

The spatial distribution of major and trace elements of surface sediments in the northeastern Beibu Gulf of the South China Sea

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Abstract

A multi-index analysis including grain size, major and trace elements is performed on the surface sediments from the northeastern Beibu Gulf to trace the sources of the sediments and to understand the controlling factors for elements distribution. The mean grain size exhibits a wide variation ranging from 0.09Φ to 8.05Φ with an average value of 5.33Φ. The average contents of major elements descend in an order of $c(\text{SiO}_2) > c(\text{Al}_2\text{O}_3) > c(\text{Fe}_2\text{O}_3) > c(\text{CaO}) > c(\text{MgO}) > c(\text{K}_2\text{O}) > c(\text{Na}_2\text{O}) > c(\text{TiO}_2) > c(\text{P}_2\text{O}_5) > c(\text{MnO})$, while those of trace elements exhibit a descending order of $c(\text{Sr}) > c(\text{Rb}) > c(\text{V}) > c(\text{Zn}) > c(\text{Cr}) > c(\text{Pb}) > c(\text{Ni}) > c(\text{Cu}) > c(\text{As})$. On the basis of elementary distribution characteristics and statistical analyses, the study area is divided into the four zones: Zone I is located in the northeastern coastal area of the gulf, which receives large amount of fluvial materials from local rivers in Guangxi and Guangdong, China, and the Qiongzhou Strait; Zone II is located in the center of the study area, where surface sediments exhibits a multiple source; Zone III is located in the Qiongzhou Strait, where surface sediments are dominated by materials from the Zhujiang River and Hainan; Zone IV is located in the southwest of the study area, where surface sediments are mainly originated from the Red River and Hainan. The statistical analyses of sediment geochemical characteristics reveal that the grain size, which is mainly influenced by hydrodynamics and mineral composition of terrigenous materials, is the leading factor controlling the elementary distribution. Meanwhile, impacts from anthropogenic activities and marine biogenic process will also be taken into consideration.

Key words: grain size, major and trace elements, Beibu Gulf, spatial distribution, sediment source

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1 Introduction

The provenance of sediments and sedimentary rocks is a key index to reconstruct regional paleoclimate, paleoceanography and tectonic history. Most marine sediments in the marginal sea are composed of terrigenous materials that are transported by rivers and/or wind from the surrounding continent (Wang et al., 1999). Compared with the riverine inputs, the eolian supply was a minor source in the marginal seas, especially for the areas far away from the source and dominant atmospheric wind pathways, such as the South China Sea (Boulay et al., 2007). The complicated sedimentary processes make it hard to distinguish the differences between terrigenous sediments and those with a marine source. In this regard, geochemical analyses, specifically those based on elemental geochemistry, have been an effective way to identify sediment provenance (e.g., McLennan et al., 1993; Mange and Morton, 2007; Li et al., 2016). Meanwhile, elemental compositions of marine sediments are controlled by many complex factors, including mineralogical compositions in source

rocks, grain size, sediment sorting, post-depositional diagenesis, as well as anthropogenic inputs (Calvert, 1976; Li et al., 2016).

Over the past few decades, lots of research have been focused on the flux and transport process of riverine sediments in marginal seas (e.g., Nittrouer et al., 1986; Allison et al., 2000; Liu et al., 2004, 2009, 2007b; Xue et al., 2010). Recent studies have been mainly focused on large river systems and only few of them discussed transport process of sediments from relative small rivers. In this study we focus on the Beibu Gulf, which is a semi closed marginal sea surrounded by northern Vietnam and Guangxi, Guangdong and Hainan, China (Fig. 1).

The Beibu Gulf is heavily influenced by the East Asian monsoon system making it an ideal place to understand the source (weathering), transport, and sink of sediments. The main objectives of the present study are to: (1) characterize the spatial distribution of major and trace elements in the surface sediments of the northeastern Beibu Gulf, (2) understand the source of the modern sediments in the study area, and (3) evaluate sedimento-

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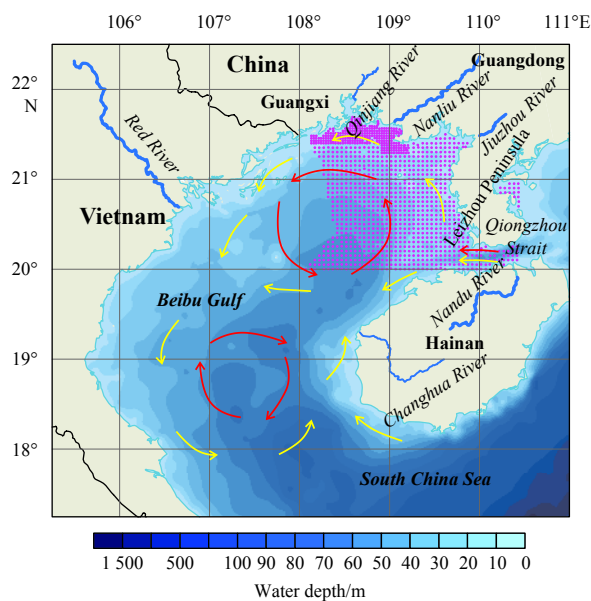


Fig. 1. A map of the study area showing the water depth overlaid with locations of surface sediment samples ($n=1\ 202$), and seasonal variations of circulation patterns in the Beibu Gulf. The red arrows represent circulation pattern in summer and the yellow arrows represent circulation pattern in winter. Modified after Gao et al. (2017).

logical and geochemical factors that control the distribution patterns of the major and trace elements.

2 Regional background

The Beibu Gulf is located in the northwestern South China Sea (SCS), covering waters from approximately 17°N to 22°N and from 105°E to 110°E (Fig. 1). It is surrounded by the Leizhou Peninsula, Qiongzhou Strait, Hainan, and northern Vietnam, and extends to the Guangxi coast in the north, with an area of approximately 1.3×10^5 km² (Gao et al., 2017). The water depth in the Beibu Gulf is typically less than 100 m, with a mean depth of 40 m. The Beibu Gulf is characterized by tropical-subtropical monsoon climate with an average temperature of 23°C and annual precipitation of 1 300–2 500 mm. A large number of rivers discharge into the Beibu Gulf, such as the Red River, Qionjiang River, Nanliu River, Nandu River, Jiuzhou River and others, which also provide the main sediment source. Bedrock around the Beibu Gulf consists mainly of Pre-Quaternary granite and Late Quaternary basalt (Ma et al., 2002).

Circulation in the Beibu Gulf is characterized by contrasting patterns during the summer and winter monsoon seasons (Fig. 1). The summer season brings a large anticyclonic eddy in the southern gulf and a cyclonic gyre in the northern gulf, with a boundary located around 19°30'N (Gao et al., 2015). Flows are northward along the eastern part of the upper gulf and westward along the northern coastline. In winter, the gulf-wide circulation is cyclonic, which nests a cyclonic gyre in the southern gulf. Circulation in fall is similar to that in winter. However, the cyclonic gyre in the southern gulf in fall is stronger than that in winter, which can intrude to the area around 19°N. The current off the coast of Vietnam and northwestern coast of Hainan is weaker in fall than that in winter. The current off the northwestern coast of Hainan is found to be southwestward instead of northeastward (Gao and Chen, 2014; Gao et al., 2017). Additionally, strong cur-

rents enter the gulf via the Qiongzhou Strait from the east all year round, with the maximum strength in winter (Shi, 2014).

3 Materials and methods

A total of 1 202 surface sediments were collected in the north-eastern Beibu Gulf jointly by Second Institute of Oceanography, Ministry of Natural Resources and South China Sea Branch of State Oceanic Administration in 2007 (samples locations are shown in Fig. 1). The samples were stored at 4°C immediately after collection. Sediment grain size was measured using a Mastersizer-2000 laser particle size analyzer (analysis range: 0.01–2 000.00 μm). For the pre-treatment of a grain size analysis, excess H₂O₂ (30%) and HCl (1 mol/L) were added to remove the organic matter and carbonate in bulk samples, respectively. Then 5–10 mL sodium hexametaphosphate (0.5 mol/L) was added to let the sediment disperse. The preparation and measurement of the grain size were carried out by the Key Laboratory of Submarine Geosciences, State Oceanic Administration, China.

A total of 305 samples were chosen for geochemical analysis. Major (SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, K₂O, Na₂O, TiO₂, P₂O₅ and MnO) and trace elements (Ni, Cu, Zn, Pb, Cr, Rb, Sr, V and As) were identified using an X-ray fluorescence spectrometer (XRF) and an inductively coupled plasma mass spectrometer (ICP-MS) at the Institute of Geophysical and Geochemical Exploration, Chinese Academy of Geological Sciences, China, respectively. Prior to chemical analysis, the samples were dried below 105°C, crushed to less than 200 mesh size (74 μm) in an agate mortar, and stored in clean polyethylene bags at room temperature for major elements analysis. For trace elements analysis, precisely 0.25 g of each sample was put in a Teflon bomb with an acid mixture (5:4:1 V (HNO₃) + V (HCl) + V (HF)) (Loring and Rantala, 1992) and then heated to 120°C for 12 h on a heating plate. The acid digestion was repeated until only a negligible amount of white residue remained. Then, the solution was evaporated to dry and extracted with HNO₃. The standard sediment samples (GSD-9 and GSD-10) were analyzed for data quality assurance and control. The results show that the errors are mostly less than 5% for the major and trace elements.

4 Results

4.1 Grain size of surface sediments

The grain size distribution of surface sediments in the north-eastern Beibu Gulf is shown in Fig. 2. The average contents of sand, silt and clay fractions are 33%, 47% and 20%, respectively. The silt and clay fractions exhibit similar distribution patterns, having the high content in the center of the study area. The sand fraction shows a contrary distribution pattern, with the highest value in the Qiongzhou Strait, along the coast and the relict deposit on the middle of Beibu Gulf (Fig. 2). The mean grain size (M_z) varies from 0.09Φ to 8.05Φ with a mean value of 5.33Φ, the spatial distribution pattern shows similar characteristics of silt fraction's (Fig. 2).

4.2 Features of elemental contents

The average contents of the major elements, in a descending order, are as follows: SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, K₂O, Na₂O, TiO₂, P₂O₅ and MnO (Fig. 3; Table 1). The content of SiO₂ is more than 63.00% of the major elements. And the content of Al₂O₃ is between 0.44%–21.70%, with an average of 12.88%. The contents of other major elements are generally less than 5.00%. The average contents of the trace elements in a descending order are as follows: Sr, Rb, V, Zn, Cr, Pb, Ni, Cu and As (Fig. 4; Table 1).

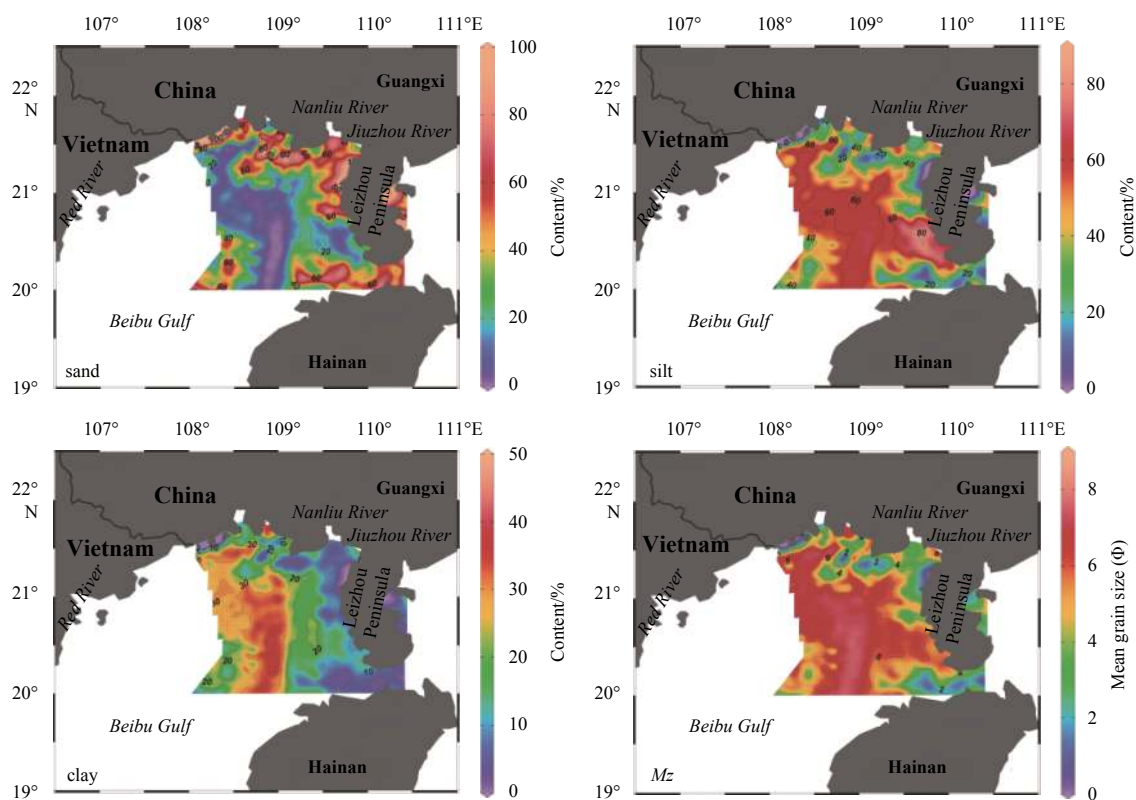


Fig. 2. Distribution patterns of the contents of sand, silt and clay, and mean grain size in the surface sediments of the study area.

The major and trace elements exhibit various distribution patterns in the study area (Figs 3 and 4). Overall, most elements exhibit a similar pattern with that of silt fraction, excluding SiO_2 , CaO , MnO , Sr and As (Figs 2–4). SiO_2 is the dominant element, and the content decreases from greater than 70.00% along the coastal zone to less than 60.00% in the center of the study area. Such variation corresponds to decreases of sand fraction and As content. In contrast, Al_2O_3 content is more than 15.00% in the center of study area and west of the Leizhou Peninsular. And Al_2O_3 content decreases to less than 10.00% in the Qiongzhou Strait, along the coastal zone and southeast of the Leizhou Peninsular. This spatial distribution pattern corresponds to that of silt fraction. The distribution patterns of Fe_2O_3 , MgO , K_2O , Na_2O , TiO_2 , P_2O_5 , Rb , V , Zn , Cr , Pb , Ni and Cu are similar with that of Al_2O_3 . For instance, Fe_2O_3 shows an increasing trend from north to south. CaO and Sr are mostly abundant in sandy deposit, especially on the shelf off the Nanliu River Estuary, the exits of the Qiongzhou Strait, and relict deposit in the middle of the Beibu Gulf. The content pattern of MnO is also similar, although with a less abundance, to those of CaO and Sr .

4.3 Pearson correlation

Pearson correlation coefficients (r) between major elements, trace elements, and grain size data were calculated and displayed in Table 2. Most elemental contents exhibit a strong positive correlation with the content of silt fraction, except for SiO_2 , CaO , MnO , Sr and As . A strong correlation was found between CaO and Sr contents.

4.4 Cluster and principal component analysis

Bulk elemental contents were standardized using Z scores before a cluster analysis. An R-mode hierarchical cluster analysis showed a correlation among elements and identified several

suites (Fig. 5), with Cluster I including Ni , Cr , V , TiO_2 , K_2O , Rb , Al_2O_3 , Cu , Zn , Fe_2O_3 , Pb and P_2O_5 , Cluster II including MgO and Na_2O , and Cluster III including CaO and Sr . For the rest elements, MnO , As , and SiO_2 belongs to Clusters IV, V and VI, respectively. Clusters I and II are strongly positively correlated with the silt fraction (Table 2). SiO_2 from Cluster VI is highly affiliated with the sand fraction. To analyze the provenances of the sediments, we also use a Q-mode hierarchical cluster analysis to group samples with a similar petrographical characteristic. Combining with the samples location and the surrounding environment, we divide the study area into four zones (Fig. 6).

We performed principal component analysis on elemental contents and Mz . To maximize the sum of the variances of the squared loadings, a varimax rotation was used in principal components calculation. The top three principal components explained 83.9% of the total variances. Table 3 presents the factor loading results: F1 (52.2% of variance) shows high positive loadings of Al_2O_3 , Fe_2O_3 , TiO_2 , P_2O_5 , K_2O , Ni , Cu , Zn , Pb , Rb , Cr and V , and high negative loading of SiO_2 . Scores of F1 display a similar distribution pattern with that of Mz (Figs 2 and 7). The low F1 scores are calculated along the coastal zone and relict deposit in the center of Beibu Gulf (Fig. 7). F2 (16.8% of variance) displays high positive loadings of MgO and Na_2O , and a moderate negative loading of As . The pattern of F2's score is similar with that of F1 (Fig. 7). F3 (14.9% of variance) exhibits high positive loadings of CaO , MnO and Sr . Scores of F3 correlate well with the distribution of CaO , MnO and Sr (Figs 3, 4 and 7).

5 Discussion

5.1 Sediment provinces

The western Pacific marginal seas are mainly covered by biogenic, volcanogenic and especially terrigenous sediments, and

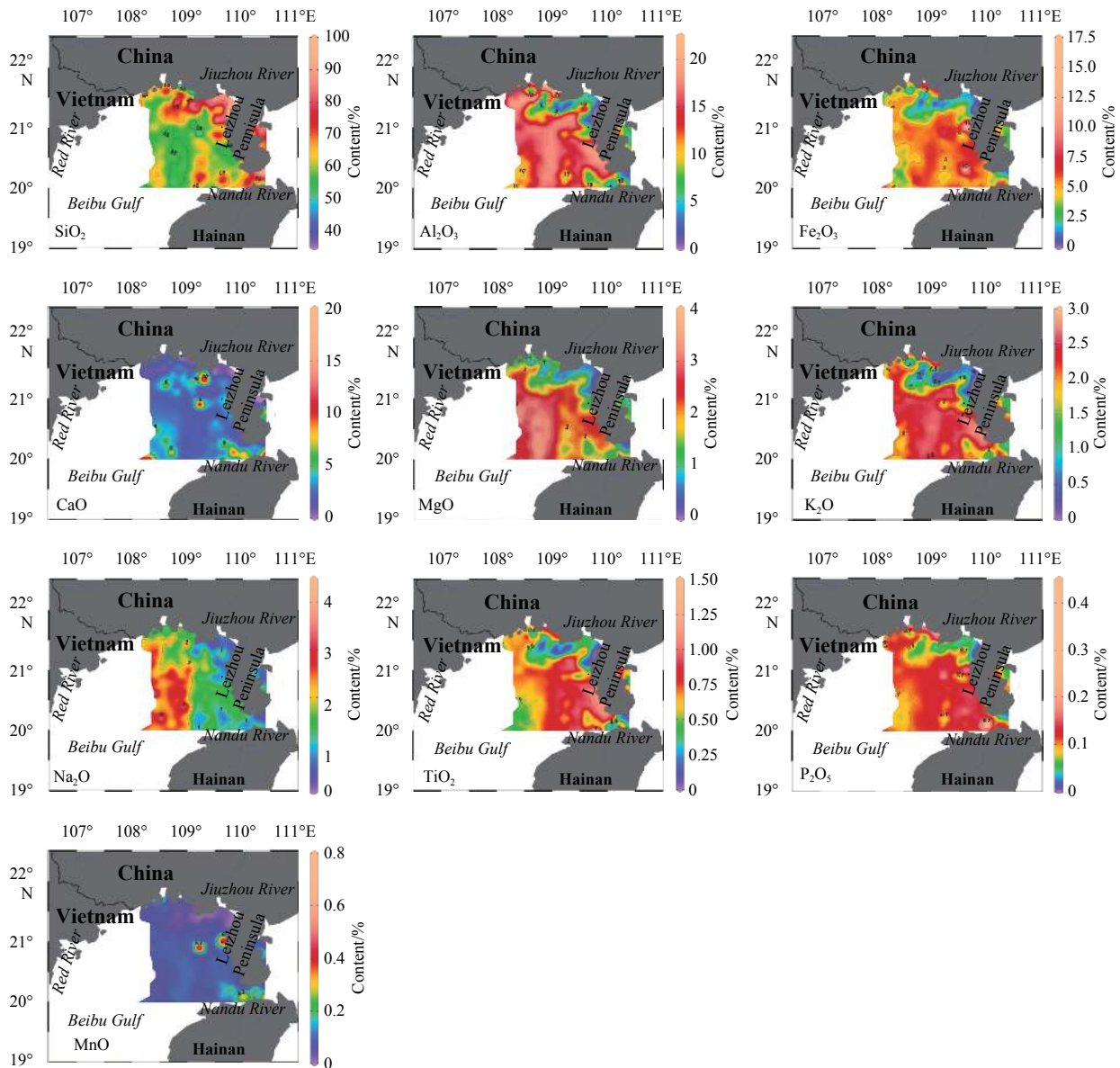


Fig. 3. Distribution patterns of major elements in the surface sediments of the study area.

the fluvial contribution is dominated in the terrigenous component (Wang, 1999). The major element composition of marine sediments can be used to discuss the source of terrigenous materials through assessing the state of chemical and physical weathering. The chemical composition of weathering products of the river basin is expected to demonstrate well-established concepts on mobility of various elements during weathering processes (Nesbitt et al., 1980; Singh et al., 2005; Liu et al., 2007a). The identification and evaluation of major element mobility during weathering was done with the help of elemental ratios calculated with respect to the least mobile element aluminium. The ratio of the content of element X and $c(\text{Al}_2\text{O}_3)$ in the samples divided by the ratio of the same element content in upper continental crust (UCC) gives the following element ratio (Singh et al., 2005):

$$\text{Element ratio}(X) = \frac{[c(X)/c(\text{Al}_2\text{O}_3)]_{(\text{samples})}}{[c(X)/c(\text{Al}_2\text{O}_3)]_{(\text{UCC})}}$$

This element ratio refers to the relative enrichment or deple-

tion of the element, i.e., being greater than 1 indicates enrichment, being less than 1 indicates depletion and equaling 1 indicates no change in the relative abundance of element.

According to the previous studies based on clay minerals and rare earth elements, the Zhujiang River, and Red River, Hainan, small rivers in Guangxi and Guangdong, and Qiongzhou Strait are the potential provenances for the northeastern Beibu Gulf sediments (e.g., Dou et al., 2012; Zhou et al., 2014). Figure 8 displays the element ratios calculated from average major element contents normalized to the UCC. As demonstrated, the samples from Zones I, II and III, east exit of Qiongzhou Strait (Cui et al., 2015), Zhujiang River and Red River (Liu et al., 2007a) show a similar chemical mobility with little difference. The mobility of silica is critical for understanding of chemical weathering. The SiO_2 content is depleted in the Zhujiang River sediments but rather stable in the sediments from the Red River, east exit of the Qiongzhou Strait, and Zone I, suggesting stronger chemical weathering occurring in the Zhujiang River basin. The highly mobile elements calcium and sodium from Zhujiang River and Red

Table 1. Contents of major and trace elements in the surface sediments of the northeastern Beibu Gulf

	Minimum	Maximum	Average
SiO ₂	39.84	96.71	63.45
Al ₂ O ₃	0.44	21.70	12.88
Fe ₂ O ₃	0.14	16.92	4.69
CaO	0.18	17.51	2.95
MgO	0.16	3.55	2.03
K ₂ O	0.09	2.77	1.93
Na ₂ O	0.13	4.12	1.79
TiO ₂	0.03	1.36	0.62
P ₂ O ₅	0.01	0.41	0.11
MnO	0.01	0.76	0.08
Sr	11.55	1 148.70	148.82
Rb	4.80	156.90	92.33
V	5.00	164.00	72.82
Zn	7.10	115.80	69.98
Cr	5.90	106.40	63.11
Pb	3.90	112.60	28.37
Ni	0.90	61.66	24.96
Cu	1.70	58.65	17.10
As	1.63	97.48	11.37

Note: The unit for SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, K₂O, Na₂O, TiO₂, P₂O₅ and MnO is %; the unit for Sr, Rb, V, Zn, Cr, Pb, Ni, Cu and As is µg/g.

River, and Zone I show similar low values related to their chemical weathering. The CaO content is obviously enriched in Zone IV and western bank of Hainan sediments (Cui et al., 2015) (Fig. 8), indicating a relatively weak weathering environment. In contrast

to sodium, potassium is preferentially absorbed by clay minerals in the sediments (Zhao and Yan, 1994). In comparison, more depleted potassium in Zhujiang River sediments suggests stronger chemical weathering. The calculation of the element ratios indicates that sediments in Zone I experience strongest chemical weathering, followed by those from Zones II and III, while sediments deposited in Zone IV experience the weakest chemical weathering (Fig. 8). The degree of chemical weathering can be estimated by the chemical index of alternation (CIA) (Nesbitt and Young, 1982):

$$CIA = \frac{c(Al_2O_3)}{c(Al_2O_3) + c(CaO^*) + c(Na_2O) + c(K_2O)} \times 100.$$

Using molecular proportions and with CaO* representing calcium oxide in silicates only (Nesbitt and Young, 1989). This value is thought to quantify the state of chemical weathering of the rocks by referring to the loss of labile elements such as sodium, calcium, and potassium (Liu et al., 2007a). The CIA values are well correlated with the $c(K_2O)/[c(Na_2O) + c(CaO)]$ molar ratio for sediments in the study area as well as those from their potential provenances (Fig. 9).

On the basis of the Q-mode cluster analysis and distribution of major and trace elements, we divided the study area into four zones (Fig. 6). Zone I is located in the northeastern coastal area of the gulf, around the Guangxi and Guangdong coastal areas. Through analyzing the distribution pattern of SiO₂ (Fig. 3), rivers in Guangxi and Guangdong, such as Nanliu River, Qinjiang River and Jiuzhou River (Fig. 1), should contribute sediments to this zone. Combining with the circulation patterns (Fig. 1) and plots in Fig. 9, the contribution from the Qiongzhou Strait should also

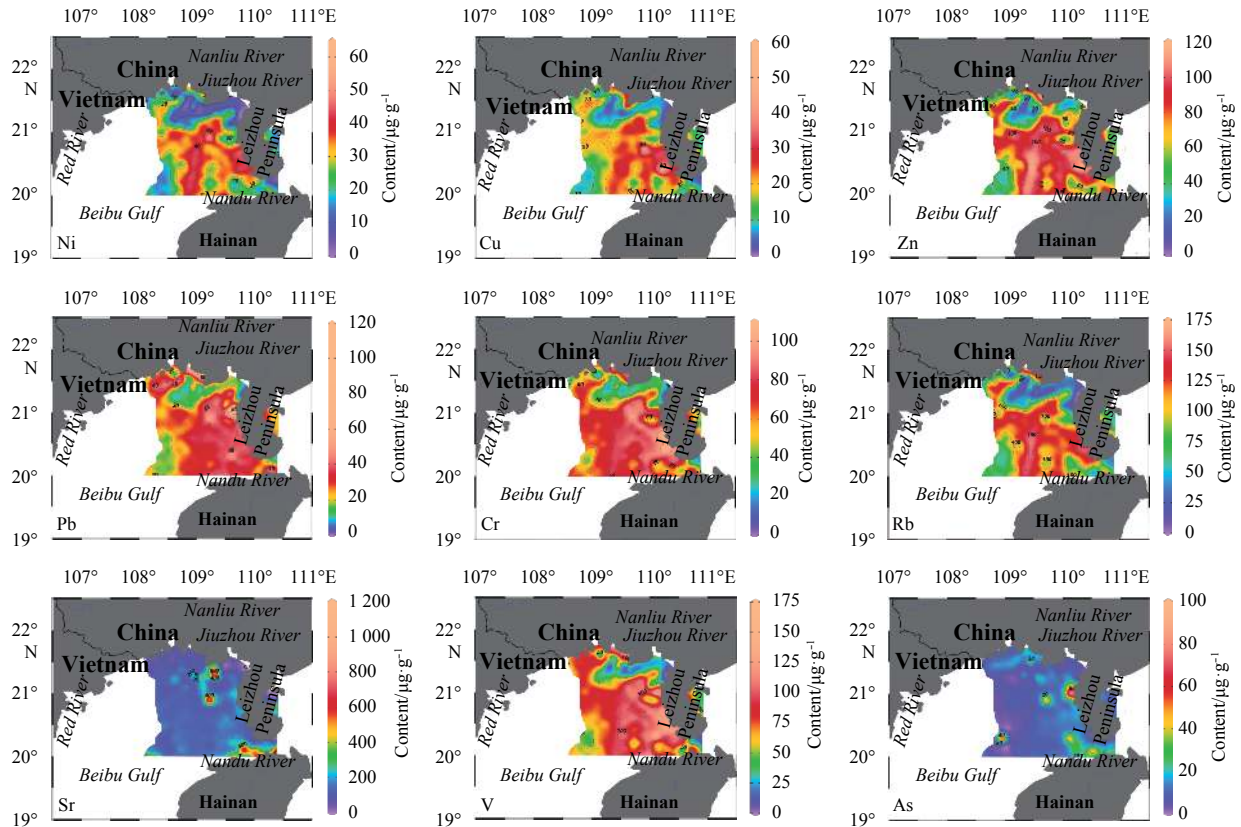


Fig. 4. Distribution patterns of the trace elements in the surface sediments of the study area.

Table 2. Pearson correlation matrix of element concentrations and mean grain size

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	MnO	TiO ₂	P ₂ O ₅	K ₂ O	Na ₂ O	Ni	Cu	Zn	Pb	Rb	Cr	Sr	V	As	Sand	Silt	Clay	Mz (Φ)		
SiO ₂	1.000																								
Al ₂ O ₃	-0.845 ¹⁾	1.000																							
Fe ₂ O ₃	-0.742 ¹⁾	0.613 ¹⁾	1.000																						
CaO	-0.161 ¹⁾	-0.331 ¹⁾	0.072	1.000																					
MgO	-0.847 ¹⁾	0.729 ¹⁾	0.589 ¹⁾	0.049	1.000																				
MnO	-0.299 ¹⁾	0.008	0.496 ¹⁾	0.482 ¹⁾	0.144 ²⁾	1.000																			
TiO ₂	-0.688 ¹⁾	0.820 ¹⁾	0.656 ¹⁾	-0.271 ¹⁾	0.566 ¹⁾	0.111 ²⁾	1.000																		
P ₂ O ₅	-0.715 ¹⁾	0.635 ¹⁾	0.759 ¹⁾	0.094	0.464 ¹⁾	0.535 ¹⁾	0.682 ¹⁾	1.000																	
K ₂ O	-0.820 ¹⁾	0.885 ¹⁾	0.683 ¹⁾	-0.200 ¹⁾	0.821 ¹⁾	0.127 ²⁾	0.857 ¹⁾	0.653 ¹⁾	1.000																
Na ₂ O	-0.634 ¹⁾	0.566 ¹⁾	0.179 ¹⁾	-0.064	0.741 ¹⁾	-0.115 ²⁾	0.227 ¹⁾	0.165 ¹⁾	0.477 ¹⁾	1.000															
Ni	-0.824 ¹⁾	0.822 ¹⁾	0.790 ¹⁾	-0.106	0.762 ¹⁾	0.337 ¹⁾	0.833 ¹⁾	0.715 ¹⁾	0.876 ¹⁾	0.376 ¹⁾	1.000														
Cu	-0.645 ¹⁾	0.742 ¹⁾	0.646 ¹⁾	-0.213 ¹⁾	0.512 ¹⁾	0.175 ¹⁾	0.812 ¹⁾	0.660 ¹⁾	0.753 ¹⁾	0.184 ¹⁾	0.844 ¹⁾	1.000													
Zn	-0.643 ¹⁾	0.739 ¹⁾	0.673 ¹⁾	-0.192 ¹⁾	0.588 ¹⁾	0.207 ¹⁾	0.759 ¹⁾	0.596 ¹⁾	0.779 ¹⁾	0.214 ¹⁾	0.891 ¹⁾	0.833 ¹⁾	1.000												
Pb	-0.611 ¹⁾	0.631 ¹⁾	0.822 ¹⁾	-0.089	0.311 ¹⁾	0.430 ¹⁾	0.683 ¹⁾	0.732 ¹⁾	0.587 ¹⁾	0.007	0.710 ¹⁾	0.703 ¹⁾	0.696 ¹⁾	1.000											
Rb	-0.785 ¹⁾	0.898 ¹⁾	0.701 ¹⁾	-0.282 ¹⁾	0.742 ¹⁾	0.136 ²⁾	0.851 ¹⁾	0.661 ¹⁾	0.936 ¹⁾	0.414 ¹⁾	0.931 ¹⁾	0.829 ¹⁾	0.895 ¹⁾	0.694 ¹⁾	1.000										
Cr	-0.810 ¹⁾	0.803 ¹⁾	0.829 ¹⁾	-0.073	0.705 ¹⁾	0.292 ¹⁾	0.873 ¹⁾	0.750 ¹⁾	0.884 ¹⁾	0.288 ¹⁾	0.940 ¹⁾	0.846 ¹⁾	0.842 ¹⁾	0.757 ¹⁾	0.893 ¹⁾	1.000									
Sr	-0.183 ¹⁾	-0.232 ¹⁾	0.160 ¹⁾	0.880 ¹⁾	-0.008	0.603 ¹⁾	-0.114 ²⁾	0.238 ¹⁾	-0.121 ²⁾	-0.174 ¹⁾	0.065	-0.020	0.024	0.125 ²⁾	-0.116 ²⁾	0.060	1.000								
V	-0.782 ¹⁾	0.824 ¹⁾	0.853 ¹⁾	-0.169 ¹⁾	0.589 ¹⁾	0.294 ¹⁾	0.906 ¹⁾	0.778 ¹⁾	0.829 ¹⁾	0.242 ¹⁾	0.895 ¹⁾	0.831 ¹⁾	0.809 ¹⁾	0.823 ¹⁾	0.856 ¹⁾	0.933 ¹⁾	-0.012	1.000							
As	-0.047	-0.111 ²⁾	0.397 ¹⁾	0.221 ¹⁾	-0.204 ¹⁾	0.577 ¹⁾	-0.028	0.368 ¹⁾	-0.116 ²⁾	-0.291 ¹⁾	0.066	0.055	0.034	0.432 ¹⁾	-0.057	0.092	0.329 ¹⁾	0.183 ¹⁾	1.000						
Sand	0.662 ¹⁾	-0.738 ¹⁾	-0.489 ¹⁾	0.218 ¹⁾	-0.648 ¹⁾	-0.069	-0.530 ¹⁾	-0.447 ¹⁾	-0.669 ¹⁾	-0.548 ¹⁾	-0.634 ¹⁾	-0.520 ¹⁾	-0.565 ¹⁾	-0.419 ¹⁾	-0.672 ¹⁾	-0.568 ¹⁾	0.136 ²⁾	-0.586 ¹⁾	0.115 ²⁾	1.000					
Silt	-0.632 ¹⁾	0.761 ¹⁾	0.463 ¹⁾	-0.296 ¹⁾	0.623 ¹⁾	-0.006	0.635 ¹⁾	0.446 ¹⁾	0.705 ¹⁾	0.470 ¹⁾	0.671 ¹⁾	0.602 ¹⁾	0.608 ¹⁾	0.432 ¹⁾	0.706 ¹⁾	0.629 ¹⁾	-0.209 ¹⁾	0.636 ¹⁾	-0.172 ¹⁾	-0.934 ¹⁾	1.000				
Clay	-0.608 ¹⁾	0.692 ¹⁾	0.304 ¹⁾	-0.260 ¹⁾	0.672 ¹⁾	-0.069	0.339 ¹⁾	0.261 ¹⁾	0.559 ¹⁾	0.729 ¹⁾	0.476 ¹⁾	0.314 ¹⁾	0.382 ¹⁾	0.193 ¹⁾	0.546 ¹⁾	0.376 ¹⁾	-0.275 ¹⁾	0.381 ¹⁾	-0.256 ¹⁾	-0.857 ¹⁾	0.754 ¹⁾	1.000			
Mz	-0.665 ¹⁾	0.791 ¹⁾	0.429 ¹⁾	-0.309 ¹⁾	0.701 ¹⁾	-0.056	0.586 ¹⁾	0.394 ¹⁾	0.719 ¹⁾	0.603 ¹⁾	0.636 ¹⁾	0.520 ¹⁾	0.552 ¹⁾	0.365 ¹⁾	0.698 ¹⁾	0.584 ¹⁾	-0.278 ¹⁾	0.576 ¹⁾	-0.0245 ¹⁾	-0.910 ¹⁾	0.931 ¹⁾	0.900 ¹⁾	1.000		

Note: ¹⁾ The correlation is significant at the 0.01 level (2-tailed); ²⁾ The correlation is significant at the 0.05 level (2-tailed).

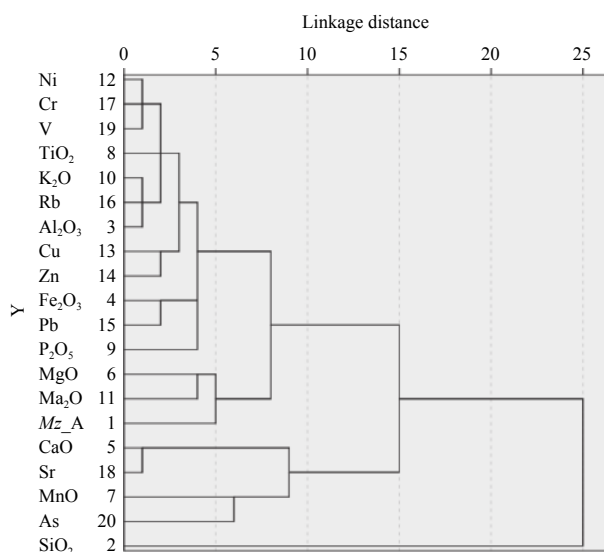


Fig. 5. R-mode hierarchical cluster analysis for the major and trace elements and mean grain size obtained using Ward's hierarchical clustering method. Linkage distances reflect the strength of correlation between two elements.

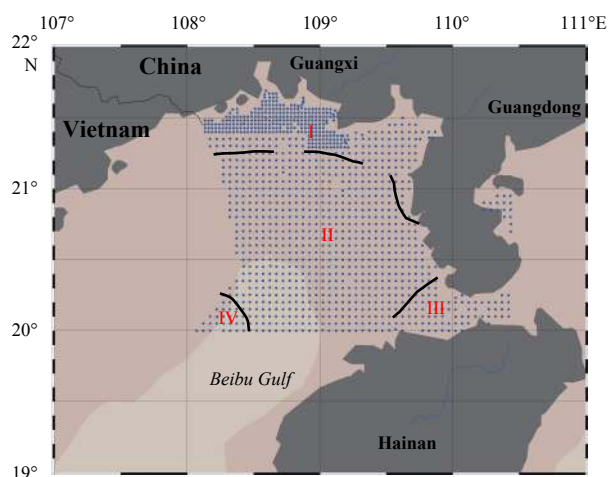


Fig. 6. Elemental geochemical zones in the study area (the dash line represents the estimated boundary of different zones).

be considered as a possible source. Therefore, the fluvial materials from rivers in Guangxi and Guangdong, and the Qiongzhou Strait are the main sources of sediments in Zone I. Zone II is located in the center of study area, where most major and trace elements are concentrated (except for SiO_2 , CaO , MnO , Sr and As , see Figs 3 and 4). Here the sediments could be from a multiple sources: the riverine materials from Guangxi are firstly deposited in the coastal area in summer, and then resuspended and transported into this zone in winter. Such “summer deposit and winter transport” mechanism is similar with that of the Huanghe River, Changjiang River, Zhujiang River, and Mekong River-derived sediments (Yang et al., 1992; Liu et al., 2004, 2006; Xue et al., 2010; Ge et al., 2014). Because of the westward currents flowing through the Qiongzhou Strait all year around (Fig. 1), sediments from east exit of the Qiongzhou Strait can be transported into this zone (Fig. 9). Moreover, the sediments from the western bank of Hainan can also be transported here (Figs 1 and 9). Zone III is

Table 3. Calculation of multiple principal components with varimax rotation

	F1	F2	F3
Mz (Φ)	0.545	0.607	-0.242
SiO_2	-0.710	-0.589	-0.288
Al_2O_3	0.801	0.477	-0.202
Fe_2O_3	0.845	0.059	0.316
CaO	-0.240	0.116	0.907
MgO	0.525	0.786	0.118
MnO	0.331	-0.194	0.766
TiO_2	0.884	0.182	-0.148
P_2O_5	0.802	0.041	0.344
K_2O	0.818	0.480	-0.081
Na_2O	0.134	0.875	-0.043
Ni	0.901	0.324	0.092
Cu	0.877	0.105	-0.073
Zn	0.861	0.171	-0.038
Pb	0.885	-0.185	0.166
Rb	0.888	0.361	-0.122
Cr	0.923	0.247	0.091
Sr	-0.033	-0.048	0.907
V	0.958	0.124	0.032
As	0.260	-0.567	0.492
Variance/%	52.2	16.8	14.9

located in the Qiongzhou Strait, where the contents of SiO_2 , MnO , CaO , Sr , Pb and As are high (Figs 3 and 4). There are strong westward currents flowing through the Qiongzhou Strait all year round, therefore, the Zhujiang River-derived sediments can be transported into the Qiongzhou Strait. Sediments from the Hainan, including those from the Nandu River and eroded from the coast, can also contribute to Zone III. Zone IV is located in the southwest of the study area, where Fe_2O_3 , CaO , K_2O , MgO , Sr and As are abundant (Figs 3 and 4). This area is part of the paleo-Red River Delta, and is covered by relict sediments (Chen and Zhang, 1986; Dou et al., 2012). Therefore, the contribution from the Red River should not be ignored. In addition, the sediments originate from Hainan and western bank coastal erosion can also be transported into this zone in winter (Figs 1 and 9).

5.2 Geochemical elements distribution and controlling factors

The cluster and principal component analysis effectively reduce the dimensionality of geochemical data. The two dimension-reduction methods produced consistent results regarding the elemental assemblages in surface sediments. Elements in Clusters I and II exhibit high positive loadings over F1 and F2, respectively. And elements in Clusters VI and V exhibit negative loadings over F1 and F2, respectively. Moreover, F3 corresponds to Clusters III and IV.

F1 and F2 mostly exhibit high positive loading for silt and clay fractions. The contents of aluminium and titanium in sea water are very low, and they are mostly regarded as terrigenous materials in marine sediments (Bruland, 1983; Goldberg and Arrhenius, 1958). Thus, F1 and F2 can be inferred as terrigenous detritus derived from weathered crustal continental rocks. The distribution patterns of these elements and Mz , along with the cluster and principal component analyses, indicate that the grain size is the most important factor controlling the distribution of elements in these two groups (Figs 2–5, Table 2). Fine-grained sediments are rich in Al_2O_3 , Fe_2O_3 , TiO_2 , P_2O_5 , K_2O , MgO , Na_2O , Ni , Cu , Zn , Pb , Rb , Cr and V , while coarse-grained sediments have high SiO_2 and

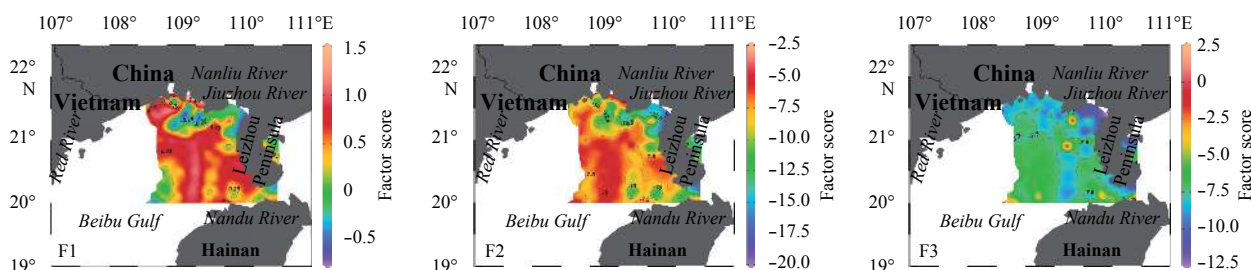


Fig. 7. Factor scores of the three principal components in the study area.

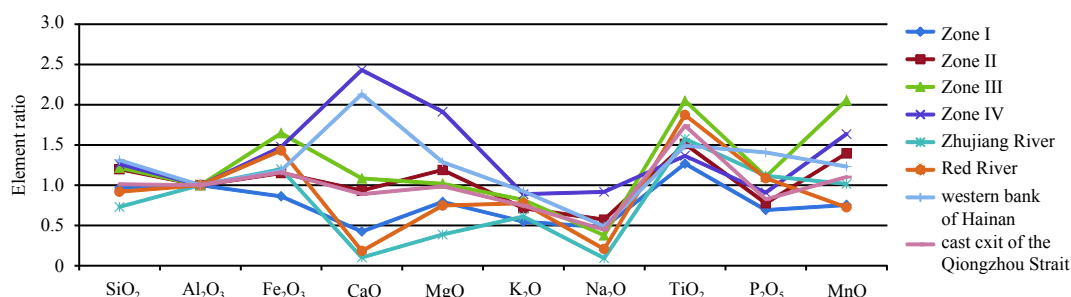


Fig. 8. Element ratios of samples from the study area. Data from the Zhujiang River (Liu et al., 2007a), the Red River (Liu et al., 2007a), the western bank of Hainan (Cui et al., 2015), and the east exit of the Qiongzhou Strait (Cui et al., 2015) are plotted for comparison as the potential provenances.

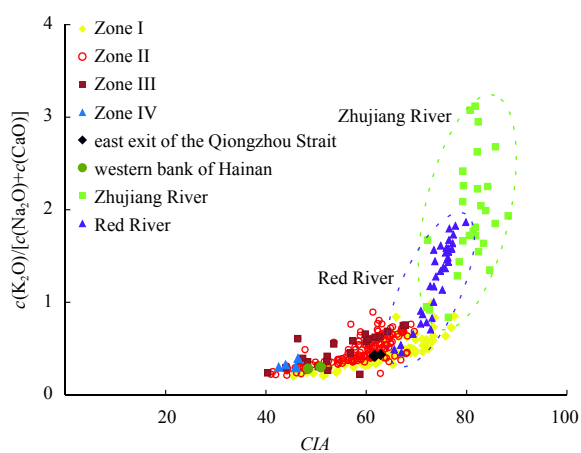


Fig. 9. Correlations of chemical index of alteration (CIA) with $c(\text{K}_2\text{O})/[c(\text{Na}_2\text{O})+c(\text{CaO})]$ molar ratio in study area and potential sediment provenances (Liu et al., 2007a; Cui et al., 2015).

As contents. The characteristics of the grain size are mostly controlled by a hydrodynamic environment and the mineral composition of terrigenous components (e.g., Self, 1977; Gao and Collins, 1992; Gao, 2009). The strong hydrodynamics in coastal area leads to deposition of coarse-grained sediments (Zone I, Figs 2 and 6). Xie et al. (2014) indicated that Nandu River-derived sediments were mainly influenced by flood-induced jet currents and alongshore tidal currents passing through the Qiongzhou Strait, which are mainly composed of sand. Meanwhile, the potential vorticities between the inflow from the southern gulf circulation and outflow in the Qiongzhou Strait were essentially cancelled each other (Gao et al., 2015). Sand, which is transported from the Qiongzhou Strait, would be deposited in the strait and its west exit (Zone III, Figs 2 and 6). Coarse-grained sediments contain more quartz, which raises SiO_2 content while

dilute that of other elements. Therefore, the SiO_2 content has a high value in these two zones (Fig. 3). On the other hand, riverine materials experienced the processes of transportation, deposition, resuspension, transportation, and redeposition, and the sorting effect results the fine-grained sediments to be deposited in the center of the study area (Zone II, Figs 2 and 6). Aluminium mostly resides in aluminum silicates, which are detrital minerals dominated by clay minerals (Zhao and Yan, 1994). The Al_2O_3 content is high in Zone II. The aluminum silicates are one of the most important carriers of absorbed metals in the nearshore sediments (Zhao and Yan, 1994; Jonathan et al., 2004). Meanwhile, the isomorphism phenomenon makes some metallic element ions (such as Ni^{2+} , Cr^{3+} , and so on) are easily substituted by the ions (such as Mg^{2+} , Fe^{3+} , and so on) from silicates (Zhao and Yan, 1994). Accordingly, Fe_2O_3 , K_2O , MgO , Na_2O , Ni , Cu , Zn , Pb , Rb , Cr and V contents are positively correlated with Al_2O_3 content (Table 3).

Anthropogenic activity is another important factor affecting the spatial variations of elements, especially that of heavy metal. Rivers flowing through catchments with rapid industrial and economic developmental are ideal carriers of heavy metal (Zhang et al., 2017). The Cu , Cr , Pb , Zn and As contents are found to be much higher than their background values in most of the samples (Fig. 4). Especially in the estuary and Zone III, the high values are centered off the estuaries in Guangxi and Hainan, which indicates impacts from human activities.

F3 displays significant positive loadings for CaO , Sr and MnO . Because of the similar ionic radius of Ca^{2+} and Sr^{2+} , the phenomenon of isomorphism is widespread (Zhao and Yan, 1994). The variations of these two elements are always synchronism, and they are mainly biogenic sourced. The highest F3 scores present around the Weizhou Island off the Guangxi coast. As flourishing coral reef platforms are reported in the center gulf (Wang et al., 2016), the relict deposit could be introduced by coral debris (Fig. 7). The MnO content is also controlled by the ox-

ide content in the environment, except for the riverine inputs and sediments transportation process. The manganese would deposit as an authigenic oxide in the oxic environment (Wei et al., 2003). The distribution pattern of MnO content is similar with that of CaO and Sr, which indicates that the high value areas are oxic environment that favorite the authigenic manganese deposition.

6 Conclusions

We performed the grain size, major and trace elements analyses on surface sediments from the northeastern Beibu Gulf in the South China Sea. Most elements, except for SiO₂, CaO, MnO, Sr and As, exhibit a similar spatial distribution with that of silt fraction. On the basis of the Q-mode cluster analysis and the elements distribution, the study area was divided into four zones: Zone I is located in the northeastern coastal area of the gulf, where sediments are mainly from the rivers in Guangxi and Guangdong, and the Qiongzhou Strait; Zone II is located in the center of the study area, and the sediments here have a multiple source; Zone III is located in the Qiongzhou Strait, which is dominated by sediments from the Zhujiang River and Hainan Island; Zone IV is located in the southwest of the study area, and the sediments here mainly originated from the Red River and Hainan. Our analysis reveals that while the grain size, which is mainly controlled by the hydrodynamics and mineral composition, is the dominant factor for the elements distribution in the Beibu Gulf, impacts from the anthropogenic activity and the marine biogenic process should be also taken into consideration.

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