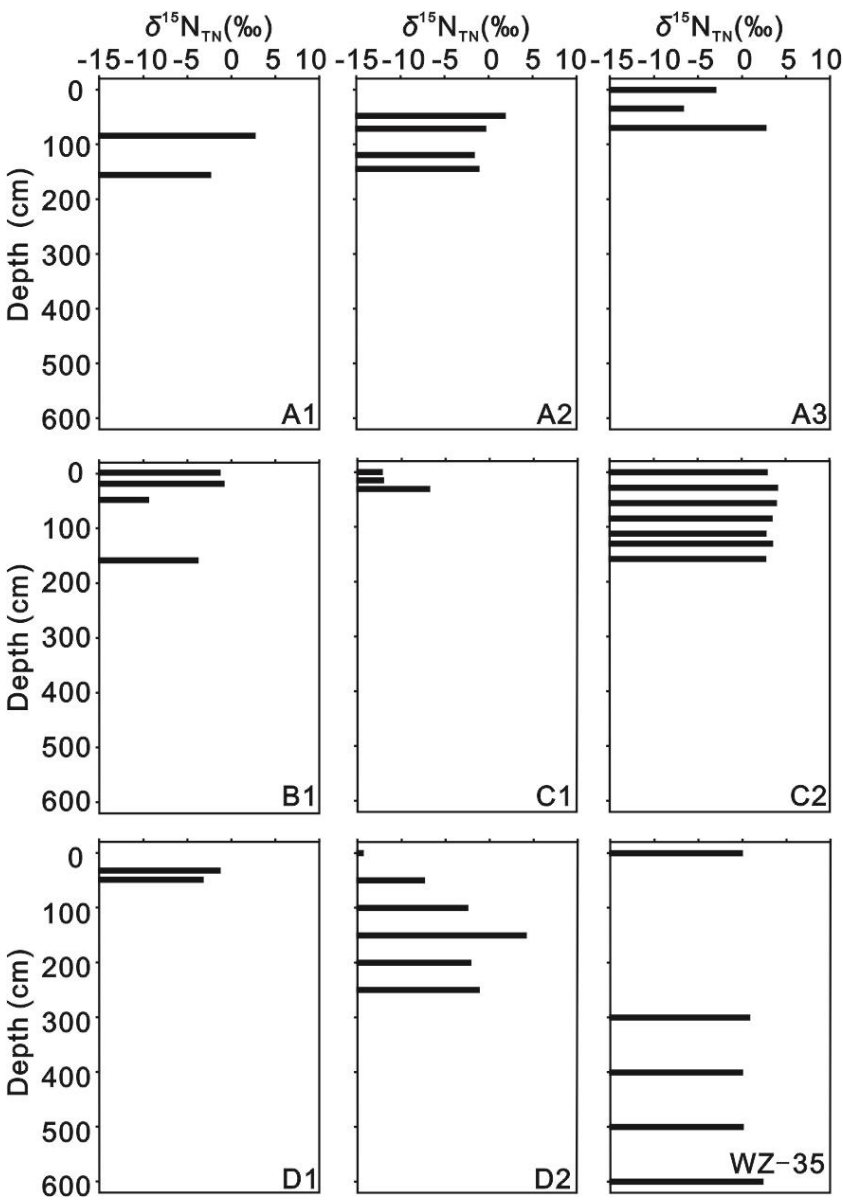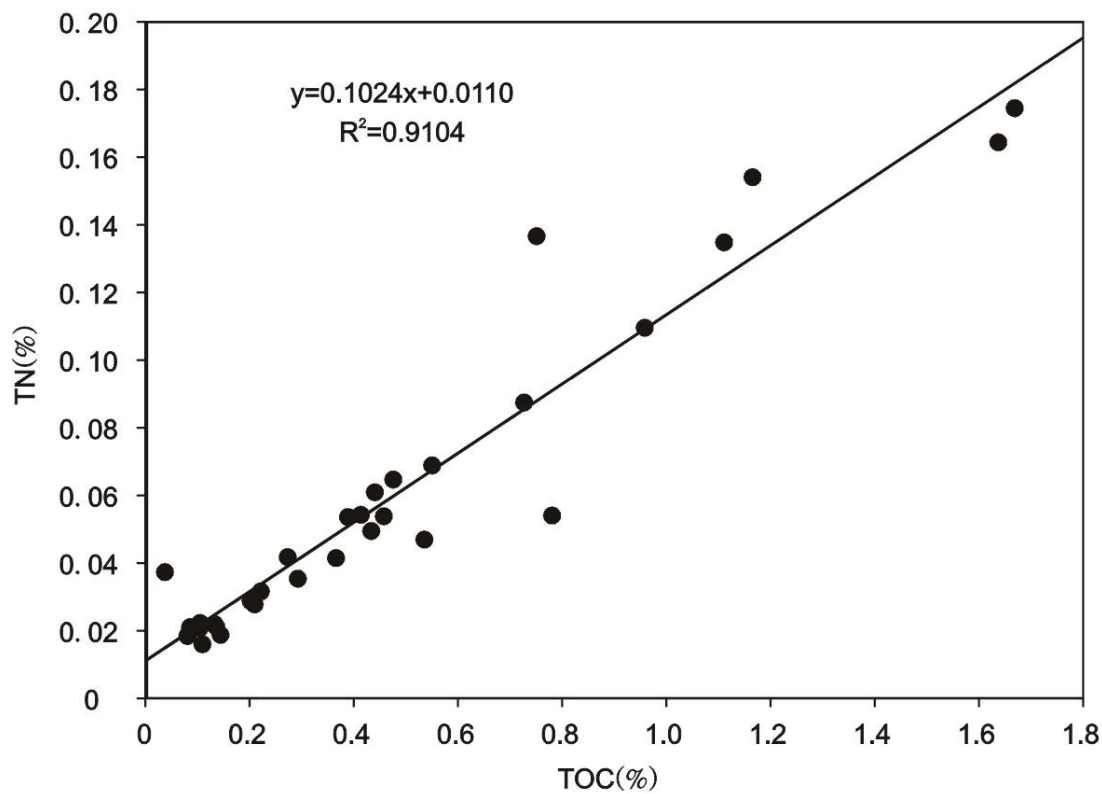**Figure 8.** Distribution of $\delta^{15}N_{TN}$ of the core sediments

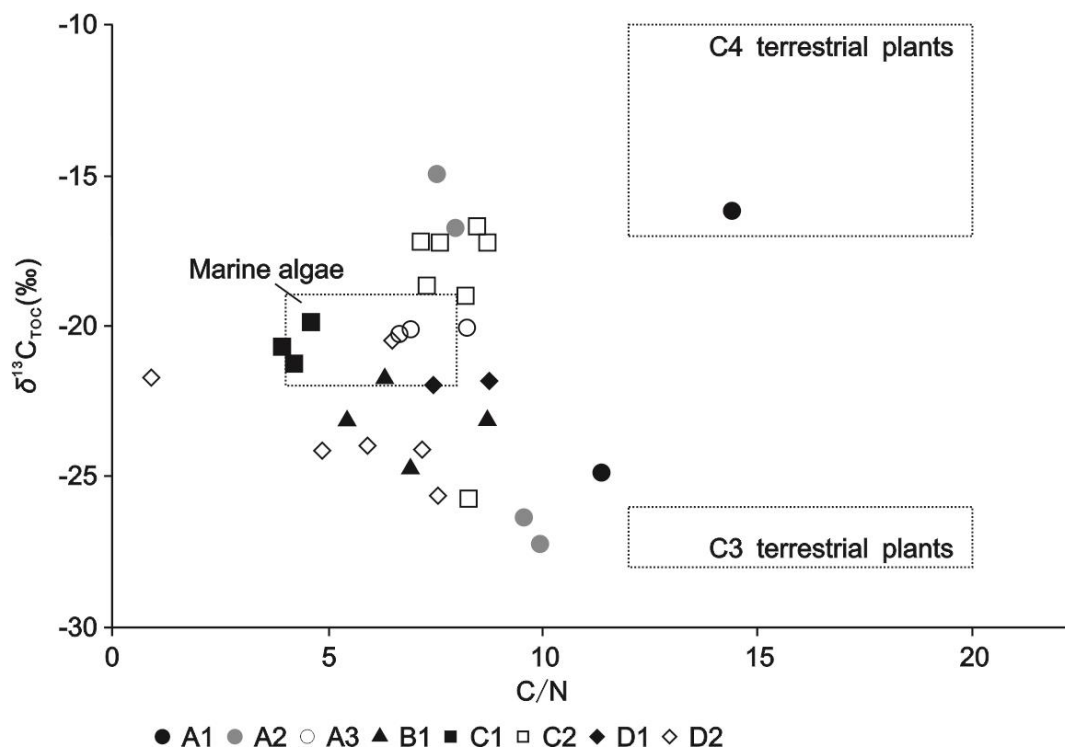**Figure 9.** The relationship between TOC and TN of the core sediments on Weizhou Island

Figure 10. Distribution of $\delta^{13}C_{TOC}$ and C/N of the core sediments in the correlation plots of
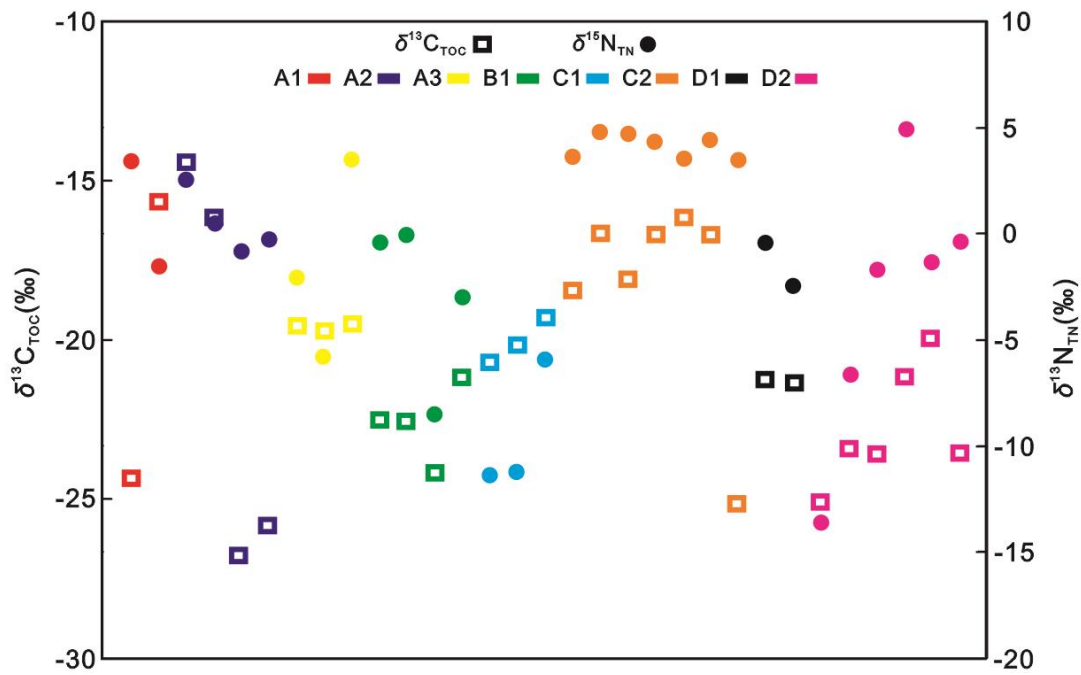
difference organic sources

Figure 11. Distribution of $\delta^{13}C_{TOC}$ and $\delta^{15}N_{TN}$ of core sediments
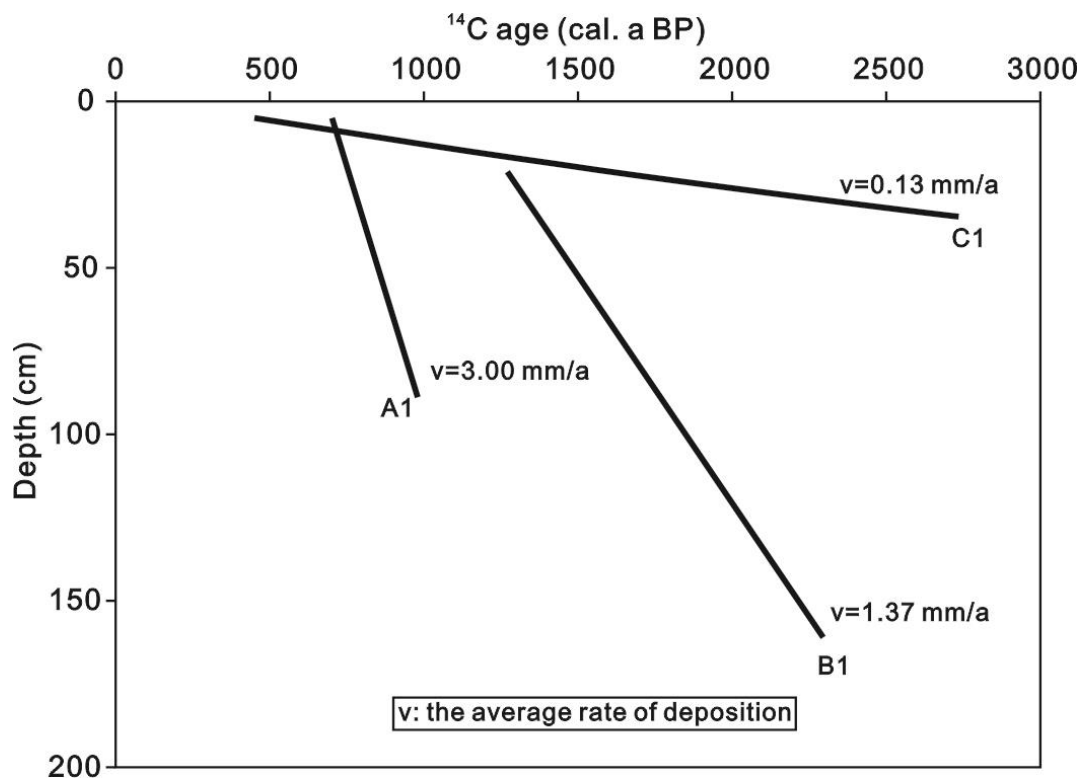

Figure 12. ^{14}C dating age of the coral sediments with their average deposition rate
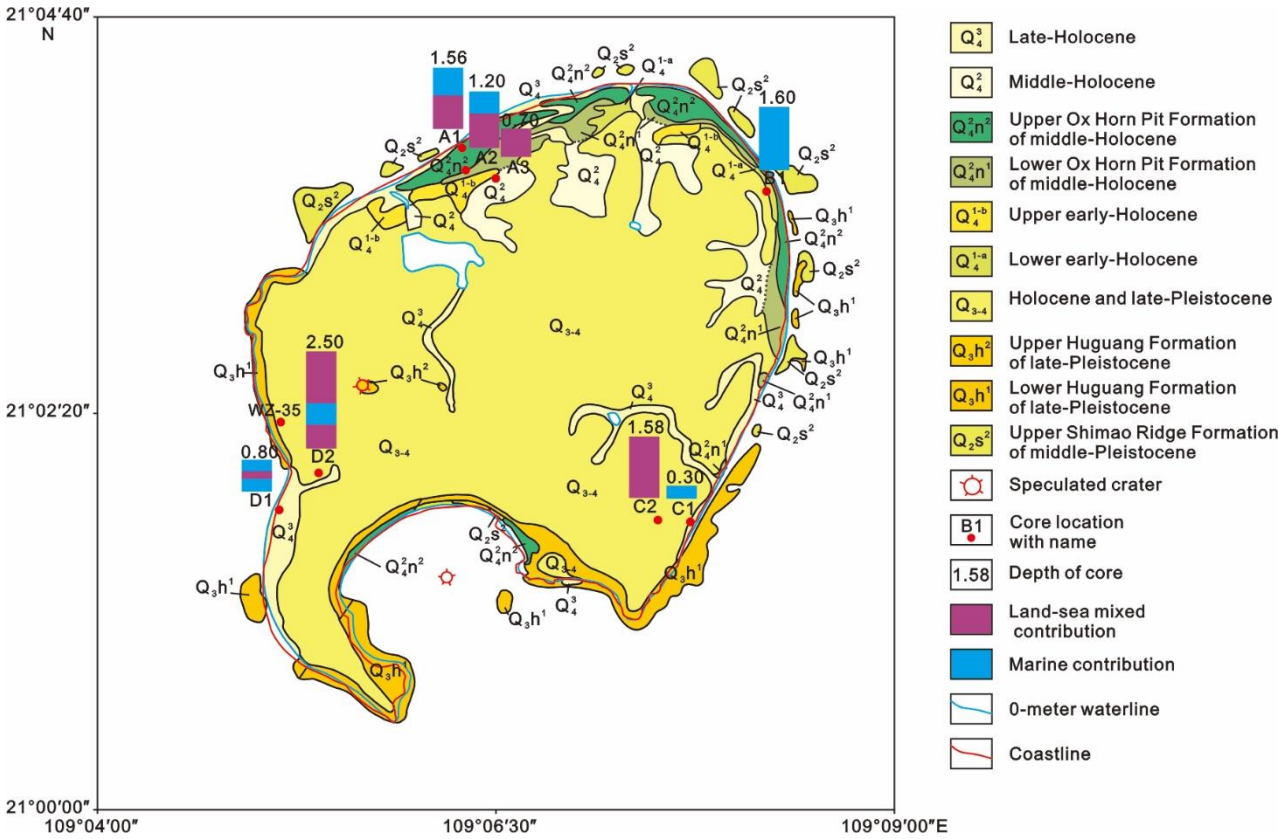
Figure 13. Schematic diagram of the source of the core sediments on Weizhou Island.

The stratum information is color-coded in the figure. Also, the coastline and 0-meter waterline are

marked in the figure.

Table Legends

Table 1. Information of core sampling on Weizhou Island

Core	Depth (cm)	Number of sample	Measured analysis	Location
A1	156	14	TIC, TOC, TN and ^{14}C age	21°03'55.86"N，109°06'20.40"E
A2	144	7	TIC, TOC and TN	21°03'48.07"N，109°06'22.31"E
A3	70	3	TIC, TOC and TN	21°03'45.54"N，109°06'33.56"E
B1	210	6	TIC, TOC, TN and ^{14}C age	21°03'40.10"N，109°08'16.04"E
C1	30	3	TIC, TOC, TN and ^{14}C age	21°01'42.93"N，109°07'47.41"E
C2	168	7	TIC, TOC and TN	21°01'42.97"N，109°07'36.08"E
D1	80	6	TIC, TOC, TN and ^{14}C age	21°01'46.72"N，109°05'11.11"E
D2	250	6	TIC, TOC and TN	21°01'59.91"N，109°05'25.48"E
WZ-35	600	5	TIC, TOC and TN	21°02'19.40"N，109°05'12.25"E

Table 2. Radiocarbon dating data of coral debris sample of the core sediments

Sample code	Depth (cm)	Beta	AGE(BP) (years)	Material measured
A1-1	0	470544	720 ± 30	coral
A1-8	84	470541	1000 ± 30	coral
B1-2	20	470547	1290 ± 30	coral
B1-5	160	470545	2310 ± 30	coral
C1-1	0	470549	450 ± 30	coral
C1-2	15	470538	1490 ± 30	coral
C1-3	30	470537	2750 ± 30	coral
D1-1	0	470552	1220 ± 30	coral
D1-4	48	470551	1200 ± 30	coral
D1-5	64	470550	1050 ± 30	coral

Table 3. List of C/N ratios of the core sediments

Sample code	Depth (cm)	C/N	Sample code	Depth (cm)	C/N	Sample code	Depth (cm)	C/N
A1-1	84	11.38	B1-5	160	6.32	D1-4	48	7.45
A1-7	156	14.42	C1-1	0	4.21	D2-1	0	7.55
A2-1	48	7.55	C1-2	15	3.92	D2-2	50	5.92
A2-2	72	7.96	C1-3	30	4.59	D2-3	100	4.87
A2-4	120	9.94	C2-1	0	8.21	D2-4	150	0.90
A2-5	144	9.55	C2-2	28	7.21	D2-5	200	6.48
A3-1	0	6.92	C2-3	56	7.32	D2-6	250	7.19
A3-2	35	6.67	C2-4	84	7.58	WZ35-1	0	3.50
A3-3	70	8.22	C2-5	112	8.46	WZ35-2	300	4.94
B1-1	0	8.73	C2-6	140	8.73	WZ35-3	400	5.08
B1-2	20	5.47	C2-7	168	8.28	WZ35-4	500	5.03
B1-3	50	6.94	D1-3	32	8.77	WZ35-5	600	6.31

Supplementary Materials: Table S1: Distribution of TIC, TOC, TN and their isotopic compositions in sediment under the study, Table S2: 14C-age of coral in sediment under the study.

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6 References

1. de Haas, H.; van Weering, T.C.E.; de Stieger, H. Organic carbon in shelf seas: sinks or sources, processes and products. *Cont. Shelf Res.* **2002**, *22*, 691-717.
2. Yang, Q.C.; Zhang, X.S.; Xu, X.Y.; Asrar, G.R. An Analysis of Terrestrial and Aquatic Environmental Controls of Riverine Dissolved Organic Carbon in the Conterminous United States. *Water* **2017**, *9*.
3. Meyers, P.A. Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes. *Org. Geochem.* **1997**, *27*, 213-250.
4. Yu, F.L.; Zong, Y.Q.; Lloyd, J.M.; Huang, G.Q.; Leng, M.J.; Kendrick, C.; Lamb, A.L.; Yim, W.W.S. Bulk organic delta C-13 and C/N as indicators for sediment sources in the Pearl River delta and estuary, southern China. *Estuar. Coast. Shelf Sci.* **2010**, *87*, 618-630.
5. Li, Y.X.; Zhang, L.J.; Xue, L.; Fan, W.H.; Liu, F.W.; Yang, H. Spatial Variation in Aragonite Saturation State and the Influencing Factors in Jiaozhou Bay, China. *Water* **2020**, *12*.
6. Lupon, A.; Catalan, N.; Marti, E.; Bernal, S. Influence of Dissolved Organic Matter Sources on In-Stream Net Dissolved Organic Carbon Uptake in a Mediterranean Stream. *Water* **2020**, *12*.
7. Zhang, Y.F.; Li, D.W.; Wang, K.; Xue, B. Contribution of Biological Effects to the Carbon Sources/Sinks and the Trophic Status of the Ecosystem in the Changjiang (Yangtze) River Estuary Plume in Summer as Indicated by Net Ecosystem Production Variations. *Water* **2019**, *11*, 16.
8. Li, X.G.; Song, J.M.; Yuan, H.A. Inorganic carbon of sediments in the Yangtze River Estuary and Jiaozhou Bay. *Biogeochemistry* **2006**, *77*, 177-197.
9. Xie, X.L.; Wang, Y.Z.; Zhang, P.Y.; Gao, X.L. Fractionation of inorganic carbon in surface sediments of Daya Bay and Sishili Bay areas. *Environ. Chem.* **2011**, *6*,

1108-1113. (In Chinese)

10. Zhang, D.H.; Zhao, L.S. *Geochemistry*; Zhang, B.R., Chen, Y.L., Mao, S.D., Yang, Z.F., Hou, Q.Y., Yuan, G.L. Eds.; Geological Publishing House, China 2013; pp. 388-394. (In Chinese)

11. Lamb, A.L.; Wilson, G.P.; Leng, M.J. A review of coastal palaeoclimate and relative sea-level reconstructions using delta C-13 and C/N ratios in organic material. *Earth-Sci. Rev.* **2006**, *75*, 29-57.

12. Sampei, Y.; Matsumoto, E. C/N ratios in a sediment core from Nakaumi Lagoon, southwest Japan - usefulness as an organic source indicator. *Geochem. J.* **2001**, *35*, 189-205.

13. Brodie, C.R.; Casford, J.S.L.; Lloyd, J.M.; Leng, M.J.; Heaton, T.H.E.; Kendrick, C.P.; Zong, Y.Q. Evidence for bias in C/N, delta C-13 and delta N-15 values of bulk organic matter, and on environmental interpretation, from a lake sedimentary sequence by pre-analysis acid treatment methods. *Quat. Sci. Rev.* **2011**, *30*, 3076-3087.

14. Perdue, E.M.; Koprivnjak, J.F. Using the C/N ratio to estimate terrigenous inputs of organic matter to aquatic environments. *Estua. Coast. Shelf Sci.* **2007**, *73*, 65-72.

15. Krull, E.; Haynes, D.; Lamontagne, S.; Gell, P.; McKirdy, D.; Hancock, G.; McGowan, J.; Smernik, R. Changes in the chemistry of sedimentary organic matter within the Coorong over space and time. *Biogeochemistry* **2009**, *92*, 9-25.

16. Rumolo, P.; Barra, M.; Gherardi, S.; Marsella, E.; Sprovieri, M. Stable isotopes and C/N ratios in marine sediments as a tool for discriminating anthropogenic impact. *J. Environ. Monitor.* **2011**, *13*, 3399-3408.

17. Tang, H.J.; Ke, Z.X.; Yan, M.T.; Wang, W.J.; Nie, H.Y.; Li, B.X.; Zhang, J.P.; Xu, X.R.; Wang, J. Concentrations, Distribution, and Ecological Risk Assessment of Heavy Metals in Daya Bay, China. *Water* **2018**, *10*.

18. Liu, X.T.; Ge, C.D.; Zhou, X.Q.; Huang, M.; Tang, M.; Li, Y.L. Nitrogen geochemical characteristics and their implications on environmental change in the lagoon sediments of the Dongdao Island of Xisha Island in South China Sea. *Haiyang Xuebao* **2017**, *39*, 43-54. (In Chinese)

19. Gao, X.L.; Yang, Y.W.; Wang, C.Y. Geochemistry of organic carbon and nitrogen in surface sediments of coastal Bohai Bay inferred from their ratios and stable isotopic signatures. *Mar. Pollut. Bull.* **2012**, *64*, 1148-1155.

20. Bejugam, P.; Nayak, G.N. Source and depositional processes of the surface sediments and their implications on productivity in recent past off Mahanadi to Pennar River mouths, western Bay of Bengal. *Paleogeogr. Paleoclimatol. Paleoecol.* **2017**, *483*, 58-69.

21. Zhan, Q.; Wang, Z.H.; Xie, Y.; Xie, J.L.; He, Z.F. Assessing C/N and delta C-13 as indicators of Holocene sea level and freshwater discharge changes in the subaqueous Yangtze delta, China. *Holocene* **2012**, *22*, 697-704.

22. Liu, J.H.; Li, G.Z.; Nong, H.Q. Features of geomorphy and Quaternaty geology

of the Weizhou Island. *Jour. Guangxi Acad. Sci.* **1991**, *1*, 27-36. (In Chinese)

23. Qi, F.Q.; Li, G.Z.; Sun, Y.F.; Liang, W.; Du, J. Basic geomorphologic features of the Weizhou Island of the Beibu Bay. *Advan. Mar. Sci.* **2003**, *1*,41-50. (In Chinese)

24. Li, C.N.; Wang, F.Z. Holocene volcanic effusion in Weizhou Island and its geological significance. *Miner. Petrol.* **2004**, *4*, 28-34. (In Chinese)

25. Yu, Z.T.; Wang, X.j.; Zhao, C.Y.; Lan, H.Y. Spatial variations of inorganic carbon and isotopes in the surface sediment of the Lake Bosten. *Jour. Lake Sci.* **2015**, *27*, 250-257. (In Chinese)

26. Gao, Y.K.; Wang, H.Y.; Cheng, Y.; Liu, H.Y.; Zhu, C.Y. Climatic and environment changes in more than the past 1800 years as recorded by isotopic carbon and nitrogen in organic matter of sediments from western Foye Chi (Buddha Pond) on Taibai Mountain. *Acta Sci. Nat. Univ. Pek.* **2018**, *56*, 94-104. (In Chinese)

27. Ji, W.H.; Guo, N.C.; Xu, J.; Yu, H.; Niu, Y. Carbon and nitrogen isotope characterization and source analysis of sediments from shallow lakes in the middle of Yangtze River. *Jour. Hydroeco.* **2018**, *39*, 8-15. (In Chinese)

28. Li, X.G.; Song, J.M. Source, removal and transformation of carbon in marine sediments. *Studia Mar. Sci.* **2004**, *46*, 106-117. (In Chinese)

29. Cao, H.S.; Zhang, Z.P.; He, W.T.; Huang, X.; Pu, S.Q. Study on the change process of the ecological encirnment in the Zhanjiang Bay through the organic carbon isotope technique. *Jour. Ocean Technol.* **2020**, *39*, 57-63. (In Chinese)

30. Prahl, F.G.; Ertel, J.R.; Goni, M.A.; Sparrow, M.A.; Eversmeyer, B. Terrestrial organic-carbon contributions to sediments on the Washington Margin. *Geochim. Cosmochim. Acta* **1994**, *58*, 3035-3048.

31. Bordovskiy, O.K. Sources of organic matter in marine basins. *Mar. Geol.* **1965**, *3*, 5-31.

32. Chen, M.; Zeng. J.; Yang, W.F. The eco-environmental changes in China coastal seas elucidated from isotope tracers. *Haiyang Xuebao* **2018**, *40*, 32-41. (In Chinese)

33. Maksymowska, D.; Richard, P.; Piekarek-Jankowska, H.; Riera, P. Chemical and isotopic composition of the organic matter sources in the Gulf of Gdansk (Southern Baltic Sea). *Estuar. Coast. Shelf Sci.* **2000**, *51*, 585-598.

34. Lin, G.H. *Stable isotope ecology*; Higher Education Press, 2013; pp. 37-266.(In Chinese)

35. Emerson, S.; Hedges, J.I. Processes controlling the organic carbon content of open ocean sediments. *Paleoceanography* **1988**, *3*, 621-634.

36. Thimdee, W.; Deein, G.; Sangrungruang, C.; Nishioka, J.; Matsunaga, K. Sources and fate of organic matter in Khung Krabaen Bay (Thailand) as traced by delta C-13 and C/N atomic ratios. *Wetlands* **2003**, *23*, 729-738.

37. Oleary, M.H. Carbon isotopes in photosynthesis. *Bioscience* **1988**, *38*, 328-336.

38. Ruiz-Fernandez, A.C.; Hillaire-Marcel, C.; Ghaleb, B.; Soto-Jimenez, M.;

Paez-Osuna, F. Recent sedimentary history of anthropogenic impacts on the Culiacan River Estuary, northwestern Mexico: geochemical evidence from organic matter and nutrients. *Environ. Pollut.* **2002**, *118*, 365-377.

39. Owens, N.J.P. Natural Variations in 15 N in the Marine Environment. *Adv. Mar. Biol.* **1988**, *24*, 389-451.

40. Vizzini, S.; Savona, B.; Caruso, M.; Savona, A.; Mazzola, A. Analysis of stable carbon and nitrogen isotopes as a tool for assessing the environmental impact of aquaculture: a case study from the western Mediterranean. *Aquac. Int.* **2005**, *13*, 157-165.

41. Xiong, H.X.; Zong, Y.Q.; Qian, P.; Huang, G.Q.; Fu, S.Q. Holocene sea-level history of the northern coast of South China Sea. *Quat. Sci. Rev.* **2018**, *194*, 12-26.

42. Yao, Y.T.; Harff, J.; Meyer, M.; Zhan, W.H. Reconstruction of paleocoastlines for the northwestern South China Sea since the Last Glacial Maximum. *Sci. China. Earth. Sci.* **2009**, *52*, 1127-1136.

43. Zhao, N.; Shen, D.S.; Shen, J.W. Formation Mechanism of Beach Rocks and Its Controlling Factors in Coral Reef Area, Qilian Islets and Cays, Xisha Islands, China. *J. Earth Sci.* **2019**, *30*, 728-738.

44. Shen, J.W.; Wang, Y.; Zhao, N.; Yang, H.Q.; Fu, F.X.; Jin, Y.B. Carbonate sedimentary characteristics of the beach rocks around Qilian Islets and Cays, Xisha Islands: Implication for coral reef development and decline. *Paleogeogr. Paleoclimatol. Paleoecol.* **2017**, *474*, 264-278.

45. Mo, Y.J. Development of coastal landform in Weizhou Island. *Tropic. Geog.* **1989**, *3*, 243-248. (In Chinese)

46. Jiwarungrueangkul, T.; Liu, Z.F.; Zhao, Y.L. Terrigenous sediment input responding to sea level change and East Asian monsoon evolution since the last deglaciation in the southern South China Sea. *Glob. Planet. Change* **2019**, *174*, 127-137.