

## Relative REE abundances of porewater in Pacific pelagic sediment: estimation by equilibrium calculations based on REE composition of Mn-oxide and apatite components

Masamichi TAKEBE<sup>1)\*</sup> and Koshi YAMAMOTO<sup>2)</sup>

- 1) Department of Sciences, Matsue National College of Technology, 4-14, Nishi-ikuma-cho, 690-8518, Japan  
Fax +81-852-36-5182 \*: takebe@matsue-ct.jp  
2) Graduate School of Environmental Studies, Nagoya University, Furo, Chikusa, Nagoya 464-8601, Japan

### Abstract

In order to reveal REE mobilization in sediment during early diagenesis, we estimate the REE composition of porewater in Pacific sediments deposited in the Equatorial area. The Pacific sediment was divided chemically into leachate 1 (extracted by alkaline  $\text{Na}_2\text{S}_2\text{O}_4$ ), leachate 2 (extracted by 0.17 M HCl) and residue. The leachate 1, leachate 2 and residue consist mainly of Mn oxide, carbonate fluorapatite (CFA), and detrital materials, respectively. The Mn oxide and CFA component are considered to provide information about REE composition of porewater. Assuming that Mn oxide and CFA in the sediment were in chemical equilibrium with the porewater in terms of REE, the REE composition (REE/Gd ratio) of the porewater in the sediment was estimated from the REE abundance of the leachate 1 and 2. The estimated REE pattern (REE/Gd ratio) of the porewater shows La depletion and Ce enrichment relative to the deep-seawater. The difference of REE composition between deep-seawater and porewater suggests that REE in pelagic sediment is mobilized during early diagenesis.

**Key words:** REE composition, Porewater, Pelagic sediment, Equilibrium calculation

### 1. Introduction

Whereas REEs are generally believed to behave conservatively in sediment, several studies reported that REEs are mobilized during diagenesis. For example, Murray *et al.* (1991) discussed the mobility of light REE in Japan Sea sediments. Milodowski and Zalasiewicz (1991) reported that REEs in Paleozoic sedimentary rocks are concentrated in authigenic monazite, xenotime and apatite, which are generated during early diagenesis. Hence, the behavior of REE during diagenesis is essential to interpret the REE composition of sediments. To evaluate REE behavior during early diagenesis, we need more knowledge about the REE chemistry of porewater. However, there have been very few studies about the REE chemistry of porewater because of sampling and analytical difficulty due to low concentrations of REE in porewater. (Sholkovitz *et al.*, 1989; 1992; Haley and Klinkhammer, 2003).

Takebe (2005) conducted sequential chemical leaching experiment for Pacific sediments (Fig. 1). Fig. 2 shows the REE compositions of L1 (leachate by alkaline  $\text{Na}_2\text{S}_2\text{O}_4$ ), L2 (leachate by 0.17 M HCl) and R3 (residue) by the sequential leaching experiments in Takebe (2005)

The L1 leachate originates mainly from Mn oxide and its Mn content accounts for 65~85 % of the bulk Mn content. The shapes of the REE patterns and sizes of the Ce anomalies of the L1 leachate are similar to those of diagenetic Mn nodules (Fig. 3a: Calvert *et al.*, 1987; Ohta *et al.* 1999). Takebe (2005) concluded that the REEs of the L1s were associated with Mn oxide deposited during early diagenesis.

The L2 leachates are considered to be derived mainly from biogenic CFA. The L2 leachates contain 60~90 % of the bulk phosphorus. It is known that biogenic CFA scarcely contains REEs in a living body, but concentrates REEs after sedimentation (Toyoda and Tokonami, 1990). The REE patterns of

the L2 leachates normalized to deep-seawater REE abundances (SA5-5149m; Zhang and Nozaki, 1996) show large positive Ce anomalies (Fig. 3b). Considering that REE incorporation into CFA from solution may not be related to redox reaction of Ce and that REEs have similar chemical properties to each other, the REE distribution coefficient between the solution and CFA may not show a Ce anomaly. Deep-seawater is not, therefore, appropriate as a solution that interacted with the CFA in terms of REE. An alternative candidate for the solution is porewater. Toyoda and Tokonami (1990) suggested that a large contribution of porewater likely contributes to the high REE concentrations of fish teeth in pelagic sediments. Taking into account the positive Ce anomalies shown in Fig. 3b, the porewater should show a Ce enrichment relative to the deep-seawater. In fact, there are many reports showing that porewater are enriched in Ce relative to seawater (Sholkovitz *et al.*, 1989; 1992; Haley and Klinkhammer, 2003).

The PAAS normalized REE patterns of the R3 residues show negative Ce anomalies and positive Eu anomalies. R3 residues are the component not extracted by the reducing agent and acid. Thus the negative Ce anomalies in the R3 residue probably indicate the contribution of authigenic clay deposited from sea or porewater, and the Eu anomalies suggest the influence of basaltic detrital materials from oceanic island or andesitic eolian dust from American continent (Takebe, 2005; Nakai *et al.*, 1993).

In this study, we calculate the REE composition of porewater in Pacific sediment, based on the analyzed REE compositions of Mn oxides and CFA examined in the sediments by Takebe (2005).

## 2. Samples and methods

Examined samples (NB7 and 59P159) were collected from the Western and Equatorial Pacific during NH 90-1 and GH 80-1 cruises, respectively, by the Geological Survey of Japan (NB7: 14°N 138°E, 11 cm below sea floor (cmbsf), 59P159: 1°N 171°W, 15 cmbsf; Fig. 1). These samples were from the seabed deeper than 5000 m and rarely contain Ca-carbonate. The sampling sites of NB7 and 59P159 are in areas with abundant biogenic productivity (Leinen *et al.*, 1986). Takebe (2005) reported that these samples show high phosphorous concentrations reflecting enrichment of biogenic CFA.

Each sample was divided into three fractions by a sequential leaching method, following the similar procedure to that of Toyoda and Masuda (1991). The analytical method in this study is summarized below, and the details were reported in Takebe and Yamamoto (2003) and Takebe (2005). A sample was leached with Na-dithionite solution under alkaline conditions maintained by  $\text{Na}_2\text{CO}_3$  and the resulting leachate was named leachate 1 (L1). The residue was subsequently leached with 0.17 M HCl, and the leachate was named leachate 2 (L2). The residue was digested by HF-HClO<sub>4</sub>, fused finally with  $\text{Na}_2\text{CO}_3$ , and named R3.

The REE concentrations of bulk, L1 leachate, L2 leachate and R3 residue were measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS; HP4500). There was no correction made for the total blank of REEs during the procedure because of its negligible contribution (< 1 %). REE concentrations were recalculated on an ignition loss-free basis. This recalculation does not affect the discussion in this study, because all the elements in

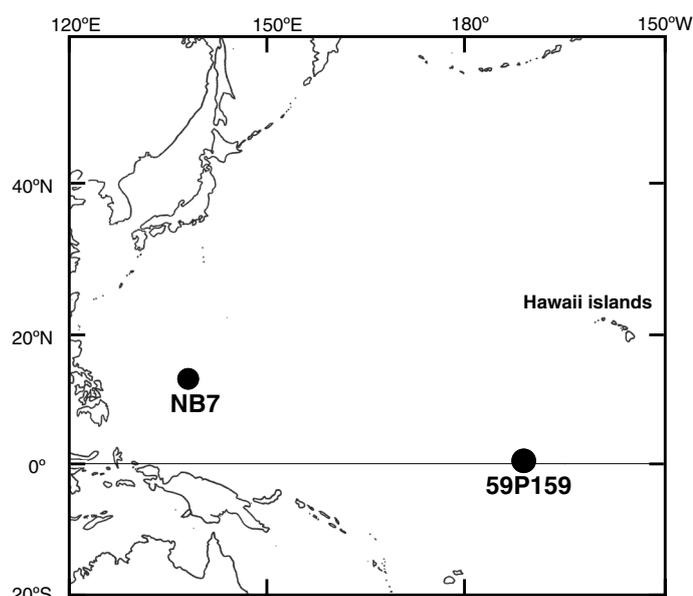


Fig. 1. Location map of analyzed samples.

the sample are corrected by the same factor. The recalculated concentrations are used for the following discussions. Raw data were reported in Takebe (2005). The difference between the REE concentration of the bulk analysis and the sum of the REE concentrations in L1 leachate, L2 leachate and R3 residue was less than 5 %.

To depict REE patterns, the REE composition of Post-Archean Australian average shale (PAAS: Nance and Taylor, 1976; Taylor and McLennan, 1985) was used for normalization.

### 3. Results and Calculation

REE abundances in each fraction are presented in Table 1 and Fig. 2. On the basis of the REE abundance of the L1 leachates (Mn oxide components), we estimate the REE/Gd ratio of the porewater except for the Ce/Gd ratio, assuming that chemical equilibrium was established between the Mn oxide and porewater. Ce/Gd ratio of porewater is hard to estimated from Ce content in Mn oxide component, because  $Ce^{3+}/(Ce^{3+}+Ce^{4+})$  ratio in the component is unclear. Subsequently, the distribution coefficient of REE ( $K_{d_{REE}}/K_{d_{Gd}}$ ) between the CFA and porewater is estimated by the REE/Gd ratio of the L2 leachates (CFA component) and porewater. After that, the Ce/Gd ratio of the porewater is evaluated from the pattern of the distribution coefficient. Reason for focusing REE ratios (REE/Gd ratios) is that we can omit the estimation of uncertain activity of  $H_2O$  and activity coefficients of REE in porewater.

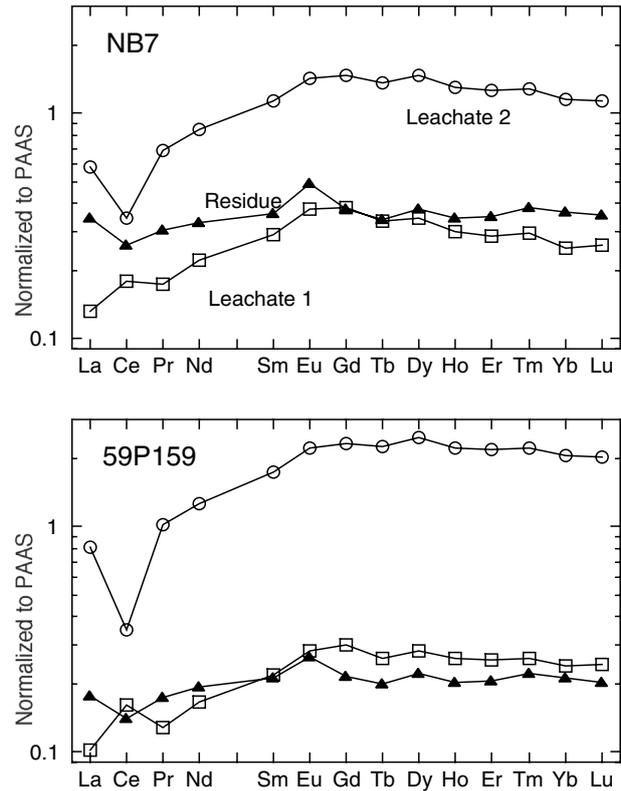


Fig. 2. PAAS-normalized REE patterns of the leachates and residue.

#### 3.1. REE/Gd Ratio of Porewater, except for Ce/Gd Ratio

Assuming that the changes of temperature and pressure cause negligible effects on the REE partitioning between Mn oxide and solution, we carry out the following calculation under the simplifying conditions of 25°C and 1 atm. Incorporation of REE into diagenetic Mn oxide from solution is expressed by the following reaction (Kawabe *et al.*, 1999):



where Ln stands for REE. The equilibrium constant of Eq. (1) can be written as

$$K_{Ln(OH)_3 \cdot nH_2O} = (a_{Ln^{3+}} \cdot a_{H_2O}^{3+n}) / a_{Ln(OH)_3 \cdot nH_2O} \cdot a_{H^+}^3, \quad (2)$$

where “a” is the activity for respective species. When the activities of  $Ln^{3+}$  and  $Ln(OH)_3 \cdot nH_2O$  are expressed in terms of the molar concentration of  $Ln^{3+}$  in solution, the molar fraction of  $Ln(OH)_3 \cdot nH_2O$  in Mn oxide and the respective activity coefficients, Eq. (2) can be re-written as the following equation,

**Table 1.** REE concentrations (ppm) of bulk sample, leachates and residue.

	NB7					59P159				
	Leachate 1	Leachate 2	Residue	total	bulk	Leachate 1	Leachate 2	Residue	total	bulk
La	5.06	22.2	13.0	40.2	38.8	3.86	31.0	6.69	41.5	41.0
Ce	14.5	27.5	20.9	62.9	60.5	13.0	27.7	11.2	51.9	52.9
Pr	1.54	6.13	2.70	10.4	9.93	1.14	9.14	1.55	11.8	11.8
Nd	7.10	27.2	10.6	44.9	43.0	5.31	40.9	6.22	52.4	52.3
Sm	1.63	6.34	2.02	9.99	9.57	1.22	9.76	1.19	12.2	12.1
Eu	0.413	1.58	0.536	2.53	2.41	0.308	2.48	0.292	3.08	3.05
Gd	1.78	6.93	1.77	10.5	9.96	1.40	11.1	1.02	13.5	13.5
Tb	0.257	1.06	0.262	1.57	1.50	0.201	1.74	0.154	2.10	2.03
Dy	1.51	6.48	1.65	9.65	9.21	1.23	10.9	0.977	13.1	12.9
Ho	0.301	1.31	0.341	1.95	1.87	0.259	2.24	0.203	2.70	2.64
Er	0.833	3.69	1.01	5.54	5.33	0.743	6.36	0.596	7.70	7.49
Tm	0.118	0.514	0.153	0.784	0.750	0.104	0.899	0.0891	1.09	1.04
Yb	0.706	3.26	1.03	4.99	4.82	0.671	5.82	0.596	7.09	6.95
Lu	0.112	0.488	0.152	0.752	0.732	0.106	0.884	0.0870	1.08	1.03

“total” is sum of leachates and residue.

$$K_{\text{Ln}(\text{OH})_3 \cdot n\text{H}_2\text{O}} = ([\text{Ln}^{3+}] \cdot \gamma_{\text{Ln}^{3+}} \cdot a_{\text{H}_2\text{O}}^{3+n}) / (X_{\text{Ln}(\text{OH})_3 \cdot n\text{H}_2\text{O}} \cdot \lambda_{\text{Ln}(\text{OH})_3 \cdot n\text{H}_2\text{O}} \cdot a_{\text{H}^+}^3), \quad (2')$$

where  $[\text{Ln}^{3+}]$  and  $X_{\text{Ln}(\text{OH})_3 \cdot n\text{H}_2\text{O}}$  are the molar concentration of  $\text{Ln}^{3+}$  in porewater and the molar fraction of  $\text{Ln}(\text{OH})_3 \cdot n\text{H}_2\text{O}$  in the Fe-Mn oxide, respectively.  $\gamma$  and  $\lambda$  denote activity coefficients in porewater and Fe-Mn oxide, respectively. Although values of  $\gamma_{\text{Ln}^{3+}}$  and  $\lambda_{\text{Ln}(\text{OH})_3 \cdot n\text{H}_2\text{O}}$  are not strictly constant across the REE series, they may be presumed to be approximately constant. Normalization of Eq. (2') by that for Gd leads to the following form,

$$K_{\text{Ln}(\text{OH})_3 \cdot n\text{H}_2\text{O}} / K_{\text{Gd}(\text{OH})_3 \cdot n\text{H}_2\text{O}} = ([\text{Ln}^{3+}] / [\text{Gd}^{3+}]) / (X_{\text{Ln}(\text{OH})_3 \cdot n\text{H}_2\text{O}} / X_{\text{Gd}(\text{OH})_3 \cdot n\text{H}_2\text{O}}). \quad (2'')$$

The left side of Eq. (2'') can be estimated from the distribution coefficients ( $K_{d,\text{Ln}}$ ) between Fe-Mn oxyhydroxide precipitate and NaCl solution (Kawabe *et al.*, 1999). The  $K_d$  value is defined by the following equation.

$$K_{d,\text{Ln}} = X_{\text{Ln}} / [\text{Ln}]_{\text{total}}, \quad (3)$$

where  $[\text{Ln}]_{\text{total}}$  and  $X_{\text{Ln}}$  are the REE concentration in solution and molar fraction of REE in Fe-Mn oxyhydroxide, respectively. Because almost all dissolved REE is present as  $\text{REE}^{3+}$  under their experimental conditions (Kawabe *et al.*, 1999), Eq. (3) can be re-written as follows:

$$K_{d,\text{Ln}} = X_{\text{Ln}} / [\text{Ln}^{3+}]. \quad (4)$$

Normalized by the equation for Gd, Eq. (4) is expressed as follows:

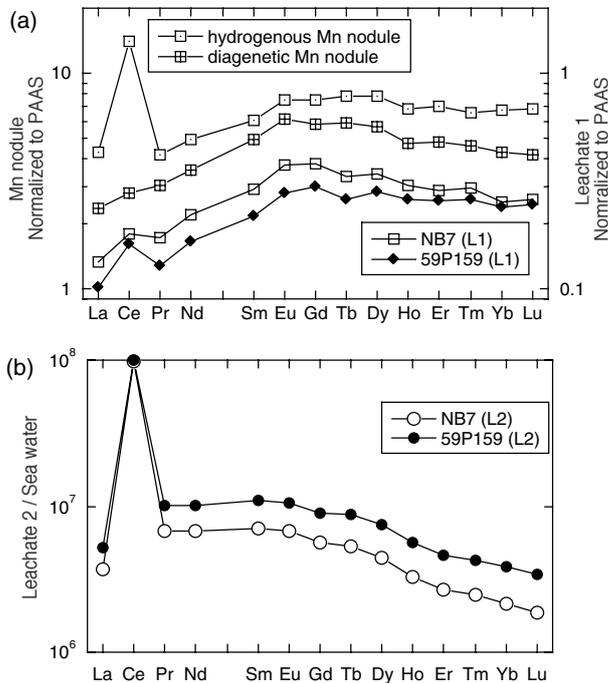
$$K_{d,\text{Ln}} / K_{d,\text{Gd}} = (X_{\text{Ln}} / X_{\text{Gd}}) / ([\text{Ln}^{3+}] / [\text{Gd}^{3+}]). \quad (4')$$

Considering  $X_{\text{Ln}} = X_{\text{Ln}(\text{OH})_3 \cdot n\text{H}_2\text{O}}$ , we obtain the following equation from Eqs. (2'') and (4').

$$X_{\text{Ln}(\text{OH})_3 \cdot n\text{H}_2\text{O}} / X_{\text{Gd}(\text{OH})_3 \cdot n\text{H}_2\text{O}} = K_{\text{Gd}} / K_{\text{Ln}} \quad (5)$$

Therefore, the left side of Eq. (2''), i.e. the ratio of the equilibrium constants of Eq. (1), can be calculated from the  $K_{\text{Ln}}$  values of Kawabe *et al.* (1999). The  $K_{\text{Ln}}/K_{\text{Gd}}$  ratios other than the  $K_{\text{Ce}}/K_{\text{Gd}}$  ratio are independent of the mole fractions of Fe and Mn in Fe-Mn oxyhydroxide, whereas  $K_{\text{Ce}}/K_{\text{Gd}}$  ratio is dependent on these mole fractions (c.f. Kawabe *et al.*, 1999). In order to simplify the problem, Ce is omitted in the following calculation. The calculated  $K_{\text{Ln}}/K_{\text{Gd}}$  ratios are presented in Table 2.

The fraction of  $\text{REE}^{3+}$  and  $\text{REE}(\text{III})$ -complexes in porewater was calculated (Fig. 4). In the calculation, we assume that pH is 7.84, salinity is 35 ‰, and the concentrations of total- $\text{CO}_2$ , Na, Ca, Mg, Cl, and  $\text{SO}_4^{2-}$  are  $3.10 \times 10^{-3}$  mol/kg, 0.468 mol/kg,  $10.0 \times 10^{-3}$  mol/kg,  $50.2 \times 10^{-3}$  mol/kg, 19.3 ‰ and  $23.3 \times 10^{-3}$  mol/kg, respectively. For these data, we refer to literatures published concerning porewater in Pacific sediments without Ca-carbonate (Presley and Culp, 1973, Gieskes and Johnson, 1980). Calculated concentrations of  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  are  $4.50 \times 10^{-5}$  mol/kg and  $1.87 \times 10^{-3}$  mol/kg, respectively. The stoichiometric constants of dissociation of carbonic acid in seawater (salinity = 35) at 5°C are calculated according to the equation reported by Millero (1995). The stoichiometric constants of complexation of metals other than REE are obtained from data at ionic strength = 0.7 and 25°C by Millero and Schreiber (1982). The activity coefficients of  $\text{REE}^{3+}$ -complexes are calculated under the conditions of ionic strength = 0.7 and 25°C, following Millero and Schreiber (1982) and Millero (1992). The activity coefficients of the other ions in seawater (salinity = 35) at 5°C are obtained from Millero and Pierrot (2002). Stability constants of REE-complexes are refer to Mironov *et al.* (1982), Millero (1992), and Ohta and Kawabe (2000b). An adjustment between concentration values in mol/kg and mol/l was not made because it would have caused insignificant differences in the results. As shown in Fig. 4, the



**Fig. 3.** (a) PAAS-normalized REE pattern of hydrogenous and diagenetic Mn nodules and leachate 1. Plots of Mn nodules are average of analytical data of respective Mn nodules. The data are quoted from Ohta *et al.* (1999). (b) REE patterns of Leachate 2 normalized to deep-seawater (SA5-5149m; Zhang and Nozaki, 1996).

**Table 2.** Equilibrium constants ( $K_{\text{Ln}}$ ) relative to  $K_{\text{Gd}}$  between Fe-Mn oxyhydroxide and solution, and their 90% confidence limits.

	$K_{\text{Ln}} / K_{\text{Gd}}$	
La	3.66	± 0.12
Pr	1.13	± 0.04
Nd	0.957	± 0.029
Sm	0.616	± 0.014
Eu	0.665	± 0.015
Gd	1.00	
Tb	0.810	± 0.016
Dy	0.787	± 0.018
Ho	0.871	± 0.015
Er	0.810	± 0.021
Tm	0.640	± 0.024
Yb	0.506	± 0.019
Lu	0.556	± 0.021

These are calculated from data of Kawabe *et al.* (1999)

following approximation is possible.

$$[\text{Ln}]_{\text{total}} = [\text{Ln}(\text{CO}_3)_2^-] + [\text{LnCO}_3^+]. \quad (6)$$

Ohta and Kawabe (2000a) reported that a similar approximation is also valid under seawater conditions.

REE(III)-complexes are formed according to the following reactions.



Complex formation constants of Eqs. (7) and (8) are written as follows, respectively:

$$K_{\text{Ln}(\text{CO}_3)_2^-} = a_{\text{Ln}(\text{CO}_3)_2^-} / (a_{\text{Ln}^{3+}} \cdot a_{\text{CO}_3^{2-}}^2). \quad (9)$$

$$K_{\text{LnCO}_3^+} = a_{\text{LnCO}_3^+} / (a_{\text{Ln}^{3+}} \cdot a_{\text{CO}_3^{2-}}). \quad (10)$$

Eqs. (9) and (10) can be re-written as the following equations, using molar concentrations and activity coefficients for the respective species,

$$K_{\text{Ln}(\text{CO}_3)_2^-} = ([\text{Ln}(\text{CO}_3)_2^-] \cdot \gamma_{\text{Ln}(\text{CO}_3)_2^-}) / ([\text{Ln}^{3+}] \cdot [\text{CO}_3^{2-}]^2 \cdot \gamma_{\text{Ln}^{3+}} \cdot \gamma_{\text{CO}_3^{2-}}^2). \quad (9')$$

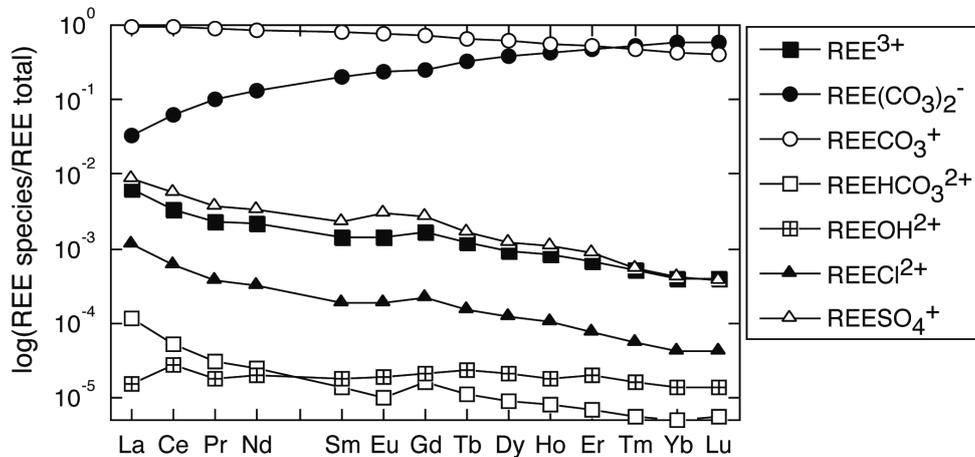
$$K_{\text{LnCO}_3^+} = ([\text{LnCO}_3^+] \cdot \gamma_{\text{LnCO}_3^+}) / ([\text{Ln}^{3+}] \cdot [\text{CO}_3^{2-}] \cdot \gamma_{\text{Ln}^{3+}} \cdot \gamma_{\text{CO}_3^{2-}}). \quad (10')$$

Assuming  $\gamma_{\text{Ln}(\text{CO}_3)_2^-} = \gamma_{\text{LnCO}_3^+}$  (c.f. Cantrell and Byrne, 1987), we obtain the following equation from Eqs. (9') and (10').

$$[\text{Ln}(\text{CO}_3)_2^-] = (K_{\text{Ln}(\text{CO}_3)_2^-} / K_{\text{LnCO}_3^+}) \cdot [\text{LnCO}_3^+] \cdot [\text{CO}_3^{2-}] \cdot \gamma_{\text{CO}_3^{2-}}. \quad (11)$$

From Eqs. 6) and 11),  $[\text{Ln}]_{\text{total}}$  is expressed as,

$$[\text{Ln}]_{\text{total}} = [\text{LnCO}_3^+] \cdot \{ (K_{\text{Ln}(\text{CO}_3)_2^-} / K_{\text{LnCO}_3^+}) \cdot [\text{CO}_3^{2-}] \cdot \gamma_{\text{CO}_3^{2-}} + 1 \}. \quad (12)$$

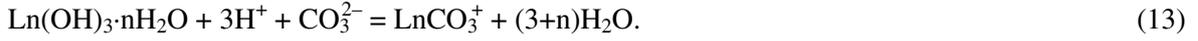


**Fig. 4.** Calculated concentration ratios of  $\text{REE}^{3+}$  and other  $\text{REE}^{3+}$ -complexes to total dissolved REE in porewater. Assumptions for this calculation are presented in text.

Normalized by the equation for Gd, Eq. 12) is expressed as,

$$\begin{aligned} ([\text{Ln}]_{\text{total}} / [\text{Gd}]_{\text{total}}) &= ([\text{LnCO}_3^+] / [\text{GdCO}_3^+]) \cdot \\ &\{ (\mathbf{K}_{\text{Ln}(\text{CO}_3)_2^-} / \mathbf{K}_{\text{LnCO}_3^+}) \cdot [\text{CO}_3^{2-}] \cdot \gamma_{\text{CO}_3^{2-}} + 1 \} / \{ (\mathbf{K}_{\text{Gd}(\text{CO}_3)_2^-} / \mathbf{K}_{\text{GdCO}_3^+}) \cdot [\text{CO}_3^{2-}] \cdot \gamma_{\text{CO}_3^{2-}} + 1 \}. \end{aligned} \quad (12')$$

From the chemical equations of (1) and (8), incorporation of REE into diagenetic Mn oxide from the porewater is also expressed by the following reaction



Equilibrium constant of chemical reaction (13), can be written as follow.

$$\mathbf{K}_{\text{Ln}(\text{OH})_3 \cdot n\text{H}_2\text{O} - \text{LnCO}_3^+} = ([\text{LnCO}_3^+] \cdot \gamma_{\text{LnCO}_3^+} \cdot a_{\text{H}_2\text{O}}^{3+n}) / (X_{\text{Ln}(\text{OH})_3 \cdot n\text{H}_2\text{O}} \cdot a_{\text{H}^+}^3 \cdot [\text{CO}_3^{2-}] \cdot \gamma_{\text{CO}_3^{2-}}). \quad (14)$$

The right hand equation of Eq. (14) can also be obtained from the equilibrium constants of Eqs. (2') and (10').

$$\mathbf{K}_{\text{Ln}(\text{OH})_3 \cdot n\text{H}_2\text{O}} \cdot \mathbf{K}_{\text{LnCO}_3^+} = ([\text{LnCO}_3^+] \cdot \gamma_{\text{LnCO}_3^+} \cdot a_{\text{H}_2\text{O}}^{3+n}) / (X_{\text{Ln}(\text{OH})_3 \cdot n\text{H}_2\text{O}} \cdot a_{\text{H}^+}^3 \cdot [\text{CO}_3^{2-}] \cdot \gamma_{\text{CO}_3^{2-}}). \quad (15)$$

Assuming that  $\gamma_{\text{LnCO}_3^+}$  is constant across the REE series, the following equation can be obtained from Eq (15) normalized by the equation for Gd.

$$\begin{aligned} &([\text{LnCO}_3^+] \cdot X_{\text{Gd}(\text{OH})_3 \cdot n\text{H}_2\text{O}}) / ([\text{GdCO}_3^+] \cdot X_{\text{Ln}(\text{OH})_3 \cdot n\text{H}_2\text{O}}) \\ &= (\mathbf{K}_{\text{Ln}(\text{OH})_3 \cdot n\text{H}_2\text{O}} \cdot \mathbf{K}_{\text{LnCO}_3^+}) / (\mathbf{K}_{\text{Gd}(\text{OH})_3 \cdot n\text{H}_2\text{O}} \cdot \mathbf{K}_{\text{GdCO}_3^+}). \end{aligned} \quad (16)$$

Eq (16) can be transformed into following equation.

$$\begin{aligned} &([\text{LnCO}_3^+] / [\text{GdCO}_3^+]) \\ &= (\mathbf{K}_{\text{Ln}(\text{OH})_3 \cdot n\text{H}_2\text{O}} \cdot \mathbf{K}_{\text{LnCO}_3^+} \cdot X_{\text{Gd}(\text{OH})_3 \cdot n\text{H}_2\text{O}}) / (\mathbf{K}_{\text{Gd}(\text{OH})_3 \cdot n\text{H}_2\text{O}} \cdot \mathbf{K}_{\text{GdCO}_3^+} \cdot X_{\text{Ln}(\text{OH})_3 \cdot n\text{H}_2\text{O}}) \end{aligned} \quad (16')$$

From Eqs. (12') and (16'), we obtained the following equation.

$$\begin{aligned} ([\text{Ln}]_{\text{total}} / [\text{Gd}]_{\text{total}}) &= (\mathbf{K}_{\text{Ln}(\text{OH})_3 \cdot n\text{H}_2\text{O}} / \mathbf{K}_{\text{Gd}(\text{OH})_3 \cdot n\text{H}_2\text{O}}) \cdot (X_{\text{Ln}(\text{OH})_3 \cdot n\text{H}_2\text{O}} / X_{\text{Gd}(\text{OH})_3 \cdot n\text{H}_2\text{O}}) \\ &\cdot (\mathbf{K}_{\text{Ln}(\text{CO}_3)_2^-} \cdot [\text{CO}_3^{2-}] \cdot \gamma_{\text{CO}_3^{2-}} + \mathbf{K}_{\text{LnCO}_3^+}) / (\mathbf{K}_{\text{Gd}(\text{CO}_3)_2^-} \cdot [\text{CO}_3^{2-}] \cdot \gamma_{\text{CO}_3^{2-}} + \mathbf{K}_{\text{GdCO}_3^+}). \end{aligned} \quad (17)$$

Using Eq. (17), we could calculate the Ln/Gd ratio of porewater from the  $\mathbf{K}_{\text{d}_{\text{Ln}}}/\mathbf{K}_{\text{d}_{\text{Gd}}}$  ratio (Table 2) and the Ln/Gd ratio of the Mn oxide (L1).

The results of the calculations are presented in Table 3 and Fig. 5a (except for Ce/Gd ratio). The calculated error caused by the analytical error of the Ln/Gd ratio is smaller than the size of points plotted in Fig 5a. There is no significant difference in the calculated Ln/Gd ratio of the porewater between NB7 and 59P159. The calculated porewater shows La depletion relative to the deep-seawater. Except for the La/Gd ratio, the calculated Ln/Gd ratio of the porewater is similar to the ratio of deep-seawater (SA5-5149 m: Zhang and Nozaki, 1996).

### 3.2. Distribution coefficient of REE between CFA and porewater

Using the calculated Ln/Gd ratio of the porewater, we can evaluate the Gd-normalized distribution

**Table 3.** Ln/Gd ratios of pore water and their 90 % confidence limits.

	NB7	59P159
La	2.86 ± 0.10	2.78 ± 0.09
Ce		
Pr	0.727 ± 0.028	0.683 ± 0.026
Nd	3.09 ± 0.09	2.94 ± 0.09
Sm	0.698 ± 0.016	0.666 ± 0.015
Eu	0.184 ± 0.004	0.175 ± 0.004
Gd	1.00	1.00
Tb	0.165 ± 0.003	0.164 ± 0.003
Dy	1.19 ± 0.03	1.24 ± 0.03
Ho	0.291 ± 0.005	0.320 ± 0.006
Er	0.934 ± 0.024	1.06 ± 0.03
Tm	0.139 ± 0.005	0.156 ± 0.006
Yb	0.841 ± 0.032	1.02 ± 0.04
Lu	0.148 ± 0.005	0.177 ± 0.007

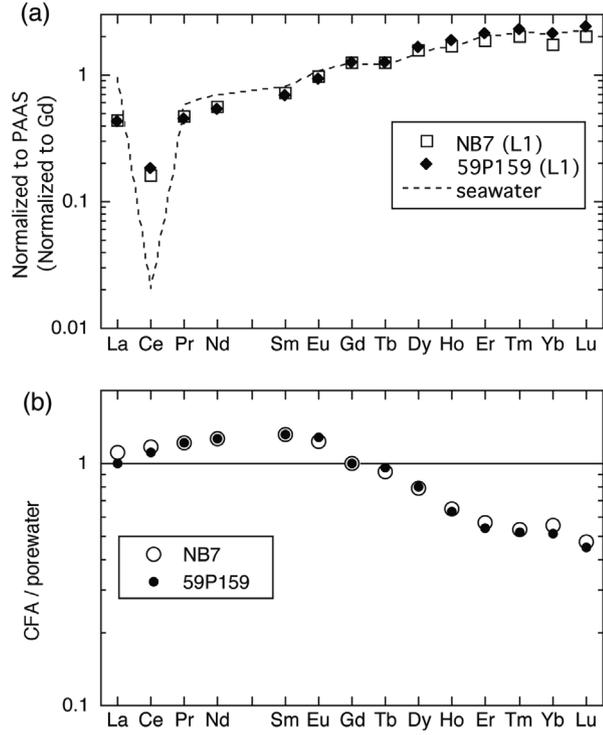
**Table 4.** Distribution coefficient ( $K_{d_{Ln}}$ ) relative to  $K_{d_{Gd}}$  between CFA and porewater, and their 90% confidence limits.

	NB7	59P159
La	1.12 ± 0.04	1.01 ± 0.03
Ce	1.17	1.10
Pr	1.22 ± 0.04	1.21 ± 0.04
Nd	1.27 ± 0.04	1.26 ± 0.04
Sm	1.31 ± 0.03	1.32 ± 0.03
Eu	1.24 ± 0.03	1.28 ± 0.03
Gd	1.00	1.00
Tb	0.925 ± 0.018	0.961 ± 0.019
Dy	0.786 ± 0.017	0.797 ± 0.018
Ho	0.647 ± 0.011	0.632 ± 0.011
Er	0.570 ± 0.014	0.542 ± 0.014
Tm	0.534 ± 0.019	0.521 ± 0.019
Yb	0.559 ± 0.020	0.517 ± 0.019
Lu	0.476 ± 0.017	0.450 ± 0.016

coefficient ( $K_{d_{Ln}}/K_{d_{Gd}}$  ratio) between the CFA (L2) and porewater. The estimated  $K_{d_{Ln}}/K_{d_{Gd}}$  ratios are presented in Table 4 and Fig. 5b. Although the Ce/Gd ratio of the porewater is unclear, the  $K_{d_{Ce}}/K_{d_{Gd}}$  ratio can be estimated from the following equation, assuming that the distribution coefficient shows no Ce anomaly.

$$\log(K_{d_{Ce}} / K_{d_{Gd}}) = (\log(K_{d_{La}} / K_{d_{Gd}}) + \log(K_{d_{Pr}} / K_{d_{Gd}})) / 2. \quad (18)$$

The pattern of the  $K_{d_{Ln}}/K_{d_{Gd}}$  ratio (Fig. 5b) shows a slight increase from La to Sm and a distinct decrease from Sm (1.3) to Lu (0.45~0.48).



**Fig. 5.** (a) Comparison of REE/Gd ratios between calculated porewater and deep seawater. The Ce/Gd ratio was calculated after the calculation of distribution coefficient of REE between CFA and porewater. (b) Distribution coefficient ( $K_{d_{REE}}/K_{d_{Gd}}$ ) of REE between CFA and porewater. The  $K_{d_{REE}}/K_{d_{Gd}}$  was calculated from Eq. (18) assuming that the distribution coefficient shows no Ce anomaly.

### 3.3. Ce /Gd Ratio of Porewater

On the basis of the  $Kd_{Ce}/Kd_{Gd}$  ratio, we can estimate the Ce/Gd ratio of the porewater, assuming that the contributions of components other than CFA to the Ce content of the L2 leachates are negligible. The REE/Gd ratio of the porewater is shown in Fig. 5(a). The size of the negative Ce anomaly of the porewater is smaller than that of the deep-seawater (SA5-5149 m; Zhang and Nozaki, 1996).

## 4. Discussion

### 4.1. Ce anomaly

The calculated REE concentration in porewater shows a smaller negative Ce anomaly than those in the deep-seawater. In fact, Sholkovitz (1989, 1992) and Haley and Klinkhammer (2003) observed that porewater has smaller Ce anomaly relative to bottom seawater. The smaller Ce anomaly implies the preferential Ce release from sediment to porewater (Haley and Klinkhammer, 2003). It is known that suspended particles are effective carriers of REE from seawater to sediment (Murphy and Dymond, 1984; Moffet, 1993; Sholkovitz *et al.*, 1994). Suspended particles coated by Fe-Mn oxyhydroxide and organic matter adsorb REE while sinking through the water column (Moffet, 1993; Sholkovitz *et al.*, 1994). In particular, Ce is effectively adsorbed on suspended particles relative to the other REEs due to the oxidation of Ce(III) to Ce(IV), which is less soluble in oxic seawater (Sholkovitz *et al.*, 1994). As a result, suspended particles show positive Ce anomalies (Sholkovitz *et al.*, 1994). After sedimentation, the particles derived from the seawater column may release Ce due to the degradation of organic matter and Fe-Mn oxyhydroxide during early diagenesis. This process is considered to cause the smaller Ce anomaly of the porewater in the Pacific sediments than that of the deep-seawater.

### 4.2. La depletion

The La depletion estimated by us is actually observed by Haley and Klinkhammer (2003) in porewater of deep-sea sediments, suggesting that our estimation is valid. The calculated porewater shows La depletion relative to the deep-seawater. The La depletion in porewater in pelagic sediment is also inferred from the fact that diagenetic Mn nodules usually show La depletion relative to hydrogenous ones (Fig. 3a; Ohta *et al.*, 1999). The suspended particles, that are responsible for the Ce enrichment in the porewater, are also considered to affect the distributions of other REE in the porewater.

Ohta and Kawabe (2000b) reported that the pattern of the REE distribution coefficient between Fe-Mn oxyhydroxide and seawater shows La depletion, which becomes distinct with decreasing total carbonate concentration. Equatorial Pacific sediments are generally enriched in organic carbon (Ohkouchi *et al.*, 1997). Porewater in equatorial sediments may have a higher total carbonate concentration than seawater due to the degradation of organic matter in the sediment (c.f. Libes, 1992). Thus, the suspended particles with Fe-Mn oxyhydroxide coatings adsorb REE in seawater with lower total carbonate content and, then after sedimentation, the particles release REEs into porewater with higher total carbonate content. As a result, the La migration from seawater to porewater via the suspended particles may be small relative to the flux of the other light-REEs. These processes may cause the La depletion of the porewater in the Pacific sediment.

Another possible reason for the La depletion of the porewater is that authigenic materials in the sediment preferentially take up La from the porewater. However the Mn oxide (L1) and CFA (L2) in the Pacific sediments do not show enough La enrichment to explain the La depletion of the porewater. The R3 residues of NB7 and 59P159 are considered to contain authigenic materials, because the R3 residues show negative Ce anomalies (Fig. 2), which cannot be explained by the contributions of detrital materials (Takebe, 2005). Because R3 is not extractable by a reducing agent and 0.17M HCl, the authigenic materials might be barite and/or clay minerals.

#### 4.3. Distribution coefficient of REE between CFA and porewater

There has been no satisfactory explanation as to how biogenic CFA concentrates REE from ambient solution, although several hypotheses have been proposed (Shemesh, 1990; Grandjean-Léuyer *et al.*, 1993; Reynard *et al.*, 1999). Koeppenkastrop and De Carlo (1992) performed a REE sorption experiment with synthetic hydroxyapatite under seawater conditions, and reported that the distribution coefficient showed a slight increase from La to Nd and a distinct decrease from Nd to Lu. Taking into account the similarity of the ionic radii between the middle-REE<sup>3+</sup> and Ca<sup>2+</sup>, they considered that lattice substitution causes preferential sorption of the middle-REE onto hydroxyapatite relative to other REEs. This mechanism may also influence the REE abundance of the biogenic CFA, because the  $K_{d_{Ln}}/K_{d_{Gd}}$  ratio of the CFA in this study also shows the maximum value for a middle-REE (Sm). On the other hand, the  $K_{d_{La}}/K_{d_{Lu}}$  ratio (5.1) obtained experimentally by Koeppenkastrop and De Carlo (1992) is twice higher than the ratio (2.2~2.5) of our study. Moreover, the Kd values of Koeppenkastrop and De Carlo (1992) range from  $1 \times 10^5$  to  $1 \times 10^6$ , while the Kd value for the CFA in the present study is estimated to be up to  $\sim 10^9$  because of the high La concentrations in the CFA (> 3000 ppm: Takebe, 2005) and the low concentration in deep-seawater (5~6 ppt: Zhang and Nozaki, 1996). These large differences may be caused by the fact that Koeppenkastrop and De Carlo (1992) and this study do not take complexation into consideration in the  $K_{d_{Ln}}$  calculation. In addition, it is reported that variations in crystallinity, carbonate content and F order in the apatite lattice potentially influence the REE abundances in fish apatite in sediment (Shemesh, 1990).

### 5. SUMMARY

In this study, we estimate the REE composition of porewater in Pacific sediment, based on the REE compositions of Mn oxides and CFA component analyzed by Takebe (2005), assuming that Mn oxide and CFA in the sediment were in chemical equilibrium with the porewater in terms of REE.

At first, we estimate the REE/Gd ratio of the porewater except for the Ce/Gd ratio, on the basis of the REE abundance of Mn oxide component. In the calculation, we assumed that REE are mainly dissolved as  $\text{Ln}(\text{CO}_3)_2^-$  and  $\text{LnCO}_3^+$  in porewater, according to the equilibrium calculation. After the estimation of REE composition of porewater, the distribution coefficient of REE ( $K_{d_{\text{REE}}}/K_{d_{\text{Gd}}}$  ratio) between the CFA and porewater is calculated from the REE/Gd ratio of CFA component and porewater. Subsequently, the Ce/Gd ratio of the porewater is evaluated from the pattern of the distribution coefficient.

Our calculated REE composition of porewater shows La depletion and a small negative Ce anomaly relative to deep-seawater (SA5-5149m: Zhang and Nozaki, 1996) when normalized to PAAS, whereas the REE/Gd ratio except for La and Ce is similar to the ratio of the deep seawater. The La depletion is actually observed in porewater (Haley and Klinkhammer, 2003). The difference of REE composition of deep-seawater and porewater suggest that REE in pelagic sediment is mobilized during early diagenesis.

### Acknowledgements

We especially wish to express my gratitude to K. Tanaka, Hiroshima University, who contributed with suggestion and criticism. We also express my gratitude to R. Metcalfe, Quintessa Japan for their patience in revising the English version of this paper. The surface sediments used in this study were collected during GH 80-1 Cruises of the Geological Survey of Japan, and NH 90-1 Cruises of the Northwest Pacific Carbon Cycle Study (NOPACCS) assigned to the Kansai Environmental Engineering Center Co. Ltd. (KEEC) by the New Energy and Industrial Technology Development Organization (NEDO). A. Nishimura, Geological Survey of Japan kindly gave us these Pacific sediments.

## References

- Calvert, S. E., Piper, D. Z., Baedecker, P.A., 1987. Geochemistry of the rare earth elements in ferromanganese nodules from DOMES Site A, northern equatorial Pacific. *Geochim. Cosmochim. Acta* **51**, 2331-2338.
- Cantrell, K. J., Byrne, R. H., 1987. Rare earth element complexation by carbonate and oxalate ions. *Geochim. Cosmochim. Acta* **51**, 597-605.
- Grandjean-Lécuyer, P., Feist, R., Albarède, F., 1993. Rare earth elements in old biogenic apatites. *Geochim. Cosmochim. Acta* **57**, 2507-2514.
- Gieskes, J. M., Johnson, J., 1980. Interstitial-water studies, Leg 58. In: Lee, M., Stout, J. N. (eds) Initial Reports of the Deep Sea Drilling Project, **58**, 607-610.
- Haley, B. A., Klinkhammer, G. P., 2003. Complete separation of rare earth elements from small volume seawater samples by automated ion chromatography: method development and application to benthic flux. *Marine Chem.* **82**, 197-220.
- Kawabe, I., Ohta, A., Ishii, S., Tokumura, M., Miyauchi K., 1999. REE partitioning between Fe-Mn oxyhydroxide precipitates and weakly acid NaCl solutions: Convex tetrad effect and fractionation of Y and Sc from heavy lanthanides. *Geochem. J.* **33**, 167-179.
- Koeppenkastrop, D., De Carlo, E., 1992. Sorption of rare-earth elements from seawater onto synthetic mineral particles: An experimental approach. *Chem. Geol.* **95**, 251-263.
- Leinen, M., Heath, G. R., Biscaye, P. E., Kolla, V., Thiede, J., Dauphin, J., P., 1986. Distribution of biogenic silica and quartz in recent deep-sea sediments. *Geology* **14**, 199-203.
- Libes, S., 1992. An introduction to marine biogeochemistry, John and Sons, Inc., 734pp..
- Millero, F. J., 1992. Stability constants for the formation of rare earth inorganic complexes as a function of ionic strength. *Geochim. Cosmochim. Acta* **56**, 3123-3132.
- Millero, F. J., 1995. Thermodynamics of the carbon dioxide system in the oceans, *Geochim. Cosmochim. Acta* **59**, 661-677.
- Millero, F. J., Schreiber, D. R., 1982. Use of the ion pairing model to estimate activity coefficients of the ionic components of natural water. *Ame. J. Sci.* **282**, 1508-1540.
- Millero, F., Pierrot, D., 2002. Speciation of metals in natural waters, In: Gianguzza A., Pelizzetti, E., Sammartano, S. (eds) Chemistry of marine water and sediments, Springer, pp. 194-221.
- Milodowski, A. E., Zalasiewicz, J. A., 1991. Redistribution of rare earth elements during diagenesis of turbidite/hemipelagite mudrock sequences of Llandovery age from central Wales. In: Morton, A. C., Todd, S. P., Haughton, P. D. W. (eds) Developments in Sedimentary Provenance Studies, Geological Society, London, Special Publication, **57**, 101-124.
- Mironov, V. E., Avramenko, N. I., Koperin, A. A., Blokhin, V. V., Eike, M. Yu., Lasyev, I. D., 1982, Thermodynamics of the formation reaction of the monochloride complexes of the rare earth metals in aqueous solutions. *Koord. Kim.* **8**, 636-638.
- Mofett, J. W., 1993. A radiotracer study of cerium and manganese uptake onto suspended particles in Chesapeake Bay. *Geochim. Cosmochim. Acta* **58**, 695-703.
- Murphy, K., Dymond, J., 1984. Rare earth element fluxes and geochemical budget in the eastern equatorial Pacific. *Nature* **307**, 444-447.
- Murray, R. W., Buchholtz ten Brink, M. R., Brumsack, H. -J., Gerlach, D. C., Russ III, G. P., 1991. Rare-earth elements in Japan Sea sediments and diagenetic behavior of Ce/Ce\*, results from ODP Leg 127. *Geochim. Cosmochim. Acta* **55**, 2657-2671.
- Nakai S., Halliday A. N., Rea D. K., 1993, Provenance of dust in the Pacific Ocean. *Earth Planet. Sci. Lett.* **119**, 143-157.
- Nance, W.B. and Taylor, S.R. 1976, Rare-earth element patterns and crustal evolution. 1. Australian post-Archean sedimentary-rocks, *Geochimica et Cosmochimica Acta* **40**, 1539-1551.
- Ohkouchi, N., Kawamura, K., Kawahata, H., Taira, A., 1997, Latitudinal distributions of terrestrial biomarkers in the sediments from the Central Pacific. *Geochim. Cosmochim. Acta* **61**, 1911-1918.
- Ohta, A., Kawabe, I., 2000a. Theoretical study of tetrad effects observed in REE distribution coefficients between marine Fe-Mn deposit and deep seawater, and in REE(III)-carbonate complexation constants. *Geochem. J.* **34**, 455-473.
- Ohta, A., Kawabe, I., 2000b. Rare earth element partitioning between Fe oxyhydroxide precipitates and aqueous NaCl solutions doped with NaHCO<sub>3</sub>: Determinations of rare earth element complexation constants with carbonate ions.

- Geochem. J.* **34**, 439-454.
- Ohta, A., Ishii, S., Sakakibara, M., Mizuno, A., Kawabe, I., 1999. Systematic correlation of the Ce anomaly with the Co/(Ni+Cu) ratio and Y fractionation from Ho in distinct types of Pacific deep-sea nodules. *Geochem. J.* **33**, 399-417.
- Presley B. J., Culp J. H., 1973. Interstitial water chemistry, Leg 17. In; Roth, P. N., Heriing, J. R. (eds) Initial. Reports of the Deep Sea Drilling Project, 17, 515-516.
- Reynard, B. Lécuyer, C., Grandjean, P., 1999. Crystal-chemical controls on rare-earth element concentrations in fossil biogenic apatites and implications for paleoenvironmental reconstructions. *Chem. Geol.* **155**, 233-241.
- Shemesh, A., 1990. Crystallinity and diagenesis of sedimentary apatites, *Geochim. Cosmochim. Acta* **54**, 2433-2438.
- Sholkovitz, E. R., Piepgras, D. J., Jacobsen B. J., 1989. The pore water chemistry of rare earth elements in Buzzards Bay sediments, *Geochim. Cosmochim. Acta* **53**, 2847-2856.
- Sholkovitz, E. R., Shaw, T. J., Schneider, D. L., 1992. The geochemistry of rare earth elements in the seasonally anoxic water column and porewaters of Chesapeake Bay. *Geochim. Cosmochim. Acta* **56**, 3389-3402.
- Sholkovitz, E.R., Landing, W. M., Lewis, B. L., 1994. Ocean particle chemistry: the fractionation of rare earth elements between suspended particles and seawater. *Geochim. Cosmochim. Acta* **58**, 1567-1579.
- Takebe, M., 2005. Carriers of rare earth elements in Pacific deep-sea sediments. *J. Geol.* **113**, 201-215.
- Takebe, M., Yamamoto, K., 2003, Geochemical fractionation between porcellanite and host sediment, *J. Geol.* **111**, 301-302.
- Taylor, S. R., McLennan, S. M., 1985. The Continental Crust: Its composition and evolution. Blackwell, London, 312pp.
- Toyoda, K., Masuda, A., 1991. Chemical leaching of pelagic sediments: Identification of the carrier of Ce anomaly. *Geochem. J.* **25**, 95-119.
- Toyoda, K., Tokonami, M., 1990. Diffusion of rare-earth elements in fish teeth from deep-sea sediments. *Nature* **345**, 607-609.
- Zhang, J., Nozaki, Y., 1996. Rare earth elements and yttrium in seawater: ICP-MS determinations in the East Caroline, Coral Sea, and South Fiji basins of the western South Pacific Ocean. *Geochim. Cosmochim. Acta* **60**, 4631-4644.

(Received: 18 Sept. 2007, Accepted: 15 Oct. 2007)