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Spatial variability in alkaline earth metals of surface sediments from the Jiulong River mouth, Southeast China: implications for hydro-sedimentary dynamic processes and sedimentary facies

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Abstract

The establishment of effective proxies for the differentiation of sedimentary facies in the tide-dominated river mouth is fundamental to the delineation of stratigraphy and the study of paleoenvironments. Geochemical signatures of the acetic acid (HAc) extractive phases of alkaline earth metals, such as Sr, Ba, and Ca, are closely related to sedimentary environments and thus provide a novel method for discriminating the sedimentary facies of river mouth. In this study, 50 surface water and surface sediment samples were obtained from different geomorphological units of the Jiulong River mouth, i.e., river channel, distributary channel, delta front, delta front slope, prodelta, and shallow marine area, and the salinity of the water, the grain size, and the Sr, Ba, and Ca contents and Sr/Ba molar ratio (Sr/Ba) in HAc leachates of the sediments were determined. Contents of alkaline earth metals in HAc leachates of surface sediments from the Changjiang (Yangtze) River coast were also collated. The goals of this study were to reveal the spatial distribution of alkaline earth metals in the Jiulong River mouth, define their depositional mechanisms, and search for effective geochemical proxies for identification of the various sedimentary facies in the fluvial to marine transition zone. The results revealed several land-to-sea gradients. The Ba content decreased rapidly from the distributary channel to the sea, and the Sr and Ca contents and Sr/Ba increased gradually with the increase in salinity. Salinity, marine biomass, and sedimentary dynamic processes, were speculated to be the main reasons for the differences in their spatial distributions. There were significant differences in Ba, Sr, Ca, and Sr/Ba between the river channel and the distributary channel, in Ca and Ba between the distributary channel and the delta front (slope), and in Sr, Ca, and Sr/Ba between the delta front (slope) and the prodelta–shallow marine region. The Sr–Ba scatterplot showed that the sediments of the river channel and alluvial plain were located as a high Ba and low Sr element-defined end-member, whereas samples of the prodelta and shallow marine formed a high Sr and low Ba end-member. These can be used as characteristic end-members indicating terrestrial facies and marine facies, respectively. The sediments of the delta plain, tidal river, distributary channel, delta front, and delta front slope are located between these two end-member regions of the scatterplot, and this region of the diagram can be used to identify land–sea transitional sedimentary facies.

Key words: Sr-Ba, sedimentary facies, tide-dominated river mouth, end-member, salinity

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1 Introduction

Rivers are the link between land and sea. They transport approximately from 150 × 10^9 t to 200 × 10^9 t of suspended sediments to the sea every year (Milliman and Syvitski, 1992), which are mainly deposited in river mouths and nearby continental

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margins, making river mouth a key area for the study of global change and land-sea interactions. As a result of Late Quaternary sea-level fluctuations, the stratigraphy of river mouth is characterized by drastic changes of sedimentary facies and uncontinuities induced by frequent erosions (Li and Wang, 1998). Therefore, the identification of sedimentary facies is the basis for the study of paleoenvironmental changes using sedimentary records at river mouth (Pan et al., 2023b). However, sedimentary facies in the tide-dominated river mouth often have similar lithologies and sedimentary structures (Gao et al., 2012; Zhan, 2012), such as those of coarse-grained sediments in distributary channels and river mouth bars, fine-grained sediments in delta fronts slope, tidal flats, and flood-dominated channels, which make reconstruction of the paleoenvironments difficult. The similar lithologies and sedimentary structures also hinder studies such as sea-level reconstruction, identification of marine intrusions and paleostorm events, and environmental changes at coastal archaeological sites (Zhan, 2012; Wang et al., 2012, 2013). Therefore, finding effective proxies to distinguish sediment successions formed in different sedimentary geomorphological units in present-day river mouth is a top priority to improve the identification of sedimentary facies in land–sea transitional zones.

In the land-sea transitional environment such as tide-dominated river mouth, the alkaline earth metals Sr, Ba, and Ca and the Sr/Ba molar ratio (Sr/Ba) in sediments are very sensitive to changes in depositional environment. Sr is highly active and enriched in seawater, marine organisms, and marine sediments (Bowen, 1956; Cho et al., 1999; Zwolsman and Van-Eck, 1999; Alfonso et al., 2006). Ca has properties similar to those of Sr, is also enriched in marine environments, having a significant positive correlation with Sr content. Both elements are positively correlated with water column salinity (Coffey et al., 1997; Cho et al., 1999; Zwolsman and Van-Eck, 1999; Wang, 1996; Wang et al., 2001; Dorval et al., 2005; Mohan and Walther, 2015). Ba is enriched in fresh water but has low values in seawater, which is attributable to the fact that when salt water and fresh water mix, the Ba^{2+} in the fresh water readily reacts with SO_4^{2-} in the seawater to form $BaSO_4$ precipitate (Wang, 1996; Shi et al., 2003). Ba content is thus negatively correlated with the salinity of the water. Therefore, marine sediments have higher Sr/Ba, and terrestrial sediments have lower ratios (Wang et al., 1979; Liu et al., 1984; Qian et al., 2012).

Geochemical elements in sediments mainly include exchangeable, carbonate-bound, Fe/Mn oxide-bound, organic-bound, and detrital phases (Tessier et al., 1979), among which the exchangeable and carbonate phases are closely related to the depositional environment (Wang, 1996). Wang (1996) and Wang et al. (2019a, 2019b) found that the Sr/Ba in the exchangeable and carbonate phases of sediments extracted using the dilute HAc method could better distinguish the marine and terrestrial depositional environments of the Huanghe (Yellow) River delta. Wang et al. (2021) investigated the spatial distribution of alkaline earth metals in the dilute HAc-extracted phases of surficial sediments from the Changjiang (Yangtze) River mouth and found a clear differentiation of each sedimentary facies. Huang et al. (2021a) investigated the spatial distribution of alkaline earth metals in the dilute HAc and dilute HCl-extracted phases of surficial sediments from three sedimentary environments, namely, the alluvial plain, tidal river, and saltmarsh-tidal flats in the Ningbo Plain. They found that the alkaline earth metals in the acid leachates are most sensitive to changes in the depositional environment of the coastal zone, that the results of HAc-extracted phases are not affected by the sample volumes or the measuring instruments. Huang et al. (2021a) also reported the end-member values of terrestrial and marine sediments of the East China coast, which can effectively identify the depositional environments of coastal zone. On this basis, further studies have used HAc-extracted alkaline earth metals as the indicators to investigate saltwater intrusion, extreme storm events and coastal flooding in the lowlands of eastern China coast, as well as the evolution of depositional environments and human adaptations at Neolithic sites (Huang et al., 2020, 2021b; Zhang et al., 2022; Pan et al., 2023a; Zheng et al., 2023).

The Jiulong River mouth on the southeast coast of China is a strongly tidal influenced river mouth that has formed diverse sedimentary geomorphological units under complex tidal-fluvial interactions (Fig. 1a). The sedimentary facies differentiation and Late Quaternary stratigraphic records of this river mouth remain poorly understood (Chen et al., 1998). In this study, surface sediments from different geomorphological units were collected from land to sea to characterize the distribution of alkaline earth metals in the dilute HAc leachates, explore their relationships with the hydrodynamic environments, and search for effective proxies for identifying the sedimentary facies of the tide-dominated river mouth. Results reported from the Changjiang River coast of East China Sea (Huang et al., 2020, 2021a; Wang et al., 2021; Zhang et al., 2022) were also collated to compare with the spatial distributions of alkaline earth metals in the Jiulong River mouth.

2 Regional setting

The Jiulong River is a subtropical mountain stream with a total length of 1 923 km and catchment area of 1.47×10^4 km^2 (Xu and Chen, 2010), making it the second largest river in Fujian Province, China. The main bedrock in the Jiulong River Basin is Mesozoic igneous rocks, among which the biotite granite that intruded in the Late Yanshan period are the most widespread, and the soil-forming parent rocks are mainly granitic (Yu et al., 2012). The Jiulong River Basin has a subtropical oceanic monsoon climate. It has an average annual precipitation of 1 400–1 800 mm, which is concentrated between April and September (approximately 75% of the annual precipitation), and is frequently affected by typhoons in summer and autumn (Wen et al., 2007). The runoff from the Jiulong River to the sea is also concentrated from April to September (Fig. 1b), with average annual runoff values of the main tributaries, the North River and the West River, being 8.27×10^9 m^3 and 3.70×10^9 m^3, respectively, and the average annual suspended sediment concentrations being 0.206 kg/m^3 and 0.210 kg/m^3, respectively (Comprehensive Survey Leading Group Office of Coastal and Tidal Flat Resource in Fujian Province, 1990). Semidiurnal tides occur in the Jiulong River mouth, with an average tidal range of 3.99 m and a maximum range of 6.42 m (Editorial Committee of Chinese Gulf Annals, 1993). The intrusion of the flood tide is directed toward the north bank of the river mouth, the flows of the ebb tide and runoff are directed toward the south bank (Fig. 1c), forming a counterclockwise circulation centered on the Jiyu Island (Zeng, 1987).

The Jiulong River runs into an embayment surrounded by bedrock and forms a delta at the head of the bay (Fig. 1a). The delta plain is divided by three distributary channels: the north, middle, and south channels. The north channel is gradually silting up, and the south and middle channels are currently the main channels through which runoff enters the sea. The bay is 7 km wide from north to south, narrows to about 4 km at the mouth, and the submerged topography slopes seaward at a gradient of about 2‰. In the 1970s, the government constructed

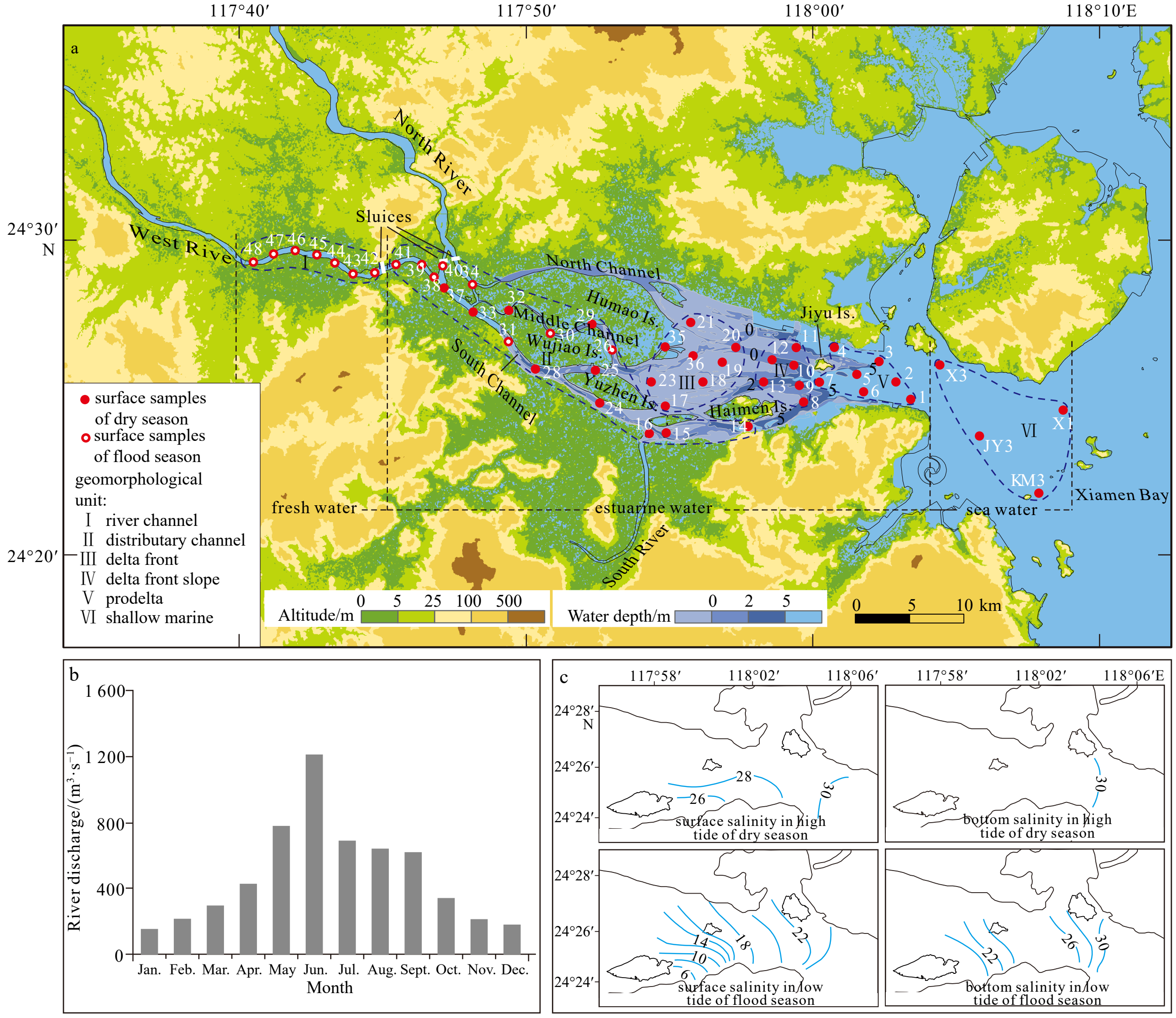

Fig. 1. The Jiulong River mouth and sampling stations (a); monthly average discharge of the Jiulong River (Wang and Jiang, 2013) (b); surface/bottom salinity distribution at high/low tide of the dry/flood season in the Jiulong River mouth (Wang et al., 1986) (c).

sluices in both the North River and the West River at the mouth of the Jiulong River (Fig. 1a) to prevent the intrusion of tides, so the river upstream of the sluices is entirely fresh water. An estuarine water area, where salt water and fresh water mix, extends from the sluice to the mouth of the embayment (Wang et al., 2022). The upper part of the embayment where delta plain presents is dominated by runoff from the south and middle channels, which are influenced by flooding tidal currents. In the lower part, high-salinity water intrusion occurs at high tide during the dry season, and the salinity is uniformly distributed vertically; both horizontal and vertical salinity gradients become significantly larger during the flood season (Fig. 1c; Wang et al., 1986). In the area east of Jiyu Island, the lower layer is occupied by high-salinity water throughout the year, and the upper layer is diluted water in summer (Wang and Jiang, 2013; Wang et al., 2022). The shallow marine area east of the bay is dominated by highly saline water throughout the year.

3 Materials and methods

3.1 *Sampling in different geomorphological units*

In this study, by considering topography and hydrology (Figs. 1a, c; Wang et al., 2022), the Jiulong River mouth was divided into six geomorphological units (Ⅰ–Ⅵ): river channel, distributary channel, delta front, delta front slope, prodelta, and shallow marine (Fig. 1a). The river channel (Ⅰ) is the area upstream of the West River sluice. The south and middle channels are the distributary channels of the delta plain (Ⅱ). Unit Ⅲ belongs to the submerged shoals of the delta front, which are mostly exposed to the water surface at low tide. Unit Ⅳ, the delta front slope, is the area from Haimen Island to Jiyu Island, where the water depth ranges from 0 m to 5 m. The water depth in the section from Jiyu Island to the mouth, which corresponds to the prodelta (Ⅴ), is mostly greater than 5 m. The shallow marine area (Ⅵ) is the Xiamen Bay east of the mouth.

Samples of surface sediment and surface seawater (Fig. 1a) were collected synchronously during two cruises in January 2020 (dry season; 35 sets) and October 2022 (flood season; 15 sets), respectively. In total, there were 50 sets of samples. Sites were numbered in the order of sample collection. Surface sediments were collected using a grab sampler, packaged in self-sealing polyethylene bags, and immediately returned to the laboratory for freezing and preservation. Surface seawater was collected in

1 L plastic bottles.

3.2 *Methodology*

For surface water salinity testing, water samples were brought back to the laboratory and immediately tested with a TK22-HWYDA-1 salinometer (salinity test range 2–42, resolution 0.000 1, precision (stability): ± 0.001 4, accuracy: ± 0.005). Surface sediments for grain-size analysis were oven-dried at 40℃, and about 0.2 g was placed into a beaker. Samples were treated with 10 mL of H_2O_2 (10%) to remove organic matter and then with 10 mL of HCl (10%) to remove calcareous material. Samples were washed with distilled water after 4 h reactions. After settling for 24 h, they were disaggregated by adding 5 mL of Calgon (sodium hexametaphosphate, 5%), followed by immersion in an ultrasonic bath for ca. 15 min. The grain size was measured using a Beckman Coulter Laser Diffraction Particle Size Analyzer (LS13320). Sediments were classified according to the grain size, with particles smaller than 4 μm as clay, 4–63 μm as silt, and larger than 63 μm as sand. Lithology of the sediment was determined according to the percentage of each component (Friedman and Sanders, 1978).

The alkaline-earth metal contents of the surface sediment samples were extracted with dilute HAc to obtain the exchangeable and carbonate phases. The pre-treatment procedure followed Huang et al. (2021a) and was as follows: the samples were lyophilized in a freeze-dryer under vacuum at a low temperature. The lyophilized samples were ground thoroughly with an onyx mortar and pestle until all samples passed through a 200 mesh sieve. 0.200 0 g specimen of each sample was placed in a 50 mL centrifuge tube. Then, 20 mL of 10% HAc solution was added to the centrifuge tube containing the sample and allowed to react at room temperature for 24 h, during which time the sample was shaken with a blender every 4 h to ensure a complete reaction. The specimen was centrifuged at a speed of 4 000 r/min for 10 min. Then, the supernatant was poured into a clean and dry crucible, and the crucible was placed on an electric hot plate (180℃) and heated until only a very small amount of liquid and orange-red solids on the walls remained. Finally, 20 mL of nitric acid (HNO_3) with a concentration of 5‰ was added to fix the volume, and the solution was transferred to a clean centrifuge tube. An Inductively Coupled Plasma Mass Spectrometer (ICP-MS, Agilent 7500 cx) was used to determine the Sr, Ba, and Ca contents, and the Sr/Ba was calculated from the results. The instrumental error was <6%. The analytical process was monitored using the AGV-2, BCR-2, and BHVO-2 standards and a blank sample to ensure that the test results were reliable.

4 Results

4.1 *Spatial distribution of surface water salinity*

Salinity measurements of surface water from the Jiulong River mouth showed the trend of increasing salinity from land to sea (Table 1, Fig. 2) and that the salinity of waters in the northern part of the bay (e.g., Sites 2–4, 20 and 21) was higher than that in the southern part, reflecting flood tidal current intrusion into the river mouth from the northern side. The small difference between the flood and dry seasons suggests that the sluices regulate freshwater discharge. Salinity values in the river channel (Sites 42–48) were close to 0, with a mean value of 0.1. The salinity in the distributary channel (Sites 14–16, 24–26, 28–34, and 37–41) increased seaward from 0.92 to 21.3, with a mean value of 8.45. In this unit, low values of salinity (mean 1.91) occurred at seven Sites at the top of the delta (Sites 33–34 and 37–41). Salinity increased rapidly at the south and middle channels (Sites 28–32), where it had a mean value of 6.56. It further increased in the lower part of the south channel (Sites 14–16, Salinity > 20, mean 20.83) and the lower part of the middle channel (Sites 25, 26, and 29, range from 9.54 to 15.94, mean 13.09). The salinity range of the delta front (Sites 17–21, 23, 35, and 36) was from 15.9 to 27.5, with a mean value of 21.78, while that of the northern stations (Sites 20, 21) exceeded 25 and that of the southern stations (Sites 17–19, 23) ranged from 15.9 to 21.5, with a mean value of 19.55. Salinity values in the delta front slope (Sites 8–13) were similar to those of the delta front, ranging from 17.6 to 23.5, with a mean value of 21.8, but there was a smaller difference between north and south. Salinity values in the prodelta (Sites 1–7) increased again, ranging from 22.2 to 29.2, with a mean value of 25.74, with higher values in the north and lower values in the south. The average values of three Sites in the north (Sites 2–4) and four Sites in the south (Sites 1, 5–7) were 29 and 23.3, respectively. The shallow marine environments (Sites X3, JY3, X1, and KM3) had

Table 1. Salinity distribution of surface water in the Jiulong River mouth

Geomorphological unit	Number of samples	Salinity		
		Min.	Max.	Average
River channel	7	0.1	0.1	0.1
Distributary channel	18	0.92	21.3	8.45
Delta front	8	15.9	27.5	21.78
Delta front slope	6	17.6	23.5	21.8
Prodelta	7	22.2	29.2	25.74
Shallow marine	4	22.2	29.0	26.3

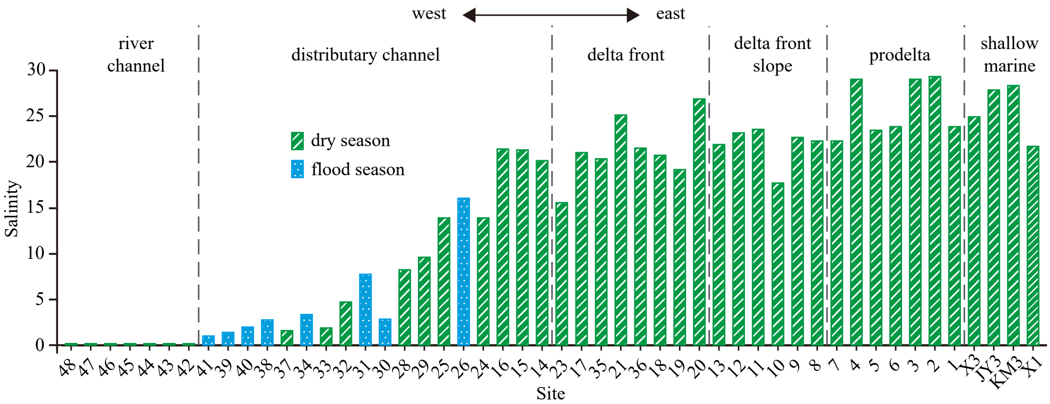

Fig. 2. Salinity distribution of surface water in the Jiulong River mouth.

the highest salinity, ranging from 22.2 to 29.0, with a mean value of 26.3.

4.2 *Distribution characteristics of surface sediment grain size and types*

Grain size of surface sediments in the Jiulong River mouth does not show a clear trend of distribution among geomorphological units. Grain sizes are finer in river channel and distributary channel, and are coarser with large variations between sites in geomorphological units seaward (Table 2, Figs 3a and b). Lithologies of all samples were dominated by clayey silt at 62%, followed by sandy silt at 22% and sand at 10%. The mean grain size showed the highest values in delta front facie, with an average value of 133.1 μm. The facies of prodelta, delta front slope and shallow marine also have coarser sediments with average values of mean grain size of 55.6 μm, 39.4 μm and 44.4 μm, respectively. Mean grain size showed lower values in river channel and distributary channels, with average values of 19.4 μm and 36.0 μm, respectively (Fig. 3b).

4.3 *Spatial distribution of alkaline earth metals*

The distribution of the alkaline earth metals Sr, Ba, and Ca and the Sr/Ba in the surface sediments of the Jiulong River mouth varied significantly among the different geomorphological units (Table 2, Fig. 3). The Ba content decreased seaward, and the Sr, Ca, and Sr/Ba values generally increased from land to sea.

Ba content was significantly high in the river channel, with a mean value of 150.91 mg/kg (Fig. 3c), but it decreased rapidly from west to east in the distributary channels, with a mean value of 30.47 mg/kg. Ba content was significantly low in the four geomorphological units from the delta front to the shallow marine, with mean values of 9.08 mg/kg, 5.41 mg/kg, 5.09 mg/kg, and 5.48 mg/kg, respectively.

Sr content was lowest in the river channel (Fig. 3d), where it had a mean value of 8.72 mg/kg, and increased significantly toward the distributary channels with a mean value of 23.24 mg/kg. The Sr content increased again in the delta front and delta front slope, where it had mean values of 30.84 mg/kg and 30.94 mg/kg, respectively. The Sr content presented the highest values, with means of 42.12 mg/kg and 44.72 mg/kg, in the prodelta and shallow marine units, respectively.

The Ca content was lowest in the river channel, with a mean value of 12.92 g/kg (Fig. 3e), but it increased to 25.07 g/kg in the distributary channels and showed higher and similar values in the delta front and delta front slope, where it had mean values of 36.10 g/kg and 36.86 g/kg, respectively. The Ca content increased rapidly to significantly high values of 77.12 g/kg and 95.76 g/kg in the prodelta and shallow marine units, respectively.

The mean Sr/Ba was only 0.06 in the river channel, but it tended to increase rapidly to the east in the distributary channels, where it had a mean value of 2.44 (Fig. 3f). It increased further to 4.23 and 6.23 in the delta front and delta front slope, respectively. The Sr/Ba was significantly high in the prodelta and shallow marine areas, with average values of 9.64 and 11.79, respectively.

5 Discussion

5.1 *Mechanisms of spatial variation in alkaline earth metals*

Salinity of surface seawater is dynamics and instantaneous, representing short-time scale processes in comparison to the surface sediments, which change over longer time scales. However, because the freshwater discharge from the Jiulong River is regulated by the sluices, the seasonal variations in salinity are likely to be small (Yu et al., 2019). The comparison of salinity during the flood season and dry season shown in Fig. 2 supports this speculation. Therefore, in this study, we analyzed the correlations between surface water salinity and contents and ratios of alkaline earth metals. The result showed that Sr and Sr/Ba were significantly and positively correlated with salinity, with R^2 values of 0.617 2 and 0.515 9, respectively (Figs 4a, d). Ca was also positively correlated with salinity, with R^2 of 0.32 (Fig. 4c). Ba was negatively correlated with salinity (Fig. 4b), with R^2 of 0.380 2. The p values in the statistical analyses were all less than 0.01 (Fig. 4), indicating highly significant correlations. These analyses indicate that the salinity of the water mass is an important factor controlling the distribution of alkaline earth metals in surface sediments. However, the Ba content presented consistently low values in environments with water salinity >15, suggesting that Ba cannot be used to discriminate among higher salinity water masses and their associated sedimentary environments.

We also analyzed the correlations between grain size and contents and ratios of alkaline earth metals. The results showed very weak effect of grain size (Fig. S1). We then compared the alkaline earth metals between the geomorphological units and found that there were more significant differences (Fig. 5). We propose that salinity, marine biomass and sedimentary dynamic processes are important factors affecting the variations among the geomorphological units. The high Ba and low Sr and Ca characteristics of the river channel indicate that the sluice of the West River completely blocked salinity intrusion, causing the river channel to have typical characteristics of terrestrial facies end-member elements. The rapidly decreasing Ba content in the distributary channels of the delta plain indicates strong desorption (Coffey et al., 1997; Wang et al., 2015). Previous studies have

Table 2. Distribution of mean grain size and alkaline earth metals content in surface sediments of the Jiulong River mouth

Geomorphological unit	Characteristic parameter	Mean grain size/μm	Ba/(mg·kg^{-1})	Sr/(mg·kg^{-1})	Ca/(g·kg^{-1})	Sr/Ba molar ratio
River channel	Average	19.4	150.91	8.72	12.92	0.06
	Range	9.1–32.1	14.39–230.90	1.39–14.31	6.73–18.86	0.05–0.97
Distributary channel	Average	36.0	30.47	23.24	25.07	2.44
	Range	9.0–323.4	4.45–229.70	11.07–34.85	12.07–49.97	0.08–6.60
Delta front	Average	133.1	9.08	30.84	36.10	4.23
	Range	11.5–381.6	4.30–15.38	21.71–47.73	15.80–64.52	1.41–8.97
Delta front slope	Average	39.4	5.41	30.94	36.86	6.23
	Range	7.4–116.1	4.04–7.52	19.42–44.68	16.05–69.73	2.58–11.06
Prodelta	Average	55.6	5.09	42.12	77.12	9.64
	Range	12.5–163.0	3.34–7.96	21.40–52.45	13.03–179.30	2.79–14.28
Shallow marine	Average	44.4	5.48	44.72	95.76	11.79
	Range	23.0–66.8	2.73–11.29	37.17–54.86	56.40–190.00	3.29–19.47

Fig. 3. Distribution of grain size, lithology and alkaline earth metals in surface sediments of the Jiulong River mouth.

shown that Ba desorption occurs mainly in low salinity environments (mostly salinity ⩽5; Wang et al., 2021). Measurements of surface water salinity in this study showed that the salinity already exceeded 5 (Fig. 2) in the middle and lower parts of the distributary channels (east of Site 31). The sharp decrease in Ba content occurred precisely in the upper part of the distributary channels (west of Site 31). Thus, the desorption of Ba in the Jiulong River mouth also occurs mainly in environments with salinity ⩽5. The increases in Sr and Ca in this geomorphological unit reflect the transport of Sr and Ca in seawater, marine organ-

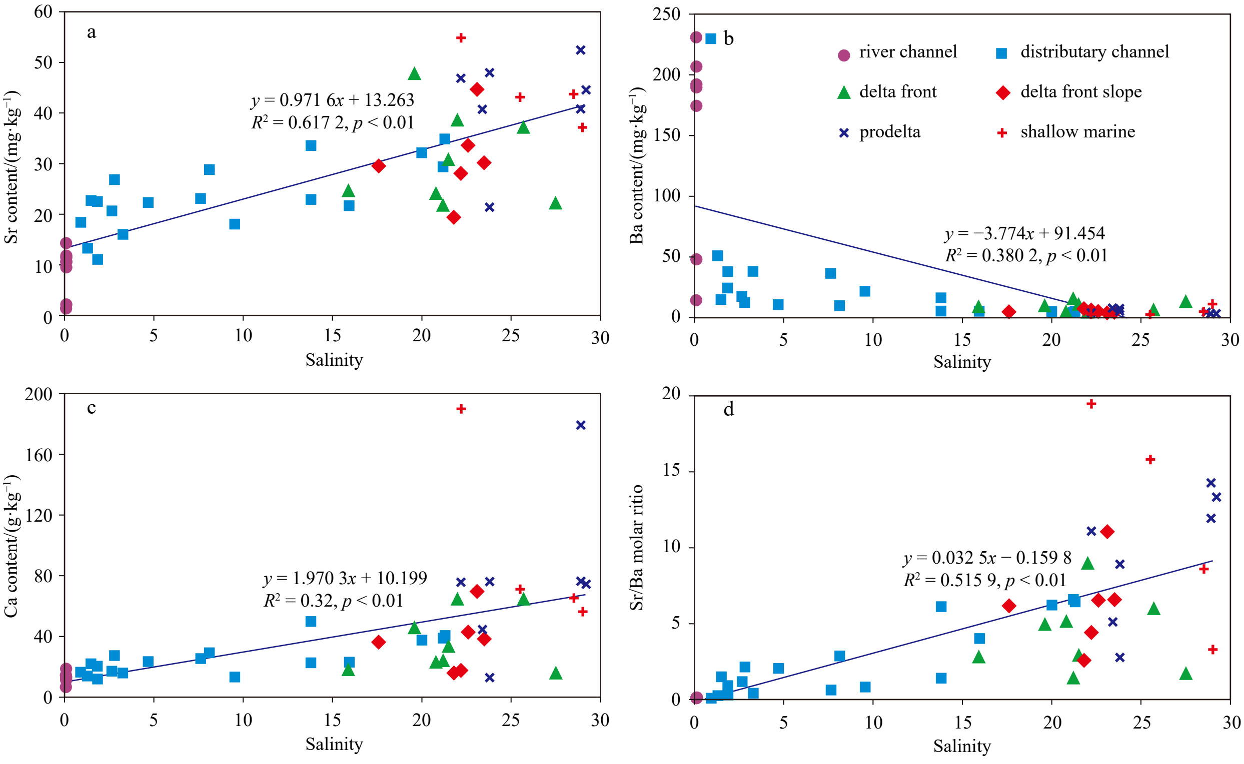

Fig. 4. Correlation between alkaline earth metals in surface sediments and surface water salinity in the Jiulong River mouth.

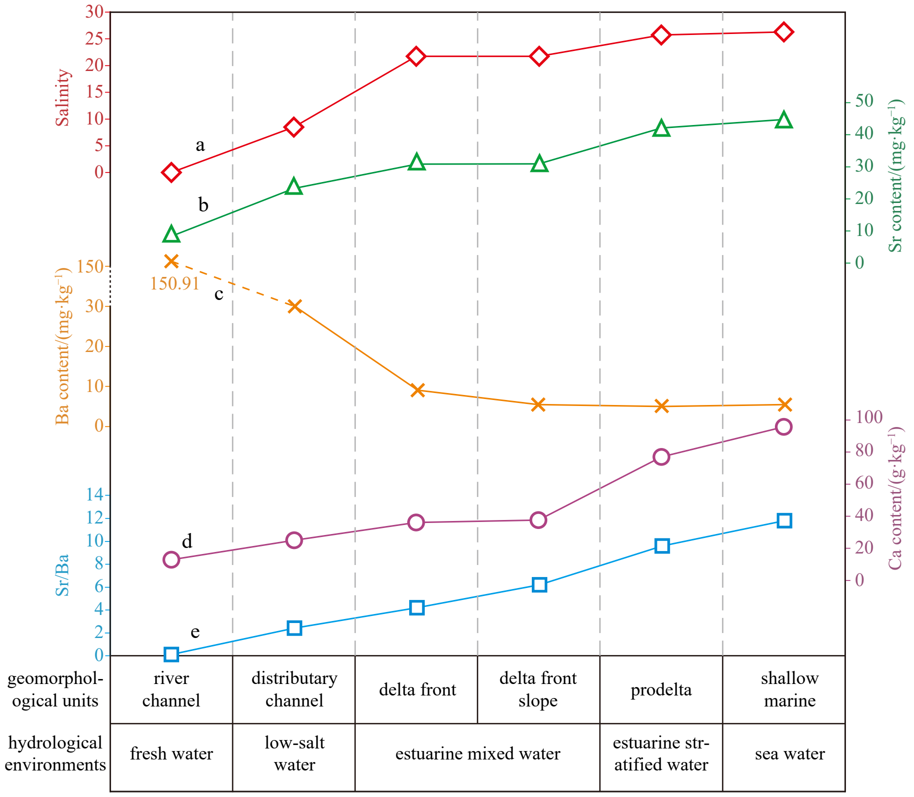

Fig. 5. Average values of salinity and alkaline earth metals in different geomorphological units and hydrological environments in the Jiulong River mouth.

isms, or marine sediments by the flood tides to the upper part of the distributary channels (Kim et al., 1999), indicating the function of tidal pumping in the landward dispersal and trapping of marine-sourced suspended sediments.

The low Ba contents from the delta front to the shallow marine area indicate that there are no new sources of Ba and that the

Ba in the sediments of the Jiulong River mouth is input mainly from terrestrial sources. The significant increases in Sr and Ca in the delta front and delta front slope reflect the trapping of marine-sourced sediments, suggesting that dynamic processes such as tidal pumping and estuarine circulation make an important contribution to the sedimentation mechanism of the delta front. In addition, it may also indicate an increase in marine biological productivity. In the prodelta and shallow marine area, the Sr and Ca contents increased again, which may be mainly due to the increased contribution of marine organisms, as the apparent stratification of the upper diluted water and the lower hypersaline water in this area is favorable to marine algal blooms (Deng et al., 2019; Li, 2019) and thus can support higher marine planktonic and benthic biomass. Further study in the future is suggested to examine this speculation.

5.2 *End-member characteristics of alkaline earth metals and indicators of sedimentary facies*

To investigate the geomorphological environmental differentiation of alkaline earth metals in the Jiulong River mouth quantitatively, box plots and independent sample *t*-tests were used to determine the differences in the above proxies among the river channel, distributary channel, delta front (slope), and prodelta–shallow marine areas (Table 3; Fig. 6). The results showed that *p* values of Ba were less than 0.05, reflecting significant differences, between the river channel and distributary channel and between the distributary channel and delta front (slope) (Fig. 6a) but were greater than 0.05, indicating nonsignificant differences, between the delta front (slope) and prodelta-shallow marine area. The *p* values of Sr between the river channel and distributary channel and between the delta front (slope) and prodelta-shallow marine area were all less than 0.01, reflecting very significant differences (Fig. 6b); and the *p* value between the distributary channel and the delta front (slope) was 0.059, reflecting a nonsignificant difference between these two datasets, which may reflect the widespread deposition of marine-sourced sediments supplied by the flood tide to these geomorphological units. The *p* values of Ca between the river channel and distributary channel and between the distributary channel and delta front (slope) were all less than 0.01, indicating very significance (Fig. 6c). The value between the delta front–delta front slope and prodelta–shallow marine area was less than 0.05, reflecting a significant difference between the two datasets. The *p* values of Sr/Ba between the river channel and distributary channel and between the delta front (slope) and prodelta–shallow marine area were less than 0.01 (Fig. 6d), reflecting very significant differences, and the value between the distributary channel and delta front (slope) was 0.077, reflecting a non-significant difference between these two datasets. In summary, there were significant differences in Ba, Sr, Ca, and Sr/Ba between the river channel and the distributary channel, significant differences in Ca and Ba between the distributary channel

Table 3. Results of *t*-test (*p* values) on alkaline earth metals and Sr/Ba molar ratio between sedimentary geomorphological environments at the Jiulong River mouth

Alkaline earth metals	River channel vs. distributary channel	Distributary channel vs. delta front (slope)	Delta front (slope) vs. prodelta-shallow marine
Ba	0.045	0.007	0.091
Sr	0.001	0.059	0.002
Ca	0.004	0.008	0.016
Sr/Ba	0.008	0.077	0.009

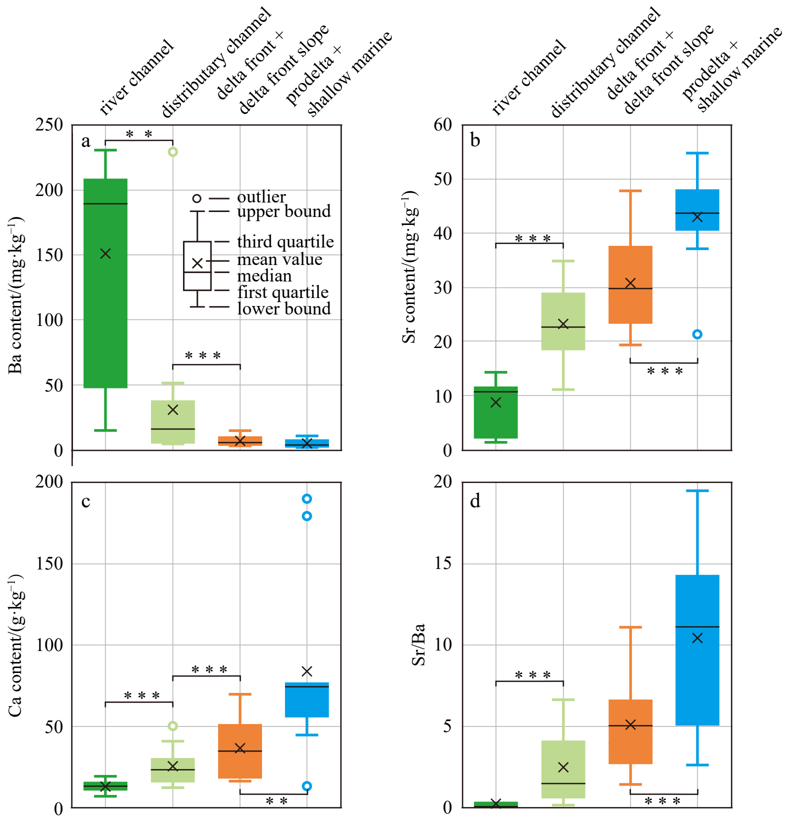

Fig. 6. Box-and-whisker plots of alkaline earth metals and Sr/Ba molar ratio. Very significant ($p < 0.01$) and significant ($0.01 < p < 0.05$) differences between independent data groups measured by *t*-tests are indicated by *** and **, respectively.

and the delta front (slope), and significant differences in Sr, Ca, and Sr/Ba between the delta front (slope) and prodelta–shallow marine area.

Based on the results of the significance tests mentioned above, the Sr-Ba scatter plot was used for end-member element analysis of the sediments in the Jiulong River mouth. The results showed (Fig. 7a) that the river channel forms a high Ba and low Sr end-member region and that the prodelta–shallow marine area is typified by high Sr and low Ba. These two regions do not overlap and are obviously different, so they can be used as terrestrial facies and marine facies end-member element groups, respectively. The distributary channel and the delta front (slope) are located in the area between these two end-members, showing the characteristics of the land-sea transitional environment. Among these, the distributary channel unit is more toward the terrestrial facies end-member and the delta front (slope) is closer to the marine facies end-member.

In order to validate the terrestrial and marine end-members of Sr and Ba contents, we further compared with previous studies of alkaline earth metals reported from different geomorphological settings of the Changjiang River coast (Figs 7b, c; Huang et al., 2020, 2021a; Wang et al., 2021; Zhang et al., 2022). Sediments collected from the Jiulong River channel and the alluvial plain of the Changjiang River coast all have higher but with a wide range of Ba contents and lower Sr contents. Sediments of prodelta and shallow marine of the Jiulong River mouth contain similar high Sr values and very low Ba values with those of the Changjiang River prodelta, while the sediments of inner continental shelf and relict sand off the Changjiang River mouth contain higher Sr values, supporting the enrichment of Sr in the marine environment. The distributary channel and delta front (slope) of this study and the tidal river, delta plain, and delta front of the Changjiang River coast are located in the area between these two end-members, showing features of the land-sea transition zone. Therefore, the spatial distribution of alkaline earth metals in the Jiulong River mouth are in general consistent with those on the world's mega river coast, reflecting that alkaline earth metals of Sr, Ba, Ca and Sr/Ba are effective proxies for identifying sedimentary facies in the tide-dominated river mouth.

6 Conclusions

(1) The content of the alkaline earth metal Ba in the Jiulong River mouth decreases from land to sea, while the contents of Sr and Ca and the Sr/Ba increase gradually toward the sea. The alkaline earth metals and theirs have significant characteristic values in different geomorphological units. The Ba content in the river channel is more than 50 mg/kg, the Sr content is less than 15 mg/kg, and the Sr/Ba approaches 0. The Ba content of the distributary channel is about 30 mg/kg, and the Sr/Ba is less than 5. The Sr content in the delta front and front slope is about 30 mg/kg, the Ca content is about 35 g/kg, and the Sr/Ba is about 5. In the prodelta and shallow marine regions, the Sr content is higher than 40 mg/kg, the Ca content is about 80 g/kg, and the Sr/Ba is about 10.

(2) The salinity, marine biomass, and sedimentary dynamic processes in the Jiulong River mouth are suggested to be the main factors explaining the differences in their spatial distribution. The Ba content decreases rapidly in the upper part of the distributary channel, indicating a strong desorption effect in a low-salinity environment.

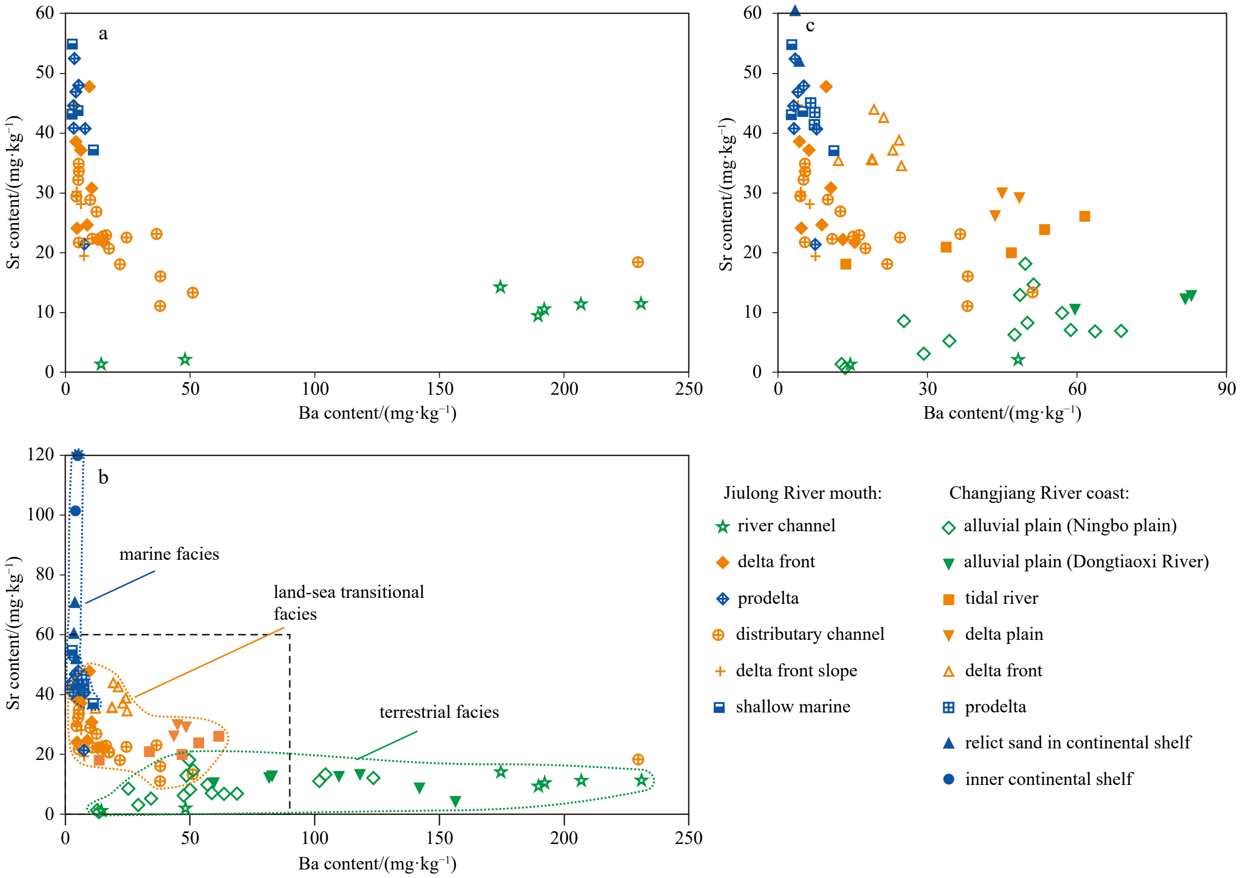

Fig. 7. Distribution of alkaline earth metals of surface sediments from the Jiulong River mouth (a) and the Changjiang River coast (b, c).

(3) Significant differences in Ba, Sr, Ca, and Sr/Ba were observed between the river channel and the distributary channel, significant differences in Ca and Ba occurred between the distributary channel and the delta front (slope), and significant differences in Sr, Ca, and Sr/Ba occurred between the delta front (slope) and the prodelta–shallow marine region. The Sr-Ba scatter plot can distinguish sedimentary environments of terrestrial facies, land-sea transitional facies, and marine facies. In this plot, the river channel facies were located at a high Ba and low Sr end-member position, and the prodelta–shallow marine facies were at a high Sr and low Ba end-member position. These results can be used as representative terrestrial facies and marine facies element end-members, respectively. The distributary channel and the delta front (slope) located between these two end-members, and this region of the diagram can be considered as representing land–sea transition facies.

References

Alfonso J A, Martínez M, Flores S, et al. 2006. Distribution of trace elements in offshore sediments of the Orinoco Delta. Journal of Coastal Research, 223(3): 502–510

Bowen H J M. 1956. Strontium and Barium in sea water and marine organisms. Journal of the Marine Biological Association of the United Kingdom, 35(3): 451–460, doi: 10.1017/S0025315400010298

Chen Wenrui, Lan Dongzhao, Chen Chenghui. 1998. Late Quaternary diatom and sea level changes in estuarine plain of the Jiulong River. Acta Oceanologica Sinica, 17(4): 509–518

Cho Y G, Lee C B, Choi M S. 1999. Geochemistry of surface sediments off the southern and western coasts of Korea. Marine Geology, 159(1–4): 111–129, doi: 10.1016/S0025-3227(98)00194-7

Coffey M, Dehairs F, Collette O, et al. 1997. The behaviour of dissolved Barium in estuaries. Estuarine, Coastal and Shelf Science, 45(1): 113–121

Comprehensive Survey Leading Group Office of Coastal and Tidal Flat Resource in Fujian Province. 1990. Comprehensive Investigation Report of Coastal and Tidal Flat Resource in Fujian Province (in Chinese). Beijing: China Ocean Press

Deng Zhirui, He Qing, Safar Z, et al. 2019. The role of algae in fine sediment flocculation: In-situ and laboratory measurements. Marine Geology, 413: 71–84, doi: 10.1016/j.margeo.2019.02.003

Dorval E, Jones C M, Hannigan R. 2005. Chemistry of surface waters: Distinguishing fine-scale differences in sea grass habitats of Chesapeake Bay. Limnology and Oceanography, 50(4): 1073–1083, doi: 10.4319/lo.2005.50.4.1073

Editorial Committee of Chinese Gulf Annals. 1993. Chinese Gulf Annals (the First Book of Eight) (in Chinese). Beijing: China Ocean Press, 174

Friedman G M, Sanders J E. 1978. Principles of Sedimentology. New York: Wiley

Gao Xiaoqin, Wang Zhanghua, Li Lin, et al. 2012. Magnetic properties of surficial sediments and distribution of authengenic iron sulfide in modern tidal flat at Yangtze estuary. Journal of Palaeogeography (in Chinese), 14(5): 673–684

Huang Jing, Lei Shao, Tang Liang, et al. 2020. Mid-Holocene environmental change and human response at the Neolithic Wuguishan site in the Ningbo coastal lowland of East China. The Holocene, 30(11): 1591–1605, doi: 10.1177/0959683620941070

Huang Jing, Li Yongning, Ding Fengya, et al. 2021b. Sedimentary records of mid-Holocene coastal flooding at a Neolithic site on the southeast plain of Hangzhou Bay, East China. Marine Geology, 431: 106380, doi: 10.1016/j.margeo.2020.106380

Huang Jing, Zheng Tongtong, Wang Aihua, et al. 2021a. Comparison of different extraction methods for alkaline earth metals and its implications: a case study of the surficial sediments from Ningbo Plain. Journal of East China Normal University (Natural Science) (in Chinese), (2): 73–84

Kim G, Yang H S, Church T M. 1999. Geochemistry of alkaline earth elements (Mg, Ca, Sr, Ba) in the surface sediments of the Yellow Sea. Chemical Geology, 153(1–4): 1–10, doi: 10.1016/S0009-2541(98)00149-1

Li Gang. 2019. Fast acclimation of phytoplankton assemblies to acute salinity stress in the Jiulong River Estuary. Acta Oceanologica Sinica, 38(8): 78–85, doi: 10.1007/s13131-019-1389-3

Li Congxian, Wang Pinxian. 1998. Study of Late Quaternary Stratigraphic Framework in the Yangtze Estuary (in Chinese). Beijing: Science Press, 1

Liu Yingjun, Cao Liming, Li Zhaolin, et al. 1984. Element Geochemistry (in Chinese). Beijing: Science Press, 360–372

Milliman J D, Syvitski J P M. 1992. Geomorphic/tectonic control of sediment discharge to the ocean: the importance of small mountainous rivers. The Journal of Geology, 100(5): 525–544, doi: 10.1086/629606

Mohan J A, Walther B D. 2015. Spatiotemporal variation of trace elements and stable isotopes in subtropical estuaries: II. Regional, local, and seasonal salinity-element relationships. Estuaries and Coasts, 38(3): 769–781, doi: 10.1007/s12237-014-9876-4

Pan Yu, Sun Guoping, Lei Shao, et al. 2023a. Geochemical characteristics of alkaline earth metals in the sediments of Neolithic sites in the eastern Ningshao Plain and implications for the saltwater intrusion. Marine Geology & Quaternary Geology (in Chinese), 43(6): 169–180

Pan Dadong, Zhang Lianghui, Lin Yongchong. 2023b. Temporal spatial distribution and source of organic matter in tidal flat surficial sediments and their implications for sedimentary environment identification in the Jiulong River Estuary. Haiyang Xuebao (in Chinese), 45(2): 85–97

Qian Lijun, Chen Hongde, Lin Liangbiao, et al. 2012. Geochemical characteristics and environmental implications of middle Jurassic Shaximiao Formation, Western Margin of Sichuan Basin. Acta Sedimentologica Sinica (in Chinese), 30(6): 1061–1071

Shi Zhongsheng, Chen Kaiyuan, Shi Jun, et al. 2003. Feasibility analysis of the application of the ratio of strontium to barium on the identifying sedimentary environment. Fault-Block Oil & Gas Field (in Chinese), 10(2): 12–16

Tessier A, Campbell P G C, Bisson M. 1979. Sequential extraction procedure for the speciation of particulate trace metals. Analytical Chemistry, 51(7): 844–851, doi: 10.1021/ac50043a017

Wang Aihua. 1996. Discriminant effect of sedimentary environment by the Sr/Ba ratio of different exising forms. Acta Sedimentologica Sinica (in Chinese), 14(4): 168–173

Wang Qian, Chang Fengming, Li Tiegang, et al. 2015. Application of planktonic foraminiferal Ba/Ca ratios to quantitatively reconstruct paleosalinity of surface ocean waters over the Amazon fan. Quaternary Sciences (in Chinese), 35(2): 383–389

Wang Zhanghua, Chen Zhongyuan, Li Luqian, et al. 2001. Spatial and temporal distribution of trace elements in Yangtze Estuary, China: Significance of diluted setting. Chinese Science Bulletin, 46(S1): 65–72, doi: 10.1007/BF03187239

Wang Cui, Ding Yi, Guo Zhouhua, et al. 2022. Spatial-temporal distribution of total organic carbon and its transportation in the Jiulong River Estuary. Scientific Reports, 12(1): 9395, doi: 10.1038/s41598-022-13268-0

Wang Yiyou, Guo Wenying, Zhang Guodong. 1979. Application of some geochemical indicators in determining of sedimentary environment of the Funing Group (Paleogene), Jin-Hu depression, Kiangsu province. Journal of Tongji University (in Chinese), 7(2): 51–60

Wang Weiqiang, Huang Shanggao, Gu Deyu, et al. 1986. Mixing characters of fresh water with sea water in the Jiulong Jiang Estuary, Fujian. Taiwan Strait (in Chinese), 5(1): 10–17

Wang Jinyuan, Jiang Yuwu. 2013. The distribution of salinity and the dynamic process of salt flux in Jiulong River estuary. Journal of Xiamen University: Natural Science (in Chinese), 52(6): 835–841

Wang Aihua, Liu Jiankun, Xu Naicen, et al. 2019a. A new technology for selective extraction of sedimentogenic strontium and barium from terrigenous clastic sediments. Geology in China (in Chinese), 46(3): 670–671

Wang Aihua, Liu Jiankun, Zhang Fei, et al. 2019b-03-05. A new method for selective extraction of sedimentogenic strontium and barium from terrigenous clastic sediments: CN, 201611260917.0 (in Chinese)

Wang Aihua, Wang Zhanghua, Liu Jiankun, et al. 2021. The Sr/Ba ratio response to salinity in clastic sediments of the Yangtze River Delta. Chemical Geology, 559: 119923, doi: 10.1016/j.chemgeo.2020.119923

Wang Zhanghua, Zhan Qing, Long Haiyan, et al. 2013. Early to mid-Holocene rapid sea-level rise and coastal response on the southern Yangtze delta plain, China. Journal of Quaternary Science, 28(7): 659–672, doi: 10.1002/jqs.2662

Wang Zhanghua, Zhuang Chencheng, Saito Y, et al. 2012. Early mid-Holocene sea-level change and coastal environmental response on the southern Yangtze delta plain, China: implications for the rise of Neolithic culture. Quaternary Science Reviews, 35: 51–62, doi: 10.1016/j.quascirev.2012.01.005

Wen Kegang, Song Dezhong, Cai Shishu. 2007. Meteorological Disasters in China (Fujian) (in Chinese). Beijing: China Meteorological Press, 12–16

Xu Yonghang, Chen Jian. 2010. Uranium-lead dating of detrial zircons from the Minjiang and Jiulong Estuaries in the western coast of the Taiwan Strait: implication for its provenance. Haiyang Xuebao (in Chinese), 32(4): 110–117

Yu Dan, Chen Nengwang, Krom M D, et al. 2019. Understanding how estuarine hydrology controls ammonium and other inorganic nitrogen concentrations and fluxes through the subtropical Jiulong River Estuary, S. E. China under baseflow and flood-affected conditions. Biogeochemistry, 142(3): 443–466, doi: 10.1007/s10533-019-00546-9

Yu Xingguang, Liu Zhenghua, Ma Zhiyuan, et al. 2012. Ecological Environment and Ecosystem Management in the Jiulong River Estuary (in Chinese). Beijing: China Ocean Press, 9

Zeng Gang. 1987. Characteristics of the distribution of the currents in the Xiamen Harbour. Journal of Oceanography in Taiwan Strait (in Chinese), 6(1): 1–5

Zhan Qing. 2012. The Early to Mid-Holocene sea-level reconstruction and sedimentary environmental response of the Yangtze Delta plain, China (in Chinese)[dissertation]. Shanghai: East China Normal University

Zhang Wentong, Zheng Tongtong, Wang Zhanghua, et al. 2022. Reconstruction of coastal flooding processes and human response at the end of the Liangzhu Culture, East China. Quaternary Science Reviews, 293: 107705, doi: 10.1016/j.quascirev.2022.107705

Zheng Tongtong, Lei Shao, Wang Zhanghua, et al. 2023. Prehistoric sea-salt manufacture as an adaptation strategy to coastal flooding in East China. Quaternary Science Reviews, 302: 107966, doi: 10.1016/j.quascirev.2023.107966

Zwolsman J J G, Van-Eck G T M. 1999. Geochemistry of major elements and trace metals in suspended matter of the Scheldt estuary, Southwest Netherlands. Marine Chemistry, 66(1–2): 91–111, doi: 10.1016/S0304-4203(99)00026-2

Supplementary information:

Fig. S1. Correlation between alkaline earth metals and mean grain size of surface sediments in the Jiulong River mouth.

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