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Magnetic Characteristics of Surface Sediments of Liaodong Bay, China

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Abstract Analysis of magnetic properties of marine surface sediments has been gradually proved to be one of the effective means for researching the source of marine sediments. In this paper, samples from 39 sites in Liaodong Bay were collected to analyze the magnetic characteristics of the surface sediments. Magnetic study indicated that the surface sediments of the Liaodong Bay are characterized by magnetite. In the middle and eastern part and the southwest corner of the Bay, the main magnetic grains were coarse multi-domain and pseudo-single-domain particles, while in other areas single-domain and pseudo-single-domain particles constitute the majority. Based on grain size and environmental magnetism data, the content of magnetic minerals has a positive correlation with the hydrodynamic environment when the magnetic mineral domain is finer. However, the content of magnetic minerals is in a complex relationship with the hydrodynamic environment in the coarse magnetic domain of magnetic minerals found in central Liaodong Bay and places outside the Fuzhou Bay, implying that the strong hydrodynamic environment accelerates the sedimentation of coarse magnetic minerals. Based on geographic pattern of magnetic properties, it can be inferred that the main provenance of the surface sediments of the Liaodong Bay is the surrounding rivers, and the comparative analysis indicates that Yellow River substances maybe also exist in the bay.

Key words magnetic characteristics; grain size; provenance; Liaodong Bay; surface sediments

1 Introduction

Environmental Magnetism, as an emerging interdisciplinary branch of geoscience, is an integrated combination of geology, magnetism and environmental sciences. Since the 1970s, great achievements have been made on magnetic studies of marine sediments. Magnetic characteristics of sediments can directly show the content, type, particle size and other information of the magnetic minerals. Such factors are related to sediment provenance, transportation, sediment dynamics and redeposition process, and indirectly related to climate changes and human activities (Zhang *et al*., 1995).

The Liaodong Bay possesses complex hydrodynamic conditions, which bring it a complicated surface sediment distribution. Various researches have been made by scientists on the sources of surface sediment in different ways including sedimentary methods (Xu *et al*., 2012; Dou *et al*., 2014; Qiao *et al*., 2010), numerical experiments (Wang *et al*., 2012) and geochemistry measurement (Li *et al*., 2010), but the provenance still remains a controversial issue. In this study, we investigated the environmental magnetic properties of the surface sediments in the Liaodong Bay, in order to provide environmental magnetic evidences for potential provenance of surface sediments of the Liaodong Bay. This will be of great significance for further research on analysing the evolution process of the transport and formation of the surface sediment in Liaodong Bay and Bohai Sea and evaluating the contribution of the rivers flowing into Liaodong Bay and that of the Yellow River.

Many studies have been made on the application of rock and mineral magnetic method in the research of sediment transportation and deposition. Alagarsamy (2009) studied the magnetic mineralogy and geochemistry of surface sediments on the continental shelf of India, as well as the concentrations of heavy metals and their impact on the coastal environment, and concluded with the factors that control the concentrations of heavy metals in the east and west coast of India. Tian *et al*. (2013) carried out a magnetic study on the surface sediments from the seafloor surrounding Hainan Island. It is found that the low-frequency magnetic susceptibility and frequency magnetic susceptibility have a significant spatial difference, and their combination can effectively indicate provenance variation

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of nearshore surface sediments. Wang *et al*. (2010) researched the magnetic characteristics of muddy sediments in the northeastern part of China Seas, including the continental shelf near South Korea, and discussed the sources of the muddy sediment and its transport model via grain fractions. Liu *et al*. (2007) made a detailed magnetic study on the fine-grain-size surface sediments taken from the muddy area to the north of Shandong Peninsula and in the 'Fujian-Zhejiang coast muddy area', which reveals the differences in magnetic characteristics among varied provenance areas. Kim *et al*. (2013) measured various magnetic parameters including concentration, mineral composition, and grain size of surface sediments collected from northern East China Sea at 98 regularly spaced sites. The relevant statistical analysis yielded four clusters, demonstrating that the sediments in the study area can be distinguished by magnetism. Their study identified the provenance of fine-grained sediments in the northern East China Sea. Based on the previous practical use of environmental magnetism, the provenance of surface sediments of the Liaodong Bay will be analyzed via environmental magnetism in this study.

2 Study Area

Located in the northern Bohai Sea, the Liaodong Bay is the northernmost semi-enclosed shallow bay in China, where the bottom topography is relatively flat and slightly inclined from the coast to the central part of the bay, with an average depth of less than 15 m, except for the center of the bay, which may reach a depth over 30 m. The water depth on the west side is deeper than that on the east. The western Liaodong Bay is rather shallow, with numerous sandbanks and a straight shoreline (Sun, 2008). A great quantity of young sediments deposited in the Liaodong Bay comes from surrounding rivers, and the recent sediment discharged into the bay is about 40×10^{6} t yr^{-1} on average (Qiao *et al*., 2010).

Reciprocating flow dominates the Liaodong Bay, with the mainstream generally being parallel to the shoreline (Gu and Xiu, 1996). The velocity of tidal current in the Liaodong Bay ranges from 1 to 1.5 m s^{-1} in general. A strong tidal current occurs in the southeast and the velocity of the strongest tidal current may reach 2.5 m s^{-1} in the Laotieshan channel (Luan *et al*., 2012) (Fig.1). The Liaodong Bay possesses a rather weak circulation system composed of the remaining current of the Yellow Sea warm current and the Bohai Sea coastal current. Except for some particular months in summer, the remaining Yellow Sea warm current invades into the central Bohai Sea and extends to the west coast, and then is divided into the north and the south branches. The north branch flows northward along the west coast of the Liaodong Bay, forming a clockwise circulation. However in summer, the north branch of the remaining Yellow Sea warm current flows northward along the east coast of the Bay and forms a counter-clockwise circulation (Luan *et al*., 2012; Wan, 2003) (Fig.1).

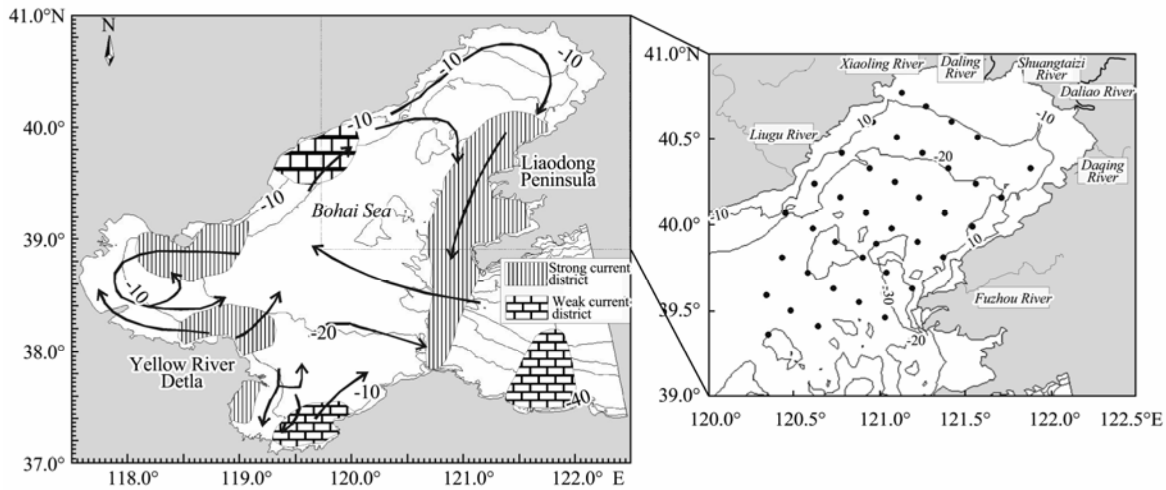

Fig.1 The distribution of currents in Liaodong Bay (Gu and Xiu, 1996) and the circulation system except for summer (Qu, 1994), and location of sampling sites.

3 Methods

In September 2012, surface sediments (upper 5 cm) were collected from the Liaodong Bay using a grab sampler aboard the vessel *Xianyu-No.1* during the marine geology cruise in the Liaodong Bay, and 39 sites were basically homogeneously east-northeastward distributed in the Liaodong Bay and a small part of central Bohai Sea (Fig.1).

3.1 Grain Size Measurement

The laser grain size analyzer of UK Mastersizer 2000 was used for grain size analysis of 31 samples in Qingdao Institute of Marine Geology. Firstly, 10 g of dry samples were picked out after being dried at 60℃. Secondly, the samples were continuously soaked in a solution of 10% H_2O_2 and 0.1 mol L^{-1} hydrochloric acid for 12 h to wipe away organic matters and $CaCO_3$. Then 10 mL of sodium hexametaphosphate solution at a concentration of 0.05

mol L^{-1} was added. Finally, the sample was completely dispersed with an ultrasonic for 10 min and then put into the equipment for grain size analysis.

3.2 Magnetic Measurements

Magnetic susceptibility measurements were completed at Ocean University of China, while other environmental magnetic parameters were measured in Qingdao Institute of Marine Geology. The samples were dried in an oven at a temperature of less than 40℃ and gently tapped with an agate mortar and pressed into powder. Then about 5 g of the sample were weighed and placed into a polyethylene film. For magnetic measurements, 39 samples were prepared by shaping the dried sediments into non-magnetic plastic cubes of 8 cm^3. All the samples were analyzed for low and high frequency magnetic susceptibilities (χ_{lf} and χ_{hf}), anhysteretic remanent magnetization (ARM), and stepwise acquisition of isothermal remanent magnetization (IRM).

The values of χ_{lf} and χ_{hf} were measured with a Bartington Instruments MS2 magnetic susceptibility meter, with frequencies set at 0.47 kHz and 4.7 kHz, respectively. The frequency-dependent magnetic susceptibility (χ_{fd}) was then calculated with the formula of $\chi_{\text{fd}} = (\chi_{\text{lf}} - \chi_{\text{hf}})/\chi_{\text{lf}} \times 100(\%)$. The ARM was induced using a Dtech 2000 alternating-field (AF) demagnetizer with the ARM attachment at a peak AF of 100 mT, in a superimposed steady 0.04 mT direct current (DC) field. The susceptibility of ARM (χ_{ARM}) was calculated by normalizing ARM to a DC-biasing field. For samples, IRM acquisition experiments were performed by stepwise increasing DC fields up to 1.5 T (25 steps), using an ASC IM-10–30 impulse magnetizer. In the present study, the IRM acquired at 1.5 T was referred to as saturation IRM (SIRM). The remaining samples acquired IRMs at DC fields of 20 mT, −100 mT and −300 mT. Two reverse fields (−100 mT, −300 mT) were then used to evaluate the parameter *S* in the form of ratios:

$$S_{-100}=100\times(SIRM-IRM_{-100\text{mT}})/(2\times SIRM),$$

and

$$S_{-300}=100\times(SIRM-IRM_{-300\text{mT}})/(2\times SIRM).$$

All the remanence measurements were made on AGICO JR-6A spinner magnetometer.

4 Results

4.1 Magnetic Minerals

Magnetic susceptibility (χ) and saturation isothermal remanence (SIRM) can reflect the content of magnetic minerals. However, SIRM is mainly affected by ferrimagnetic minerals and incomplete antiferromagnetic minerals. Except for one particularly anomalous data point, a strong positive correlation (R^2=0.695) was found between χ and SIRM (Fig.2). Therefore, the magnetic properties of the surface sediments of the study area were mainly dominated by ferrimagnetic minerals.

S_{-300} and S_{-100} reflect the relative proportions of ferrimagnetic minerals and incomplete antiferromagnetic minerals, which rise with the increase of the content of ferrimagnetic mineral (Shi *et al.*, 2007; Canbay *et al.*, 2010). When S_{-100}>70%, or S_{-300}>90%, it means that the dominant minerals are ferrimagnetic minerals. In the study area, the maximum value of S_{-100} was 88.89% and the minimum value was 70.79%. All the values of S_{-100} were greater than 70% with an average at 84.11% (Fig.3). However, the maximum value of S_{-300} was 98.59%. Only at one site the S_{-300} value was lower than 90% and the average value reached 94.4% (Fig.3). This also proves that the magnetic characteristics of the surface sediments in the study area were dominated by the ferrimagnetic minerals.

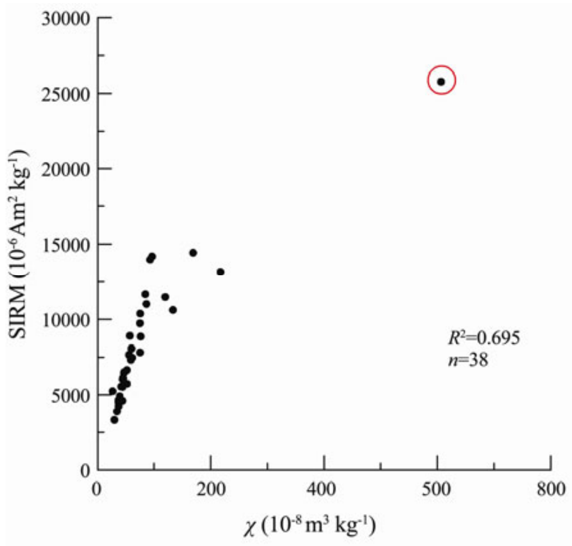

Fig.2 The correlation between magnetic parameters (*SIRM* and χ) of Liaodong Bay surface sediments (the red circles represent the anomalous data point).

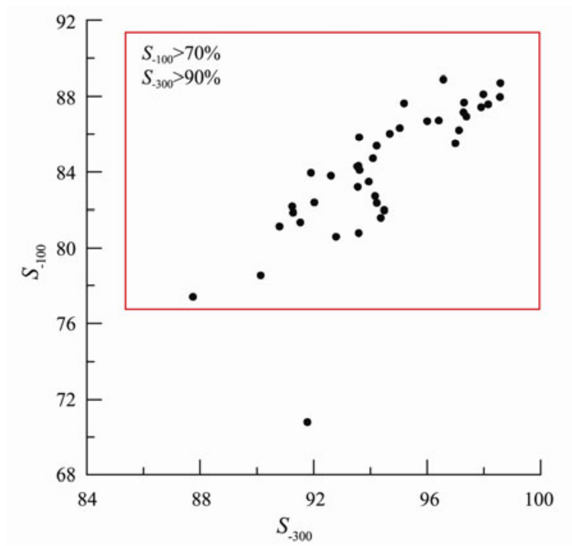

Fig.3 The scatter diagram of magnetic parameters (S_{-100} and S_{-300}) of Liaodong Bay surface sediments.

The *κ-t* curves of representative samples were obtained *via* heating-cooling cycles from room temperature up to 700℃ (Fig.4). The *κ-t* curve shows that the volume susceptibility κ increased when heated from room temperature to around 300℃, and then decreased when the temperature continuously increased from 300℃ to around 400℃. When the temperature reached 580℃, κ decreased abruptly. It is the unblocking phenomenon since the sample has been heated up to the Curie temperature of magnetite. Hence, the sediments may be divided into two types by κ-t curves. For the first type, κ values increased significantly when the sample was heated from around 510℃ (L36), the main reason being the Hopkins effect of single-domain magnetite. However, the phenomenon above was not evident in the other type. In the cooling process, the curves of the two types were quite similar. When the temperature dropped from 590℃ to around 490℃, the κ value significantly increased, and was greater than that in the heating process in this temperature range, indicating that a large amount of magnetite has been formed during the heating process (Liu *et al*., 2007). As the temperature dropped from 490℃ to room temperature, the κ value decreased slowly and was finally stabilized. In summary, the magnetic minerals in the surface sediments of the Liaodong Bay were dominated by magnetite.

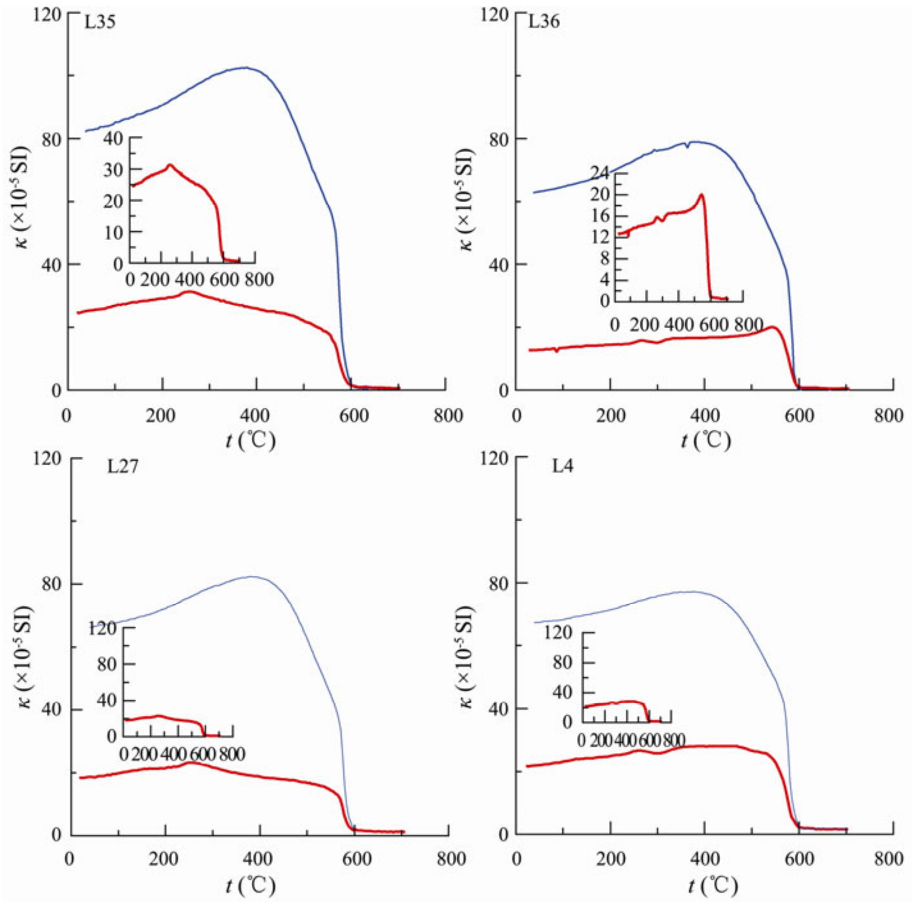

Fig.4 The κ-t curve of typical surface sediment samples of Liaodong Bay (Inset shows the heating curve only).

4.2 Magnetic Concentration

In environmental magnetism studies, the magnetic susceptibility (χ) and IRM are regarded as the best parameters to indicate the characteristics of magnetic minerals. Magnetic susceptibility is affected by the grain size, types and content of magnetic minerals, in particular the enrichment of ferrimagnetic minerals (such as magnetite) (Qu, 1994). In the study area, magnetic susceptibility values were generally within the range of 30×10^{-8}–110×10^{-8} m^3 kg^{-1} and averaged at 79.31×10^{-8} m^3 kg^{-1}. The maximum value of 606.56×10^{-8} m^3 kg^{-1} was found in the middle of the Liaodong Bay near Fuzhou Bay, while the minimum value, as low as 24.46×10^{-8} m^3 kg^{-1}, occurred in the northern part of the Liaodong Bay. In conclusion, higher magnetic susceptibility values occurred in the east and southwest corner of the Liaodong Bay, which may indicate the enrichment of ferrimagnetic minerals, while lower magnetic susceptibility values were found in the north and west of the Bay (Fig.5a).

SIRM mainly depends on the content and type of ferromagnetic minerals as well as grain size of the samples (Jiang *et al*., 2004). It gradually decreases as the grain size gets larger. Single-domain magnetic particles have the strongest SIRM and the SIRM value of super-paramagnetic minerals is zero. Different from magnetic susceptibility, the SIRM values are not affected by paramagnetic and diamagnetic minerals. In the study area, the distribution of SIRM was similar to χ with the highest SIRM larger than 20000×10^{-6} Am^2 kg^{-1} (Fig.5b). Thus, ferrimagnetic minerals were mainly located in the east and southwest corners of the Liaodong Bay, and the region with lower ferrimagnetic mineral content was the northern and western parts of the Bay.

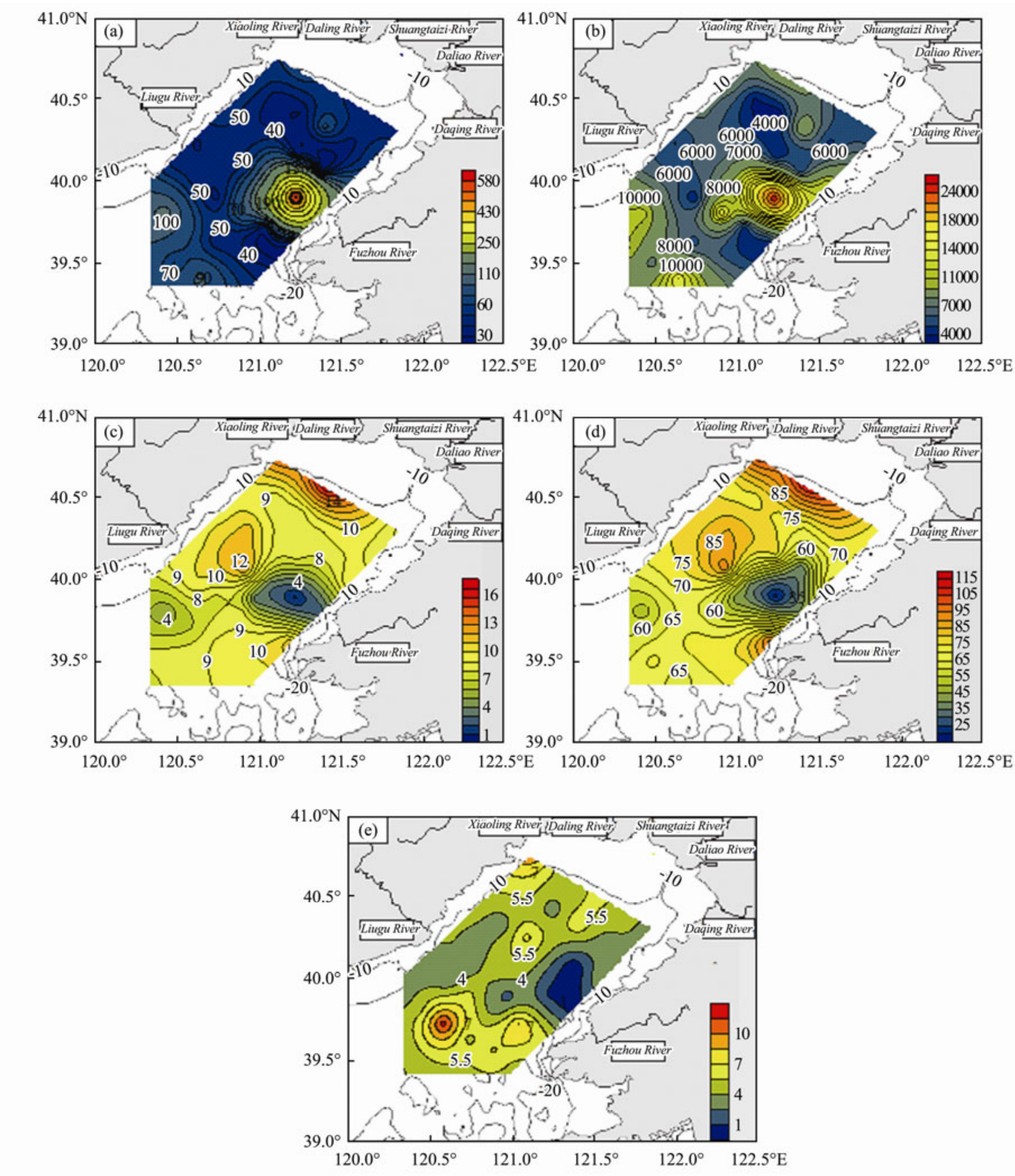

Fig.5 The distribution of magnetic parameter contours of Liaodong Bay surface sediments a) mass magnetic susceptibility (χ) (unit: $10^{-8}\,m^3\,kg^{-1}$); b) SIRM (unit: $10^{-6}\,Am^2\,kg^{-1}$); c) χ_{ARM}/χ; d) $\chi_{ARM}/SIRM$ (unit: $10^{-5}\,m\,A^{-1}$); e) χ_{fd}%.

4.3 Magnetic Grain-Size

The ratio of χ_{ARM}/χ can indicate the grain size of ferrimagnetic minerals. A higher ratio indicates the richness of single-domain particles, while a lower ratio reflects the presence of multi-domain or super-paramagnetic particles (Banerjee *et al*., 1981; King *et al*., 1982). The ratio of $\chi_{ARM}/SIRM$ is not affected by super-paramagnetic grains, so the lower ratio reflects the multi-domain grains (Shi *et al*., 2007). The parameters χ_{fd}% may reflect the existence of super-paramagnetic particles and their relative content. In the mid-east region and southwest corner of the Liaodong Bay, the magnetic parameters were characterized by $\chi_{ARM}/\chi<10$ and $\chi_{ARM}/SIRM<60\times10^{-5}$ m A^{-1}, indicating that the ferrimagnetic minerals were dominated by pseudo-single-domain and multi-domain magnetic particles in this region (Figs.5c and 5d). In other parts of the Liaodong Bay, the parameters were different from the above ones, suggesting that the pseudo-single-domain and single-domain magnetic particles dominated the ferrimagnetic mineral grains in these regions (Figs.5c and 5d). In addition to the eastern Liaodong Bay, the range of χ_{fd}% in the study area varied from 3% to 8%, with an average value of 4.73%, indicating the presence of super-paramagnetic (SP) grains (Fig.5e).

Based on the hysteresis loop measurements, the M_{rs}/M_s and H_{cr}/H_c were calculated and plotted in the Day diagram (Day *et al*., 1977). Typical samples were mainly in the range of pseudo-single-domain and multi-domain, with some of the samples located near the bottom right corner of the diagram, indicating the possible presence of super-paramagnetic particles (Fig.6).

4.4 Grain Size of Sediments

The grain size of marine sediment is a joint result of sediment provenance, hydrodynamic conditions, topography and other factors of the sedimentary area, and, therefore, the grain size can be a significant parameter to define the depositional environment (Wan, 2003). Through an analysis on the median size of surface sediments and the percentages of sand, silt and clay in the study area, it was found that the sediment was coarser in the eastern and mid-west regions of Liaodong Bay, and finer in other regions (Fig.7). Gu and Xiu (1996) found that strong currents exist in the eastern area of the Liaodong Bay, which may be the reason for coarsening sediment grain size, while in the mid-west, the coarse sediments may be related to the substances from the Liugu River.

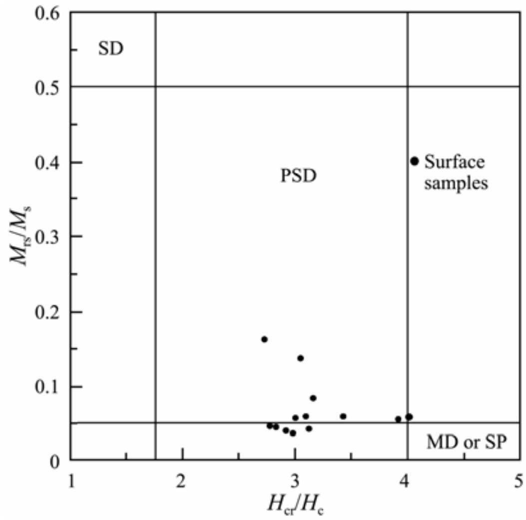

Fig.6 The diagram of M_{rs}/M_s and H_{cr}/H_c for some surface sediment samples of Liaodong Bay.

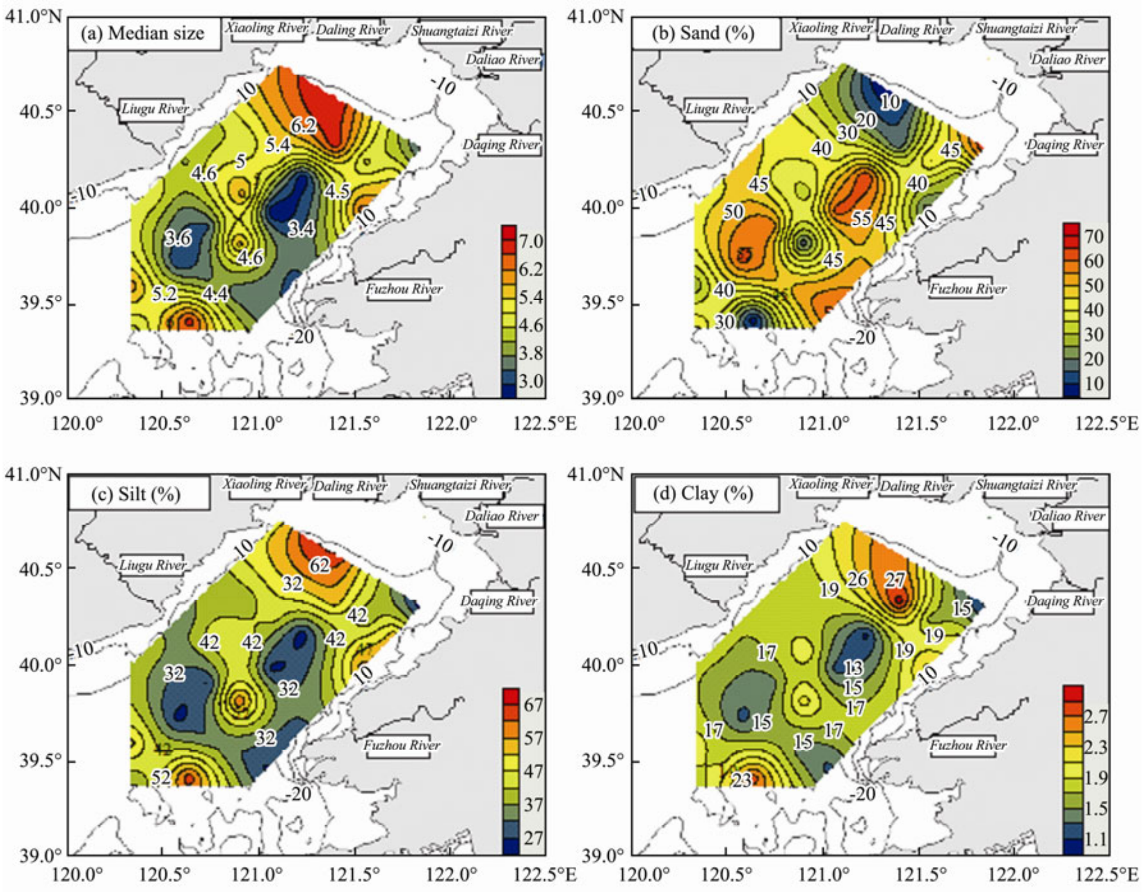

Fig.7 The grain size distribution and contents of surface sediments in the Liaodong Bay: a) The median size (unit: Φ); b) The sand content (%); c) The silt content (%); d) The clay content (%).

5 Discussion

5.1 Responses of Magnetic Characteristics to the Sedimentary Environment

Numerous studies showed a good correlation between grain size and magnetic parameters (Zhang *et al*., 2001; Wang *et al*., 1996; Clifton *et al*., 1999; Oldfield, 1994; Jia *et al*., 2000; Yang and Li, 2002). Through a correlation analysis on the magnetic susceptibility values in the surface sediments and the median size as well as sand, silt and clay contents (Fig.8), it was found that magnetic susceptibility had the highest positive correlation with silt content, followed by the second and third highest positive correlations with the clay content and the median diameter (Φ). However, it was negatively correlated with sand content. It indicates to a certain extent a close relationship between the magnetic mineral content of sediments and sedimentary environment. Generally, the weak hydrodynamic environment can result in a finer sediment grain size and a higher content of magnetic mineral.

Apart from grain sizes, some other factors also have significant influence on the magnetic properties. This study shows a remarkable relationship between magnetic mineral content and magnetic domains. According to χ_{ARM}/χ and $\chi_{ARM}/SIRM$, we divided the samples into fine magnetic domain and coarse magnetic domain. As for the former, the magnetic minerals mainly consist of single-domain and pseudo-single-domain groups, and the magnetic mineral content has a positive correlation with χ_{ARM}/χ and $\chi_{ARM}/SIRM$. Therefore, with the magnetic domains getting finer, the magnetic mineral content increases (Fig.9). Conversely, when the magnetic domains are relatively coarse, with the magnetic mineral getting coarser, the magnetic mineral content increases (Fig.10). The reason is that under the strong hydrodynamic environment the coarse magnetic mineral is easier to deposit and preserve than the fine magnetic mineral. Thus, in addition to grain size, magnetic domain is also considered as an important factor in the research of magnetic mineral content.

In the northern part of the study area, the fine-grained sediments are mainly from the rivers to the north of the Liaodong Bay, where the magnetic domains are smaller with the sediment grain size becoming gradually coarser from north to south, and its magnetic mineral content is also getting lower. In the western part of the study area, however, the magnetic domains are smaller and the sediment grain size from nearshore to offshore is also getting finer, though the change is not obvious. As a result, the magnetic mineral content is also altered a little. In the eastern part, the sediment grain is coarse due to the strong hydrodynamic condition. According to the magnetic domain information achieved in the middle of the Liaodong Bay and outside the Fuzhou Bay, its magnetic domains are very coarse, resulting in the enrichment of magnetic minerals and forming an area with high magnetic mineral content. However, Liaodong Shoal is an area with low content of magnetic minerals, as the magnetic mineral domains become significantly finer. In the southwestern part of the study area, due to the presence of two fine-grained sediment depocenters and their smaller magnetic domains, these two areas are endowed with high content of magnetic minerals.

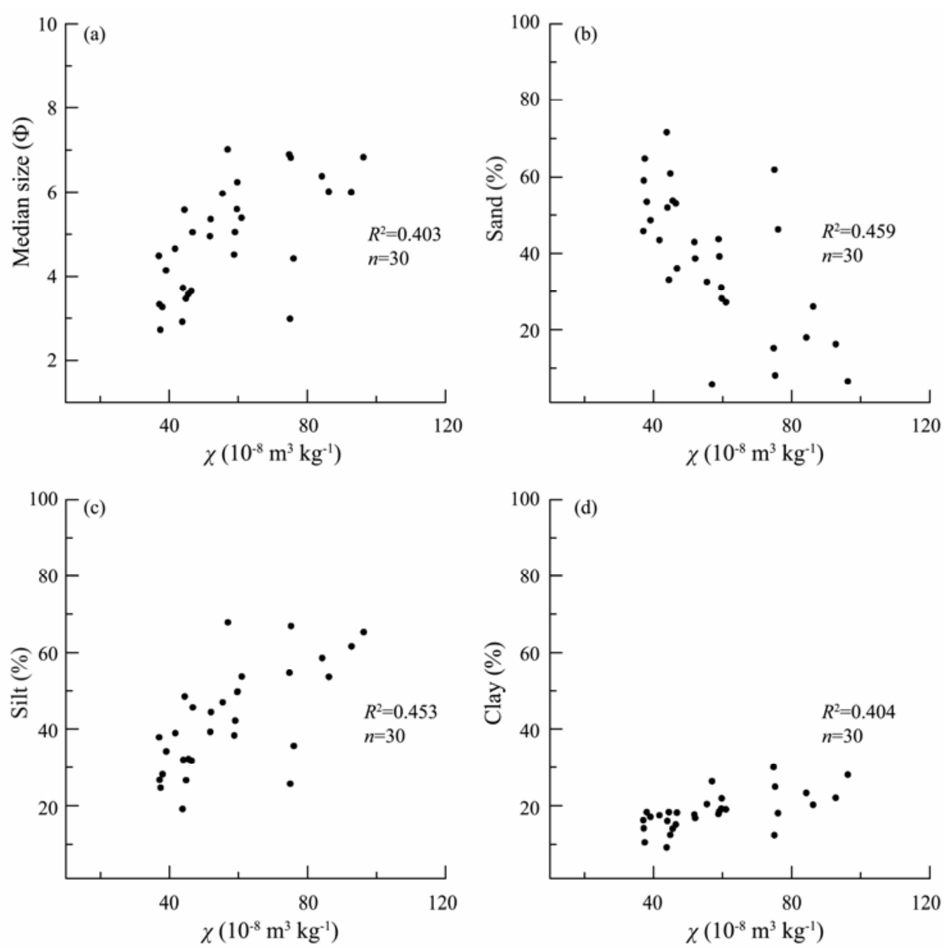

Fig.8 Correlation between magnetic susceptibility (χ) and size parameters: a) χ and median size (Φ); b) χ and sand content (%); c) χ and silt content (%); d) χ and clay content (%).

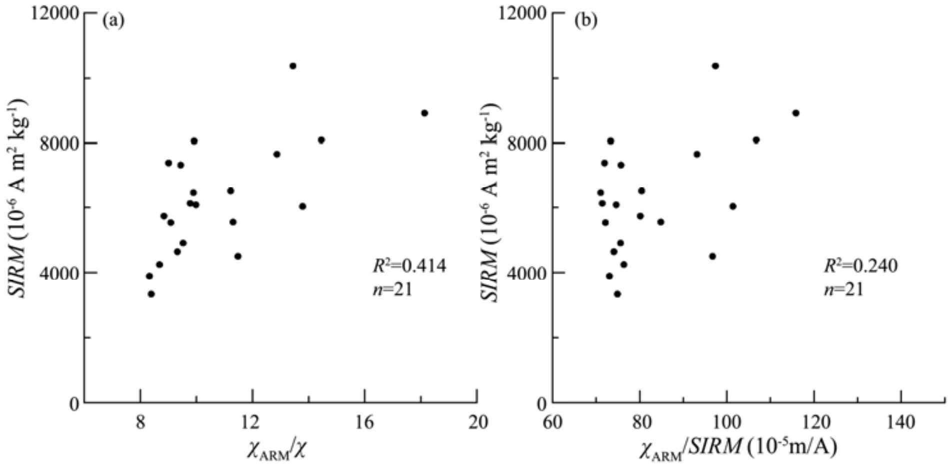

Fig.9 Correlation between magnetic susceptibility (χ) and fine magnetic domains of magnetic minerals: a) χ and χ_{ARM}/χ; b) χ and $\chi_{ARM}/SIRM$.

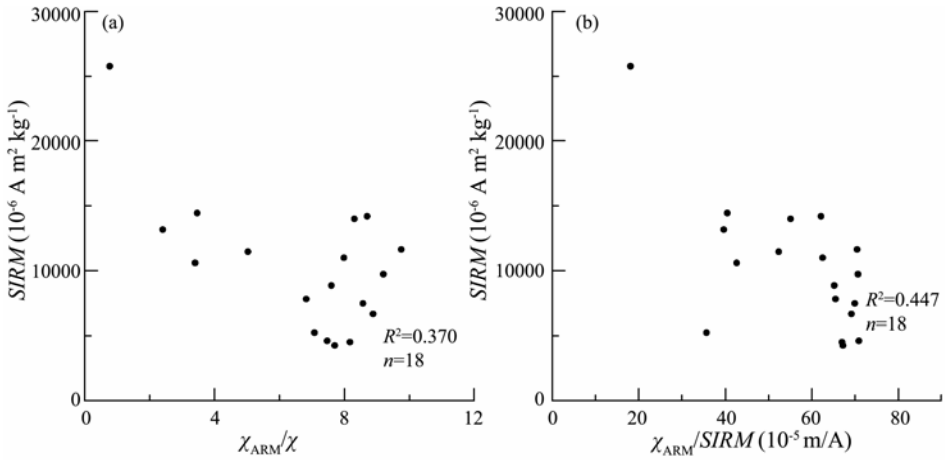

Fig.10 Correlation between magnetic susceptibility (χ) and coarse magnetic domain magnetic minerals: a) χ and χ_{ARM}/χ; b) χ and $\chi_{ARM}/SIRM$.

5.2 Provenance

Previous studies have indicated that the deposits of the Liaodong Bay are from multiple sources, including neighboring rivers, offshore currents, erosion of coastal islands and rocks. However, river input is the most prominent contributor (Qiao *et al*., 2010; Qin *et al*., 1985). Most sediments in the northern part of the Liaodong Bay consist of silt and clay, and the provenance of sediments is mainly from the surrounding rivers, such as the Daliao River, Xiaoling River, Daling River, Shuangtaizi River and so on. These sediments, under the effect of coastal currents and the resistance from tidal current (Qin *et al*., 1985; Song *et al*., 1997), are characterized by the decrease in fine fraction (silt and clay) towards the middle part, along with a gradual increase in coarse-grained components, which is consistent well with the magnetic trends of this region. In the west coast sea near the Liugu River estuary, sediments are mainly from the river itself and the dominating component is sand. The distribution of sediments is mainly controlled by alongshore currents (Qin *et al*., 1985). In the central and eastern sea areas of the Liaodong Bay, surface sediments are mainly affected by the tidal current. The fine sediments (clay and silt) have continually been washed away by the long-term tide action, leading to a high sand content in the surface sediments. In the southwest corner of the Liaodong Bay, the sediments are mainly the suspended matters from the north coastal current. Near the Liaodong Shoal, the sediments are mainly the coarse particles eroded and transported through the Bohai Strait (Xu *et al*., 2012).

Comparison had been made previously on the magnetic characteristics of surface sediment of the Liaodong Bay with those of the surface sediments of the Yellow River estuary (Wang *et al*., 2004) and the suspended matters from the Yellow River (Li *et al*., 2012) and the muddy area to the north of Shandong Peninsula (Liu *et al*., 2007) (Figs.11–12). It is found that the magnetic characteristics of the study area are similar to those of the Yellow River surface sediments and suspended matters. However, the comparison with Shandong Peninsula muddy area shows that the magnetic mineral content of the muddy area is consistent with that of the study area, but the magnetic domain is coarser and the ferrimagnetic mineral content is higher. So the main provenance of surface sediments in the Liaodong Bay is the surrounding rivers, where substantial Yellow River substances may exist.

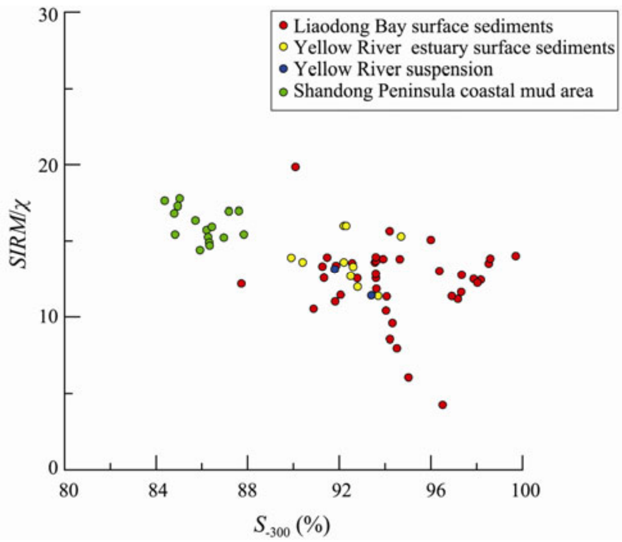

Fig.11 S_{-300} versus *SIRM*/χ, for samples from the surface sediments of Liaodong Bay and other areas.

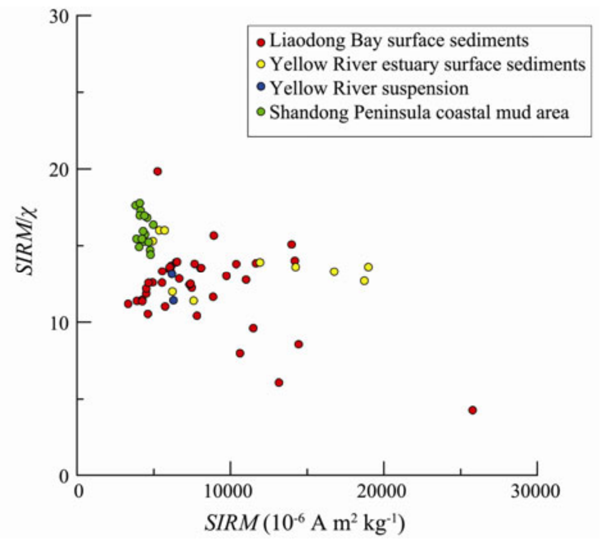

Fig.12 *SIRM* versus *SIRM*/χ, for samples from the surface sediments of Liaodong Bay and other areas.

6 Conclusions

1) The magnetic susceptibility (χ) and *SIRM* values are higher in the mid-east and southwest corner of the Liaodong Bay, owing to the enrichment of ferrimagnetic minerals, while these values are lower in the north and west of the Liaodong Bay.

2) Magnetic characteristics of the Liaodong Bay surface sediments are dominated by ferrimagnetic minerals. Magnetite is the main type of ferrimagnetic mineral.

3) There are super-paramagnetic (SP) grains in the surface sediments of the Liaodong Bay. In the mid-east and southwest corner of the Bay, the ferrimagnetic minerals are mainly composed of coarse multi-domain and pseudo-single-domain particles, while in other regions, the single-domain and pseudo-single-domain particles constitute the majority.

4) The study found that grain size is an important factor to sediment magnetic mineral content with a positive correlation with silt content, clay content and median diameter (Φ), and has a negative correlation with sand content. Meanwhile, magnetic domain also influences the content of magnetic minerals. When the magnetic domain is fine, the fine magnetic mineral is easier to accumulate than coarse magnetic mineral. Conversely, for a coarse magnetic domain, the coarse magnetic mineral tends to deposit easier than the fine magnetic mineral.

5) Correlation analysis of the magnetic characteristics suggests that the main provenance of surface sediments of the Liaodong Bay is the substances from surrounding rivers, with a part from the Yellow River.

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