

Mechanisms of incorporation of rare earth elements into ferromanganese concretions*

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Abstract: The equilibrium between ferromanganese concretions and sea water is assumed to explain the composition of rare earth elements (REE) in ferromanganese concretions. The enrichment of REE in the four end-members of ferromanganese concretions is in the order: hydrogenous > oxic-diagenetic > suboxic-diagenetic > hydrothermal. The lower enrichment of REE in oxic-diagenetic nodules than in hydrogenous crusts, in contrast to transition metals, is ascribed to the lower concentration of REE in interstitial water than in sea water or to greater retention of REE than of transition metals in sedimentary phases during diagenesis. The correlation between REE and Fe in concretions is attributed to their similar supply mechanisms to concretions and not to the incorporation of REE into the iron-oxide phase of concretions. REE are incorporated not only into the iron-oxide phase but also into the manganese oxide phase. Distribution coefficients of REE between ferromanganese concretions and sea water have a maximum at Sm and decrease monotonically from Sm to La and from Sm to Lu. This phenomenon is explained by the combination of two factors. The adsorption of free ions of REE on oxides increases from La to Lu, depending on their hydrolysis constants. On the other hand, the proportion of free ions of REE to the total decreases from La to Lu, depending inversely on their stability constants with carbonate or some organic ligands. The incorporation of Ce into ferromanganese concretions is controlled by the redox potential of the environments.

1. Introduction

Since the first excellent work by GOLDBERG *et al.* (1963), much data have been accumulated on rare earth elements (REE) in marine ferromanganese concretions (GLASBY, 1972/73; PIPER, 1974; CORLISS *et al.*, 1978; ADDY, 1979; ELDERFIELD and GREAVES, 1981; ELDERFIELD *et al.*, 1981a, b; APLIN, 1984; MURPHY and DYMOND, 1984; CALVERT *et al.*, 1987; GLASBY *et al.*, 1987; INGRI and PONTÉR, 1987). However, mechanisms of incorporation of REE into ferromanganese concretions have not been well documented.

Ferromanganese concretions are classified into hydrogenous, oxic-diagenetic, suboxic-diagenetic and hydrothermal varieties, on the basis of the composition of transition metals and mineralogy

(BONATTI *et al.*, 1972; DYMOND *et al.*, 1984). Typical ferromanganese concretions of hydrogenous origin occur as crusts on seamounts, which are enriched in Fe and Co, and depleted in Cu. Their mineral form is vernadite (δ -MnO₂). Nodules of oxic-diagenetic origin are buried in siliceous ooze or clay and have the highest contents of transition metals. Their mineral form is todorokite. Nodules of suboxic-diagenetic origin occur in hemipelagic environments or shallow-water continental margins. The nodules are characterized by low contents of transition metals and their mineral form is todorokite. Hydrothermal ferromanganese oxide deposits occur usually as crusts in hydrothermal regions and have low contents of transition metals. Their mineral form is todorokite or birnessite.

Ferromanganese concretions on seamounts have the highest contents of REE and are extremely enriched in Ce (APLIN, 1984). In nodules of oxic-diagenetic origin, the contents of REE and the enrichment of Ce are intermediate between hydrogenous and suboxic-

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diagenetic nodules (Wahine survey area, ELDERFIELD *et al.*, 1981a; DOMES Site A, thin sediment valley nodules, CALVERT *et al.*, 1987). Ferromanganese concretions of suboxic-diagenetic origin have low contents of REE and low enrichment of Ce (Loch Fyne, GLASBY, 1972/73; MANOP Site H, MURPHY and DYMOND, 1984). Hydrothermal manganese and iron oxide deposits are characterized by extremely low contents of REE and extremely low enrichment of Ce (the Galapagos Rift, CORLISS *et al.*, 1978).

GOLDBERG *et al.* (1963) attributed the enrichment of Ce (relative to La) to the oxidation of Ce^{3+} to Ce^{4+} . They found that the enrichment of REE in ferromanganese concretions relative to sea water has its maximum at Sm, and decreases monotonically from Sm to Lu and from Sm to La (except Ce). The decrease from Sm to Lu was ascribed to the increasing stability of heavy REE (HREE) complexes with ligands in sea water but the decrease from Sm to La was not clearly explained. ELDERFIELD *et al.* (1981a) attributed the correlation between REE and P to the incorporation of REE into a phosphatic phase in nodules. However, this is not the case, because there is no correlation between REE and P in crusts on seamounts (APLIN, 1984). The correlation between REE and Fe has been attributed to the incorporation of REE into the iron oxyhydroxide phase in ferromanganese concretions (ELDERFIELD *et al.*, 1981a, b; CALVERT *et al.*, 1987; GLASBY *et al.*, 1987). However, the manganese oxide phase must play an important role in the incorporation of REE, because REE contents in almost pure iron oxide deposits are only two times higher than those in almost pure manganese oxide deposits at the Galapagos Rift (CORLISS *et al.*, 1978).

TAKEMATSU *et al.* (1989) explained the wide compositional variety of transition metals in marine ferromanganese concretions by assuming that the oxide phases are in equilibrium with sea water or interstitial water with respect to transition metals and by considering the chemical form of transition metals in sea water and the sorptive properties of the oxides. The same concepts are applied to REE in marine ferromanganese concretions in this paper. Usually, chondrite- or shale-normalized REE patterns are used in discussions of the distribution of REE in

marine environments. However, this method does not clarify the mechanisms of incorporation of REE into ferromanganese concretions. Instead, distribution coefficients of REE between ferromanganese concretions and sea water are used, as developed by GOLDBERG *et al.* (1963).

2. Sources of REE in ferromanganese concretions

There are three sources of REE in ferromanganese concretions: 1) directly from sea water (hydrogenous), 2) from interstitial water as the result of diagenetic decomposition of settling particles (diagenetic), and 3) from hydrothermal fluids (hydrothermal).

Several papers were published on the concentrations of REE in sea water (HØGDAHL *et al.*, 1968; ELDERFIELD and GREAVES, 1982; PIEPGRAS and WASSERBURG, 1982; DE BAAR *et al.*, 1983, 1985; KLINKHAMMER *et al.*, 1983). Vertical distribution of REE in the Pacific and Atlantic Oceans mimics that of nutrients. However, the concentrations of REE except Ce in deep-sea water of the Pacific Ocean are about two times higher than those of the Atlantic Ocean and that of Ce in the former is four times lower than that in the latter (Table 1). The relative concentration of each REE in deep-sea water is different in the Pacific and Atlantic Oceans. The difference of REE in origin in the Pacific and Atlantic Oceans is evident from the isotopic composition of Nd in sea water. The $\epsilon_{Nd}(0)$ values of sea water in the Pacific and Atlantic Oceans are ca. -3 and ca. -12 , respectively. These differences are reflected in ferromanganese concretions (PIEPGRAS *et al.*, 1979; PIEPGRAS and WASSERBURG, 1980; GOLDSTEIN and O'NIONS, 1981; PIEPGRAS and WASSERBURG, 1982). Despite large variations of REE in sea water, the average concentrations of REE in deep-sea water (1,000-3,250 m) of the Pacific Ocean (DE BAAR *et al.*, 1985) are used as representative of sea water in this study, because most of ferromanganese concretions dealt with in this study are from the Pacific Ocean.

REE are removed from sea water and transported to the sea floor by settling particles which are the raw materials of diagenetic ferromanganese concretions. Unfortunately, data on REE

Table 1. Concentrations of rare earth elements in sea water of the Pacific and Atlantic Oceans (p mol per kg sea water).

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Ho	Tm	Yb	Lu
Pacific, VERTEX II Site (18 °N, 108 °W): DE BAAR <i>et al.</i> (1985)												
15—750 m (9)	26	14	3.3	16	2.8	0.79	4.3	0.62	1.1	0.59	3.7	0.63
	±10	±5	±0.7	±3	±0.5	±0.17	±0.8	±0.12	±0.3	±0.16	±1.3	±0.24
1,000—3,250 m (8)	51	4.2	7.3	34	6.8	1.8	9.9	1.6	3.6	2.0	13	2.4
	±13	±1.5	±1.6	±9	±1.6	±0.5	±2.5	±0.4	±0.8	±0.4	±2	±0.4
Atlantic (28°01'N, 25°59'W): ELDERFIELD and GREAVES (1982)												
0—900 m (6)	23	26	—	21	4.3	0.75	4.9	—	—	—	3.9	—
	±8	±20	—	±7	±1.1	±0.10	±0.9	—	—	—	±0.5	—
1,000—3,000 m (4)	28	19	—	23	4.4	0.96	6.1	—	—	—	5.0	—
	±5	±7	—	±3	±0.5	±0.05	±1.0	—	—	—	±0.2	—
4,500 m (1)	54	55	—	46	8.3	1.2	8.3	—	—	—	5.2	—
Atlantic (33°58'N, 58°05'W): DE BAAR <i>et al.</i> (1983)												
10—981 m (8)	16	39	3.7	—	3.4	0.70	—	0.72	1.7	0.80	4.4	0.70
	±4	±29	±0.6	—	±0.2	±0.06	—	±0.04	±0.2	±0.14	±0.5	±0.08
1,179—3,264 m (6)	32	18	4.6	—	3.5	0.76	—	0.78	1.7	0.84	4.8	1.0
	±10	±4	±0.7	—	±0.6	±0.15	—	±0.12	±0.3	±0.14	±0.9	±0.2
4,328—4,427 m (3)	82	48	11	—	7.8	1.7	—	1.5	2.6	1.2	7.2	1.6
	±2	±6	±0.2	—	±0.2	±0.01	—	±0.1	±0.1	±0.1	±0.2	±0.03

Table 2. Distribution coefficients of REE between settling particles and deep-sea water and Sm-normalized distribution coefficients, together with those of sediments, ferromanganese nodules and crusts (from MURPHY and DYMOND, 1984).

	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu
Settling particles								
DC($\times 10^6$)	0.41±0.20	6.2±3.0	0.99±0.42	0.63±0.33	0.68±0.38	0.46±0.21	0.25±0.13	0.21±0.11
DCnSm	0.63±0.03	10 ±0.6	1.8 ±0.8	1.0	1.0 ±0.05	0.76±0.13	0.41±0.07	0.33±0.04
Sediments								
DC($\times 10^6$)	4.8 ±0.4	61 ±3	6.3 ±2.5	7.0 ±0.2	6.3 ±0.4	4.8 ±0.4	3.0 ±0.1	2.6 ±0.0
DCnSm	0.68±0.06	8.7±0.5	0.90±0.35	1.0	0.90±0.05	0.69±0.06	0.42±0.02	0.37±0.0
Nodule tops								
DC($\times 10^6$)	5.1 ±1.7	73 ±31	6.5 ±1.8	6.9 ±2.1	6.5 ±1.9	4.6 ±1.3	2.6 ±0.6	2.0 ±0.5
DCnSm	0.74±0.24	11 ±4	0.95±0.27	1.0	0.95±0.27	0.66±0.19	0.38±0.09	0.29±0.07
Nodule bottoms								
DC($\times 10^6$)	1.7 ±0.3	19 ±3	2.0 ±0.2	2.2 ±0.4	1.9 ±0.04	1.5 ±0.4	0.91±0.18	0.76±0.17
DCnSm	0.77±0.13	8.5±1.5	0.93±0.09	1.0	0.86±0.02	0.67±0.18	0.41±0.08	0.35±0.08
Crusts								
DC($\times 10^6$)	19 ±0.6	340 ±17	23 ±0.8	24 ±1	23 ±0.4	14 ±0.4	8.4 ±0.3	6.6 ±0.4
DCnSm	0.79±0.02	14 ±0.7	0.95±0.03	1.0	0.96±0.02	0.60±0.02	0.35±0.01	0.28±0.02

DC and DCnSm denote the distribution coefficient and Sm-normalized distribution coefficient, respectively.

in settling particles are scarce and available only from MANOP Site H (MURPHY and DYMOND, 1984). In Table 2, distribution coefficients (DC) of REE between settling particles and deep-sea water in the Pacific Ocean, and DC of REE normalized to that of Sm (DCnSm) are given, together with those of sediments, ferromanganese nodules and crusts from MANOP Site H. The

contents of REE in settling particles increase with the depth of traps and only DCnSm are meaningful. Anomalous contents of Nd in settling particles are due to greater analytical errors for Nd (MURPHY and DYMOND, 1984). DC of REE are different among settling particles, sediments, ferromanganese nodules and crusts, but DCnSm are almost the same except for Ce. This indicates insignificant fractionation of indivi-

dual REE from one another during diagenesis. DCnSm of Ce is in the order: crusts > nodule tops > settling particles > sediments > nodule bottoms. This is probably the order of redox potential in the environments.

Unfortunately, the concentrations of REE in interstitial water of deep-sea sediments have not been published, only those in a reducing sediment core of Buzzards Bay (ELDERFIELD and SHOLKOVITZ, 1987). However, the concentrations of REE in interstitial water can be supposed from the difference in the contents of REE between nodule tops and bottoms. In the case of transition metals, ferromanganese nodules of oxic-diagenetic origin from MANOP Site S (DYMOND *et al.*, 1984) have higher contents of transition metals on the bottoms than on the tops, where the concentrations of transition metals in interstitial water are higher than those in overlying bottom water (KLINKHAMMER *et al.*, 1982). On the other hand, in the suboxic-diagenetic environments such as MANOP site H, nodule tops have higher contents of transition metals than nodule bottoms (DYMOND *et al.*, 1984), where the concentrations of transition metals in interstitial water are indistinguishable from those in overlying bottom water or lower (KLINKHAMMER, 1980). In nodules from the northern equatorial Pacific between the Clarion and Clipperton Fracture Zones and the southern equatorial Pacific, the contents of REE are higher in the top sub-samples than in the bottom sub-samples, while the contents of Ni and Cu are lower in the former than in the latter (ELDERFIELD *et al.*, 1981b). From the contents of Ni and Cu, these nodules are of oxic-diagenetic origin. At MANOP Site H, the contents of REE and transition metals in nodule tops are higher than in nodule bottoms (DYMOND *et al.*, 1984; MURPHY and DYMOND, 1984). This means that in contrast to transition metals, the concentrations of REE in interstitial water are lower than those in overlying bottom water both in oxic-diagenetic and suboxic-diagenetic environments.

In the reducing nearshore sediment core of Buzzards Bay, the concentrations of REE in interstitial water are much higher than those in overlying sea water and increase with depth, resembling the concentrations of the nutrients (ELDERFIELD and SHOLKOVITZ, 1987). From

the composition of REE in interstitial water, properties of carrier phases of REE in the water column can be deduced, because settling particles are formed in sea water, transported to the sea floor and decomposed in the sediment. These processes are the same in nearshore and deep-sea environments. Accordingly, the concentrations of REE in interstitial water are divided by those in overlying sea water, and the calculated concentration ratios of REE are further divided by that of Sm (Fig. 1). The main carrier phase has the uptake maximum at Sm, as the settling particles at MANOP Site H (Table 2). The carrier phase is probably biogenic amorphous silica, because the concentration of silicate in interstitial water is an order of magnitude higher than that of phosphate at any depth in the sediment (ELDERFIELD and SHOLKOVITZ, 1987) and because the distribution of REE in the deep-sea water column mimics that of silicate (DE BAAR *et al.*, 1983; KLINKHAMMER *et al.*, 1983). The content of Sm in SiO₂ is calculated to be about 1 ppm from their concentrations in interstitial water, while that in diatom is 1.6 ppm (ELDERFIELD and GREAVES, 1983). Another carrier phase is probably organic matter. In the deep sea, such an organic phase is regenerated in the water column. According to ELDERFIELD and SHOLKOVITZ (1987), the sediment of Buzzards Bay is anoxic and black, with a thin (1 mm) brown oxic layer. The sediment particles are probably coated with iron sulfide. REE released from settling particles may not be adsorbed on such reducing sediment particles and remain in interstitial water, because REE contents in hydrothermal sulfide are extremely low (ELDERFIELD and GREAVES, 1983). The composition of REE in reducing interstitial water, as observed at depth in the Buzzards Bay sediment, will be the juvenile type composition of REE in oxic- and suboxic-diagenetic sediments. Actually, REE released into interstitial water from settling particles will be readily adsorbed on manganese and iron oxides in oxic environments.

Hydrothermal solutions are strongly enriched in light REE (LREE) relative to sea water and display a pronounced positive Eu anomaly (MICHARD *et al.*, 1983). Such anomaly is evident in hydrothermal iron oxide crusts but not clear in hydrothermal manganese oxide crusts (CORLISS

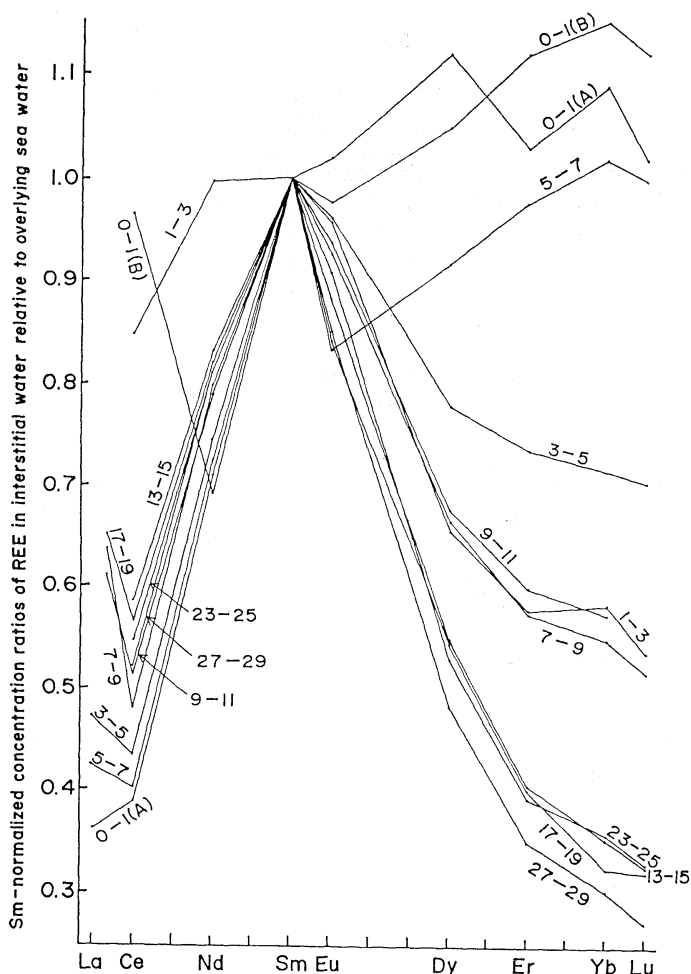


Fig. 1. Sm-normalized concentration ratios of REE in interstitial water relative to overlying sea water (from ELDERFIELD and SHOLKOVITZ, 1987). Numbers in the figure denote depth ranges in a Buzzards Bay sediment core (cm).

et al., 1978). The difference is probably attributed to the fact that iron oxides are precipitated earlier than manganese oxides from oxygenated hydrothermal solutions (EDMOND *et al.*, 1979).

3. REE composition of ferromanganese concretions of four different origins

Selected ferromanganese concretions of hydrogenous, oxic-diagenetic, suboxic-diagenetic and hydrothermal origins are crusts on seamounts from the Line Islands Archipelago (APLIN, 1984), nodules from DOMES Site A (CALVERT *et al.*, 1987), nodules from MANOP Site H (MURPHY and DYMOND, 1984) and

hydrothermal crusts from the Galapagos Rift (CORLISS *et al.*, 1978), respectively (Table 3). Valley nodules in siliceous, thin Quarternary sediments and highlands nodules from DOMES Site A (CALVERT and PIPER, 1984) are of oxic-diagenetic and hydrogenous-oxic diagenetic origins, respectively, because the composition of transition metals and mineralogy in the former is almost the same as that from MANOP Site S (DYMOND *et al.*, 1984) and that in the latter is almost the same as that from MANOP Site R (DYMOND *et al.*, 1984). DC of REE of the four end-members are shown in Fig. 2. The enrichment of REE is in the order: hydrogenous

Table 3. Contents of REE in the four end-members of ferromanganese concretions, distribution coefficients of REE between concretions and deep-sea water and Sm-normalized distribution coefficients of REE.

	Mn (%)	Fe (%)	La (ppm)	Ce (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Tb (ppm)	Yb (ppm)	Lu (ppm)
Hydrogenous: Crusts on seamounts, Line Islands (APLIN, 1984)										
	21.3	17.4	307	1,100	261	54	14	—	28	4.2
	±4.9	±3.8	±77	±575	±73	±17	±4		±4	±0.6
DC (x10 ⁶)			43	1,900	53	54	52		13	10
DCnSm			0.80	34	0.99	1.0	0.96		0.24	0.19
Hydrogenous-oxic diagenetic: Nodules on highlands, DOMES Site A (CALVERT <i>et al.</i> , 1987)										
	19.2	10.9	176	575	181	43.3	10.0	7.27	19.2	2.65
	±3.3	±1.2	±30	±152	±24	±5.7	±1.5	±1.19	±2.4	±0.35
DC (x10 ⁶)			25	980	37	43	37	29	8.7	6.3
DCnSm			0.57	23	0.85	1.0	0.85	0.67	0.20	0.15
Oxic diagenetic: Nodules in valley, thin Quaternary sediments, DOMES Site A (CARVERT <i>et al.</i> , 1987)										
	24.0	5.86	87	197	103	23.4	5.66	4.32	11.3	1.58
	±1.6	±0.43	±13	±53	±15	±3.3	±0.73	±0.67	±1.9	±0.25
DC (x10 ⁶)			12	330	21	23	21	17	5.1	3.8
DCnSm			0.53	14	0.90	1.0	0.90	0.74	0.22	0.16
Suboxic diagenetic: Nodules in hemipelagic sediments, MANOP Site H (MURPHY and DYMOND, 1984)										
Nodule tops	35.0	4.07	36	43	32	6.9	1.76	1.14	5.7	0.85
	±3.4	±1.58	±12	±18	±9	±2.1	±0.50	±0.33	±1.4	±0.20
DC (x10 ⁶)			5.1	73	6.5	6.9	6.5	4.6	2.6	2.0
DCnSm			0.74	11	0.95	1.0	0.86	0.67	0.41	0.35
Nodule bottoms	44.6	0.84	12	11	10	2.2	0.51	0.37	2.0	0.32
	±1.6	±0.14	±2	±2	±1	±0.4	±0.01	±0.10	±0.4	±0.07
DC (x10 ⁶)			1.7	19	2.0	2.2	1.9	1.5	0.91	0.76
DCnSm			0.77	8.5	0.93	1.0	0.86	0.67	0.41	0.35
Hydrothermal: Crusts on hydrothermal mounds, the Galapagos Rift (CORLISS <i>et al.</i> , 1978)										
Manganese oxides	49.9	0.30	3.0	2.5	—	0.47	0.13	0.08	0.57	0.13
	±1.6	±0.15	±0.8	±1.2		±0.17	±0.03	±0.01	±0.10	±0.03
DC (x10 ⁶)			0.43	4.2		0.47	0.48	0.30	0.26	0.31
DCnSm			0.96	9.9		1.0	1.1	0.70	0.59	0.71
Iron oxides	7.85	27.5	6.7	4.2	—	0.79	0.27	0.15	0.99	0.12
	±0.79	±0.2	±0.1			±0.25	±0.08	±0.02		±0.04
DC (x16 ⁶)			0.94	7.2		0.79	0.98	0.58	0.45	0.29
DCnSm			1.3	7.5		1.0	1.3	0.76	0.47	0.36

DC and DCnSm denote the distribution coefficient and Sm-normalized distribution coefficient, respectively.

> oxic-diagenetic > suboxic-diagenetic > hydrothermal, while that of transition metals is in the order: oxic-diagenetic > hydrogenous > suboxic-diagenetic > hydrothermal (DYMOND *et al.*, 1984; TAKEMATSU *et al.*, 1989). As found by GOLDBERG *et al.* (1963), DC of REE have their maximum at Sm, except for hydrogenous ferromanganese crusts. The enrichment of La and Eu in hydrothermal iron oxide deposits is due to the fact that hydrothermal solutions are strongly enriched in LREE relative to sea water and have a pronounced positive Eu anomaly

(MICHARD *et al.*, 1983). The smaller anomaly in hydrothermal manganese oxides is caused by the fact that manganese oxides are precipitated later than iron oxides from oxygenated hydrothermal solutions (EDMOND *et al.*, 1979). The order of Ce enrichment (hydrogenous > oxic-diagenetic > suboxic-diagenetic > hydrothermal) is due to the redox potential of depositional environments. In this respect, Ce is similar to Co (PIPER, 1988).

Any model for the mechanism of incorporation of REE into ferromanganese concretions must

explain the two aspects: 1) the lower enrichment of REE in oxic-diagenetic concretions than in hydrogenous concretions, in contrast to the

greater enrichment of transition metals in the former than in the latter, and 2) the maximum at Sm in DC of REE.

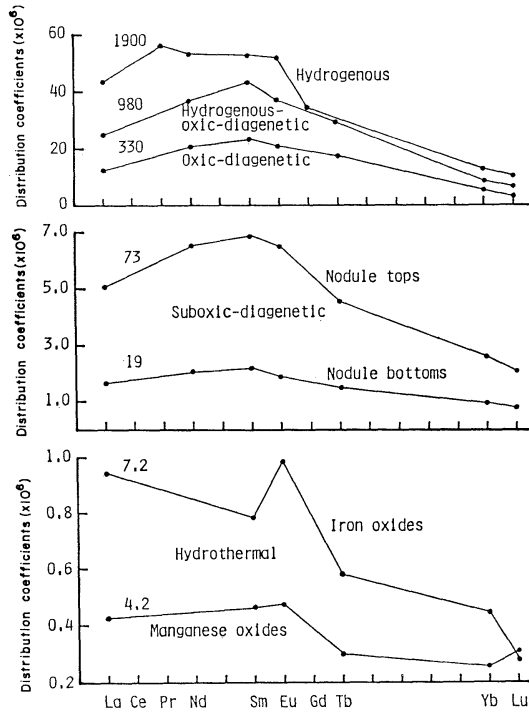


Fig. 2. Distribution coefficients of REE between ferromanganese concretions of different origins and Pacific deep-sea water (see Table 3).

4. Mechanisms of incorporation of REE into ferromanganese concretions

The lower enrichment of REE in oxic-diagenetic concretions than in hydrogenous concretions is probably attributed to great retention of REE in sedimentary components, which are released from settling particles. This is consistent with the assumption that concentrations of REE in interstitial water are lower than those in deep-sea water, as described before. The evidence is found in REE contents of the deep-sea sediments. The contents of REE in nodules and associated sediments from Wahine survey area (ELDERFIELD *et al.*, 1981a), Area C between the Clarion and Clipperton Fracture Zones (GLASBY *et al.*, 1987) and DOMES Site A (CALVERT *et al.*, 1987; PIPER *et al.*, 1987) are given in Table 4. From the composition of transition metals and mineralogy in nodules (CALVERT *et al.*, 1978; ELDERFIELD *et al.*, 1981b; CALVERT and PIPER, 1984), nodules in these areas are of oxic-diagenetic origin. The contents of REE in the bulk sediments are almost the same as those in the nodules, except for Ce. However, REE contents in the non-lithogenous (authigenic) fraction of the sediments are more than two times higher

Table 4. Contents of REE in oxic-diagenetic nodules, associated siliceous sediments and the lithogenous fraction of the sediment.

	Mn (%)	Fe (%)	La (ppm)	Ce (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Gd (ppm)	Tb (ppm)	Yb (ppm)	Lu (ppm)
Wahine survey area (siliceous ooze): ELDERFIELD <i>et al.</i> (1981a)											
Nodules	25.9	6.65	87.5	293	125	29.8	7.19	28.5	—	13.0	—
	±1.1	±1.62	±17.3	±103	±26	±7.4	±1.60	±5.4		±2.7	
Sediments	0.55	4.10	71.3	93.0	101	25.6	6.36	26.5	—	13.8	—
	±0.30	±0.60	±11.0	±5.6	±12	±3.7	±1.16	±3.9		±2.0	
Area C (siliceous ooze): GLASBY <i>et al.</i> (1987)											
Nodules	—	4.74	93	344	134	33.3	7.8	—	4.0	12.9	1.8
		±0.39	±10	±76	±33	±6.2	±1.4		±0.9	±2.1	±0.4
Sediments		3.86	69	75	69	17.6	4.5	—	2.8	9.0	1.5
		±0.34	±44	±15	±47	±9.3	±2.6		±1.9	±5.2	±0.8
DOMES Site A (siliceous thin Quaternary sediment): CALVERT <i>et al.</i> (1987), PIPER <i>et al.</i> (1987) and PIPER (1988)											
A nodule	25.1	5.31	88	188	104	20.2	5.71	—	4.32	11.6	1.63
A sediment	1.21	4.90	79	80	91	23	5.7	—	4.0	12.4	1.9
Lithogenous fraction	—	—	24	48	—	4.2	—	—	—	2.2	—

than those in the nodules, because the lithogenous fraction in deep-sea sediments constitutes more than 80% of the bulk sediments in weight (TAKEMATSU, 1978) and the contents of REE in the lithogenous fraction of deep-sea sediments are low and comparable to those in continental shales (PIPER, 1988). On the other hand, the contents of transition metals in ferromanganese nodules are more than an order of magnitude higher than those in the associated bulk sediments. This indicates that in contrast to transition metals most of REE released from settling particles during diagenesis are readily taken up by sedimentary phases before reaching ferromanganese concretions.

ELDERFIELD *et al.* (1981a) concluded from the correlation between REE and both of P and Fe in nodules from Wahine survey area that REE are incorporated into both of a phosphatic phase and an iron phase in nodules. However, this is not the case. The correlation is attributed to the supplies of REE, Fe and P to nodules in proportional rates from interstitial water. Phosphate is preferentially adsorbed on ferric oxides (CROSBY *et al.*, 1984) and no correlation is found between REE and P in crusts from the Line Islands Archipelago (APLIN, 1984). REE contents in modern biogenic phosphates are very low ($Nd < 150$ ppb), and high REE contents in sedimentary phosphates are ascribed to the presence of the Fe-oxide phase (SHAW and WASSERBURG, 1985).

Manganese oxides as well as iron oxides must be the important phase to control REE contents. The evidence is found in hydrothermal regions where both of Mn-oxides and Fe-oxides are precipitated separately. Hydrothermal iron oxides are more influenced by hydrothermal solutions than hydrothermal manganese oxides, at the Galapagos Rift, as is evident from their REE distribution patterns (Fig. 2.). The concentration of Sm in hydrothermal solutions is about 10^2 times higher than that in deep-sea water (MICHARD *et al.*, 1983). Therefore, iron oxides must be precipitated from sea water with a higher concentration of Sm than manganese oxides. Nevertheless, at the Galapagos Rift, hydrothermal iron oxides have only about two times higher content of Sm than hydrothermal manganese oxides, although the purity of the former

is lower than that of the latter (CORLISS *et al.*, 1978). DE BAAR *et al.* (1985) suggested from the correlation between REE and Mn near the oxygen minimum layer in the water column that Mn-oxide serves as a REE carrier. Therefore, manganese oxides play an important role in controlling REE contents. The relationship between REE and Fe (ELDERFIELD *et al.*, 1981a; GLASBY *et al.*, 1987) is fundamentally attributed to their similar supply mechanisms to nodules. REE and Fe are trapped in sedimentary phases during diagenesis, as discussed later.

The amounts of elements adsorbed on oxides depend on the products of their surface complex formation constants and concentrations of their free ions. The surface complex formation constants of cationic elements on oxides (MnO_2 , Fe_2O_3 , SiO_2 and probably clay minerals) depend on their first hydrolysis constants (SCHINDLER *et al.*, 1976; LI, 1981; SCHINDLER, 1981). The concentrations of cationic free ions are inversely related to their stability constants of inorganic

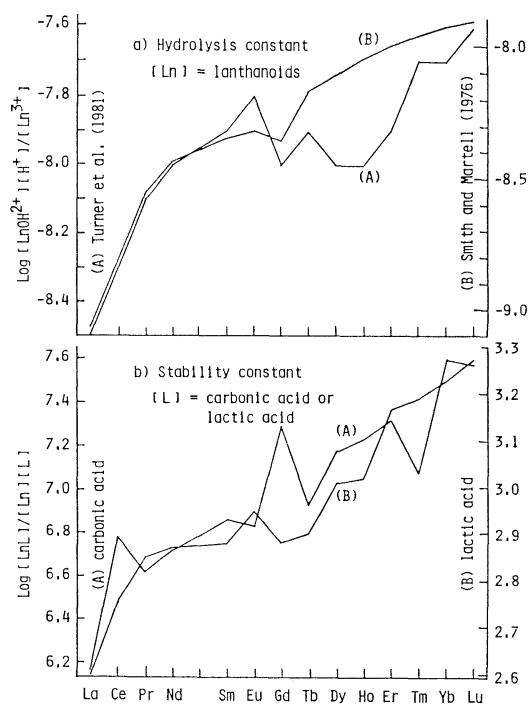


Fig. 3. a) Hydrolysis constants of REE (SMITH and MARTELL, 1976; TURNER *et al.*, 1981). b) Stability constants of REE with carbonic acid (TURNER *et al.*, 1981) and lactic acid (SILLÉN and MARTELL, 1971).

and organic ligands. In Fig. 3, the first hydrolysis constants of REE (SMITH and MARTELL, 1976; TURNER *et al.*, 1981) are plotted in the order of atomic number, together with their stability constants with carbonic acid (TURNER *et al.*, 1981) and lactic acid (SILLÉN and MARTELL, 1971). According to BRULAND (1983), the main species of REE in oxygenated sea water are carbonate complexes. Lactic acid is used for the separation of REE from one another (GOLDBERG *et al.*, 1963; SCHMITT *et al.*, 1963), and has some analogy to humic acid, because humic acid has carboxyls, phenolic and alcoholic hydroxyls as functional groups (SCHNIZER and KHAN, 1972).

Hydrolysis constants of REE increase almost monotonically from La to Lu. This means that the adsorption ability of the free ions of REE on oxides increases from La to Lu. On the other hand, the proportion of the free ions of REE to the total decreases from La to Lu, because their stability constants of carbonate and lactate complexes increase from La to Lu. The combination of these two effects must cause the Sm maximum in DC of REE.

The first hydrolysis constants ($\log *K_1$) of Mn, Co, Ni, Cu and Zn are -10.6, -9.65, -9.86, -8.00 and -8.96, respectively, while that of La is -8.50, which is the lowest among REE (TURNER *et al.*, 1981). This indicates that REE are more readily adsorbed on oxides than transition metals except Cu. This is the reason why the REE contents of the non-lithogenous fraction in oxic-diagenetic sediments are higher than those in the associated ferromanganese nodules, in contrast to transition metals, as described before. Cu is mostly present in organic form in deep-sea water (BUCKLEY and VAN DEN BERG, 1986) and interstitial water (HEGGIE *et al.*, 1986), and organically-bound metals are inhibited from being incorporated into oxides (PRICE, 1967; VAN DEN BERG, 1982; CALVERT *et al.*, 1987).

The DC of La and Lu normalized to that of Sm (DCnSm) varies largely from area to area (Table 3). There are many factors influencing DCnSm: 1) relative concentrations of REE in sea water in contact with ferromanganese concretions, 2) ligands in sea water which form complexes with REE, and 3) carriers of REE in the water column. Interstitial water is probably

depleted in LREE and HREE relative to sea water, if the carrier of REE is oxides such as biogenic SiO₂, Mn- and Fe-oxides, as is observed in the Buzzards Bay sediment core (ELDERFIELD and SHOLKOVITZ, 1987). However, DCnSm in nodules buried in the sediment will be almost the same as that in the carrier phase, because almost all of REE released from the carrier phase will be readily taken up by nodules and sediment particles coated with manganese and iron oxides (a closed system). Peculiar Ca-P-rich iron-oxide concretions were found in Barents Sea, which have extremely low DCnSm of LREE (including Ce) and HREE, extremely high contents of REE and low contents of transition metals (INGRI, 1985; INGRI and PONTÉR, 1987). The genesis is not clear but a possible mechanism is as follows. Settling particles rich in diatoms are transported to the sea floor (< 200 m), which are depleted in LREE and HREE relative to sea water. Settling particles are regenerated in less oxidizing bottom environment where iron oxides are stable and manganese oxides are unstable. Iron oxides scavenge REE and P from bottom water of which REE composition is similar to that of settling particles (an open system). In this way, the iron-oxide concretions are probably subject to the two-step depletion of LREE and HREE.

The first hydrolysis constant of Ce⁴⁺ is about eight orders of magnitude larger than that of Ce³⁺ (SMITH and MARTELL, 1976; TURNER *et al.*, 1981). The large DCnSm of Ce in ferromanganese concretions is, therefore, attributed to the higher adsorption ability of Ce⁴⁺ than Ce³⁺ on oxides. The content of Ce in nodules from abyssal hills in the Atlantic Ocean (ADDY, 1979) is about four times higher than that from highlands at DOMES Site A (CALVERT *et al.*, 1987) in spite of the fact that the contents of the other REE are almost the same. This difference is ascribable to the fact that the concentration of Ce in the Atlantic deep-sea water is about four times higher than that in the Pacific deep-sea water. DCnSm of Ce in the Atlantic nodules (ca. 9), calculated by using the concentrations of REE in the Atlantic deep-sea water, is rather low relative to that in the corresponding Pacific nodules (ca. 23). The higher concentration of Ce in the Atlantic deep-sea water is

probably attributed to the lower abundance of ferromanganese concretions in the Atlantic Ocean compared to the Pacific Ocean.

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希土類元素の鉄マンガン団塊への編入機構

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要旨: 鉄マンガン酸化物と海水が希土類元素に関して平衡状態にあるものと仮定して、鉄マンガン団塊中の希土類元素の組成を説明した。4つの起源の異なる鉄マンガン団塊中における希土類元素の濃縮順序は、海水起源>酸化した続成起源>亜酸化した続成起源>熱水起源であった。遷移元素と異なり、海水起源の団塊より酸化した続成起源の団塊中において希土類元素の濃縮程度が低い原因は、海水中より間隙水中において希土類元素の濃度が低いか、あるいは希土類元素が遷移元素より続成作用中に堆積物構成成分に保持され、鉄マンガン団塊に供給されないためである。これは粘土鉱物も含めた酸化物に対する希土類元素の吸着親和力が遷移元素のそれより強いことに起因する。団塊中における希土類元素と鉄の相関は希土類元素が鉄酸化物相に存在するためではなく、希土類元素と鉄の団塊への供給機構が似ているためである。希土類元素は鉄酸化相ばかりでなく、マンガン酸化物相にも同様に取り込まれる。鉄マンガン酸化物と海水との間の希土類元素の分配係数は、原子番号順に、LaからSmに向かって単調に増加し、Smで極大になった後Luに向かって減少する。この現象は2つの因子の組合せによって説明できる。酸化物に対する希土類元素の遊離イオンの吸着は、それらの加水分解定数に依存して、LaからLuに向かって増加する。一方、遊離イオンの割合は、炭酸あるいは有機物配位子との安定度定数に逆比例して、LaからLuに向かって減少する。Ceの鉄マンガン団塊への濃縮は環境の酸化還元電位によって支配される。