

## NOTE

# Rare earth elements, Sr, Ba, Fe, and major cation concentrations in some living foraminiferal tests collected from Iriomote Island, Japan: An exploration for trace element behavior during biogenic calcium carbonate formation

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Rare earth elements (REE), Sr, Ba, Fe, Mg, Ca, Na, and K concentrations in three kinds of living foraminiferal tests collected from Iriomote Island, Japan were measured in order to obtain some qualitative aspects of trace element behavior during biogenic CaCO<sub>3</sub> formation. The obtained results were examined using the sample/seawater concentration ratios, which can be considered as a measure of total effect of element incorporation into biogenic CaCO<sub>3</sub> in marine environments. On a sample/seawater concentration ratio vs. ionic radius diagram, the foraminifera/seawater ratios of trivalent REEs and divalent Mg, Ca and Sr fall on their respective curves having peaks near the Ca ionic radius. This is consistent with the most widely accepted theory that solid/liquid partition coefficients are largely controlled by the sizes of the host site in the crystal and the substituting cation, such that a cation that has the most suitable size for the site can enter the crystal most easily. On the other hand, the foraminifera/seawater ratios of Fe and Ba show higher values than those expected from the crystal structure control model, which might be caused by insoluble precipitates such as Fe-hydroxides and barite. It is interesting that the concentrations of REEs in foraminifera are correlated with those of Fe, which suggests coprecipitation of REE with Fe-hydroxide. Such coprecipitation of REE might have occurred in seawater, followed by uptake of Fe-hydroxides by foraminiferal food micro-organisms. After digestion of such food, the dissolved REEs in intracellular fluid might have fractionated as CaCO<sub>3</sub> crystallization proceeds, and the combined crystal structure and ionic radius effect becomes conspicuous forming a peak on the foraminifera/seawater ratio vs. ionic radius diagram.

Keywords: foraminifera, rare earth elements, calcium carbonate, partitioning, biomineralization

## INTRODUCTION

Foraminifera are single-celled protists that live usually in marine environments either on the sea floor or in the surface waters. They have shell-like agglutinated or secreted outer protective layer, called a test. The test is mainly composed of calcium carbonate, calcite, and thus can be preserved in sedimentary environments. Because sizes of foraminifera are relatively small (usually sub-millimeter size), they are almost ubiquitously found in sedimentary cores as a major microfossil group and have been used for various geological purposes (e.g., Sen Gupta, 1999; Scott *et al.*, 2001).

A typical example is deciphering of the past climate variations using oxygen isotopic compositions of foraminiferal shells (e.g., Shackleton and Opdyke, 1973;

Emiliani and Shackleton, 1974). It is interesting that Sr and Mg concentrations in foraminiferal shells as well as those in corals can also reflect past oceanic temperatures (e.g., Elderfield *et al.*, 1996; Lea, 1999; Lea *et al.*, 1999; Marshall and McCulloch, 2002; Alibert *et al.*, 2003; McConnell and Thunell, 2005). Moreover, Ba in foraminiferal shells may provide useful information about seawater alkalinity (Lea, 1993; Henderson, 2002), and some other elements such as Cd, F, Li, U and B have been examined from paleo-environmental view points (e.g., Delaney *et al.*, 1985; Rosenthal *et al.*, 1997; Russell *et al.*, 2004; Hintz *et al.*, 2006; Hönisch *et al.*, 2007).

Although trace element partitioning between solid and liquid is basically controlled by the size of cation site of the crystal structure and ion sizes in the substituting elements, (e.g., Onuma *et al.*, 1968; Blundy and Wood, 2003), it is likely that some other factors such as charges of substituting ions, complexation, and hydration changes around trace elements may operate in aquatic environments. Moreover, living materials like foraminifera con-

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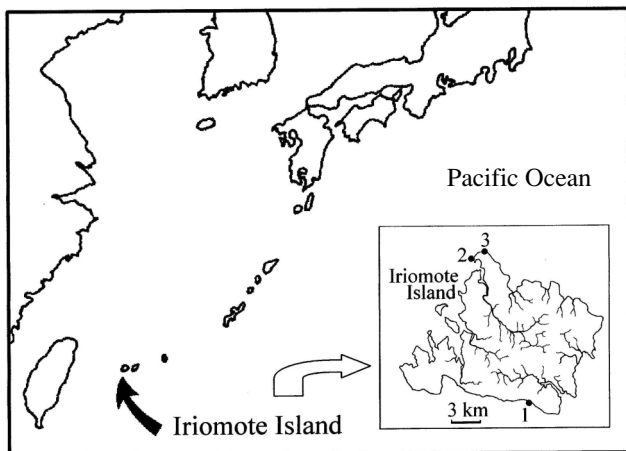


Fig. 1. Location map of Iriomote Island and analyzed samples (numbers refer to locality numbers in Table 1).

tain body fluid which mediate solid (shell) and liquid (seawater) along with complex vital effects (e.g., Rimstidt *et al.*, 1998). Aside from applicability of trace element data to paleo-environmental studies, mechanisms on trace element partitioning with respect to biogenic  $\text{CaCO}_3$  would be interesting. In order to understand the trace element partitioning behaviors, rare earth elements (REE) are considered to be useful, because they have similar chemical properties but somewhat different ionic radius. However, REE data on foraminiferal tests are limited (Palmer, 1985; Haley and Klinkhammer, 2002; Haley *et al.*, 2005).

Palmer (1985) measured REEs in mixed species assemblages of foraminifera tests taken from Atlantic Ocean sediment core tops and showed that about 90% of the REEs measured in the non-detrital phase reside in the coating phase, an authigenic Fe–Mn-rich phase adsorbed onto the surface of the test following the death of the organism. Palmer and Elderfield (1986) examined REEs and Nd isotopic compositions in ferromanganese oxide coatings of Cenozoic foraminifera and concluded that the distribution of REEs in Cenozoic foraminifera not cleaned by chemical methods is dominated by the chemistry of post-burial diagenetic phases that coat the original, biogenically precipitated calcite. Haley and Klinkhammer (2002) developed a novel flow-through method for cleaning and dissolving foraminiferal shell and pointed out that REEs have proven to be highly concentrated in the refractory contaminant phases rather than in the coating phases. Haley *et al.* (2005) further developed several different cleaning protocols for the core foraminiferal samples, measured REE distribution coefficients, and concluded that planktonic and benthic foraminiferal REEs can be used for reconstructing surface water circulation

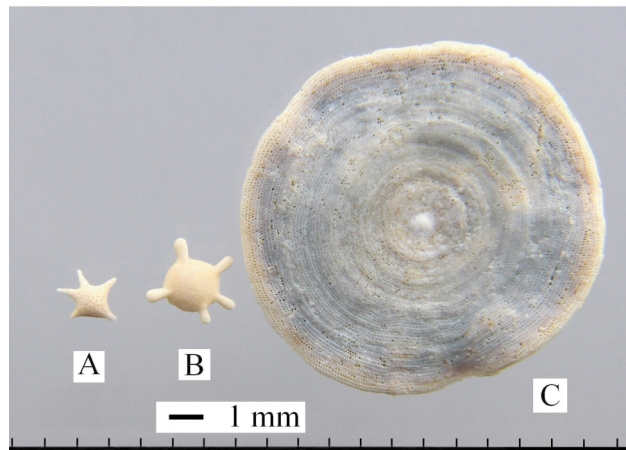


Fig. 2. Photograph showing examples of three kinds of foraminifera samples. A: *Baculogypsina*, B: *Calcarina*, C: *Marginopora*. Scale bar is 1 mm.



Fig. 3. Photograph showing the coral sample (*Acropora*). Scale bar is 1 cm.

and productivity, and organic carbon flux to the seafloor, respectively. These studies have focused on fossil foraminifera and coatings on them, but studies on living foraminifera which are not affected by post-mortem coatings seem to be sparse.

It is known that relatively large living foraminifera occur in the near shore area of the Okinawa district, Japan (e.g., Sugihara *et al.*, 2006; Hohenegger, 2006; Raja *et al.*, 2007; Yordanova and Hohenegger, 2007). Moreover, three kinds of relatively large foraminifera, especially star-shaped foraminiferal test called Hoshi-suna in

Table 1. Analytical results (ppm)

Sample name	SW-1	SW-2	Bacul-1	Bacul-2	Calc-1	Marg-1	Coral-1
	seawater	seawater	Baculogypsina	Baculogypsina	Calcarina	Marginopora	Acropora
Locality	2	3	1	3	3	3	3
Date	22/6/06	10/7/07	10/4/84	10/7/07	10/7/07	10/7/07	22/12/06
Na	1.07E+04	1.10E+04	3.96E+03	3.59E+03	6.93E+03	8.30E+03	3.95E+03
K		4.10E+02	9.66E+01	1.09E+02	9.58E+01	4.54E+01	6.30E+01
Mg	1.21E+03	1.30E+03	2.51E+04	3.43E+04	2.99E+04	3.12E+04	1.09E+03
Ca	4.17E+02	4.20E+02	3.01E+05	3.62E+05	3.65E+05	3.64E+05	3.91E+05
Mg/Ca (mmol/mol)			1.38E+02	1.56E+02	1.35E+02	1.41E+02	4.60E+00
Mn				9.62E+00	2.16E+00	2.05E+01	
Fe	5.80E-03	4.40E-03	9.25E+01	3.76E+01	2.22E+01	3.83E+01	3.36E+00
Sr		9.66E+00	2.40E+03	1.81E+03	1.74E+03	1.45E+03	8.69E+03
Ba	1.02E-02	5.57E-03	5.18E+00	3.73E+00	3.63E+00	5.50E+00	1.29E+01
La	2.47E-06	5.22E-06	1.76E-01	1.31E-01	5.54E-02	1.77E-01	8.79E-03
Ce	2.18E-06	4.16E-06	5.63E-01	3.04E-01	2.00E-01	3.23E-01	1.42E-02
Nd	2.13E-06	3.74E-06	2.57E-01	1.81E-01	1.13E-01	1.80E-01	8.65E-03
Sm	5.01E-07	7.82E-07	6.86E-02	4.71E-02	2.87E-02	3.85E-02	1.99E-03
Eu	8.26E-08	1.13E-07	1.48E-02	1.14E-02	7.19E-03	8.85E-03	4.16E-04
Gd	6.89E-07	9.64E-07	7.51E-02	5.73E-02	3.38E-02	4.19E-02	2.30E-03
Dy	7.79E-07	9.54E-07	6.04E-02	4.95E-02	1.99E-02	3.26E-02	2.36E-03
Er	5.81E-07	6.93E-07	3.23E-02	2.74E-02	1.13E-02	1.87E-02	1.82E-03
Yb	4.37E-07	6.04E-07	2.08E-02	1.86E-02	7.64E-03	1.16E-02	1.32E-03
Lu	9.96E-08	9.09E-08	3.75E-03	2.84E-03	1.08E-03	1.67E-03	2.91E-04

Japanese, can be obtained easily in beach sand of Iriomote Island, Okinawa prefecture, Japan (e.g., Fujita, 2001). This island is located in the southern part of the East China Sea (ca., 123.5°E and 20.4°N; see Fig. 1), and belongs to subtropical oceanic climate, and is fringed by coral-reefs. The surface water temperatures around the island are inferred to be similar to those for the adjacent Sekisei-youko area, a global coral reef monitoring site, and their reported values for a few study areas, for example, are 29.3–28.4°C for the August average temperatures and 22.5°C for the January one (NNEO, 2007). These foraminifera as well as some corals are considered to be suitable for exploratory research for REE incorporation behaviors from seawater to foraminiferal shell or coral skeletons. In the present study, we have measured some trace elements including REEs in three kinds of larger foraminifera to examine trace element incorporation mechanisms during biogenic CaCO<sub>3</sub> formation processes.

#### SAMPLES AND ANALYTICAL METHODS

All of the samples used in this study were collected at the seashores of Iriomote Island (Fig. 1). Two Baculogypsina, one Calcarina, one Marginopora, one coral (Acropora) and two seawater samples were used in this study (Figs. 2 and 3). The Baculogypsina sample specimens (Bac1-1) were separated by hand picking from the beach sands collected at the southern sampling site (#1) on April 10, 1984. For the other foraminiferal samples, Bac1-2 (Baculogypsina), Calc-1 (Calcarina), and Marg-1

(Marginopora), the fresh specimens were selected from the beach sands of locality #3 (Fig. 2). One coral specimen (Coral-1) is an Acropora colony fragment collected at #3 (Fig. 3). Surface seawater samples from two sites at the seashore of Iriomote Island were collected with a polyethylene bucket, immediately filtered through a 0.45 μm membrane filter into polyethylene bottles, and acidified with HCl.

The foraminifera specimens were crushed using agate mortar, sonicated repeatedly with ethanol in ultrasonic bath until clear appearance was obtained, then dried, and sorted between 100 and 200 mesh nylon sieves. The cleaning method used in the present study is rather simple in comparison with the procedures used in the fossil foraminiferal studies (e.g., Barker *et al.*, 2003). However, our method can be considered to be sufficient for the present study, because the specimens used are basically living foraminifera, and thus the post-mortem development of secondary coatings are minimal influence. The coral sample was firstly crushed with a large ceramic mortar, and major parts of the clean fragments selected were crushed and powdered using an agate ball mill.

The powder samples of about 1 to 3 g were dissolved by HCl and HNO<sub>3</sub> mixture in Savillex® teflon container, followed by HF–HClO<sub>4</sub> treatment. After dryness, HCl was added to obtain HCl solution and stocked in a polyethylene bottle. An appropriate amount of aliquot was taken from this stock solution for further analyses described below.

The concentrations of the major cations (Na, K, Ca,

and Mg) were determined by atomic absorption spectroscopy using Sr as interference suppressor. REE, Ba, Sr and Rb were measured by mass-spectrometric isotope dilution using a thermal ionization mass spectrometer. The latter method has been used widely for the accurate determination of trace elements in geochronology and in trace element geochemistry for rocks and water samples (e.g., Terakado and Masuda, 1979; Otsuka and Terakado, 2003; Nakajima and Terakado, 2003; Ogata and Terakado, 2006). Co-precipitation with Fe-hydroxide was used for trace element separation from major cations (e.g., Masuda and Ikeuchi, 1979), and conventional ion exchange column method was applied for further purification and separation of trace elements. About one kilogram of seawater was used for REE measurements.

All of the acids were purified by sub-boiling several times in a quartz glass distillation vessel. The  $\text{Fe}^{3+}$  solution was prepared by dissolving pure Fe powder, followed by purification on a cation exchange column. The ammonia solution was purified by room temperature distillation. The total analytical blanks were sufficiently low, but for some REEs, blank corrections of approximately 10% were made at a maximum. All of the data listed in Table 1 were blank corrected. The precisions of most elements were evaluated to be less than 3%, and to be approximately 5% in the cases of Rb, Gd, Dy and Yb. The mineral compositions of  $\text{CaCO}_3$  polymorphs, calcite and aragonite, were checked by powder X-ray diffraction (XRD).

## RESULTS

The analytical results are listed in Table 1. From the XRD data, it was confirmed that the foraminifera shells are composed of high-Mg calcite, whereas the coral is completely aragonite. In Fig. 4, the relative concentrations of foraminiferal samples normalized to the seawater concentrations measured in this study, i.e., (concentration of element x in the shell)/(concentration of element x in seawater), are plotted against ionic radii (Shannon, 1976). These  $\text{CaCO}_3$ -sample/seawater concentration ratios are considered to be apparent partition coefficients between foraminiferal-test and seawater.

The foraminifera/seawater ratios for Ca range from  $7.2 \times 10^2$  to  $8.7 \times 10^2$ . They are considered to be relatively uniform. Because Ca is a major constituent element in both foraminiferal shell and seawater, their slight variations are mostly attributed to variations in Ca concentrations (or  $\text{CaCO}_3$  weights) caused by organic tissue remained in shell fragments.

The foraminifera/seawater ratios for Mg and Sr fall within the ranges from  $2.0 \times 10^2$  to  $2.7 \times 10^2$ , and  $1.5 \times 10^2$  to  $2.5 \times 10^2$ , respectively. These values are lower than

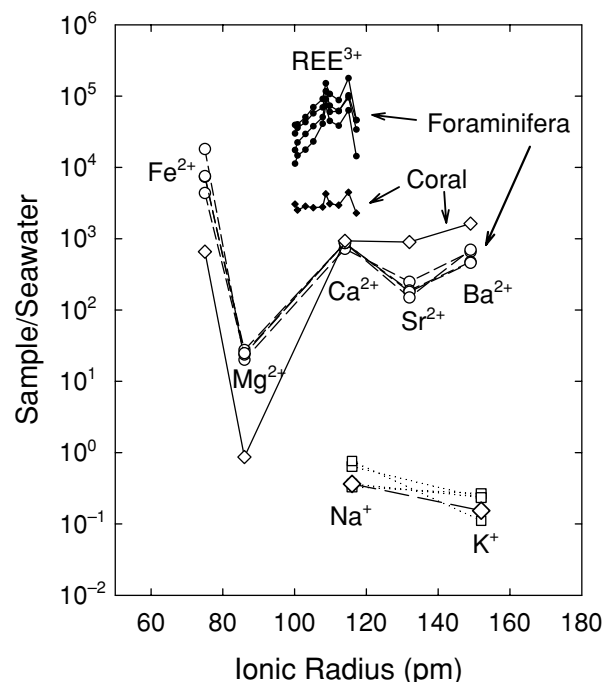


Fig. 4. Sample/seawater ratio versus ionic radius diagram for four foraminifera and one coral samples. The concentrations of the samples were normalized to the average values of two seawater samples. The ionic radii in six-fold coordination are used (Shannon, 1976).

the Ca values, and their variations are also small compared to those of Ca. The Ba foraminifera/seawater ratios are  $4.6 \times 10^2$  to  $7.0 \times 10^2$ , being somewhat higher than the Sr values. The Fe values range from  $4.4 \times 10^3$  to  $1.8 \times 10^4$ , which are considerably higher than those for Mg and Ca. The coral/seawater ratios for these divalent cations (Fe–Mg–Ca–Sr–Ba) show similar relative patterns to those for the foraminiferal data, but Fe and Mg values are lower, and Sr and Ba values are higher than those for the foraminiferal ones. The monovalent cations (Na and K) show considerably lower sample/seawater ratios than those of divalent cations.

The foraminifera/seawater ratios for the REEs are relatively high, ranging from  $1.1 \times 10^4$  to  $1.8 \times 10^5$  (Fig. 4). The REEs show a middle to light REE enriched pattern with positive Eu and Ce anomalies. The coral/seawater ratios of REEs ( $4.5 \times 10^3$ – $2.3 \times 10^3$ ) are lower than those for the foraminiferal ones, and shows almost flat pattern with positive Eu and Ce anomalies.

## DISCUSSION

The mechanisms of trace element incorporation from seawater to foraminiferal shell include several elemen-

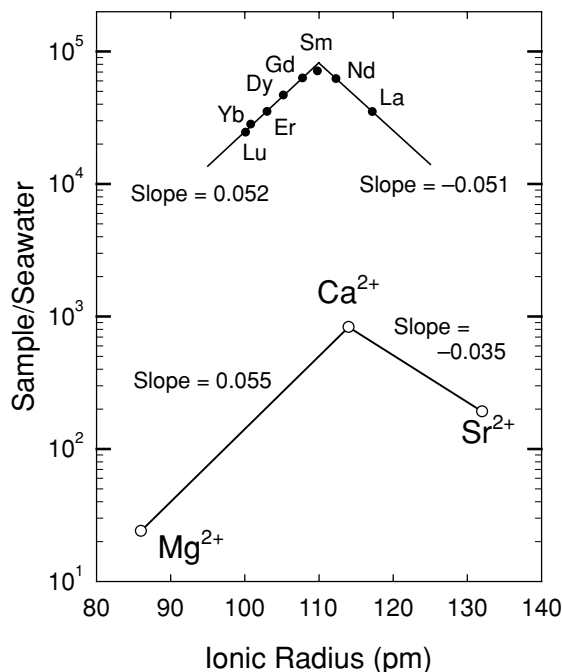


Fig. 5. Sample/seawater ratio versus ionic radius diagram for the average values of four foraminifera samples. Slopes for Lu–Yb–Er–Dy–Gd, Nd–La, Mg–Ca, and Ca–Sr spans are calculated.

tary processes: for example, ingestion of food, digestion and assimilation of food by digestive organs of foraminifera, and precipitation of shell materials mainly composed of  $\text{CaCO}_3$  from body fluids. It is likely that the foods of foraminifera are consist of wide range of micro-organisms, which also contain organic or inorganic particulate materials. Moreover, endocytosis of seawater, modification of vacuolized seawater within cytoplasm, intracellular Ca-reservoir have been discussed for foraminiferal biomineralization mechanism (e.g., Erez, 2003; de Nooijer *et al.*, 2009a, b). The apparent foraminifera/seawater partition coefficients reflect all these effects, but in spite of such complexity, the obtained foraminifera/seawater ratios seem to have distinct characteristics.

#### Crystal structure control

One striking feature, which can be seen in the foraminifera/seawater vs. ionic radius diagram (Fig. 4), is the peak-like shape that is consistent with the well known partitioning regularity concerning sizes of both cation site in crystal structure and substituting element. In general, it is widely accepted that solid/liquid partition coefficients are largely controlled by the sizes of the host site in the crystal and the substituting cation, such that a cation that has the most suitable size for the site

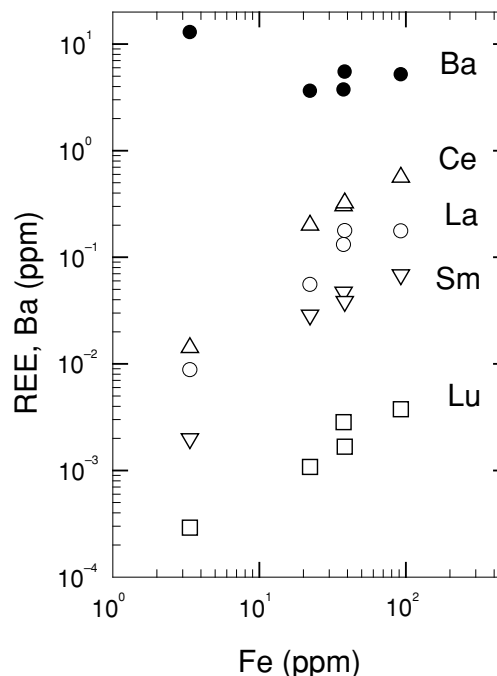


Fig. 6. Correlation between Fe and REE concentrations in the foraminifera and coral samples. Note that although La, Ce, Sm and Lu are chosen for example, the other REE data also show similar trends. Ba data are also plotted, but do not show obvious correlation.

can enter the crystal most easily (e.g., Onuma *et al.*, 1968). Theoretical considerations of trace element partitioning between solid and liquid have shown the parabolic shape for monovalent cations on the partition coefficient vs. ionic radius diagram (PC-IR diagram) (e.g., Nagasawa, 1966; Blundy and Wood, 2003). According to the crystal structure model, the elements which have ion sizes close to  $\text{Ca}^{2+}$  are most concentrated in the  $\text{CaCO}_3$  and the larger size difference ones are less concentrated. As seen in Fig. 4, Mg and Sr are less concentrated than Ca. Moreover, the foraminifera/seawater ratios of REEs show peaks near the Ca ion size.

The average REE values of four foraminifera data are plotted against ionic radius in Fig. 5 together with Mg, Ca and Sr data (note that Eu and Ce are omitted because of their anomalous behavior expected from their anomalous valence states: i.e.,  $\text{Eu}^{2+}$  and  $\text{Ce}^{4+}$ ). It is interesting that the absolute values of the slopes for the heavy REE (Lu–Gd), the light REE (La–Nd), and Mg–Ca spans are almost identical (0.052, 0.051 and 0.055, respectively), though the Ca–Sr slope is somewhat smaller (0.035). These similarities in slopes seen in Fig. 5 are consistent with the law proposed by Philpotts (1978). He pointed out on empirical grounds that in partition coefficient vs. ionic radius diagram, the curves for a particular lattice

site are parabolic near optimum radius, linear elsewhere, parallel for different valences, and mirror images on opposite sides of optimum. Our REE data seem to have a possible parabolic shape near Sm (i.e., Gd–Sm–Nd part), linear in heavy REE span (Lu–Gd), and mirror images on Lu–Gd and Nd–La sides (their slopes are 0.052 and 0.051, respectively). Moreover, the heavy REE slope is almost parallel to the Mg–Ca one (0.052 and 0.055, respectively). Therefore, these peaks on the trivalent REE and divalent Mg–Ca–Sr data are compatible with the crystal structure control model (e.g., Onuma *et al.*, 1968; Philpotts, 1978; Blundy and Wood, 2003), though there might be slight differences in the expected shapes that the researchers envisaged.

It is known that biogenic  $\text{CaCO}_3$  forms two polymorphs: i.e., calcite (trigonal) and aragonite (orthorhombic), and foraminifera and coral shells are composed of calcite and aragonite, respectively. Moreover, as for carbonate polymorphism, a trigonal structure is favored by divalent cations smaller than Ca, and an orthorhombic structure favors cations larger than Ca, and calcium carbonate itself can crystallize in either structure. In our data, the sample/seawater ratios of Mg in the foraminiferal cases (calcite) are obviously higher than those in the coral (aragonite) one (see Fig. 4). This is consistent with the crystal structure control model, because Mg has a smaller ionic radius than Ca being suitable in calcite lattice site than in aragonite one. Similarly, for Sr and Ba which are larger than Ca, the sample/seawater ratios in the foraminifera (calcite) are lower than those in the coral (aragonite), which is also consistent with the crystal structure control.

As for Na and K in Fig. 4, their lower sample/seawater ratios in comparison with divalent cations are consistent with the crystal structure control model, because ion charge has a strong influence on partition coefficients, and the partition coefficient for a substituting ion having a charge different from the optimum one has a lower partition coefficient (e.g., Blundy and Wood, 2003). The sample/seawater ratio of  $\text{K}^+$  is lower than that of  $\text{Na}^+$  which is closer to the  $\text{Ca}^{2+}$  radius, as expected from the crystal structure control model. However, the difference between Na and K seems to be rather small in comparison with Ca–Sr difference, which requires further investigations.

#### *Effect of insoluble precipitates*

The sample/seawater ratios for Fe and Ba in Fig. 4 are much higher than those expected from the Mg–Ca–Sr data on the basis of the crystal structure control theory. It is notable that the concentrations of Fe and Ba in seawater are more than three orders of magnitude lower than those of Mg, Ca and Sr which are classified into major elements in seawater (Table 1). It is well known that Fe and Ba form insoluble solids such as  $\text{Fe}(\text{OH})_3$  ( $K_{\text{sp}} = 1.8 \times 10^{-14}$ ;

Cooper, 1935) and  $\text{BaSO}_4$  ( $K_{\text{sp}} = 10^{-10.05}$ ; Monnin and Galinier, 1988), and therefore Fe and Ba are rare in the seawater. These Fe- or Ba-bearing fine particles are considered to be ingested by microorganisms along with food, and these microorganisms are further taken by foraminifera.

Moreover, it is well known that REEs tend to coprecipitate with Fe-hydroxides, and for this reason, Fe-hydroxides are used for pre-concentration of REE for analyses. Therefore it can be considered that the REEs are incorporated into foraminifera as a coprecipitated form with Fe-hydroxides. This is supported by a broad correlation between Fe and REE concentrations: for example, in Fig. 6, La, Ce, Sm, Lu, and Ba concentrations are plotted against Fe concentrations, and the REE concentrations obviously increase with increasing Fe concentrations. Such Fe-REE correlation indicates that the REEs are incorporated into foraminifera along with their foods containing Fe-hydroxides. Similarly, Ba might be incorporated into foraminifera via coprecipitation with Fe-hydroxides, but lack of correlation in the Ba–Fe scatter diagram (Fig. 6) suggests incorporation of insoluble precipitate such as  $\text{BaSO}_4$  rather than coprecipitation with Fe-hydroxides.

It can be expected from the Fe-hydroxide coprecipitation effect that the seawater-normalized REE patterns for the foraminifera should be flat, because all of the REEs must be concentrated in the Fe-hydroxides without fractionation among REEs. On the contrary to such expectation, the observed patterns show peaks as demonstrated in the average pattern in Fig. 5. This problem, however, can be reconciled by considering that the REE-coprecipitated Fe-hydroxides are digested by foraminifera, and individual REE ions are released from Fe-hydroxides, then the REE ions are partitioned between body fluid and  $\text{CaCO}_3$  shell, resulting in the fractionated REE patterns.

Although we focus on foraminifera in the present study, we would like to briefly discuss the coral REE data. Our coral REE pattern does not show obvious peak-shape corresponding to an optimum site, and thus crystal structure effect does not come out clearly. Since we analyzed only one coral sample, it may be difficult to draw a definite conclusion, but the REEs in our coral skeleton might be affected by secondary  $\text{CaCO}_3$  deposition or recrystallization during coral growth. The growth period for such coral colony skeleton is considered to be relatively long. This makes the effect of secondary  $\text{CaCO}_3$  deposition larger, and under such circumstances, the original REE pattern might have been altered by secondary REE deposition probably accompanied by Fe-hydroxide precipitation. However, further investigations are necessary for better understanding of biogenic  $\text{CaCO}_3$  materials.

## CONCLUSIONS

On the foraminifera/seawater concentration ratio vs. ionic radius diagram, the patterns for the divalent Mg–Ca–Sr and the trivalent REEs indicate effectiveness of crystal structure control on the behavior of these elements from seawater to the foraminiferal shell. On the other hand, the Fe and Ba values are much higher than those expected from the simple crystal structure control. Moreover, the concentrations of REEs in foraminifera are correlated with those of Fe. These observations can be explained by the combined effect of REE coprecipitation with Fe-hydroxides and partitioning of REEs between intracellular fluid and CaCO<sub>3</sub> shell. The insoluble Fe and Ba materials formed in seawater have been incorporated by foraminifera or by their food micro-organisms. After digestion of these REE and Fe enriched food materials, the REEs in foraminiferal intracellular fluid were distributed into CaCO<sub>3</sub> shell under crystal structure control.

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