

Geochemistry of Rare Earth Elements in the Dissolved, Acid-Soluble and Residual Phases in Surface Waters of the Changjiang Estuary

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The concentrations of rare earth elements in the dissolved, acid-soluble and residual phases in surface waters of the Changjiang Estuary were determined using ICP-MS. The main purposes of the study are to understand the estuarine geochemistry of rare earth elements and to explore water-particle interactions in the Changjiang estuarine mixing zone. The results show that there are two distinct processes operating on dissolved rare earth elements in the estuary: large scale removal at low salinities due to salt-induced coagulation and remarkable release at mid to high salinities. These processes result in modification of the effective river water flux and the systematical fractionation of the dissolved rare earth elements toward the East China Sea. The increase in concentration of dissolved rare earth elements in the mid to high salinity waters of the Changjiang Estuary suggests a sediment source in the mixing zone of the estuary, which is located over a shallow, broad shelf where there is extensive physical contact between bottom sediment and estuarine waters. Acid-soluble rare earth elements, the concentrations of which also dropped sharply in the low salinity region, appear to be controlled by salt-induced coagulation process and intense deposition of suspended particulate matter in the low salinity region. In the mid to high salinities, all acid-soluble rare earth element concentrations increase slightly with increasing salinity, suggesting that resuspension of sediments occurred. In contrast, the residual rare earth element concentrations are relatively constant with salinity variation in the Changjiang estuarine surface waters.

Keywords:

- Rare earth elements,
- Changjiang Estuary,
- removal,
- release,
- fractionation.

1. Introduction

The rare earth elements (REEs) are an extremely coherent group in terms of chemical behavior and have been investigated intensively as geochemical tracers in rivers, estuaries and oceans for characterizing water mass transportation and water mixing (Goldstein and Jacobsen, 1988; Elderfield *et al.*, 1990; Byrne and Lee, 1993; Lawrence and Kamber, 2006). Estuaries are complex biogeochemical and physically dynamic systems that act as buffers between the land and the ocean. The net flux of riverine REEs to the open ocean depends on their geochemical behavior at the estuary (Elderfield *et al.*, 1990; Sholkovitz, 1993). Geochemical studies of the REEs in an estuary always involve several objectives: (1) elucidate the geochemical processes that determined

the fate of the REEs; (2) discuss the fractionation behaviors of the REEs; and (3) estimate the net riverine contribution to the REE budget of the world oceans.

The Changjiang River is the third largest river in terms of length (6300 km) and fourth in terms of water discharge (928 km³/year) in the world. Due to intense deposition of abundant suspended material transported from the Changjiang River, the upper Changjiang Estuary is very shallow. Hence, material exchange processes frequently occur between surface waters and bottom sediments in the Changjiang estuarine mixing zone (Beardsley *et al.*, 1985; Sternberg *et al.*, 1985). These processes can alter the REE composition of surface waters. Therefore, studies of the geochemical behavior of REEs in the dissolved, acid-soluble and residual phases in the Changjiang estuarine waters are of great significance in interpreting the geochemistry of the REEs in the East China Sea and the West Pacific Ocean, and in acquiring a better understanding of geochemical processes

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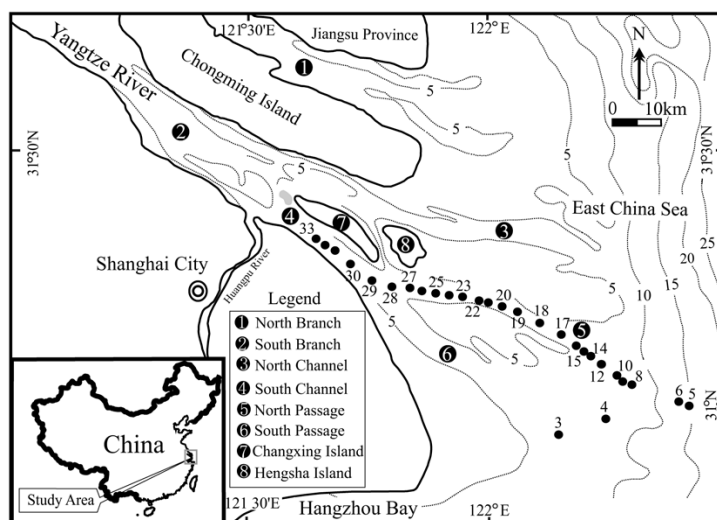


Fig. 1. Map of the Changjiang Estuary and sampling stations. Dot lines are isobaths and depth is given in meters.

such as water-particle and water-sediment interactions during estuarine mixing.

2. Sampling and Analytical Methods

A map of the Changjiang Estuary and sampling locations is given as Fig. 1. The Changjiang Estuary is separated into four long channels (North Branch, North Channel, North Passage and South Passage) by Chongming, Changxing and Hengsha islands and two submerged banks (Fig. 1). Fluvial input mainly runs through these long passages and into the East China Sea (Beardsley *et al.*, 1985; Edmond *et al.*, 1985; Pan and Sun, 1996). The North Passage, which takes on more than 50% of the discharge of the Changjiang River, is one of the major passages in the Changjiang Estuary (Pan and Sun, 1996). Thus, our sampling stations were concentrated along the North Passage (Fig. 1). Estuarine water samples were collected in surface water of the North Passage with salinity varying from 0.15 to 19 on November 4 and 5, 1998. River water from the Datong station, which is located about 650 km west of Shanghai city and is the most downstream station without tidal influence of the main channel of the Changjiang River, was also collected as the representative end-member of Changjiang river water. Sampling was done using a 10 L acid-cleaned polyethylene bucket. The samples used for the determination of the dissolved REEs were filtered through acid-cleaned 0.1 μm hollow fiber membranes (Millipore) immediately after collection and acidified to $\text{pH} < 1.6$ using Q-HCl acid and stored in 2 L high-density polyethylene bottles. Additional water samples were also obtained at each station and filtered in situ to measure major anions and cations, the latter being acidified with HNO_3 . Base cations were analyzed within one

week by graphite furnace atomic absorption spectrometry (PE.51002, PC-50) after appropriate dilution and anions by ion chromatography (Dionex ICS-90). Salinity, pH, temperature and dissolved oxygen data were obtained in situ using handy parameter sensors.

The suspended particulate matter (SPM) is an important vector for the movement of REEs within the hydrological cycle. REEs in the SPM can be further classified into a non-residual fraction adsorbed onto SPM and virtually insoluble residual REEs. Numerous methods have been used to extract different particle phases: one involves sequential removal of different phases by different chemical reagents (Tessier *et al.*, 1979); another method extracts the acid-soluble fraction including carbonates and Fe-Mn oxide coatings from the SPM with diluted acid (Sholkovitz *et al.*, 1994; Négre *et al.*, 2000). We adopted the latter method in the present study. An unfiltered estuarine water sample (2L) was directly acidified to $\text{pH} \approx 1.5$ with HCl acid after collection and filtered through 0.22 μm filters after 1 week for the determination of the acid-soluble REEs. The residual solids retained on the membrane were also collected and weighed for the concentration of SPM and residual REE measurement. The concentrations of acid-soluble REEs were directly measured by ICP-MS (Finnigan MAT ELEMENT). The concentrations of residual REEs were measured by ICP-MS after decomposition in a mixed acid (conc. HF + HNO_3 + HClO_4 volume ratio 25:50:25) at about 220°C on a hotplate for about 4–6 h.

Preconcentration and purification of dissolved REEs were performed by solvent extraction using a mixture of HDEHP (2-ethylhexyl hydrogen phosphate) and H_2MEHP (2-ethylhexyl dihydrogen phosphate) in heptane and back

Table 1. Dissolved REE concentrations in the Changjiang river water and the Changjiang estuarine surface water (pmol kg⁻¹). Corresponding salinity data are also shown.

No.	Salinity	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
River water	0.00	228.69	62.14	123.86	17.05	69.24	13.76	3.25	14.78	2.13	12.41	2.81	8.06	0.91	6.16	0.74
33	0.15	134.42	29.63	58.86	7.16	33.42	6.75	1.73	9.88	1.29	8.79	1.64	4.70	0.63	3.65	0.56
32	0.30	123.66	26.65	52.09	6.49	30.38	6.17	1.64	9.35	1.23	8.28	1.49	4.34	0.60	3.39	0.52
31	0.34	116.67	23.91	45.84	5.77	27.63	5.73	1.50	8.80	1.13	7.60	1.41	3.96	0.54	3.11	0.47
30	0.35	107.66	21.81	42.71	5.35	25.80	5.33	1.41	8.03	1.04	7.00	1.30	3.66	0.49	2.77	0.45
29	0.38	102.16	19.81	37.38	4.72	23.20	4.93	1.30	7.82	1.02	6.90	1.24	3.45	0.46	2.65	0.42
28	0.45	110.22	21.53	42.71	5.31	26.33	5.47	1.43	8.06	1.05	7.11	1.31	3.76	0.51	2.86	0.46
27	0.40	110.19	21.13	41.67	4.92	25.16	5.49	1.43	8.30	1.07	7.33	1.33	3.70	0.50	2.86	0.45
26	0.42	99.47	18.71	34.38	4.59	23.58	4.84	1.29	7.46	0.96	6.47	1.21	3.40	0.44	2.48	0.38
25	1.05	116.00	19.91	39.06	4.72	24.49	5.11	1.36	7.90	1.01	6.75	1.26	3.46	0.49	3.01	0.50
24	1.60	116.12	21.70	40.26	5.28	25.87	5.31	1.41	8.26	1.03	6.99	1.28	3.52	0.51	3.12	0.51
23	1.20	110.09	20.21	39.06	4.94	24.50	5.10	1.38	7.66	0.99	6.61	1.21	3.40	0.48	2.95	0.46
22	0.85	98.12	15.64	30.21	3.89	18.77	4.06	1.07	6.35	0.83	5.97	1.12	3.23	0.44	2.54	0.41
21	0.80	116.94	23.18	42.71	5.26	26.97	5.48	1.47	8.42	1.08	7.43	1.39	4.16	0.55	3.06	0.49
20	0.90	152.02	25.95	48.96	6.49	30.68	6.17	1.68	9.74	1.26	8.89	1.73	5.02	0.71	4.15	0.66
19	3.40	164.67	27.09	50.66	6.71	31.25	6.53	1.70	9.70	1.25	9.12	1.84	5.50	0.78	4.59	0.72
18	4.40	154.02	24.37	45.68	6.18	28.19	5.83	1.59	8.95	1.16	8.38	1.70	5.00	0.72	4.19	0.66
17	4.90	166.67	26.21	47.40	6.71	31.36	6.77	1.81	10.35	1.32	9.17	1.85	5.45	0.78	4.58	0.72
16	6.00	135.16	22.57	40.46	5.46	26.94	5.71	1.51	8.88	1.16	7.94	1.49	4.43	0.62	3.68	0.57
15	8.00	146.94	22.83	43.67	5.68	27.78	5.77	1.55	9.11	1.21	8.43	1.60	4.69	0.67	3.85	0.59
14	8.20	158.41	25.27	43.62	6.38	29.93	5.98	1.59	9.46	1.30	9.28	1.73	5.02	0.72	4.30	0.67
12	9.00	185.37	28.68	45.25	6.87	32.57	6.94	1.76	10.39	1.36	9.64	1.98	5.92	0.85	5.09	0.83
10	11.00	235.65	32.19	47.28	7.83	37.78	7.48	2.04	12.27	1.66	11.51	2.51	7.40	1.07	6.46	1.07
9	11.50	239.26	30.50	42.67	7.67	37.09	7.07	1.95	11.99	1.63	11.37	2.50	7.32	1.08	6.53	1.10
8	9.20	196.31	28.71	41.81	6.80	31.94	6.41	1.77	10.43	1.42	10.20	2.12	5.99	0.86	5.14	0.84
6	18.00	341.42	38.68	50.09	9.62	47.78	9.06	2.45	16.15	2.11	15.72	3.50	10.13	1.52	9.34	1.60
5	19.00	369.30	40.01	49.01	9.74	47.39	9.11	2.51	16.52	2.14	16.00	3.78	10.82	1.63	9.81	1.74
4	16.80	327.47	36.78	47.36	9.11	43.82	8.19	2.35	15.26	2.03	14.89	3.36	9.48	1.41	8.60	1.47
3	16.00	325.28	37.01	52.09	9.07	43.96	8.46	2.37	15.04	1.99	14.61	3.35	9.54	1.41	8.66	1.48

extraction from heptane to HCl acid before determination by ICP-MS. Indium was used as internal standard to monitor the efficiency of the chemical procedure and Rh was used to monitor the stability of ICP-MS. The following masses were used for REE measurement: ⁸⁹Y, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵¹Eu, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁷Er, ¹⁶⁹Tm, ¹⁷³Yb and ¹⁷⁵Lu. These isotopes are free of isobaric interferences and REEO⁺ and BaO⁺ are low. The analytical procedure for dissolved REEs has been described in detail by Shabani *et al.* (1990) and Zhang (1995). The entire procedure was accomplished in a Class-100 laboratory. Millipore-Q water (18.2 MΩ) and high-purity reagents were used. The blanks of the entire procedure were Y 1000, La 300, Ce 600, Pr 40, Nd 200, Sm 40, Eu 10, Gd 70, Tb 10, Dy 60, Ho 10, Er 40, Tm 4, Yb 30 and Lu 5 pmol kg⁻¹. They were about 10% for La and Ce, and 5~8% for other REEs comparing to the lowest concentrations of dissolved REEs in water samples after preconcentration. The relative standard deviations (RSD) for the determination of REEs were better than 10% in estuarine water samples and about 2% to 5% in acid-soluble and residual samples. The standard deviations for REE analysis of the standard reference solution (stock solution, CRM 130, Custom Assurance Standard, SPEX CertiPrep, Inc.) were better than ±10‰ (*n* = 11).

3. Results

3.1 Hydrology

The hydrographic properties, i.e., temperature, salinity and dissolved oxygen and the concentrations of major cations and anions, were published previously by Wang and Liu (2003). The concentrations of dissolved, acid-soluble and residual REEs are illustrated in Tables 1, 2 and 3, respectively. During water mixing in an estuary, major cations such as Ca²⁺, Mg²⁺ and Sr²⁺ are expected to behave conservatively and can be described by simple mixing of riverine and seawater end-members. In the present study, although the salinity did not display a perfectly smooth decrease as the sampling progressed upstream, the concentrations of Ca²⁺, Mg²⁺ and Sr²⁺ were strongly correlated with field salinity measurements, confirming that this data set can be treated as two-component mixing (Wang and Liu, 2003). There is no evidence of additional water input (e.g. saline groundwater) besides the riverine and seawater end-members in the Changjiang Estuary. The scatter of some salinity data as sampling that progressed upstream is attributed to a tidal current that affected our water sampling as a function of distance upstream because our samples were collected during a single day (Table 1) (Wang and Liu, 2003).

Table 2. Acid-soluble REE concentrations in surface waters of the Changjiang Estuary ($\mu\text{g g}^{-1}$).

No.	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
33	9.22	11.05	22.58	2.85	11.98	2.21	0.49	2.11	0.32	2.00	0.32	0.93	0.12	0.62	0.08
32	5.12	7.58	13.56	1.66	7.99	1.32	0.29	1.35	0.20	1.17	0.20	0.54	0.07	0.35	0.05
31	3.37	4.50	8.20	1.13	4.74	0.78	0.16	0.87	0.11	0.74	0.12	0.32	0.04	0.20	0.03
30	8.44	10.17	19.69	2.57	10.83	2.04	0.45	1.94	0.29	1.79	0.29	0.81	0.10	0.52	0.07
29	3.28	3.90	7.22	0.84	3.36	0.71	0.16	0.66	0.09	0.54	0.09	0.24	0.03	0.16	0.02
28	3.07	3.53	7.09	0.84	3.31	0.71	0.16	0.66	0.09	0.53	0.09	0.22	0.03	0.15	0.02
27	1.86	2.33	4.96	0.55	2.23	0.46	0.11	0.42	0.06	0.34	0.05	0.16	0.02	0.11	0.01
26	2.30	2.95	6.17	0.69	2.71	0.59	0.14	0.56	0.08	0.46	0.07	0.19	0.02	0.13	0.02
25	1.76	2.23	4.66	0.54	2.19	0.43	0.10	0.40	0.06	0.33	0.05	0.14	0.02	0.09	0.01
24	2.33	2.92	6.18	0.70	2.69	0.62	0.14	0.59	0.08	0.45	0.07	0.19	0.02	0.12	0.02
23	2.61	3.23	6.76	0.78	2.98	0.68	0.15	0.65	0.09	0.50	0.08	0.22	0.03	0.15	0.02
22	2.17	2.71	5.78	0.65	2.57	0.55	0.12	0.47	0.06	0.39	0.06	0.17	0.02	0.11	0.02
21	3.21	4.18	7.16	0.99	4.21	0.71	0.16	0.85	0.10	0.66	0.10	0.29	0.03	0.18	0.03
20	2.46	3.09	6.03	0.71	3.04	0.53	0.13	0.57	0.08	0.52	0.08	0.20	0.02	0.15	0.02
19	2.80	3.72	7.96	0.89	3.60	0.75	0.18	0.67	0.09	0.53	0.08	0.23	0.03	0.15	0.02
18	2.79	3.95	8.32	0.92	3.50	0.71	0.17	0.65	0.09	0.53	0.08	0.22	0.03	0.14	0.02
17	1.74	2.64	5.62	0.65	2.70	0.58	0.14	0.50	0.07	0.38	0.05	0.15	0.02	0.09	0.01
16	2.67	3.62	6.98	0.81	3.16	0.67	0.16	0.62	0.09	0.52	0.08	0.22	0.03	0.15	0.02
15	2.96	3.87	7.74	0.89	3.55	0.79	0.19	0.73	0.10	0.60	0.09	0.25	0.03	0.16	0.02
14	1.60	2.36	4.51	0.59	2.46	0.52	0.14	0.50	0.07	0.37	0.05	0.16	0.02	0.10	0.01
12	2.77	3.79	7.89	1.01	3.99	0.85	0.20	0.79	0.11	0.63	0.09	0.27	0.03	0.17	0.02
10	2.33	3.59	7.41	1.01	4.00	0.82	0.19	0.76	0.11	0.62	0.09	0.25	0.03	0.15	0.02
9	2.84	4.12	8.66	1.03	4.24	0.88	0.21	0.81	0.12	0.69	0.10	0.31	0.04	0.20	0.03
8	3.32	5.11	10.44	1.29	5.30	1.12	0.28	1.00	0.13	0.78	0.11	0.31	0.04	0.21	0.03
6	2.13	3.09	6.40	0.80	3.19	0.64	0.15	0.58	0.08	0.49	0.08	0.22	0.03	0.14	0.02
5	3.05	5.40	9.88	1.37	5.34	1.14	0.27	1.04	0.15	0.87	0.12	0.35	0.05	0.23	0.03
4	2.67	4.14	7.70	1.02	4.05	0.84	0.20	0.76	0.11	0.64	0.10	0.28	0.04	0.20	0.03
3	2.99	4.43	8.21	1.07	4.31	0.86	0.21	0.78	0.12	0.69	0.10	0.30	0.04	0.20	0.03

3.2 Estuarine behaviours of dissolved REEs

3.2.1 Dissolved REE concentrations of the river water end-member

The concentrations of dissolved REEs of the Changjiang river water end-member are given in Table 1. The results show that dissolved REE concentrations in the Changjiang river water are considerably lower than those previously reported for various river systems (Goldstein and Jacobsen, 1988; Elderfield *et al.*, 1990). For example, the concentration of dissolved Nd in the Changjiang river water is about 70 pmol kg^{-1} , which is more than an order of magnitude lower than the average value ($1360 \text{ pmol kg}^{-1}$) of previously reported Nd concentrations for rivers from Europe and America (Elderfield *et al.*, 1990). The reasons are discussed below. First, colloids and organic matter, which are the main carriers of dissolved REEs in river waters (Sholkovitz, 1992; Koeppenastrop and De Carlo, 1993), are unstable in the Changjiang river water due to high pH (7.7–8.0). This would cause a considerable decrease of the concentrations of dissolved REEs in river water. Similar observations were reported in the Ohio and Mississippi rivers

of the United States and the Indus River of Pakistan. In those rivers, the pH is high but the levels of dissolved REEs are relatively low (Goldstein and Jacobsen, 1988). In contrast, the Amazon estuarine water has lower pH but high dissolved REE concentrations (Sholkovitz, 1993).

3.2.2 Estuarine behaviours of the dissolved REEs: removal and remineralisation

The concentration and distribution of each individual REE across the salinity gradient in surface waters of the Changjiang Estuary are illustrated in Fig. 2. To distinguish estuarine geochemical processes such as removal and remineralisation from the expected river-seawater mixing, two possible conservative mixing lines (a) and (b) are shown (Fig. 3), assuming that dissolved Nd varies conservatively during mixing of the Changjiang freshwater and East China Sea surface waters. The values of end-members are for curve (a) the Nd concentration of the Changjiang river water (Table 1) and the East China Sea surface water (Tazoe *et al.*, 2006), and for curve (b) the Nd concentration of water at salinity about 3, which represents the dissolved Nd concentration after estuarine removal processes and the East China Sea surface water

Table 3. Residual REE concentrations in surface waters of the Changjiang Estuary ($\mu\text{g g}^{-1}$).

No.	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
33	11.10	20.16	41.44	4.60	16.39	2.92	0.61	1.97	0.28	1.80	0.39	1.26	0.19	1.50	0.22
32	13.29	24.40	49.71	5.50	19.87	3.51	0.72	2.32	0.33	2.15	0.47	1.50	0.22	1.76	0.26
31	13.79	25.32	50.91	5.84	21.17	3.64	0.75	2.40	0.35	2.20	0.49	1.57	0.23	1.82	0.27
30	13.41	24.86	50.64	5.66	19.87	3.49	0.73	2.36	0.34	2.16	0.47	1.52	0.23	1.80	0.27
29	14.88	27.57	56.49	6.35	22.62	3.89	0.80	2.56	0.37	2.32	0.52	1.65	0.24	1.96	0.29
28	17.84	33.69	70.13	7.72	27.53	4.81	0.96	3.08	0.45	2.85	0.64	2.03	0.30	2.41	0.36
27	17.00	32.08	65.91	7.24	25.55	4.47	0.92	2.95	0.44	2.69	0.61	1.93	0.29	2.30	0.34
26	17.14	31.80	68.44	7.52	26.62	4.61	0.93	3.04	0.44	2.75	0.62	1.97	0.29	2.32	0.35
25	18.68	35.28	73.44	7.92	28.31	5.01	1.03	3.35	0.48	3.04	0.68	2.17	0.32	2.52	0.38
24	16.69	31.22	63.89	7.10	25.45	4.41	0.90	2.87	0.42	2.61	0.58	1.87	0.28	2.22	0.33
23	15.33	28.41	59.35	6.49	23.47	4.08	0.83	2.66	0.38	2.42	0.54	1.72	0.26	2.02	0.30
22	16.95	31.51	65.26	7.32	26.17	4.56	0.93	2.95	0.42	2.65	0.60	1.91	0.29	2.29	0.34
21	13.41	24.63	50.65	5.77	20.77	3.62	0.73	2.39	0.34	2.14	0.48	1.52	0.23	1.80	0.27
20	16.95	32.10	66.49	7.47	26.49	4.61	0.92	2.91	0.43	2.68	0.60	1.88	0.29	2.26	0.34
19	19.97	37.71	76.17	8.27	29.28	5.30	1.05	3.47	0.50	3.18	0.70	2.24	0.34	2.66	0.40
18	21.35	39.58	81.37	9.09	31.51	5.54	1.12	3.67	0.53	3.34	0.74	2.37	0.36	2.85	0.43
17	20.96	39.22	81.37	8.92	32.10	5.39	1.10	3.62	0.53	3.29	0.75	2.34	0.35	2.79	0.42
16	20.96	39.58	81.10	8.92	31.17	5.39	1.10	3.62	0.52	3.28	0.74	2.32	0.35	2.74	0.43
15	20.96	39.48	80.06	8.76	31.22	5.58	1.11	3.63	0.52	3.31	0.74	2.34	0.36	2.76	0.43
14	19.08	36.35	76.49	8.47	29.80	5.01	1.05	3.43	0.49	3.08	0.68	2.21	0.33	2.59	0.39
12	20.96	38.41	79.67	8.69	30.45	5.36	1.10	3.57	0.52	3.27	0.73	2.32	0.35	2.77	0.41
10	20.35	37.71	78.70	8.77	31.17	5.28	1.08	3.57	0.51	3.24	0.73	2.28	0.34	2.71	0.41
9	19.97	37.02	79.35	8.57	30.71	5.16	1.07	3.54	0.51	3.21	0.72	2.28	0.34	2.67	0.40
8	20.16	38.06	78.28	8.73	30.97	5.27	1.07	3.55	0.52	3.23	0.73	2.28	0.34	2.71	0.41
6	19.97	37.37	77.60	8.60	30.02	5.30	1.07	3.48	0.50	3.13	0.71	2.22	0.34	2.68	0.40
5	19.61	36.35	74.41	8.12	29.61	5.19	1.03	3.40	0.49	3.12	0.70	2.19	0.33	2.61	0.39
4	17.68	32.39	68.12	7.57	26.82	4.68	0.94	3.05	0.44	2.74	0.61	1.95	0.29	2.34	0.35
3	18.34	33.69	71.23	8.03	27.83	4.93	0.97	3.11	0.45	2.87	0.64	2.03	0.31	2.41	0.36

(Tazoe *et al.*, 2006). Curve (b) is shown in the figure because it can indicate whether remineralisation occurred in the mid to high salinity regions of the Changjiang Estuary.

There are clearly separated salinity regions where different behaviour controls the relative abundance of the dissolved REEs. In the low salinity region, the concentrations of dissolved REEs decrease sharply; for example, the concentrations of Nd vary from $69.2 \text{ pmol kg}^{-1}$ in the Changjiang river water to $18.8 \text{ pmol kg}^{-1}$ in the saline waters, implying that large-scale removal of dissolved REEs did occur in that region (Table 1 and Fig. 3). The observation of rapid removal of the freshwater REE load in the Changjiang Estuary is consistent with many earlier observations in the low salinity regions in the other estuaries of the world (Elderfield *et al.*, 1990; Sholkovitz, 1993). In studies conducted during the past twenty years, salt-induced coagulation of river colloids has been established as the mechanism responsible for the removal of dissolved REEs in the low salinity region of estuaries (Elderfield *et al.*, 1990; Sholkovitz, 1993). Moreover, the extent of removal of dissolved REEs, with

total abundances reduced to 30~60% of the initial abundances in the Changjiang freshwater, follows the pattern of removal order of lighter REEs (LREE) > middle REEs (MREE) > heavy REEs (HREE), which was also previously observed in the low salinity removal process in the Amazon Estuary (Sholkovitz, 1993). These observations are also consistent with the results of experimental studies of dissolved REE with seawater (e.g. Koepenkastrup and De Carlo, 1992; De Carlo *et al.*, 1998)

From mid to high salinity regions of the Changjiang Estuary, there is a strong progressive increase in concentrations of all REEs to 150~300% of their initial abundance (Fig. 2). There must be a significant additional source supplying dissolved REEs, because all of the REE concentrations fall above the conservative mixing line (b) (Fig. 3). For example, the concentration of dissolved Nd increases gradually from $18.8 \text{ pmol kg}^{-1}$ to $47.8 \text{ pmol kg}^{-1}$ between a salinity of 3 and 19. The extent of dissolved REE release follows the order of HREE > MREE > LREE. This results in the highest salinity waters having HREE concentrations that equal or exceed those of the Changjiang river water. In previous studies, similar el-

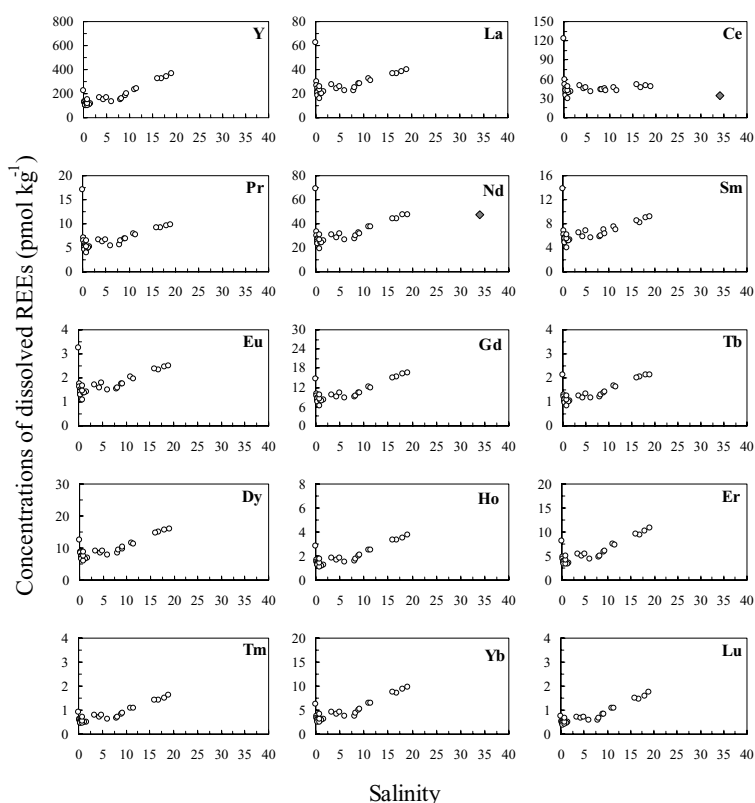


Fig. 2. Salinity distributions of the dissolved REEs in surface water of the Changjiang Estuary. Inserted dissolved Nd and Ce concentrations ($[Nd] = 47.1 \text{ pmol l}^{-1}$ and $[Ce] = 33.8 \text{ pmol l}^{-1}$) in the East China Sea (◆) surface water are taken from Tazoe *et al.* (2006).

evated REE concentrations were reported at mid- and high salinities in the Fly and Gulf of Papua estuaries (Sholkovitz and Szymczak, 2000). Moderate release of dissolved REEs were also observed in the mid to high salinity regions of the Amazon Estuary (Sholkovitz, 1993).

3.3 Estuarine behaviour of SPM, acid-soluble and residual REEs

The concentrations of SPM decrease systemically in surface water of the Changjiang Estuary from the low salinity region to the mid and high salinity ones. SPM distribution along the salinity gradient can be separated into two regions. At salinity less than three, the concentrations of SPM dropped sharply from 238 mg l^{-1} in river water to less than 50 mg l^{-1} , reflecting heavy deposition of SPM at the onset of estuarine mixing. This is due to a decrease of water velocity and the well known salt-induced coagulation of river colloids and small particles (Sholkovitz, 1978). In the mid and high salinity regions (greater than salinity three), the SPM concentrations remain as high as $15\text{--}50 \text{ mg l}^{-1}$ and no further seaward decrease was observed (Wang and Liu, 2003). On the other

hand, SPM concentrations ($0.3\text{--}6.5 \text{ mg l}^{-1}$) in the water of the East China Sea clearly show lower values than those in the Changjiang estuarine waters (Hung *et al.*, 2007). In addition, the carbon isotopic composition of SPM that was collected from the high salinity region of the Changjiang Estuary showed that those suspended particles originated mainly from the China continental area rather than being of oceanic origin (Cai *et al.*, 1992). This strongly suggests that intense resuspension of sediments mainly originating from the Changjiang River occurred in the high salinity mixing zone of the estuary (Beardsley *et al.*, 1985; Sternberg *et al.*, 1985).

The REE content of the acid-soluble phase of suspended matter in the Changjiang estuarine water is enriched by a factor of approximately 1000 to 2000 compared to that of the filtered waters. The acid-soluble fractions range from 10% to 20% of the total particulate REEs (acid-soluble REEs plus residual REEs). The concentrations of the acid-soluble REEs also drop sharply in the low salinity mixing zone of the Changjiang Estuary (Fig. 4) as the proportion of colloidal material in the SPM decreased sharply because the acid-soluble phase is mainly composed of Fe-Mn oxide colloids (Sholkovitz *et al.*,

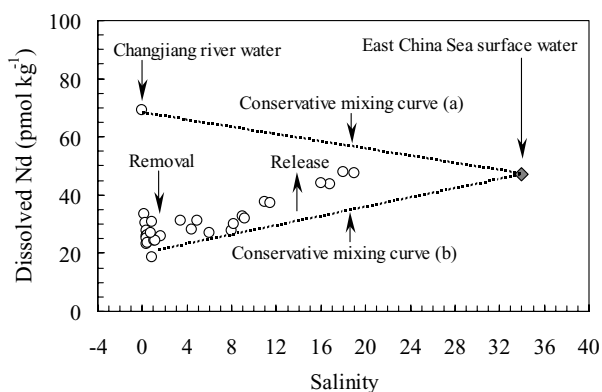


Fig. 3. Salinity distribution of dissolved Nd in surface water of the Changjiang Estuary, showing the removal process at low salinities and release at mid to high salinities (abbreviations are the same as those in Fig. 2).

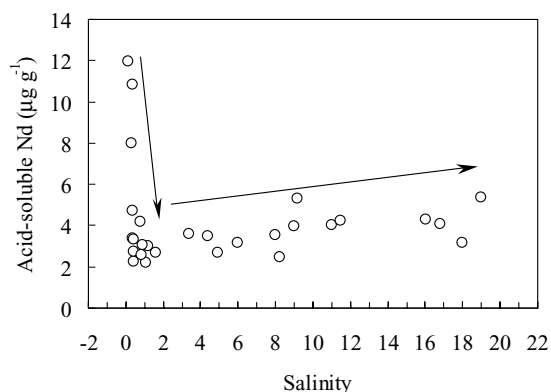


Fig. 4. Acid-soluble REE distributions in surface water of the Changjiang Estuary along the salinity gradient (only Nd is shown). Note the sharp decrease of the concentration of acid-soluble Nd in the low salinity region and slight increase in the mid to high salinities.

1994; Négre *et al.*, 2000). This implies that the REE composition of SPM at low salinities is also strongly influenced by salt-induced coagulation at the beginning of estuarine mixing. In the mid and high salinity regions (greater than salinity three), the concentrations of acid-soluble REEs increase slightly with increasing salinity (Fig. 4). This increase correlates with the increasing concentrations of SPM and dissolved REEs in the mid and high salinity regions, which is consistent with a resuspension of bottom sediments.

The concentrations of residual REEs range from $0.2 \mu\text{g g}^{-1}$ (Tm and Lu) to $80 \mu\text{g g}^{-1}$ (Ce) and represent about 80–90% of the total particulate REEs in the Changjiang estuarine water. Compared to the salinity distributions of dissolved and acid-soluble REEs, the residual REE concentrations are relatively constant as a function of salinity, meaning that the residual phase of suspended matter is composed mainly of immobile constituents.

4. Discussion

4.1 REE release mechanism in the mid and high salinity regions

The increases of dissolved REEs at high salinities that were previously reported in estuarine mixing zones of the Amazon and Fly Rivers have been attributed to the interaction of high salinity estuarine waters and sediments (Sholkovitz, 1993; Sholkovitz and Szymczak, 2000). These estuaries, located over shallow, wide shelves, are dominated by periods of strong suspension and deposition of surface sediments. There is therefore a strong physical coupling between surface waters and sediments in those estuaries. In contrast, there is no re-supply of REEs to mid and high salinity surface waters of the estu-

aries with great water depth (Sholkovitz and Szymczak, 2000). The Changjiang Estuary, however, is a high-energy system where a strong physical connection exists between benthic processes and surface water chemistry, because the upper regions of the Changjiang Estuary within salinities less than 20 are very shallow (average depth less than 6.5 m) (Fig. 1) and water-sediment interactions are very strong. This leads to energetic resuspension of bottom sediments in the Changjiang Estuary and causes a surface sediment reservoir to alternate between suspension and deposition (Pan and Sun, 1996; Li *et al.*, 2000). Sediment resuspension in the mid to high salinities of the Changjiang Estuary is evident from the high concentrations of SPM reported here and by Edmond *et al.* (1985). This process can alter the dissolved REE composition of surface waters (Sholkovitz, 1993; Sholkovitz and Szymczak, 2000). Hence, we hypothesize that the possible mechanism for the dissolved REEs release in the mid and high salinities of the Changjiang Estuary is desorption from the surface of suspended sediment during water-sediment interaction processes.

It is important to consider remineralisation of dissolved REEs in the mid and high salinities of the Changjiang, Amazon and other estuaries when calculating the net river water flux of dissolved REEs, which evolves toward the REE composition of seawater and thereby determines the residence time of REEs in the oceans. Previous studies only considered removal processes when calculating the river water flux of dissolved REEs to the oceans (Goldstein and Jacobsen, 1988; Elderfield *et al.*, 1990; Sholkovitz, 1993). However, REE removal and remineralisation are both important processes that influence the distribution of dissolved REEs in the estuaries.

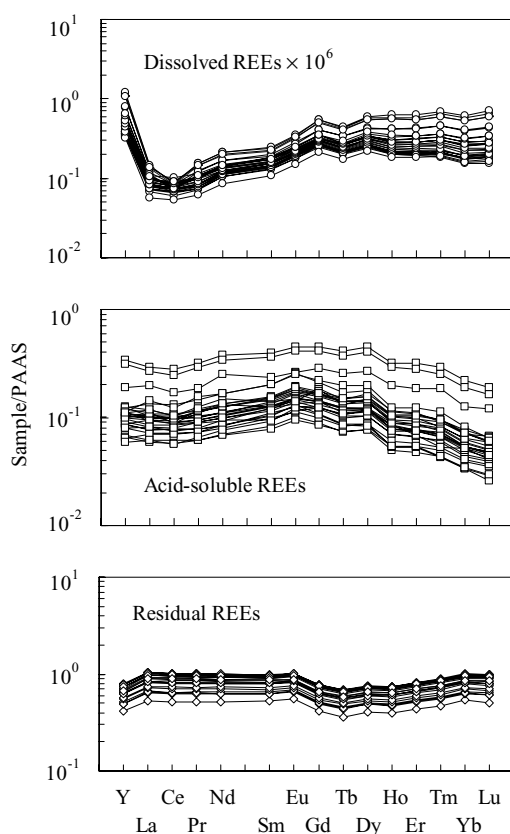


Fig. 5. Shale (PAAS) normalized patterns of dissolved, acid-soluble and residual REEs in the Changjiang estuarine surface waters.

4.2 REE fractionation

4.2.1 REE fractionation among dissolved, acid-soluble and residual phases

In waters of the Changjiang river-estuary regime, the dissolved, acid-soluble and residual REEs show different shale-normalized patterns. For example, the dissolved REEs show HREE enrichment pattern and the acid-soluble REEs show an upwardly convex pattern, while the residual material has a nearly flat REE pattern similar to shale (Fig. 5). These differences indicate that the fractionation between REEs takes place both during weathering and riverine transport.

4.2.2 LREE/HREE fractionation of dissolved REEs

As mentioned above, a significant amount of fractionation of dissolved REEs was observed to accompany the removal process in the low salinity region of the Changjiang Estuary. The LREE fraction shows the largest removal efficiencies of 71–77%. Removal of the MREE fraction is only slightly less efficient (60–75%), whereas HREE removal is markedly lower (44–58%). Although it is difficult to identify release order among HREEs, MREEs and LREEs in release process at higher

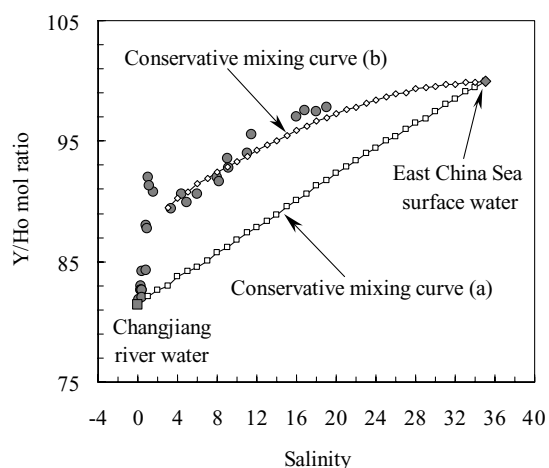


Fig. 6. Diagram showing the relationship between Y/Ho molar ratio and salinity. The end-member values of the two possible conservative mixing curves are for curve (a) the Y and Ho concentrations of the Changjiang river water (Table 1) and the East China Sea surface water, and for curve (b) the Y and Ho concentrations of the saline water at salinity 3 in the Changjiang Estuary and the East China Sea surface water.

salinities, we extrapolate that even conservative estuarine mixing can also adduce progressive HREE enrichment from low to high salinities, because seawater always has more enriched HREE than that of estuarine surface waters. Thus, the combined result of the removal, release and mixing processes progressively enriches estuarine water in the heavier REEs relative to fresh water from the Changjiang River.

4.2.3 Y/Ho ratios of dissolved phase

The Y/Ho molar ratio of dissolved REEs in the Changjiang estuarine waters is plotted against salinity in Fig. 6 along with two possible conservative mixing curves (a) and (b). The end-member values for curve (a) are the Y and Ho concentrations of the Changjiang river water and the East China Sea surface water, and for curve (b) the Y and Ho concentrations of water at salinity three in the Changjiang Estuary and the East China Sea surface water. Since there are no data of the Y/Ho ratio of the East China Sea surface water directly available from previous studies, an extrapolated value of 100 is adopted here. Nozaki *et al.* reported a value of 104 for the Y/Ho molar ratio of Kuroshio surface water (Nozaki *et al.*, 1997). On the other hand, Tazoe *et al.* found a value of 96 for the Y/Ho molar ratio in Kuroshio surface water just after mixing with the East China Sea surface water (Tazoe *et al.*, 2007). In our opinion, therefore, the value of the Y/Ho ratio of the East China Sea surface water falling within the 96–104 range with an average value of 100 is reasonable. This value is also approached by the Y/Ho ratio (97)

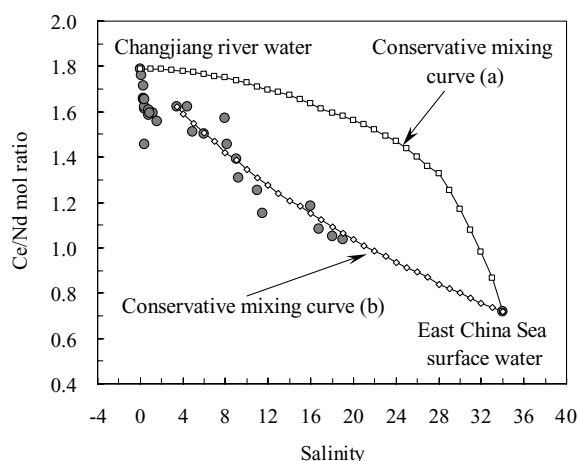


Fig. 7. Diagram showing the relationship between Ce/Nd molar ratio and salinity. The end-member values of the two possible conservative mixing curves are for curve (a) the Ce and Nd concentrations of the Changjiang river water (Table 1) and the East China Sea surface water, and for curve (b) the Ce and Nd concentrations of the saline water at salinity 3 in the Changjiang Estuary and the East China Sea surface water (Tazoe *et al.*, 2006).

of the high salinity water in the present study. Saline water (salinity 3) was chosen as one of the end-members of the conservative mixing curves (b) because it represents the concentration of dissolved REEs just after the previously described removal process. In our dataset for the estuary, the initial freshwater Y/Ho ratio of about 80 increases sharply to more than 90 upon mixing with seawater. Figure 6 shows that all Y/Ho ratios plot above the calculated mixing curve (a). However, those Y/Ho ratios in the mid to high salinities are nearly consonant with the conservative mixing curve (b), which suggests that fractionation between Y and Ho is not evident in the mid to high salinity areas of the Changjiang Estuary (Fig. 6). This indicates that fractionation between the Y and Ho in the Changjiang river-estuarine regions is most significant in the low salinity removal process. This is because Y and Ho have differential abilities to use the f orbital to form surface adsorption or solution complexes. Ho has a much greater propensity than Y to form strong surface complexes for bonding to coagulated colloids in removal processes at low salinities (Byrne and Lee, 1993).

4.2.4 Cerium anomaly of dissolved REEs

During water mixing in the Changjiang Estuary, Ce shows a negative anomaly in contrast to its neighbors La and Pr (or Nd). The magnitude of the negative Ce anomaly (0.98–0.49) increases with increasing salinity throughout the estuarine mixing zone. To discuss the fractionation behavior of Ce compared to its neighbors, the Ce/Nd ratio was chosen as an indicator because previous work has

indicated that La anomalies may influence the more traditionally used Ce anomaly, which compares the behavior of Ce with both La and Nd (Lawrence and Kamber, 2006). Figure 7 shows the distribution of Ce/Nd molar ratios in the Changjiang estuarine surface waters as a function of salinity. Two possible conservative mixing curves are also shown in the figure, following the approach previously described. The Ce/Nd ratios lie under the mixing curve (a), showing that fractionation between Ce and Nd must occur during Changjiang estuarine mixing; however, those Ce/Nd ratios in the mid to high salinities are just consonant with the conservative mixing curve (b), suggesting that fractionation is not evident in the mid to high salinity regions of the Changjiang Estuary (Fig. 7). The progressive Ce depletion toward the East China Sea in the mid and high salinity regions seems to be due to estuarine water progressively mixing with the East China Sea surface water, which has a more negative Ce anomaly. Therefore, it is concluded that, during Changjiang estuarine mixing, the Ce anomaly mainly formed at low salinities. It seems that, during the low salinity removal process, Ce is more rapidly removed from the water relative to Nd and as a consequence, fractionation of Ce compared to its neighbors occurred.

5. Conclusions

(1) Considerable removal of dissolved REEs was observed at low salinities in the Changjiang Estuary due to salt-induced coagulation of river colloids. Furthermore, interactions between water and suspended particles and sediments in a shallow part of the estuary, where salinity ranges from 8 to 19, lead to release of dissolved REEs. These processes both significantly alter the riverine water flux of REEs to the ocean and REE composition in seawater.

(2) In the low salinity mixing zone of the Changjiang Estuary, sharp falls in the acid-soluble REE concentrations reflect that the REE compositions of SPM in the low salinities are also strongly influenced by salt-induced coagulation during estuarine mixing. Moreover, the slight increases of acid-soluble REE concentrations in the mid to high salinity mixing zone indicate that the resuspension of sediments occurred. In marked contrast, the REE compositions of residual phases are relatively constant with salinity variation.

(3) Preferential removal of dissolved LREEs at low salinities and preferential release of HREEs at mid to high salinities occurred during estuarine mixing in the Changjiang Estuary. Taken together, these observations favor progressive HREE enrichment of dissolved REEs as compared to the original REE composition of the freshwater. Controlling by removal and release processes, Ce anomaly and Y/Ho fractionation were also taking place during estuarine mixing.

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