Rare earth element partitioning between Fe oxyhydroxide precipitates and aqueous NaCl solutions doped with NaHCO₃: Determinations of rare earth element complexation constants with carbonate ions

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The distribution coefficients of rare earth elements (REEs; all lanthanides except Pm, Y and Sc) between Fe oxyhydroxide precipitates and 0.5 M NaCl solutions with NaHCO₃ (0.0–12.0 mM) at 25°C and 1 bar have been determined. This experimental system is a simple model for REE partitioning between deep-sea ferromanganese nodules and seawater. The distribution coefficients, $K_d(\text{REE: precipitate/solution})$, show systematic variations with increasing NaHCO₃ concentrations. We have determined REE(III)-carbonate complexation constants from the experimental distribution coefficients as a function of NaHCO₃ concentration and pH. The REE(III)-carbonate complexation constants show almost the same series variations as reported values obtained by the solvent-extraction method, although our results by the precipitation method are rather higher by 1.0–1.5 in log unit than the literature data at zero ionic strength.

INTRODUCTION

Rare earth elements (REEs) are highly enriched in marine ferromanganese nodules (Piper, 1974; Elderfield *et al.*, 1981; Ohta *et al.*, 1999) and ferromanganese crusts (De Carlo and McMurtry, 1992; Bau *et al.*, 1996). The removal of REE by Fe-Mn oxyhydroxides from seawater into marine suspending particles and sediments is an important geochemical process. In order to investigate the incorporation of seawater REE into deep-sea nodules and crusts, Koeppenkastrop and De Carlo (1992) reported the experimental results of sorption of REEs from seawater onto Fe oxyhydroxides and Mn oxides. Bau (1999) has recently reported an experimental study of the sorption of REEs from spring water with low salinity and low pH onto Fe oxyhydroxides.

In seawater, the dissolved REE species are mainly $\text{REECO}_3^+(\text{aq})$ and $\text{REE}(\text{CO}_3)_2^-(\text{aq})$ (Byrne and Sholkovitz, 1996). It is very important to ex-

amine how REE(III)-carbonate complexation affects the REE partitioning process in seawater. Kawabe *et al.* (1999a, b) reported preliminary experimental results of REE partitioning between Fe oxyhydroxide precipitates and NaCl solutions with and without carbonate ions. They emphasized that the lanthanide tetrad effect is associated with the distribution coefficients of REEs between Fe oxyhydroxide precipitates and NaCl solutions. They analyzed their experimental results using the refined spin-pairing energy theory, RSPET, (Jørgensen, 1979; Kawabe, 1992). Although Kawabe *et al.* (1999b) estimated the complexation constants for $\text{REE}(\text{CO}_3)_2^-$ from their experimental results, they could not estimate those for REECO_3^+ from the preliminary data. REE(III)-carbonate complexation constants have been reported by Byrne and co-workers (Cantrell and Byrne, 1987a, b; Lee and Byrne, 1992, 1993; Byrne and Lee, 1993; Liu and Byrne, 1995, 1998). They determined the stability constants using the

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solvent-extraction method of Lundqvist (1982). Solvent-extraction is a classical method for determining stability constants, but the extraction system itself does not correspond to a particular natural reaction system. On the other hand, our Fe oxyhydroxide precipitation method is not frequently used for determining stability constants. However, the precipitation reaction itself has immediate geochemical importance.

The purposes of this paper are: (1) to present more detailed experimental data for REE partition coefficients between Fe oxyhydroxides and NaCl solutions with and without NaHCO_3 , (2) to determine REE(III)-carbonate complexation constants including those for all lanthanides except Pm, Y and Sc, by the precipitation method, and (3) to compare the complexation constants with those determined by solvent-extraction method.

EXPERIMENTAL

The experimental method was based on that of Kawabe *et al.* (1999a, b). For determining REE distribution coefficients between Fe oxyhydroxide precipitates and aqueous NaCl solutions, a mixed REE(III) solution containing 10 mg/l of each lanthanide except Pm, Y and Sc, and an Fe(III) solution with 100 mg/l were prepared. All the metal solutions have the same HCl concentration of 0.2 M. A NaHCO_3 (0.119 M) solution for REE(III)-carbonate complexation was also prepared.

Iron(III) oxyhydroxide precipitates were formed in NaCl (0.50 ± 0.02 M) solutions by adding 15 ml of the Fe(III) solution and 10 ml of the mixed REEs(III) solution to approximately 500 ml of the NaCl solution. Their pH were adjusted to be about 6.0 ± 0.5 by using dilute NaOH and HCl solutions. In order to examine the effect of REE(III)-carbonate complexation on the distribution coefficients, variable volumes (3.0–50.0 ml) of the NaHCO_3 solution were added to the NaCl solutions adjusted their pH to about 6.5 ± 0.5 . Iron oxyhydroxide precipitates formed in the NaCl solutions were gently stirred with magnetic stirrers in glass flasks placed in a water bath with a constant temperature ($25.0 \pm 0.1^\circ\text{C}$). Stirring was

continued from 3 to 145 hours.

After the measurement of the final pH of each NaCl solution by using a HORIBA D-12 pH meter, the precipitate and solution were separated by filtration. The pH of each solution was determined within ± 0.01 to 0.03. The precipitate on the filter was dissolved with HCl. Iron was separated from REEs by using the cation-exchange technique with a Bio-Rad AG 50WX8 (200–400 mesh) column ($\phi = 1 \text{ cm} \times 11 \text{ cm}$), and Fe and REE were determined by a SEIKO SPS-1500R ICP-AES spectrometer.

Dissolved REEs in each NaCl solution were coprecipitated with Fe(III) oxyhydroxide by adding 14 mg of Fe(III) and adjusting its pH to about 6.5. For the purpose of satisfactory recovery of dissolved REEs, this coprecipitation was repeated for the filtrate. The first and second precipitates were dissolved in HCl. The recovered REEs in Fe(III) solution were purified by cation-exchange chromatography, and then determined by ICP-AES as above. The accuracy of REE and Fe analyses by ICP-AES was about 1–5%.

In order to characterize the mixed precipitates of Fe and REEs, we examined the FT-IR spectra of Fe oxyhydroxide precipitates with and without REE. The Fe oxyhydroxide precipitate without any REE, and Fe oxyhydroxide precipitates with mixed REEs and with only Nd were prepared for FT-IR analyses. The Fe(III) (15 mg), Fe(III) (15 mg) plus mixed REEs(III) (16 mg), and Fe(III) (15 mg) plus Nd(III) (16 mg) were added to respective experimental NaCl solutions, and then their precipitates were formed in the 0.5 M NaCl solutions without NaHCO_3 and with NaHCO_3 of 1.4 mM. The experimental solutions doped with NaHCO_3 of 1.4 mM have a carbonate ion concentration similar to those of seawater. The final pH of the solutions with and without NaHCO_3 were about 8.0 and 6.5, respectively. The precipitates were filtered by $0.2 \mu\text{m}$ membrane filter and dried at 50 – 60°C . In order to examine the presence of carbonate ion, the FT-IR spectra of reagent CaCO_3 were also obtained as a reference. Iron(III) precipitates and mixed precipitates of Fe plus REEs and of Fe plus Nd, and CaCO_3 were mixed with

KBr, and then their diffuse reflection spectra were recorded on a Bio-Rad FTS-6000 FT-IR spectrometer. The absorption spectra of these samples were obtained as the difference of the diffuse reflection spectra between the respective samples and KBr.

RESULTS

Aging effect on $\log K_d(\text{REE})$ and pH of the experimental system

We examined the variations of $\log K_d(\text{REE})$ and pH in the systems with and without NaHCO_3 against the reaction times of Fe oxyhydroxide precipitates in NaCl solutions. The pH in the system without NaHCO_3 were adjusted to be about 6.5. In the case of the experimental system with NaHCO_3 , NaHCO_3 concentrations were adjusted to 1.4 mM after pH adjustment to 6.5~7.0. In Fig. 1, $\log K_d(\text{Gd})$ and pH in the systems with and without NaHCO_3 are plotted against the reaction time. Each $K_d(\text{REE})$ value is calculated as $X_{\text{REE}}/[\text{REE}]$, where X_{REE} denotes the mole fraction of each REE given by $\text{REE}/(\text{Fe} + \sum \text{REE})$ in the mixed precipitate, and $[\text{REE}]$ stands for REE concentration (mol/liter) in the solution. The $\log K_d(\text{Gd})$ and pH

Fig. 1. The aging behavior of $\log K_d(\text{Gd})$ and pH in experimental solutions with and without NaHCO_3 .

in both systems with and without NaHCO_3 once decreased for the first 3~6 hours, but they gradually increased and became constant after 72 hours. Figure 2 shows the series variations of $\log K_d(\text{REE})$ in the systems with and without NaHCO_3 . The series variations of $\log K_d(\text{REE})$ are almost parallel to one another irrespective of the reaction time in both cases with and without NaHCO_3 . The series variation of $\log K_d(\text{REE})$ is almost independent of the reaction time of precipitate in solution, but $\log K_d(\text{REE})$ and pH became constants after 72 hours in our systems. As we will discuss later, pH is a very important factor controlling the REE partitioning reaction. We adopted the $K_d(\text{REE})$ values in the runs with reaction times of 135~145 hours.

FT-IR characterization of REE coprecipitated with Fe oxyhydroxides

Kawabe *et al.* (1999a, b) expressed the REE coprecipitated with Fe oxyhydroxides as $\text{REE}(\text{OH})_3 \cdot n\text{H}_2\text{O}_{(\text{ss})}$. However it has been reported

Fig. 2. The series variation of $\log K_d(\text{REE})$ in the Fe(III) precipitate-solution systems with different aging times. The two cases of the experimental solutions with and without NaHCO_3 are shown.

that REE(III) precipitates from REE(III) solutions with carbonate ion are hydroxycarbonates, $\text{REEOHCO}_3 \cdot n\text{H}_2\text{O}_{(\text{c})}$, and hydrated carbonate, $\text{REE}_2(\text{CO}_3)_3 \cdot n\text{H}_2\text{O}_{(\text{c})}$, (Caro and Lemaitre-Blaise, 1969; Meinrath and Takeishi, 1993; Gamsjäger *et al.*, 1995). These REE phases have been obtained from REE(III) solutions in contact with atmospheric air and CO_2 , and pH of the experimental solutions were 4.0–7.0. In our experiment, however, REEs were incorporated into the Fe oxyhydroxide precipitate at the pH range of 5.6–8.7. It is difficult to characterize this kind of precipitate by X-ray powder diffraction because of its amorphous nature. We examined the possible presence of $\text{REEOHCO}_3 \cdot n\text{H}_2\text{O}_{(\text{c})}$ or $\text{REE}_2(\text{CO}_3)_3 \cdot n\text{H}_2\text{O}_{(\text{c})}$ in the mixed precipitates of Fe and REEs by FT-IR spectroscopy. Figure 3 shows the results of FT-IR spectra of Fe oxyhydroxide precipitate and mixed precipitates of Fe and all REEs and of Fe and Nd. Because the IR-active modes of carbonate ion are almost common to any carbonate minerals, we also plotted our FT-IR spectra of CaCO_3 as the representative spectra of carbonate ion. FT-IR spectra of CaCO_3 in Fig. 3 shows the strongest three peaks to be: $\nu_3 = 1437\text{--}1457\text{ cm}^{-1}$, $\nu_2 = 877\text{ cm}^{-1}$ and $\nu_4 = 713\text{ cm}^{-1}$. $\text{REEOHCO}_3 \cdot n\text{H}_2\text{O}_{(\text{c})}$ and $\text{REE}_2(\text{CO}_3)_3 \cdot n\text{H}_2\text{O}_{(\text{c})}$ have characteristic IR spectra consisting of strong bands around $\nu_3 = 1410\text{--}1500\text{ cm}^{-1}$, $\nu_2 = 810\text{--}860\text{ cm}^{-1}$ and $\nu_4 = 710\text{--}760\text{ cm}^{-1}$ (Caro and Lemaitre-Blaise, 1969; Dexpert and Caro, 1974; Caro *et al.*, 1972). The REE or Nd contents were $1.7\text{--}3.5 \times 10^{-5}$ mol per 1 g of Fe-REE-KBr or Fe-Nd-KBr mixed powder samples for FT-IR analysis. We have confirmed that the strongest three peaks of CaCO_3 were able to be satisfactorily obtained when the CaCO_3 contents were $0.8\text{--}1.0 \times 10^{-5}$ mol per 1 g of CaCO_3 -KBr mixed powder samples.

In Fig. 3, the peaks at $2300\text{--}2400\text{ cm}^{-1}$ and 1380 cm^{-1} indicate contamination by CO_2 and H_2O , respectively, in the samples and KBr. Differences of the absorbance in these peaks among samples indicate different contents of CO_2 and H_2O . As shown in Fig. 3, the FT-IR spectra of the mixed precipitates of Fe and REE and of Fe and

Fig. 3. FT-IR spectra of Fe oxyhydroxide precipitate, Fe oxyhydroxides coprecipitated with mixed REEs, Fe oxyhydroxides coprecipitated with Nd, and CaCO_3 . The X value for CaCO_3 is 0.0. [A] Fe: Fe oxyhydroxide precipitate without any REEs and $X = 0$, [B] Fe-REE: Fe oxyhydroxide coprecipitated with mixed REEs in the solution without NaHCO_3 at $\text{pH} = 6.5$ and $X = 0.54$, [C] Fe-Nd: Fe oxyhydroxide coprecipitated with Nd in the solution without NaHCO_3 at $\text{pH} = 6.5$ and $X = 0.45$, [D] Fe-REE: Fe oxyhydroxide coprecipitated with mixed REEs in the solution with NaHCO_3 of 1.4 mM at $\text{pH} = 8.0$ and $X = 1.16$, and [E] Fe-Nd: Fe oxyhydroxide coprecipitated with Nd in the solution with NaHCO_3 of 1.4 mM at $\text{pH} = 8.0$ and $X = 0.93$.

Nd are similar to those of Fe oxyhydroxide. The mixed precipitates of Fe and REEs and of Fe and Nd, however, do not show the three characteristic peaks of carbonate ion (ν_3 , ν_2 and ν_4) shown by the IR spectra of CaCO_3 or reported by Caro and Lemaitre-Blaise (1969), Dexpert and Caro (1974), and Caro *et al.* (1972). The FT-IR spectra of the mixed precipitates of Fe and REEs and of Fe and Nd also do not coincide with those of $\text{REE}(\text{OH})_3$ or REEOOH (Klevtsov *et al.*, 1967). From the FT-IR results, the coprecipitates of Fe and REEs are

Fig. 4. Experimental results of $\log K_d(\text{REE})$ in 0.5 M NaCl solutions without NaHCO_3 .

rather homogeneous. We will write the coprecipitates as $(\text{Fe}, \text{REE}) (\text{OH})_3 \cdot n\text{H}_2\text{O}$ in this study.

REE partitioning coefficients between Fe oxyhydroxide precipitates and NaCl solutions without NaHCO_3

We have determined REE partitioning coefficients between Fe oxyhydroxides and NaCl solutions without NaHCO_3 over the pH range from 5.6 to 6.6. Experiments at $\text{pH} > 7.0$ were not carried out in order to avoid contamination of the aqueous solutions by atmospheric CO_2 and the complexation of heavy REE^{3+} with OH^- . The experimental results for $\log K_d(\text{REE})$ for Ln, Y and Sc are shown in Fig. 4. They commonly show heavy REE enrichment features and they are parallel to one another. All the variation patterns exhibit convex tetrad curves, small positive Ce anomalies, $\log K_d(\text{Y})$ smaller than $\log K_d(\text{Ho})$, and $\log K_d(\text{Sc})$ values much larger than those of the other REEs. These characteristics are in agreement with those reported by Bau (1999) and Kawabe *et al.* (1999a).

The REE concentration (mol/liter) in each experimental NaCl solution determined analytically is the sum of the concentration of free REE^{3+} ion and those of minor REE complexes like $\text{REECl}^{2+}_{(\text{aq})}$ and $\text{REEOH}^{2+}_{(\text{aq})}$,

$$\begin{aligned} [\text{REE}]_{\text{total}} &= [\text{REE}^{3+}_{\text{aq}}] + [\text{REECl}^{2+}_{\text{aq}}] \\ &\quad + [\text{REEOH}^{2+}_{\text{aq}}] \\ &= [\text{REE}^{3+}_{\text{aq}}] \cdot (1 + \psi), \end{aligned} \quad (1)$$

where

$$\psi = \beta_{\text{REECl}^{2+}} \cdot [\text{Cl}^-]_{\text{aq}} + \beta_{\text{REEOH}^{2+}} \cdot [\text{OH}^-]_{\text{aq}}, \quad (2)$$

$\beta_{\text{REECl}^{2+}}$ and $\beta_{\text{REEOH}^{2+}}$ are the complex formation constants for the respective complexes. Experimental partition coefficients, $K_d(\text{REE})$, are written as follows;

$$\begin{aligned} K_d(\text{REE}) &= X_{\text{REE}} / [\text{REE}]_{\text{total}} \\ &= X_{\text{REE}} / \{ [\text{REE}^{3+}_{\text{aq}}] \cdot (1 + \psi) \}. \end{aligned} \quad (3)$$

The $K_d(\text{REE})$ values for REE in our experiments are related to the equilibrium constants for the following ligand-exchange reactions;

The equilibrium constant for Eq. (4) is expressed by

$$\log K_{(4)} = \log \left[\left\{ \frac{a_{\text{REE}(\text{OH})_3 \cdot n\text{H}_2\text{O}}}{a_{\text{REE}^{3+}}} \right\} \cdot \left\{ \frac{a_{\text{H}^+}^3}{a_{\text{H}_2\text{O}}^{3+n}} \right\} \right]. \quad (5)$$

The distinction between REE concentration values in (mol/kg) and (mol/liter) is insignificant in our experimental solutions, because concentrations are quite low. Therefore, the activities of $\text{REE}(\text{OH})_3 \cdot n\text{H}_2\text{O}_{(\text{ss})}$ and $\text{REE}^{3+}_{(\text{aq})}$ are expressed in terms of $[\text{REE}^{3+}_{\text{aq}}]$ in (mol/liter) and the mole fraction of $\text{REE}(\text{OH})_3 \cdot n\text{H}_2\text{O}_{(\text{ss})}$ in the mixed precipitate, and the respective activity coefficients;

$$a_{\text{REE}(\text{OH})_3 \cdot n\text{H}_2\text{O}} = \lambda_{\text{REE}(\text{OH})_3 \cdot n\text{H}_2\text{O}} \cdot X_{\text{REE}(\text{OH})_3 \cdot n\text{H}_2\text{O}}, \quad (6)$$

and

$$a_{\text{REE}^{3+}} = \gamma_{\text{REE}^{3+}} \cdot [\text{REE}^{3+}]_{\text{aq}}. \quad (7)$$

From Eqs. (6) and (7), Eq. (5) can be re-written in the form;

$$\begin{aligned} \log K_{(4)} = & \log \left\{ \frac{X_{\text{REE}(\text{OH})_3 \cdot n\text{H}_2\text{O}}}{[\text{REE}^{3+}]_{\text{aq}}} \right\} - 3\text{pH} \\ & - (3+n) \log a_{\text{H}_2\text{O}} + \log \left\{ \frac{\lambda_{\text{REE}(\text{OH})_3 \cdot n\text{H}_2\text{O}}}{\gamma_{\text{REE}^{3+}}} \right\}. \end{aligned} \quad (8)$$

Because the ionic strengths are almost constant in all the runs, we can assume that $a_{\text{H}_2\text{O}}$ and $\gamma_{\text{REE}^{3+}}$ is approximately constant among all the runs. The $X_{\text{REE}(\text{OH})_3 \cdot n\text{H}_2\text{O}}$ values varied from 0.08 to 0.2 at pH range from 5.6 to 6.6, but we can consider that $\lambda_{\text{REE}(\text{OH})_3 \cdot n\text{H}_2\text{O}}$ is also constant among the all runs. We determined REE distribution coefficients when we doped 7–100 mg of Fe(III) and 16 mg of REEs(III) into solutions at pH = 5.4–6.6. Their $X_{\text{REE}(\text{OH})_3 \cdot n\text{H}_2\text{O}}$ values varied from 0.02 to 0.2, but we could not recognize the systematic variations of $\lambda_{\text{REE}(\text{OH})_3 \cdot n\text{H}_2\text{O}}$.

Equation (8) is written by using Eq. (3) as follows;

$$\begin{aligned} & \log K_d(\text{REE}) - 3\text{pH} \\ & = \log K_{(4)} - \log (1 + \psi) + \text{constant}. \end{aligned} \quad (9)$$

Kawabe *et al.* (1999a) suggested that $\text{REECl}^{2+}_{(\text{aq})}$ and $\text{REEOH}^{2+}_{(\text{aq})}$ are not so significant relative to $\text{REEs}^{3+}_{(\text{aq})}$ except for Sc in experimental solutions with no NaHCO_3 and pH = 5~6. In the experimental 0.5 M NaCl solutions with pH = 6.0, the respective percentages of $\text{Gd}^{3+}_{(\text{aq})}$, $\text{GdCl}^{2+}_{(\text{aq})}$ and $\text{GdOH}^{2+}_{(\text{aq})}$ are 87.6%, 12.1% and 0.3%, when we

Table 1. Infinite dilution stability constants for REE complexation constants with anions at 25°C

	log K		
	REECl^{2+}	REEOH^{2+}	REEHCO_3^{2+}
La	0.48	5.10	2.02
Ce	0.47	5.60	1.95
Pr	0.44	5.60	1.89
Nd	0.40	5.67	1.83
Sm	0.36	5.81	1.75
Eu	0.34	5.83	1.60
Gd	0.33	5.79	1.72
Tb	0.32	5.98	1.71
Dy	0.31	6.04	1.72
Ho	0.30	6.01	1.73
Er	0.26	6.15	1.76
Tm	0.25	6.19	1.79
Yb	0.24	6.22	1.84
Lu	0.23	6.24	1.90
Y	0.35*	5.85*	1.73
reference	(1)	(2)	(3)

(1) Mironov *et al.* (1982).

(2) Millero (1992).

(3) Liu and Byrne (1998).

*The Y values were calculated according to Byrne and Lee (1993).

use the complexation constants of $\beta_{\text{REECl}^{2+}}$ (Mironov *et al.*, 1982) and $\beta_{\text{REEOH}^{2+}}$ (Millero, 1992) (see Table 1). We can assume that $[\text{REE}]_{\text{total}}$ is virtually equal to $[\text{REE}^{3+}]_{\text{aq}}$, namely, the $\log (1 + \psi)$ value is approximately zero. The experimental values of $\{\log K_d(\text{REE}) - 3\text{pH}\}$ except those for Sc are expected to be approximately constant over the experimental pH range (5.6~6.6). We cannot ignore the $\log (1 + \psi)$ value for Sc unlike the other REEs because of the extremely large complexation constant of $\text{ScOH}^{2+}_{(\text{aq})}$ reported by Travers *et al.* (1976).

Figure 5(a) shows $\{\log K_d(\text{REE}) - 3\text{pH}\}$ values for La, Gd, Lu and Sc plotted against pH. The $\{\log K_d(\text{REE}) - 3\text{pH}\}$ values for La, Gd and Lu decrease with increasing pH, and they become roughly constant at relatively high pH range (6.4~6.6). The pH dependence of $\{\log K_d(\text{REE}) - 3\text{pH}\}$ under more acidic conditions arises from two factors. First, the isoelectric zero point charge (ZPC) of amorphous Fe oxyhydroxide is slightly

Fig. 5. (a) The pH dependence of $\{\log K_d(\text{REE}) - 3\text{pH}\}$ values for La, Gd, Lu, and Sc in the system without NaHCO₃, (b) The pH dependence of $\log \{K_d(\text{Sc})/K_d(\text{Gd})\}$ in the system without NaHCO₃.

higher than our experimental pH range. Because amorphous Fe oxyhydroxide has a ZPC of 7.0~8.5 (Parks, 1965), the surface charge of our precipitates becomes close to zero with increasing pH. This surface charge variation with pH may affect our distribution coefficients. Second, Wood (1990) suggested that REE hydrolysis is not significant in weakly acidic pH range (<6). At low pH a portion of the REE may be precipitated by the adsorption reaction onto Fe oxyhydroxide surface. However, $\{\log K_d(\text{REE}) - 3\text{pH}\}$ values become roughly constant in the range of pH = 6.4~6.6, therefore the precipitation reaction of REE can be given by Eq. (4).

In Fig. 5(a), the $\{\log K_d(\text{Sc}) - 3\text{pH}\}$ values linearly decrease with increasing pH, which is a quite different behavior from those of the other REEs. The decrease of $\{\log K_d(\text{Sc}) - 3\text{pH}\}$ value includes the influence of the complexation of Sc^{3+} with OH^- and the apparent pH dependence of experimental distribution coefficient like the other REEs. Figure 5(b) shows $\log \{K_d(\text{Sc})/K_d(\text{Gd})\}$ plotted against the pH. In Fig. 5(b), the observed pH dependence of $\log \{K_d(\text{Sc})/K_d(\text{Gd})\}$ is possibly caused by complexation of Sc^{3+} with OH^- . The main species of Sc in our experimental solution may be $\text{Sc}^{3+}_{(\text{aq})}$, $\text{ScCl}^{2+}_{(\text{aq})}$, $\text{Sc}(\text{Cl})^{+}_{2(\text{aq})}$ and $\text{ScOH}^{2+}_{(\text{aq})}$ according to the complexation con-

stants reported by Travers *et al.* (1976). Kawabe *et al.* (1999a), however, showed that complexation constants for $\text{ScCl}^{2+}_{(\text{aq})}$ and $\text{Sc}(\text{Cl})^{+}_{2(\text{aq})}$ reported by Travers *et al.* (1976) are too large to be accepted. Because $\log (1 + \psi)$ value for Gd is nearly zero, $\log \{K_d(\text{Sc})/K_d(\text{Gd})\}$ is written as follows;

$$\begin{aligned} \log K_d(\text{Sc})/K_d(\text{Gd}) &= \log \{X_{\text{Sc}}/[\text{Sc}]_{\text{total}}\} - \log K_d(\text{Gd}) \\ &= \log \{X_{\text{Sc}}/[\text{Sc}^{3+}_{\text{aq}}]\} - \log (1 + \psi) - \log K_d(\text{Gd}), \end{aligned} \quad (10)$$

where

$$\psi = \beta_{\text{ScOH}^{2+}} \cdot [\text{OH}^{-}_{\text{aq}}]. \quad (11)$$

From the pH dependence of $\log \{K_d(\text{Sc})/K_d(\text{Gd})\}$ in Fig. 5(b), we calculated $\log \beta_{\text{ScOH}^{2+}}$ to be 7.61 at $I = 0.50$ using Eqs. (10) and (11). Using $\gamma_{\text{Sc}^{3+}}$ of 0.0565 (Millero and Schreiber, 1982) and $\gamma_{\text{OH}^{-}}$ of 0.657 (Millero, 1992), and assuming $\gamma_{\text{ScOH}^{2+}}$ of 0.152 (Millero, 1992), we obtained $\beta_{\text{ScOH}^{2+}}$ of 8.22 at zero ionic strength. This value is smaller than $\beta_{\text{ScOH}^{2+}}$ of 9.56 at zero ionic strength reported by Travers *et al.* (1976). The proportion of $\text{ScOH}^{2+}_{(\text{aq})}$ to total Sc in our experimental solution is 36% at pH = 5.6, 59% at pH = 6.0, and 85% at pH = 6.6.

REE partitioning coefficients between Fe oxyhydroxide precipitates and NaCl solutions doped with NaHCO₃

In our experiments, the NaHCO₃ concentrations in NaCl solutions were changed from 0.70 mM to 12.0 mM and the experimental pH range was from 7.6 to 8.7. Figure 6 shows some experimental values of $\{\log K_d(\text{REE}) - 3\text{pH}\}$ with the reaction time of precipitates in solutions of 135~145 hours. In Fig. 6, the “average values (0.0 mM)” indicates the mean values of $\{\log K_d(\text{REE}) - 3\text{pH}\}$ in the system without NaHCO₃ at the pH range of 6.4~6.6. The variation patterns of

Fig. 6. Experimental results of $\{\log K_d(\text{REE}) - 3\text{pH}\}$ for the systems of Fe oxyhydroxide precipitates and 0.5 M NaCl solutions with different NaHCO₃ concentrations (0.0–12.0 mM). The “average values (0.0 mM)” indicates the average $\{\log K_d(\text{REE}) - 3\text{pH}\}$ values in 0.5 M NaCl solutions without NaHCO₃ over the pH range from 6.4 to 6.6 (see Fig. 5(a)).

$\{\log K_d(\text{REE}) - 3\text{pH}\}$ values in the system with NaHCO₃ across the REE series have more or less convex tetrad effects, positive Ce anomalies, and $K_d(\text{Y})/K_d(\text{Ho})$ ratios less than unity in all the runs. These features are similar to the REE partition coefficients in the system without NaHCO₃ (Fig. 4). However, with increasing NaHCO₃ concentration, the $\{\log K_d(\text{REE}) - 3\text{pH}\}$ values show following systematic variations:

i) the decreases of $\{\log K_d(\text{REE}) - 3\text{pH}\}$ for heavy REE are pronounced when compared with those of light REE,

ii) the convex tetrad curves become less obvious as the NaHCO₃ concentration approaches 12.0 mM,

iii) the $\log K_d(\text{Y})/K_d(\text{Ho})$ is -0.46 when $[\text{NaHCO}_3] = 0.0$ mM, but it is -0.25 when $[\text{NaHCO}_3] = 12.0$ mM, and

iv) the decrease of $\{\log K_d(\text{Sc}) - 3\text{pH}\}$ is much greater than those of heavy REE. The $\log K_d(\text{Sc})/K_d(\text{Lu})$ decreases from 2.02 to 0.05 as $[\text{NaHCO}_3]$ increases from 0.0 mM to 12.0 mM.

These characteristics of $\{\log K_d(\text{REE}) - 3\text{pH}\}$ as a function of the NaHCO₃ concentration are caused by REE(III)-carbonate complexation in solution as pointed out by Kawabe *et al.* (1999b).

Determination of REE(III)-carbonate complexation constants

In the experimental NaCl solution doped with NaHCO₃, the total REE concentration in each solution is expressed as follows;

$$\begin{aligned}
 [\text{REE}]_{\text{total}} &= [\text{REE}^{3+}, \text{aq}] + [\text{REECl}^{2+}, \text{aq}] \\
 &\quad + [\text{REEOH}^{2+}, \text{aq}] + [\text{REEHCO}_3^{2+}, \text{aq}] \\
 &\quad + \sum_n [\text{REE}(\text{CO}_3)_n^{3-2n}, \text{aq}] \\
 &= [\text{REE}^{3+}, \text{aq}] \cdot (1 + \psi),
 \end{aligned} \tag{12}$$

where

$$\begin{aligned} \psi = & \beta_{\text{REECl}^{2+}} \cdot [\text{Cl}^-, \text{aq}] + \beta_{\text{REEOH}^{2+}} \cdot [\text{OH}^-, \text{aq}] \\ & + \beta_{\text{REEHCO}_3^{2+}} \cdot [\text{HCO}_3^+, \text{aq}] \\ & + \sum_n \beta_{\text{REE}(\text{CO}_3)_n^{3-2n}} \cdot [\text{CO}_3^{2-}, \text{aq}]^n \end{aligned} \quad (13)$$

and β 's are the complex formation constants as before. When we write each distribution coefficient in the solution with NaHCO₃ as $\{\log K_d(\text{REE}) - 3\text{pH}\}_{(\Psi \neq 0)}$, it can be re-written by using Eqs. (3), (8) and (12);

$$\begin{aligned} & \{\log K_d(\text{REE}) - 3\text{pH}\}_{(\Psi \neq 0)} \\ & = \log K_{(4)} - \log(1 + \psi)_{(\Psi \neq 0)} - (3 + n) \log a_{\text{H}_2\text{O}(\Psi \neq 0)} \\ & \quad + \log \left\{ \lambda_{\text{REE}(\text{OH})_3 \cdot n\text{H}_2\text{O}} / \gamma_{\text{REE}^{3+}} \right\}_{(\Psi \neq 0)}. \end{aligned} \quad (14)$$

Similarly, the distribution coefficient in the system without NaHCO₃, which is written as $\{\log K_d(\text{REE}) - 3\text{pH}\}_{(\Psi = 0)}$, is expressed by,

$$\begin{aligned} & \{\log K_d(\text{REE}) - 3\text{pH}\}_{(\Psi = 0)} \\ & = \log K_{(4)} - \log(1 + \psi)_{(\Psi = 0)} - (3 + n) \log a_{\text{H}_2\text{O}(\Psi = 0)} \\ & \quad + \log \left\{ \lambda_{\text{REE}(\text{OH})_3 \cdot n\text{H}_2\text{O}} / \gamma_{\text{REE}^{3+}} \right\}_{(\Psi = 0)}. \end{aligned} \quad (15)$$

The terms $\log a_{\text{H}_2\text{O}}$ and $\log \{ \lambda_{\text{REE}(\text{OH})_3 \cdot n\text{H}_2\text{O}} / \gamma_{\text{REE}^{3+}} \}$ must be approximately the same in both Eqs. (14) and (15). Hence, we obtain the following equation;

$$\begin{aligned} & \{\log K_d(\text{REE}) - 3\text{pH}\}_{(\Psi = 0)} \\ & \quad - \{\log K_d(\text{REE}) - 3\text{pH}\}_{(\Psi \neq 0)} \\ & = \log(1 + \psi)_{(\Psi \neq 0)} - \log(1 + \psi)_{(\Psi = 0)}, \end{aligned} \quad (16)$$

where

$$\begin{aligned} & (1 + \psi)_{(\Psi = 0)} \\ & = 1 + \beta_{\text{REECl}^{2+}} \cdot [\text{Cl}^-, \text{aq}] + \beta_{\text{REEOH}^{2+}} \cdot [\text{OH}^-, \text{aq}], \end{aligned} \quad (17)$$

and

$$\begin{aligned} & (1 + \psi)_{(\Psi \neq 0)} \\ & = 1 + \beta_{\text{REECl}^{2+}} \cdot [\text{Cl}^-, \text{aq}] + \beta_{\text{REEOH}^{2+}} \cdot [\text{OH}^-, \text{aq}] \\ & \quad + \beta_{\text{REEHCO}_3^{2+}} \cdot [\text{HCO}_3^-, \text{aq}] \\ & \quad + \sum_n \beta_{\text{REE}(\text{CO}_3)_n^{3-2n}} \cdot [\text{CO}_3^{2-}, \text{aq}]^n. \end{aligned} \quad (18)$$

The left-hand side of Eq. (16) corresponds to the difference between $\{\log K_d(\text{REE}) - 3\text{pH}\}_{(\Psi = 0)}$ and $\{\log K_d(\text{REE}) - 3\text{pH}\}_{(\Psi \neq 0)}$, and it can be seen graphically in Fig. 6.

We used the mean values of $\{\log K_d(\text{REE}) - 3\text{pH}\}$ in the solutions without NaHCO₃ at relatively high pH range (6.4~6.6) as the reference values of $\{\log K_d(\text{REE}) - 3\text{pH}\}_{(\Psi = 0)}$. However, it is difficult to determine all the complexation constants from Eqs. (16)–(18). In particular, $\beta_{\text{REECl}^{2+}}$, $\beta_{\text{REEOH}^{2+}}$ and $\beta_{\text{REEHCO}_3^{2+}}$ cannot be determined precisely, because they are much smaller than $\beta_{\text{REECO}_3^+}$ and $\beta_{\text{REE}(\text{CO}_3)_2^-}$ as in Millero (1992). We first corrected the values of $\{\log K_d(\text{REE}) - 3\text{pH}\}$ using literature values of $\beta_{\text{REECl}^{2+}}$, $\beta_{\text{REEOH}^{2+}}$ and $\beta_{\text{REEHCO}_3^{2+}}$. When we define Ψ as follows,

$$\Psi = \sum_n \beta_{\text{REE}(\text{CO}_3)_n^{3-2n}} \cdot [\text{CO}_3^{2-}, \text{aq}]^n, \quad (19)$$

from Eqs. (17)–(19), Ψ can be given by the following equation,

$$\begin{aligned} \Psi = & \left\{ \frac{K_d(\text{REE})_{(\Psi = 0)}}{K_d(\text{REE})_{(\Psi \neq 0)}} \right\} \cdot \left\{ \frac{a_{\text{H}^+}^{3(\Psi = 0)}}{a_{\text{H}^+}^{3(\Psi \neq 0)}} \right\} \cdot (1 + \psi)_{(\Psi = 0)} - 1 \\ & - \beta_{\text{REECl}^{2+}} \cdot [\text{Cl}^-, \text{aq}]_{(\Psi \neq 0)} - \beta_{\text{REEOH}^{2+}} \cdot [\text{OH}^-, \text{aq}]_{(\Psi \neq 0)} \\ & - \beta_{\text{REEHCO}_3^{2+}} \cdot [\text{HCO}_3^-, \text{aq}]_{(\Psi \neq 0)}. \end{aligned} \quad (20)$$

We used $\beta_{\text{REEHCO}_3^{2+}}$ values for Ln and Y at I = 0.7 (NaClO₄) and 25°C from Liu and Byrne

(1998), and they were corrected to infinite dilution according to Millero (1992). The values of $\beta_{\text{LnCl}^{2+}}$ and $\beta_{\text{LnOH}^{2+}}$ at zero ionic strength and 25°C were adopted from Mironov *et al.* (1982) and Millero (1992), respectively. Although $\beta_{\text{YCl}^{2+}}$ and $\beta_{\text{YOH}^{2+}}$ values were not reported by Mironov *et al.* (1982) and Millero (1992), we can estimate these values according to Byrne and Lee (1993). REE complexation constants with various ligands tend to have linear relationships between them (Byrne and Lee, 1993). We estimated $\beta_{\text{YCl}^{2+}}$ and $\beta_{\text{YOH}^{2+}}$ values using the experimental relationships between Y and Ho; $\log \beta(\text{Y}) = 0.024 + 0.9619 \cdot \log \beta(\text{Ho})$ at NaClO_4 0.1 M (Byrne and Lee, 1993). The estimated values for $\log \beta_{\text{YCl}^{2+}}$ and $\log \beta_{\text{YOH}^{2+}}$ at zero ionic strength and 25°C were 0.35 and 5.85, respectively. The $\log \beta_{\text{REECl}^{2+}}$, $\log \beta_{\text{REEOH}^{2+}}$ and $\log \beta_{\text{REEHCO}_3^{2+}}$ of Ln and Y are listed in Table 1. These complexation constants for each run at 0.5 M NaCl were calculated by,

$$\begin{aligned} \log \beta(I=0.5) \\ = \log \beta^0 + \log \gamma_{\text{REE}^{3+}} + \log \gamma_{\text{L}^-} - \log \gamma_{\text{REEL}^{2+}}, \quad (21) \end{aligned}$$

where β^0 is complexation constant at zero ionic strength and L^- denotes Cl^- , OH^- or HCO_3^- . The $\gamma_{\text{REE}^{3+}}$ values for Ln and Y were evaluated from Pitzer *et al.* (1978) and Millero and Schreiber (1982). Activity coefficients for anions were calculated from Millero (1992). The activity coefficients for REE complexes were calculated at $I = 0.50$ NaClO_4 from Millero (1992), because Millero (1992) did not report their values in NaCl solution. As for the correction for Sc complexation, we considered only the species of ScOH^{2+} . We used $\log \beta_{\text{ScOH}^{2+}} = 7.61$ at ionic strength = 0.50 (NaCl) and 25°C, which was estimated from our data in the preceding section.

For calculating the carbonate ion concentration in the experimental solution, we considered ion pairs of NaHCO_3^0 and NaCO_3^- . The dissociation constants for carbonic acid at infinite dilution were obtained from Millero (1979), and the association constants for $\text{NaHCO}_3^0_{(\text{aq})}$ and

$\text{NaCO}_3^-_{(\text{aq})}$ at $I = 0.5$ from Millero and Schreiber (1982). Assuming $\gamma_{\text{H}_2\text{CO}_3^0} = 1.11$ and $\gamma_{\text{H}^+} = 0.887$ from Millero and Schreiber (1982), and $\gamma_{\text{HCO}_3^-} = 0.508$ and $\gamma_{\text{CO}_3^{2-}} = 0.147$ from Millero (1992), we obtained the first and second dissociation constants of carbonate acid as $\log K'_1 = -5.96$ and $\log K'_2 = -9.74$ at $I = 0.5$. We calculated carbonate ion concentrations in our experimental solutions from the following equation;

$$\begin{aligned} [\text{NaHCO}_3]_{\text{doped}} \\ = [\text{H}_2\text{CO}_3^0_{\text{aq}}] + [\text{HCO}_3^-_{\text{aq}}] + [\text{NaHCO}_3^0_{\text{aq}}] \\ + [\text{CO}_3^{2-}_{\text{aq}}] + [\text{NaCO}_3^-_{\text{aq}}]. \quad (22) \end{aligned}$$

Figure 7 shows the variations of $\log \Psi$ against $\log [\text{CO}_3^{2-}_{\text{aq}}]$. The $\log \Psi$ values increase with increasing $\log [\text{CO}_3^{2-}_{\text{aq}}]$ values. The value of $\log \Psi$ is expressed as a function of carbonate ion concentration. When only $\text{REE}(\text{CO}_3)_n^{3-2n}_{(\text{aq})}$ is dominant in Eq. (19), it is written in a simple expression,

$$\log \Psi \approx \log \beta_{\text{REE}(\text{CO}_3)_n^{3-2n}} + n \log [\text{CO}_3^{2-}_{\text{aq}}]. \quad (23)$$

The broken lines in Fig. 7 indicate the slope of $n = 2$ in the plot of $\log \Psi$ vs. $\log [\text{CO}_3^{2-}_{\text{aq}}]$. Although the slope value for Sc is almost exactly 2, those for Gd and Lu approach 2 when carbonate ion concentration becomes 10^{-3} M. The slope value for La is less than 2 even when $[\text{CO}_3^{2-}_{\text{aq}}]$ becomes 10^{-3} . In our experimental solutions, Sc $(\text{CO}_3)_2^-_{(\text{aq})}$ is only the dominant Sc(III)-carbonate complex but the other REEs are the mixture of $\text{REECO}_3^+_{(\text{aq})}$ and $\text{REE}(\text{CO}_3)_2^-_{(\text{aq})}$. Equation (19) is actually written as follows,

$$\Psi = \beta_1 \cdot [\text{CO}_3^{2-}_{\text{aq}}] + \beta_2 \cdot [\text{CO}_3^{2-}_{\text{aq}}]^2, \quad (24)$$

where β_1 and β_2 mean $\beta_{\text{REECO}_3^+}$ and $\beta_{\text{REE}(\text{CO}_3)_2^+}$, respectively.

The REE(III)-carbonate complexation constants were calculated from Eqs. (20) and (24) by using the least-squares method. They are summarized in Table 2. The $\log \beta_1(\text{Ce})$ and $\log \beta_2(\text{Ce})$

Fig. 7. The $\log \Psi$ value, which is given by Eq. (20), plotted against $\log [\text{CO}_3^{2-}, \text{aq}]$. The broken lines indicate the slope of $\Delta(\log \Psi)/\Delta(\log [\text{CO}_3^{2-}, \text{aq}]) = 2$. The solid lines are $\log \Psi$ values given by the least-squares solutions for $\log \beta_2$ and $\log \beta_1$ (see Table 2).

Table 2. REE(III)-carbonate complexation constants at 25°C and $I = 0.5$ (NaCl)

	$\log \beta_2$	1σ	$\log \beta_1$	1σ
La	10.31	± 0.10	6.95	± 0.03
Ce*	10.87	—	7.22	—
Pr	11.24	± 0.05	7.37	± 0.03
Nd	11.39	± 0.04	7.39	± 0.03
Sm	11.75	± 0.04	7.54	± 0.03
Eu	11.83	± 0.03	7.50	± 0.03
Gd	11.76	± 0.03	7.43	± 0.03
Tb	12.03	± 0.03	7.53	± 0.03
Dy	12.20	± 0.03	7.60	± 0.04
Ho	12.30	± 0.03	7.61	± 0.04
Er	12.44	± 0.03	7.67	± 0.04
Tm	12.61	± 0.03	7.75	± 0.05
Yb	12.75	± 0.03	7.80	± 0.05
Lu	12.77	± 0.03	7.77	± 0.06
Y	12.11	± 0.03	7.54	± 0.04
Sc	15.22	± 0.03	—	—

*Ce(III)-carbonate complexation constants were interpolated from those of La, Pr and Nd.

values cannot be estimated from Eqs. (20) and (24), because a part of precipitated Ce(III) is oxidized to Ce(IV). The $\log \beta_1$ and $\log \beta_2$ values of Ce were interpolated from those for La, Pr and Nd. Although we could not calculate $\log \beta_1(\text{Sc})$

value confidently, because of the slope values of $\Delta \log \Psi / \Delta \log [\text{CO}_3^{2-}, \text{aq}]$ close to 2, its value is roughly estimated to be in the range from 8.0 to 9.5.

The $\log \beta_1$ and $\log \beta_2$ values for Y are lower than those of Ho, and they are nearly between those of Tb and Dy (Table 2). This is the reason why $\log K_d(\text{Y})$ becomes slightly closer to $\log K_d(\text{Ho})$ with increasing $[\text{NaHCO}_3]$ in Fig. 6. The $\log \beta_2$ value for Sc is the largest among all the REEs, and the difference in $\log \beta_2$ value between Sc and Lu reaches a quite large value of 2.5. In Fig. 6, there is a pronounced difference in $\{\log K_d(\text{REE}) - 3\text{pH}\}$ between Lu and Sc when CO_3^{2-} ions are actually absent, but the difference diminishes rapidly with increasing $[\text{CO}_3^{2-}, \text{aq}]$ in the solution. This is due to the large $\log \beta_2(\text{Sc})$ value. The difference of $\log K_d(\text{Sc})$ from those for heavy REE must be a good indicator of the carbonate ion concentration in aqueous solution.

REE(III)-carbonate complexation constants by Fe coprecipitation compared with those by solvent-extraction methods

We have determined REE(III)-carbonate

Table 3. *Eu(III)-carbonate complexation constants at 25 °C and zero ionic strength*

$\log \beta_2^0$	$\log \beta_1^0$	$\log (\beta_2^0/\beta_1^0)$	Source
14.02	8.86	5.16	This study
12.91	7.26	5.65	Liu and Byrne (1998)
12.94	7.32	5.62	Lee and Byrne (1992)
12.95	7.44	5.51	Rao and Chatt (1991)
13.09	7.21	5.88	Lundqvist (1982)

complexation constants for all the REEs, except for $\log \beta_1(\text{Sc})$, by the Fe oxyhydroxide precipitation method (Table 2). We compare our REE(III)-carbonate complexation constants with the previously reported data obtained by solvent-extraction methods. We cite Eu(III)-carbonate complexation constant data from Lundqvist (1982), Rao and Chatt (1991), Lee and Byrne (1992) and Liu and Byrne (1998) in Table 3. Our results and the literature values were re-calculated at infinite dilution by using the following equations:

$$\log \beta_1^0 = \log \beta_1 + \log \gamma_{\text{REECO}_3^-} - \log \gamma_{\text{REE}^{3+}} - \log \gamma_{\text{CO}_3^{2-}}, \quad (25)$$

$$\log \beta_2^0 = \log \beta_2 + \log \gamma_{\text{REE}(\text{CO}_3)_2^-} - \log \gamma_{\text{REE}^{3+}} - 2 \log \gamma_{\text{CO}_3^{2-}}. \quad (26)$$

Activity coefficients for the literature data obtained by using NaClO_4 solutions were calculated according to Millero (1992). Rao and Chatt (1991), Lee and Byrne (1992) and Liu and Byrne (1998) reported their REE(III)-carbonate complexation constants by using total $\text{CO}_3^{2-}(\text{aq})$ concentration ($[\text{CO}_3^{2-}, \text{aq}] + [\text{NaCO}_3^-, \text{aq}]$). According to Millero and Schreiber (1982), activity coefficients of total $\text{CO}_3^{2-}(\text{aq})$ are calculated from the following equation;

$$\gamma_T = \gamma_F \times [\text{CO}_3^{2-}, \text{aq}] / \{[\text{CO}_3^{2-}, \text{aq}] + [\text{NaCO}_3^-, \text{aq}]\}, \quad (27)$$

where γ_T and γ_F denote total and free activity co-

Fig. 8. The variations of $\log \beta_2^0$, $\log \beta_1^0$ and $\log (\beta_2^0/\beta_1^0)$ across the lanthanide series. The superscript "0" denotes the infinite dilution condition (Table 4). The filled symbols are our results, and the open symbols are the data obtained by the solvent-extraction method (Liu and Byrne, 1998). Our $\log \beta_1^0$ and $\log \beta_2^0$ values for Ce were interpolated from those for La, Pr and Nd.

efficients of carbonate ion, respectively. The ratio of $[\text{CO}_3^{2-}, \text{aq}] / \{[\text{CO}_3^{2-}, \text{aq}] + [\text{NaCO}_3^-, \text{aq}]\}$ is 0.533 according to Rao and Chatt (1991) and 0.457 according to Lee and Byrne (1992). We estimated $\gamma_{\text{Eu}^{3+}}$ in our 0.5 M NaCl solution from Pitzer *et al.* (1978) and Millero and Schreiber (1982), and $\gamma_{\text{CO}_3^{2-}}$ from Millero (1992). We used $\gamma_{\text{EuCO}_3^+}$ and $\gamma_{\text{Eu}(\text{CO}_3)_2^-}$ values of 0.186 at $I = 0.50$ NaClO₄ from Millero (1992), because Millero (1992) did not report values for NaCl solution.

Eu(III)-carbonate complexation constants by us and the literature data re-calculated at infinite dilution are listed in Table 3. Our $\log \beta_1^0(\text{Eu})$ and $\log \beta_2^0(\text{Eu})$ values are higher than the literature ones by 1.0~1.5. Our $\log (\beta_2^0/\beta_1^0)$ value, which is the logarithm of stepwise stability constant, is slightly lower than those ratios of the literature data by about 0.5. These differences might sug-

Table 4. REE(III)-carbonate complexation constants at 25°C and zero ionic strength

	This study			Liu and Byrne (1998)		
	$\log \beta_2^0$	$\log \beta_1^0$	$\log (\beta_2^0/\beta_1^0)$	$\log \beta_2^0$	$\log \beta_1^0$	$\log (\beta_2^0/\beta_1^0)$
La	12.52	8.33	4.19	11.58	6.52	5.07
Ce	13.06	8.58	4.49	12.05	6.86	5.20
Pr	13.43	8.73	4.70	12.37	7.03	5.35
Nd	13.59	8.75	4.84	12.46	7.08	5.39
Sm	13.95	8.90	5.05	12.82	7.25	5.57
Eu	14.02	8.86	5.16	12.91	7.26	5.65
Gd	13.95	8.78	5.17	12.76	7.17	5.59
Tb	14.22	8.88	5.34	13.05	7.23	5.82
Dy	14.38	8.95	5.44	13.18	7.33	5.85
Ho	14.48	8.96	5.52	13.27	7.32	5.95
Er	14.62	9.02	5.60	13.39	7.38	6.01
Tm	14.79	9.10	5.70	13.54	7.45	6.09
Yb	14.94	9.15	5.79	13.56	7.58	5.99
Lu	14.96	9.13	5.83	13.64	7.53	6.12
Y	14.29	8.88	5.41	12.90	7.25	5.65
Sc	17.41					

gest that we could not completely eliminate the pH dependence of reference values of $\{\log K_d(\text{REE}) - 3\text{pH}\}_{(\Psi=0)}$ (see Fig. 5(a)).

Liu and Byrne (1998) reported carbonate complexation constants for all Ln except for Pm and Y determined by the solvent-extraction method and ICP mass spectroscopic analysis of REE. We compared our results with their results in view of lanthanide series variations of the complexation constants. The REE(III)-carbonate complexation constants in this study and Liu and Byrne (1998) at infinite dilution are listed in Table 4. Figure 8 shows the series variations of $\log \beta_2^0$, $\log \beta_1^0$ and $\log (\beta_2^0/\beta_1^0)$. Our results for $\log \beta_2^0$, $\log \beta_1^0$ and $\log (\beta_2^0/\beta_1^0)$ show similar variation patterns to those by Liu and Byrne (1998). Lee and Byrne (1992) noted that stability constants of Ce, Eu, Gd, Tb and Yb do not make a smooth curves and they called this irregularity “Gd-break”. However, this “Gd-break” is the cusp of the second and the third tetrad curves according to the refined spin-pairing energy theory (RSPET) for the lanthanide tetrad effects (Peppard *et al.*, 1969; Jørgensen, 1979; Kawabe, 1992; Kawabe *et al.*, 1999a, b). The experimental results by the solvent-extraction method (Liu and Byrne, 1998)

clearly show similar tetrad effects as our data in Fig. 8. The convex tetrad effects in the series variations of $\log \beta_2^0$, $\log \beta_1^0$ and $\log (\beta_2^0/\beta_1^0)$ become less conspicuous in this order in either data sets by us or those by Liu and Byrne (1998). This decreasing order of convex tetrad effect is important to infer the relative magnitudes of Racah (E^1 and E^3) parameters for interelectron repulsion of 4f electrons in $\text{REE}^{3+}_{(\text{aq})}$, $\text{REECO}_3^{+}_{(\text{aq})}$ and $\text{REE}(\text{CO}_3)_2^{-}_{(\text{aq})}$ as discussed by Kawabe (1999).

The Fe oxyhydroxide precipitation method is not frequently applied to determining stability constants, however, we believe REE coprecipitation with Fe oxyhydroxide is quite important for understanding geochemical behavior of REE. This coprecipitation reaction can provide the REE(III)-carbonate complexation constants as we have determined here. Our $\log \beta_2^0$ and $\log \beta_1^0$ values are, however, rather higher than literature data by 1.0~1.5 and the $\log (\beta_2^0/\beta_1^0)$ ratio also does not exactly agree with literature data (Tables 3 and 4). Nevertheless, the increasing trend of REE(III)-carbonate complexation constants with the atomic number of REE and convex tetrad effects in their series variations are quite common between our results by Fe oxyhydroxide coprecipitation method

and those of Liu and Byrne (1998) by solvent-extraction method. When we consider the REE reaction between ferromanganese deposit and seawater, the $\log(\beta_2^0/\beta_1^0)$ ratio and its series variation are much more important than $\log \beta_2^0$ and $\log \beta_1^0$ values themselves. We will discuss whether our experimental study can reproduce the series variations of apparent REE distribution coefficients between ferromanganese deposit and seawater elsewhere (Ohta and Kawabe, 2000).

CONCLUSIONS

We have determined partitioning coefficients of REEs (all lanthanides except Pm, Y and Sc) between Fe oxyhydroxide precipitates and 0.5 M NaCl solutions with NaHCO_3 (0.0–12.0 mM). The experimental results are of immediate importance for considering similar geochemical reactions in natural aquatic systems involving Fe oxyhydroxide precipitates. In addition, we have shown that REE(III)-carbonate complexation constants can be determined from the REE partitioning coefficients as a function of carbonate ion concentration. Our conclusions are as follows:

(1) As the precipitates are being stirred in the solution, $\log K_d(\text{REE})$ and pH became constant within 72–140 hours in both systems with and without NaHCO_3 . The variation pattern of $\log K_d(\text{REE})$ across the series is virtually independent of the reaction time of precipitate in the solution.

(2) The FT-IR spectra of Fe(III) precipitates with all REEs(III) and Nd(III) do not exhibit any features indicative of hydrocarbonate ($\text{REEOHCO}_3 \cdot n\text{H}_2\text{O}$), hydrated carbonate ($\text{REE}_2(\text{CO}_3)_3 \cdot n\text{H}_2\text{O}$) or hydroxide ($\text{REE}(\text{OH})_3$ or REEOOH). The mixed precipitates of Fe(III) with all REEs(III) and Nd(III) show similar infrared bands to Fe(III) precipitate without any REE. The coprecipitates of Fe(III) and REEs(III) are rather homogeneous ones which could be written as $(\text{Fe}, \text{REE})(\text{OH})_3 \cdot n\text{H}_2\text{O}$.

(3) Experimental values of $\{\log K_d(\text{REE}) - 3\text{pH}\}$ obtained in the solutions without NaHCO_3 are slightly dependent on solution pH, although

their variation patterns across the REE series are parallel to each other. However, the $\{\log K_d(\text{REE}) - 3\text{pH}\}$ values become almost constant in the pH range of 6.4–6.6. The average values of $\{\log K_d(\text{REE}) - 3\text{pH}\}$ in this pH range were adopted as representative values for the system with no carbonate ion. They were used to evaluate $\log \beta_{\text{REECO}_3^+}$ and $\log \beta_{\text{REE}(\text{CO}_3)_2^-}$ (β_1 and β_2 , respectively) from experimental data for $\{\log K_d(\text{REE}) - 3\text{pH}\}$ in the system with NaHCO_3 of 0.7–12.0 mM.

(4) We have determined $\log \beta_1$ and $\log \beta_2$ for all REEs except for $\log \beta_1(\text{Sc})$ using our experimental results of $\{\log K_d(\text{REE}) - 3\text{pH}\}$ as a function of carbonate ion concentration. Although $\log \beta_1^0$, $\log \beta_2^0$ and $\log(\beta_2^0/\beta_1^0)$ values are not in exact agreement with the literature data reported by the solvent-extraction methods, their series variations across the REE series parallel those of Liu and Byrne (1998) determined by solvent-extraction method.

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