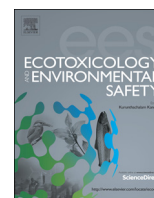




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Rare earth elements in intertidal sediments of Bohai Bay, China: Concentration, fractionation and the influence of sediment texture

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ABSTRACT

Surface sediments from intertidal Bohai Bay were assessed using a four-step sequential extraction procedure to determine their concentrations of rare earth elements (REEs) and the chemical forms in which those elements were present. The normalized ratios La/Gd and La/Yb showed that LREE contents were not significantly higher than the middle REEs or HREE contents. A negative Ce anomaly and positive Eu were observed in sand and silty sand sediments, whereas no significant Ce or Eu anomaly was found in clayey silt sediments. Residual fraction of REEs accounted for the majority of their total concentrations. Middle REEs were more easily leached than other REEs, especially in clayey silt sediment. REEs contents in the surface sediment from the intertidal Bohai Sea were consistent with data from the upper continental crust and China shallow sea sediments, indicating that they were generally unaffected by heavily anthropogenic effects from adjacent areas.

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1. Introduction

The rare earth elements (REEs) are a group of chemical elements in the periodic table with atomic numbers from 57 to 71 (Henderson, 1984; Dubinin, 2004). REEs form a coherent group of trace elements whose chemical properties change systematically and gradually across the series from La to Lu (Henderson, 1984). The coherent and predictable behavior of REEs, along with their sensitivity to pH, redox conditions and their tendency to participate in adsorption/desorption reactions, allows them to be used as input provenance markers, meteorization processes or geochemical tracers of changes in environmental conditions in water and sediments (Sholkovitz, 1992; Åstrom, 2001). REEs are useful for interpretation of diagenetic redox conditions in palaeoenvironmental research (Shields and Stille, 2001), monitoring detrital sediment sources (Grousset et al., 1998), and elucidating seawater circulation patterns (Tachikawa et al., 1999), hydrothermal fluxes (German et al., 1999), and the historic oxygenation of the oceans (Henderson, 1984; Murray et al., 1992). They are also important tools for identifying anthropogenic effects on intertidal sediment, especially those caused by unnatural liquid or

solid inputs which modify the geochemical characteristics of the sediment (Borrego et al., 2004).

Approximately 97 percent of REEs are produced in China (U.S. Geological-Survey, 2011). The industrial and agricultural usage of REEs is increasing rapidly (Xie, 1991). Even though REEs are considered to be of low toxicity, environmental contamination caused by them has already been found in some mineralized areas and soils that are affected by the long-term application of sludge (Essington and Mattigod, 1990). REEs in adequate concentrations have proven to promote crop production (Wu et al., 1983), but their effect on human health through food-chain or directly through water or air remains unclear. In recent years, the environmental behaviors of REEs have attracted increasing attention. Investigations of the background concentrations and geochemical fractionation of REEs in the environment, including sediments, soils and biological samples have been performed worldwide (e.g. Zhang et al., 1998; Leleyter et al., 1999; Cao et al., 2000; Zhang and Ishii, 2000; Yang et al., 2002; Borrego et al., 2005; Xu et al., 2010). However, information about REEs in the Bohai Sea is very scarce.

Bohai Bay is the second largest bay in the Bohai Sea, accounting for approximately one fifth of the total area of Bohai Sea. It receives industrial and domestic wastewater discharge not only from Tianjin, which is the sixth largest city in China with an urban population of approximately nine million, but also from the second largest megacity in China—Beijing. Additionally, on the western coast of Bohai Bay is located Tianjin Port, which has the fifth largest cargo throughput in

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the world. Bohai Bay receives fresh water input mainly from the Haihe River, which contributes 71.5 percent of Bohai Bay runoff (Fig. 1). Bohai Bay is a shallow water basin with a very mild-slope bottom and most of its sediments comprise fine mud. The mean water depth of Bohai Bay is around 10 m and the semi-diurnal tidal range is 0.5–2.5 m. The width of the tideland of Bohai Bay is 3–5 km and the mean velocity of the residual current is less than 0.1 m/s. The exchange of water between Bohai Bay and Bohai Sea is weak so the physical self-cleaning capacity of Bohai Bay is very poor (Tao, 2006).

As important areas that receive huge quantities of land-derived substances annually, coastal seas have attracted considerable attention. Many studies focused on the biogeochemistry of trace metals

with ecological risks—especially Cd, Cr, Cu, Hg, Pb, Ni and Zn—because they are toxic at concentrations over certain thresholds and their environmental behaviors are significantly affected by highly intense large-scale human activities (e.g. Selvaraj et al., 2004; Gao et al., 2010; Gao and Chen, 2012; Gao and Li, 2012; Zhuang and Gao, 2013; Gao et al., 2014; Zhuang and Gao, 2014). However, much less information is available about anthropogenic effects on other geochemical tracers, such as REEs in coastal marine areas. The coastal Bohai Bay is an ideal area for studying the effect of human activities on the marine environment. An investigation of the surface sediment quality and the geochemical behaviors of trace elements was carried out in the northwestern coastal Bohai Bay in May 2008, covering its intertidal and sublittoral zones and the major rivers to which it connects, and a series of papers have been published concerning the results of that investigation (Wang et al., 2011; Gao and Chen, 2012; Gao and Li, 2012; Gao et al., 2012). In the present study, both the concentrations and the fractionation of REEs in the surface sediments from intertidal Bohai Bay were determined to evaluate the response of REEs to the anthropogenic effects from surrounding areas.

2. Materials and methods

2.1. Sampling

A total of fifteen sediment samples were collected from five locations in the Bohai Bay intertidal zone in May 2008 for use in this study (Fig. 1). At each location, sampling began when the tide was lowest during the daytime of that day; beginning near the low tide line, three samples were collected in the lower intertidal zone, the middle intertidal zone and the upper intertidal zone. The undisturbed top 0–5 to 0–10 cm of the sediment was sampled and placed in acid-rinsed polyethylene zipper bags using a plastic spatula. The samples from the lower intertidal zone were labeled as A1, B1, C1, D1 and F1; those from the middle intertidal zone were labeled A2, B2, C2, D2 and F2 and those from the upper intertidal zone were labeled as A3, B3, C3, D3 and F3 (Fig. 1). All samples were stored at $\sim 4^{\circ}\text{C}$ in the dark for subsequent analysis.

2.2. Analytical methods

The sequential extraction procedure described by Rauret et al. (1999) was used herein to obtain information about the fractionations of REEs. The scheme partitions elements into four operationally defined geochemical fractions, including acid-soluble (exchangeable and bound to carbonates), reducible (bound to Fe/Mn oxyhydroxides), oxidizable (bound to organic matter and sulfides) and residual (contained within lithogenic minerals). The details of the sequential extraction protocol used in this study have been summarized in Table 1 and presented elsewhere in Gao et al. (2008, 2010).

Sample drying can reportedly change the solid phase distribution of trace elements (Rapin et al., 1986; Hjorth, 2004). Additionally, the elemental concentrations in sediments depend strongly on the grain size (Horowitz and Elrick, 1988; Howari and Banat, 2001), and a trituration treatment can potentially alter the extractability of elements (Gilliam and Richter, 1988). Therefore, wet and unground sediments were used herein in the sequential extraction procedure to reduce errors.

After the third step extraction, a mixture of concentrated HF, HNO₃ and HClO₄ (5:2:1; Li et al., 2000) was used to digest all of the remaining REEs in the residues. It was used instead of the so-called pseudototal digestion with aqua regia, which was used by Rauret et al. (1999). The total digestion of three randomly selected samples was performed by the same method as was used to determine the REEs contents in the residual fraction. The total REEs contents in sediments were estimated by summing the results for the four fractions, and they were 90–110 percent of the values obtained in the total digestion experiment.

Inductively coupled plasma mass spectrometry (Thermo X Series II) was used to determine the concentrations of REEs in this work. Five multi-element standards were used to make up a linear calibration curve. Standard solutions were run after every 30 samples to monitor and correct fluctuations of instrumental drift. The Chinese national geostandard samples of GSS-1 and GSS-8 were processed in the same way as the sample to control the analytical quality. The results matched the reference values, and the differences were all within 10 percent (most of them were within 5 percent). All plasticwares and glasswares were pre-cleaned by soaking them in 10 percent HNO₃ (v/v) for at least two days. They were then soaked and rinsed with de-ionized water. All chemicals that were used in the experiment were guaranteed to be reagent-grade or better. Blank determinations were conducted throughout the experiment for total concentration analyses and sequential extraction. All data were corrected for the dry weight of the sample.

The water content of sediments was determined gravimetrically by comparing their weights before and after an aliquot was heated at 105 °C and repeating the

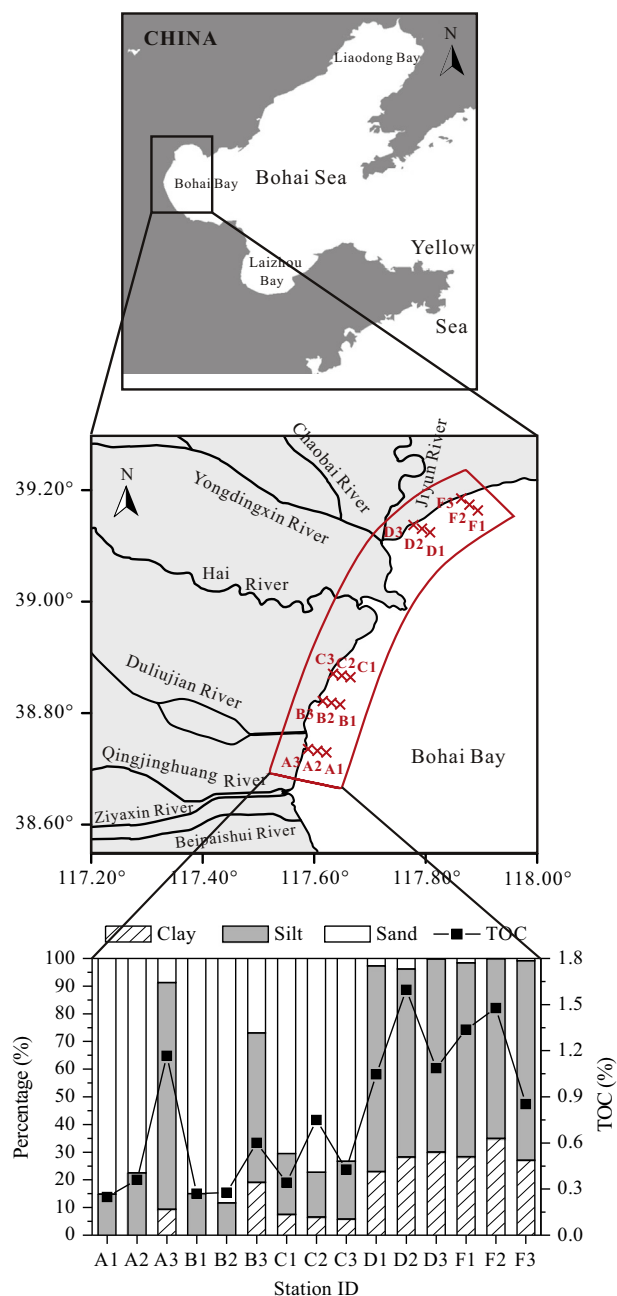


Fig. 1. Location of sampling sites in intertidal zone of Bohai Bay. The sampling sites are indicated by red crosses. A1, B1, C1, D1 and F1 were located in the lower intertidal zone, A2, B2, C2, D2 and F2 were located in the middle intertidal zone, and A3, B3, C3, D3 and F3 were located in the upper intertidal zone. The bottom panel showed the spatial variations of grain size distributions and TOC contents. (For interpretation of the reference to color in this figure, the reader is referred to the web version of this article.)

Table 1
Summary of the BCR sequential extraction protocol. For each sample, the wet weight corresponding to approximately 0.5 g dry weight based on water content measurement was used. 0.1 g residue (dry weight) from step III was used to measure Fraction 4.

Step	Fraction	Component extracted	Extraction reagent	Extraction method
I	Fraction 1, acid soluble	Exchangeable and bound to carbonates	20 ml 0.11 mol l ⁻¹ HOAc (pH 2.86)	Shaking at 22 ± 5 °C for 16 h
II	Fraction 2, reducible	Bound to Fe/Mn oxides	20 ml 0.5 mol l ⁻¹ NH ₂ OH HCl (adjusted to pH 1.5 with HNO ₃)	Shaking at 22 ± 5 °C for 16 h
III	Fraction 3, oxidizable	Bound to organic matter and sulphides	5 ml 8.8 mol l ⁻¹ H ₂ O ₂ (adjusted to pH 2.0 with HNO ₃)/another 5 ml 8.8 mol l ⁻¹ H ₂ O ₂ (adjusted to pH 2.0 with HNO ₃)/25 ml 1 mol l ⁻¹ NH ₄ OAc (adjusted to pH 2.0 with HNO ₃)	Digesting at room temperature for 1 h with occasional manual shaking, then cover the tube and heat at 85 ± 2 °C for 1 h, and then remove the cover and reduce the volume to a few milliliters/cover the tube and heat at 85 ± 2 °C for 1 h, and then remove the cover and reduce the volume to near dryness/shaking at 22 ± 5 °C for 16 h
IV	Fraction 4, residual	Within lithogenic minerals	8 ml mixture of concentrated HF, HNO ₃ and HClO ₄ (5:2:1)	Heat at a temperature of 90–155 °C for 16 h in a tightly closed digestion vessel with Teflon liner

post-heating measurements until a constant weight was obtained. The percentages of water were used to transform the substance content of the sediment from a wet-weight to a dry-weight base. The granularity of each sample was analyzed using a Malvern Mastersizer 2000 laser diffractometer that could analyze particles with sizes between 0.02 and 2000 μm. The percentages of the following three groups of grain sizes were determined to be < 4 μm (clay), 4–63 μm (silt), and > 63 μm (sand). The total organic carbon (TOC) content in the sediments was obtained by subtracting the inorganic carbon content from the total carbon, which was determined using a Shimadzu TOC-V_{CPH}/SSM-5000A and an Elementar Vario MACRO Cube CHNS analyzer, respectively.

3. Results and discussion

3.1. Sediment characteristics

The distribution of grain sizes strongly affects the geochemical behaviors of elements in sediments. As presented in Fig. 1, the sediment texture of intertidal Bohai Bay exhibits a significant spatial variation. The sediments from A3, D1–D3, and F1–F3 were dominated by silt and clay with a high TOC content. However, the sediments from A1–A2, B1–B3, and C1–C3 were dominated by sand and silt with a low TOC content. As in our earlier study (Gao and Li, 2012), which was based on the classification of Shepard (1954), the former type is called clayey silt sediment and the latter is called sand and silty sand sediments. The mean clay, silt and sand contents in sand and silty sand samples were 4.9, 22.1 and 73.0 percent, respectively, while their contents in the clayey silt samples were 25.9, 71.5 and 2.6 percent, respectively. The grain sizes in clayey silt sediments were very similar as were those in sand and silty sand sediments (Fig. 1).

3.2. REEs concentration

Table 2 presents the REEs contents in the surface sediment from intertidal Bohai Bay. As shown in the table, the REEs concentrations followed the order Ce > La > Nd > Pr > Sm and so on. The variations of REEs contents with location were small. The coefficient of variation (CV) of these contents in the sand and silty sand sediments was approximately 20 percent, while that in clayey silt sediments was about 10 percent. The smaller CV value suggests that REEs concentrations in clayey silt sediment are more uniform than those in sand and silty sand sediments. The mean REEs concentrations are generally higher in clayey silt sediment than in sand and silty sand sediments, indicating that REEs contents in sediment are strongly related to grain size. Such REEs enrichment in clay and silt fractions and their depletion in the sand fraction may be attributed to dilution by quartz and carbonate minerals (McLennan, 1989; Vital et al., 1999). Compared with those in the upper continental crust, e.g. North American Shale Composite (NASC) (Haskin et al., 1968; Gromet et al., 1984) and Post-Archean Australian Shale (PAAS) (Taylor and McLennan, 1985), and

with those in China shallow sea sediments (CSSS) (Zhao and Yan, 1994) (Table 2), the REEs contents in samples of sand and silty sand sediments were slightly lower than those in NASC, PAAS, and CSSS, while the contents in samples of clayey silt sediment were comparable with those in NASC, PAAS, and CSSS.

Table 3 presents the fourteen total REEs contents from La to Lu (ΣREE), light REEs (LREE, La to Eu) and heavy REEs (HREE, Gd to Lu), as well as the concentration ratios of LREE/HREE of the analyzed samples. In the surface sediments of intertidal Bohai Bay, ΣREE varied in the range 97.6–202.0 μg g⁻¹ with a mean of 152.1 μg g⁻¹, LREE ranged from 87.7 to 180.0 μg g⁻¹ with a mean of 136.1 μg g⁻¹, and HREE ranged from 9.9 to 22.6 μg g⁻¹ with a mean of 16.0 μg g⁻¹. LREE was 8.6 ± 0.5 times as abundant as HREE in the surface sediments. The highest ΣREE and LREE were recorded at site F2; the highest HREE was recorded at site F1, while the lowest values were always obtained at site A2. The variations of ΣREE, LREE, and HREE contents among sediments from different locations in intertidal Bohai Bay were generally small. The values of CV were 20 percent in sand and silty sand sediments and 9–11 percent in clayey silt sediment.

In coastal marine sediment, the concentration and distribution of REEs are influenced by several factors including: (1) the supply of particulate material (from a terrestrial or marine source), (2) the grain size and mineral composition of the sediment, and (3) the physical, chemical and geological processes that occur in the sediment, including changes in pH and salinity, coagulation, coprecipitation as iron hydroxides and phosphates, erosion and sedimentation (Caccia and Millero, 2007). Generally, clays contain over one and a half times as much REEs as sandstone, and the LREE/HREE ratios of sediments decrease in the order clays > sandstones > carbonates (Balashov et al., 1964; Henderson, 1984). ΣREE, LREE and HREE in clayey silt sediment were ~40 percent higher than in sand and silty sand sediments while the LREE/HREE of the former was ~10 percent lower than that of the latter, indicating that the grain size in the sediment strongly affected the REEs contents in the surface sediments from intertidal Bohai Bay (Table 3). ΣREE, LREE, HREE, and LREE/HREE in this study matched those in Huanghe River sediment (Yang et al., 2002) and fell between those in Changjiang and Po River sediments (Yang et al., 2002; Kramer et al., 2002). As indicated by Xu et al. (2010, 2012), Haihe River is the predominant source controlling the REE patterns of Bohai Bay sediment, while the environment can slightly affect the REE patterns. This conclusion may also apply to the intertidal sediment of Bohai Bay in this study.

3.3. Normalization analysis

Naturally, REEs with even atomic numbers such as Ce, Nd and Sm are more abundant than their adjacent REEs with odd atomic

Table 2

Concentrations of REEs in surface sediments from intertidal Bohai Bay: data for North American Shale Composite (NASC) (Haskin et al., 1968; Gromet et al., 1984), Post-Archean Australian Shale (PAAS) (Taylor and McLennan, 1985), and averages for China shallow sea sediments (CSSS) (Zhao and Yan, 1994). Unit is $\mu\text{g g}^{-1}$.

Sediment type	Site	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
Sand and silty sand	A1	31.9	61.7	7.43	28.4	5.22	1.09	4.26	0.70	3.80	0.81	2.19	0.39	2.24	0.35	
	A2	21.3	39.1	4.80	18.4	3.31	0.86	2.80	0.46	2.51	0.57	1.53	0.27	1.51	0.26	
	B1	27.8	54.2	6.57	24.7	4.64	1.11	3.88	0.64	3.49	0.78	2.10	0.38	2.18	0.33	
	B2	23.7	44.6	5.40	19.7	3.72	0.94	3.14	0.52	2.84	0.63	1.66	0.30	1.79	0.29	
	B3	34.3	67.8	8.20	30.5	5.66	1.14	4.84	0.76	4.03	0.90	2.35	0.43	2.43	0.39	
	C1	22.5	43.8	5.36	20.0	3.75	0.92	3.21	0.49	2.67	0.57	1.53	0.27	1.59	0.24	
	C2	24.0	46.0	5.53	20.5	3.72	0.95	3.22	0.51	2.78	0.61	1.64	0.28	1.66	0.27	
	C3	33.1	66.1	8.02	30.5	5.55	1.17	4.74	0.76	4.06	0.88	2.32	0.42	2.36	0.38	
	Mean	27.3	52.9	6.41	24.1	4.45	1.02	3.76	0.61	3.27	0.72	1.92	0.34	1.97	0.31	
	SD	5.17	11.11	1.33	5.12	0.94	0.12	0.78	0.13	0.64	0.14	0.36	0.07	0.37	0.06	
	CV (%)	19	21	21	21	21	12	21	21	20	19	19	20	19	18	
	Clayey silt	A3	32.7	68.0	8.09	29.7	5.92	1.22	5.52	0.90	4.55	1.10	2.98	0.50	2.89	0.49
		D1	34.6	69.0	8.41	31.7	6.12	1.26	5.45	0.86	4.65	1.10	2.89	0.48	2.74	0.47
		D2	34.0	72.5	8.18	30.5	6.18	1.29	5.25	0.83	4.49	1.08	2.66	0.47	2.87	0.46
D3		33.0	67.2	7.82	30.2	5.89	1.18	4.91	0.83	4.31	0.97	2.67	0.49	2.74	0.44	
F1		39.3	81.0	9.39	36.9	7.05	1.49	6.57	1.06	5.43	1.32	3.56	0.59	3.46	0.56	
F2		40.2	86.8	9.48	35.0	7.07	1.44	6.00	1.02	5.43	1.28	3.53	0.62	3.55	0.58	
F3		37.4	76.1	8.51	32.5	6.50	1.24	5.19	0.87	4.85	1.08	2.99	0.52	3.00	0.48	
Mean		35.9	74.4	8.55	32.4	6.39	1.30	5.56	0.91	4.82	1.13	3.04	0.52	3.03	0.50	
SD		3.04	7.38	0.64	2.67	0.50	0.11	0.56	0.09	0.45	0.12	0.37	0.06	0.33	0.05	
CV (%)		9	10	8	8	8	9	10	10	9	11	12	11	11	10	
NASC		31.1	66.7	7.9	27.4	5.59	1.18	5.20	0.85	5.75	1.04	3.40	0.50	3.06	0.46	
PAAS		38.2	79.6	8.8	33.9	5.55	1.08	4.66	0.77	4.68	0.99	2.85	0.41	2.82	0.43	
CSSS		33.0	67.0	7.4	29.0	5.60	1.00	5.11	0.73	3.42	0.64	1.50	0.15	2.20	0.34	

Table 3

Concentrations of total REEs (ΣREE), Light REEs (LREE: La to Eu) and Heavy REEs (HREE: Gd to Lu) (in $\mu\text{g g}^{-1}$). LREE/HREE concentration ratio, normalized La/Gd and La/Yb concentration ratios and values of δCe and δEu in surface sediments from intertidal Bohai Bay, Changjiang River and Huanghe River (Yang et al., 2002) and Po River (Kramer et al., 2002). Subscript n stands for NASC, p stands for PAAS, and c stands for CSSS.

Sediment type	Site	ΣREE	LREE	HREE	LREE/HREE	(La/Gd) _n	(La/Yb) _n	(La/Gd) _p	(La/Yb) _p	(La/Gd) _c	(La/Yb) _c	δCe_n	δEu_n	δCe_p	δEu_p	δCe_c	δEu_c	
Sand and silty sand	A1	150.5	135.7	14.7	9.21	1.25	1.40	0.91	1.05	1.16	0.95	0.94	1.05	0.92	1.08	0.93	1.23	
	A2	97.6	87.7	9.9	8.86	1.27	1.39	0.93	1.04	1.18	0.94	0.91	1.29	0.89	1.33	0.90	1.51	
	B1	132.8	119.0	13.8	8.63	1.20	1.26	0.87	0.94	1.11	0.85	0.94	1.19	0.93	1.23	0.94	1.40	
	B2	109.2	98.0	11.2	8.76	1.26	1.30	0.92	0.98	1.17	0.88	0.92	1.26	0.91	1.30	0.92	1.47	
	B3	163.7	147.6	16.1	9.15	1.19	1.39	0.87	1.04	1.10	0.94	0.95	1.00	0.93	1.03	0.94	1.17	
	C1	106.8	96.2	10.6	9.10	1.17	1.39	0.85	1.04	1.08	0.94	0.94	1.21	0.92	1.25	0.93	1.42	
	C2	111.7	100.8	11.0	9.18	1.25	1.42	0.91	1.07	1.16	0.96	0.94	1.25	0.92	1.29	0.93	1.46	
	C3	160.4	144.5	15.9	9.08	1.17	1.38	0.85	1.04	1.08	0.93	0.95	1.04	0.94	1.08	0.95	1.22	
	Mean	129.1	116.2	12.9	9.00	1.22	1.37	0.89	1.03	1.13	0.93	0.94	1.16	0.92	1.20	0.93	1.36	
	SD	26.3	23.8	2.5	0.21	0.04	0.06	0.03	0.04	0.04	0.04	0.01	0.11	0.01	0.12	0.01	0.13	
	CV (%)	20	20	20	2	4	4	4	4	4	4	2	10	2	10	2	10	
	Clayey silt	A3	164.6	145.7	18.9	7.70	0.99	1.11	0.72	0.84	0.92	0.76	0.98	0.98	0.96	1.01	0.97	1.14
		D1	169.7	151.1	18.6	8.11	1.06	1.24	0.77	0.93	0.98	0.84	0.95	1.00	0.93	1.03	0.94	1.17
		D2	170.8	152.7	18.1	8.43	1.08	1.17	0.79	0.87	1.00	0.79	1.02	1.03	1.00	1.06	1.01	1.21
D3		162.6	145.3	17.4	8.37	1.12	1.18	0.82	0.89	1.04	0.80	0.98	1.01	0.96	1.04	0.97	1.18	
F1		197.6	175.1	22.6	7.76	1.00	1.12	0.73	0.84	0.92	0.76	0.99	1.00	0.97	1.03	0.98	1.17	
F2		202.0	180.0	22.0	8.18	1.12	1.11	0.82	0.84	1.04	0.75	1.04	1.01	1.03	1.04	1.04	1.18	
F3		181.3	162.3	19.0	8.54	1.20	1.23	0.88	0.92	1.11	0.83	1.00	0.98	0.99	1.01	1.00	1.14	
Mean		178.4	158.9	19.5	8.16	1.08	1.17	0.79	0.88	1.00	0.79	1.00	1.00	0.98	1.03	0.99	1.17	
SD		15.9	14.0	2.0	0.33	0.08	0.05	0.05	0.04	0.07	0.04	0.03	0.02	0.03	0.02	0.03	0.02	
CV (%)		9	9	11	4	6	5	6	5	6	5	3	2	3	2	3	2	
Total mean		152.1	136.1	16.0	8.6	1.2	1.3	0.8	1.0	1.1	0.9	1.0	1.1	1.0	1.1	1.0	1.3	
Total SD		33.2	29.2	4.1	0.5	0.1	0.1	0.1	0.1	0.1	0.04	0.1	0.04	0.1	0.04	0.1		
Total CV (%)		22	21	25	6	8	9	8	9	8	4	11	4	11	4	11		
Changjiang River		186.6	168.3	18.3	9.2	1.1	1.5	0.8	1.2	1.0	1.1	1.0	1.0	1.0	1.0	1.1		
Huanghe River		148.0	132.8	15.2	8.7	1.1	1.3	0.8	1.1	1.0	1.0	1.0	0.9	1.0	0.9	1.0		
Po River		136.4	121.3	15.1	8.0	1.1	1.2	0.8	0.9	1.0	0.93	1.0	1.0	1.0	1.2	1.0		

Note: 1. $\delta\text{Ce} = 2 \times (\text{Ce}/\text{Ce}_{n,p, \text{ or } c}) / ((\text{La}/\text{La}_{n,p, \text{ or } c}) + (\text{Pr}/\text{Pr}_{n,p, \text{ or } c}))$.
 2. $\delta\text{Eu} = 2 \times (\text{Eu}/\text{Eu}_{n,p, \text{ or } c}) / ((\text{Sm}/\text{Sm}_{n,p, \text{ or } c}) + (\text{Gd}/\text{Gd}_{n,p, \text{ or } c}))$.

numbers. This even-odd variation in the natural abundance of elements and their isotopes is known as the “Oddo–Harkins effect” and makes it difficult to compare REEs abundance graphically. To eliminate this effect, measured REEs concentrations are customarily normalized to the REEs contents in shale in the field of

marine geochemistry. Shale is representative of the REEs composition in the upper continental crust, and therefore, this normalization can avoid complication in the variation of REEs absolute concentrations due to their natural abundance (Nozaki et al., 2000; Wood et al., 2006). However, several datasets on the mean

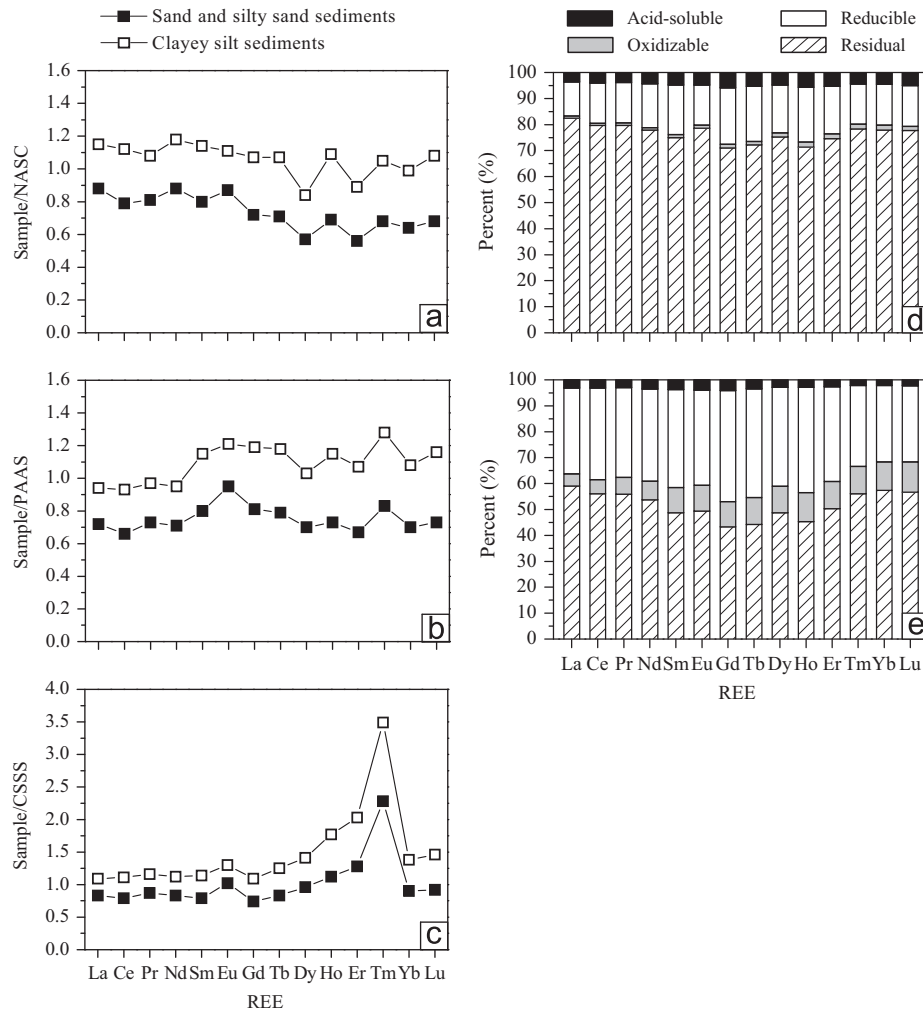


Fig. 2. NASC (a), PAAS(b) and CSSS-normalized (c) REEs patterns of sand and silty sand sediments and clayey silt sediments in intertidal Bohai Bay, based on average data. The distribution of REEs among different chemical fractions of sand and silty sand sediments (d) and clayey silt sediments (e) is also shown.

REEs contents in shale have been used for normalization in the literature (McLennan, 1989; Webb and Kamber, 2000; Chen et al., 2005; Chaillou et al., 2006). Although the major features of these datasets are similar to each other, the normalized values vary as much as ~20 percent, particularly for HREE (Alibo and Nozaki, 1999). In this study, REEs concentrations in NASC and PAAS shale were selected to normalize the measured REEs concentrations (Fig. 2a, b). REEs values in CSSS were also used for comparison (Fig. 2c).

The normalized REEs values generally exceeded 1.0 in clayey silt sediments, indicating that REEs were more abundant in this sediment than in the upper continental crust or CSSS. However, the normalized REEs concentrations were usually less than 1.0 in sand and silty sand sediments, revealing REEs depletion in such sediment relative to the upper continental crust or CSSS (Fig. 2a–c). The CSSS-normalized REEs pattern exhibited a distinct Tm maximum whereas NASC- and PAAS-normalized REEs patterns did not (Fig. 2a–c), owing to the lower Tm content in CSSS than that in NASC and PAAS (Table 2).

In the surface sediment from intertidal Bohai Bay, the normalized concentration ratios of La/Gd and La/Yb were generally uniform. They varied around 1.0, indicating that the LREE contents were not significantly higher than the middle REEs or HREE contents. However, the mean ratios in sand and silty sand sediments were always slightly higher (~10 percent) than those in clayey silt sediment. The total mean ratios were comparable to

those in the sediments from Changjiang, Huanghe and Po Rivers (Table 3).

Ce and Eu anomalies are commonly observed because these two elements are present in nature not only as trivalent ions, like all other REEs, but also with other valences (Ce^{4+} and Eu^{2+}). Ce^{3+} is apt to be oxidized to Ce^{4+} in oxygenated aqueous environment and Ce^{4+} tends to be more rapidly removed by particle scavenging than the other REEs (trivalent). Consequently, a relative depletion of Ce with respect to its REE neighbors La and Pr must occur (Sholkovitz et al., 1994; Nozaki et al., 2000). The anomalous behavior of Ce mentioned above is usually indicated by the so-called Ce anomaly (δCe), which is calculated as $\delta Ce = 2(Ce/Ce_{n, p, or c}) / [(La/La_{n, p, or c}) + (Pr/Pr_{n, p, or c})]$. Subscript n stands for NASC, p stands for PAAS, and c stands for CSSS (the same hereafter). Diagenetic remobilization of Eu is possible under conditions of reduction to Eu^{2+} at low oxidation potential and Eu is reprecipitated in the 3+ state in environments of high oxidation potential, yielding positive Eu anomalies in highly oxidized sediments (Macrae et al., 1992). Eu anomaly (δEu) is calculated as the ratio of $\delta Eu = 2(Eu/Eu_{n, p, or c}) / [(Sm/Sm_{n, p, or c}) + (Gd/Gd_{n, p, or c})]$. At sampling sites with sand and silty sand sediments, the surface sediments had negative Ce anomalies (mean value 0.92–0.94 for each δCe) and positive Eu anomalies (mean value: 1.16–1.36 for δEu) (Table 3). However, at sampling sites with clayey silt sediment, the surface sediments did not exhibit a significant Ce or Eu anomaly, and each δCe and δEu had a value of around 1.00, except for δEu_{CSSS} , which had a value of 1.17. The Ce

anomaly suggested stronger oxidation in the sand and silty sand sediments than in the clayey silt sediment. Sholkovitz et al. (1993) suggested that geologically inherited features of plagioclase feldspar and potassium feldspar have large positive Eu anomalies. Liu et al. (2007) reported relatively high potassium feldspar and plagioclase contents in sandstones from Bohai Bay. Therefore, the observed positive Eu anomaly in sand and silty sand sediments can be reasonably related to the feldspar content in the intertidal Bohai Bay. Ce and Eu anomalies in the surface sediment of the intertidal Bohai Bay, especially in the clayey silt sediment, are quite in line with those of Changjiang, Huanghe and Po River (Table 3), probably owing to their similar mineral compositions.

3.4. Fractionation

The fractionation of metals is critical to their potential toxicity and mobility (Maiz et al., 2000). The measurement of total metal concentration is undoubtedly the most effective way of evaluating the quality of sediment. However, other approaches must be used to understand the potential mobility, bioavailability and toxicity of metals in sediments, because the properties of metals in sediments depend on not only their total contents but also their physicochemical form (Gleyzes et al., 2002). The sequential extraction technique was proposed to provide information about the strength and mechanism of the association of metal with sediments (Tessier et al., 1979).

Fig. 2d and e presents the percentages of the four fractions of REEs in surface sediments from intertidal Bohai Bay. In sand and silty sand sediments, residual fraction of REEs accounted for 70.2 percent (Gd)–81.9 percent (La) of their total concentrations. In clayey silt sediments, the percentages of the residual fraction varied from 43.3 percent (Gd) to 59.0 percent (La). Dominance of residual fraction indicated that most REEs were bound to mineral lattices in surface sediments of intertidal Bohai Bay, which finding was consistent with the finding of Zhao and Yan (1994), who reported that clay minerals are important reservoirs of REEs in Chinese coastal marine sediments.

In the sand and silty sand sediments, fractions 1 to 3 accounted for 4.2–6.7, 13.1–21.7, and 0.8–2.0 percent, respectively, of the total concentrations of REEs, while in clayey silt sediments, the corresponding fractions were 2.2–4.1, 29.4–42.9, and 4.7–11.7 percent (Fig. 2d, e). The mean REEs contents in the four fractions followed the order of residual (75.9 percent) > reducible (17.4 percent) > acid soluble (5.4 percent) > oxidizable (1.4 percent) in sand and silty sand sediments, and residual (51.8 percent) > reducible (36.0 percent) > oxidizable (9.2 percent) > acid soluble (3.1 percent) in clayey silt sediments. The approximately seven-fold increase of REEs contents in oxidizable fraction in clayey silt sediments relative to sand and silty sand sediments suggested that REEs prefer to bind to organic matter and sulfides in finer sediments of the intertidal Bohai Bay.

Since cerium has an affinity towards oxides (e.g. De Baar et al., 1985; Braun et al., 1990; Tachikawa et al., 1997), an abundance of oxides can result in the positive cerium anomaly of the total sample (Leleyter et al., 1999). These results could explain why the clayey silt sediments in the intertidal Bohai Bay, which have a more reducible fraction (Fig. 2d, e), have a lesser cerium anomaly (Fig. 2a–c).

The sand and silty sand sediments, which have a more important acid-soluble fraction (Fig. 2d, e), have a more important positive europium anomaly (Fig. 2a–c). This result was similar to the finding in the Sebou River sediment (Leleyter et al., 1999). The reason lies in the affinity of europium toward carbonates since the ionic radius of Eu^{2+} is similar to Sr^{2+} (Shannon, 1976) which can provoke some Sr substitutions in carbonates (Brookins, 1989).

Table 4

Pearson correlation matrix of REEs parameters, grain size, and TOC contents.

	Clay (%)	Silt (%)	Sand (%)	TOC (%)
ΣREE ($\mu\text{g g}^{-1}$)	0.81 ^a	0.78 ^a	−0.82 ^a	0.74 ^b
LREE ($\mu\text{g g}^{-1}$)	0.81 ^a	0.77 ^a	−0.81 ^a	0.72 ^b
HREE ($\mu\text{g g}^{-1}$)	0.81 ^a	0.84 ^a	−0.86 ^a	0.80 ^a
LREE/HREE	−0.56 ^c	−0.79 ^a	0.74 ^b	−0.74 ^b
(La/Gd) _{NASC}	−0.60 ^c	−0.81 ^a	0.77 ^a	−0.77 ^a
(La/Yb) _{NASC}	−0.68 ^b	−0.79 ^a	0.78 ^a	−0.81 ^a
(La/Gd) _{PAAS}	−0.57 ^c	−0.78 ^a	0.74 ^b	−0.75 ^b
(La/Yb) _{PAAS}	−0.69 ^b	−0.79 ^a	0.79 ^a	−0.81 ^a
(La/Gd) _{CSSS}	−0.60 ^c	−0.80 ^a	0.76 ^a	−0.76 ^a
(La/Yb) _{CSSS}	−0.69 ^b	−0.78 ^a	0.78 ^a	−0.82 ^a
$\delta\text{Ce}_{\text{NASC}}$	0.85 ^a	0.74 ^b	−0.81 ^a	0.87 ^a
$\delta\text{Eu}_{\text{NASC}}$	−0.71 ^b	−0.81 ^a	0.80 ^a	−0.62 ^c
$\delta\text{Ce}_{\text{PAAS}}$	0.82 ^a	0.70 ^b	−0.77 ^a	0.82 ^a
$\delta\text{Eu}_{\text{PAAS}}$	−0.71 ^b	−0.81 ^a	0.81 ^a	−0.63 ^c
$\delta\text{Ce}_{\text{CSSS}}$	0.82 ^a	0.70 ^b	−0.77 ^a	0.82 ^a
$\delta\text{Eu}_{\text{CSSS}}$	−0.71 ^b	−0.81 ^a	0.81 ^a	−0.63 ^c
Acid-soluble REEs (%)	−0.69 ^b	−0.62 ^c	0.66 ^b	−0.62 ^c
Reducible REEs (%)	0.82 ^a	0.88 ^a	−0.89 ^a	0.92 ^a
Oxidizable REEs (%)	0.84 ^a	0.85 ^a	−0.88 ^a	0.89 ^a
Residual REEs (%)	−0.80 ^a	−0.87 ^a	0.88 ^a	−0.90 ^a

^a $P < 0.001$.

^b $0.001 < P < 0.01$.

^c $0.01 < P < 0.05$.

The percentages of residual fractions from La to Lu took on concave shapes, while the other fractions, namely acid soluble, reducible and oxidizable fractions took on convex shapes (Fig. 2d, e). This phenomenon suggests that middle REEs are more easily leached than other REEs, especially in clayey silt sediment. Many researchers have tried to determine the mechanism of middle REEs enrichment in the non-residual fractions. Gosselin et al. (1992) proposed one potential fractionation mechanism as solid-liquid exchange, which includes primary ion exchange or adsorption/desorption on mineral surfaces. Wang et al. (1994) interpreted middle REEs enrichment in the non-residual fractions as being caused by the stability of the partially filled 4f electron shells in the REEs. The middle REEs enrichment in the acid soluble and reducible fractions might be explained as a result of the middle REEs enrichment in carbonate and Fe–Mn coatings (Palmer, 1985). The middle REEs enrichment in the oxidizable fraction may be explained by the complexing ability of REEs with several kinds of carboxylic acids which roughly follow convex shapes (Zhang et al., 1998).

Table 4 presents the correlation matrix for REEs parameters, grain sizes and TOC contents. The concentrations of ΣREE , LREE, HREE, δCe and percentages of fractions 2 and 3 are positively correlated with clay, silt and TOC contents and negatively correlated with sand content. Whereas, LREE/HREE, La/Gd, La/Yb, δEu and percentages of fractions 1 and 4 are negatively correlated with clay, silt and TOC contents and positively correlated with sand content. These results show that REEs parameters are affected by both the distribution of sediment grain sizes and the amount of organic matter. Sediments with finer grains and/or higher organic matter would have higher REEs content, less LREE than middle REEs or HREE, more positive Ce anomaly and more negative Eu anomaly, more of the reducible and oxidizable fractions, and less of the acid-soluble and residual fractions.

4. Conclusions

This study investigated REEs concentrations and their chemical forms in surface sediments from the intertidal region of Bohai Bay. The results revealed that grain size and organic matter content significantly affected REEs concentrations. REEs were more abundant in sediments with finer grains and/or higher organic matter

content. Residual fractions of all REEs were the majority of their total concentration, whereas the exchangeable fraction was in a low proportion. Middle REEs are more easily leached than other REEs, especially in clayey silt sediment. REEs compositions in the intertidal Bohai Sea were consistent with data for the upper continental crust and China Shallow Sea sediments, indicating that Bohai Bay cannot be regarded as one of the highly polluted marine areas of China, at least with respect to REEs.

Although REEs not appear to be essential for living beings, they can be absorbed and speed up metabolism at low concentration. Considering that REEs have been widely used in agriculture, animal husbandry and fishery industry, and that sediment of intertidal zone, as an important reservoir of discharges from human activity, will probably absorb increasing amount of REEs, further studies are still required to discover the role of intertidal zone plays in the biogeochemical cycling of REEs and its feedback on human beings. The results of this study can provide a baseline for future comparison.

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