Tetrad effects and fine structures of REE abundance patterns of granitic and rhyolitic rocks: ICP-AES determinations of REE and Y in eight GSJ reference rocks

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All fourteen REE and Y have been determined for eight GSJ reference rocks including granitic and rhyolitic samples by ICP-AES with a preconcentration method. The two rhyolites (JR-1 and JR-2) and one granite (JG-2) exhibit convex tetrad effects of the M-type even in their chondrite-normalized REE patterns. Their tetrad effects, however, are modified from ideal ones by some step-like variations in their abundances from Tm to Lu. Similar step-like irregularities are seen commonly in chondrite-normalized patterns of other samples: granodiorites (JG-1, JG-1a, and JG-3), a fresh water lake sediment (JLk-1), and an alkali basalt (JB-1). We normalized the REE analyses for JR-1, JR-2, and JG-2 by those for JB-1, and then found that they clearly indicate quite regular convex tetrad effects of the M-type without apparent irregularities in heavy REE. The other samples, when similarly normalized by JB-1, also display analogous but less marked convex tetrad effects except for JG-3. Our present results are strong evidence for the tetrad effect in magmatic processes relevant to granitic and rhyolitic rocks formations. There are common chemical characteristics among JG-2, JR-1, and JR-2: (1) large negative Eu anomalies, and (2) rather high F contents of about 1,000 ppm. The chemical characteristics and the theoretical basis of tetrad effects may suggest that the granitic and rhyolitic rocks with the convex tetrad effects of the M-type are residual silicate melts having partitioned REE with fluids in late stages of differentiation processes. The basalt-normalization appears to be so effective for extracting tetrad effects of granitic and rhyolitic rocks. It filters off the REE characteristics common in magmatic products like the step-like irregularities in heavy REE abundances when normalized by chondrite. This makes it easier to identify lanthanide tetrad effects in magmatic rocks.

INTRODUCTION

Rare earth elements (REE) are an interesting group of elements that behave quite coherently in geochemical processes as far as they are all in the trivalent oxidation state. Despite their coherency as a group, however, individual REE can be fractionated more or less within the group by geochemical processes. The unique property of REE has been used to interpret petrogenetic processes of various rocks, so that there is a continuous interest in determining REE in rocks of various types as precisely as possible.

For the analytical purpose, radiochemical or

instrumental neutron activation analysis (RNAA or INAA), mass-spectrometric isotope dilution analysis (MS-ID), ICP-atomic emission spectrometry (ICP-AES), X-ray fluorescence spectrometry (XRF), and spark-source mass spectrometry (SSMS) have been used (Henderson and Pankhurst 1984; Potts, 1987). ICP-mass spectrometry (ICP-MS) (Hirata *et al.*, 1988) and high-performance ion chromatography (HPIC) (le Roex and Watkins, 1990) have become new techniques to analyze REE in geochemical samples. We have chosen the analytical method of ICP-AES using a scanning monochromator because of its high cost/performance, simplicity in operating such a type of ICP

spectrometers, and moderate sensitivities for REE and Y. Another reason for our choice is that all REE and Y can be determined by ICP-AES in principle (Kawabe *et al.*, 1991). The determinations of all REE and Y in geochemical samples seem to be very important in order to discuss lanthanide tetrad effects. Tetrad effects appear as subtle zig-zag variations in their chondrite-normalized abundance patterns (Masuda and Ikeuchi, 1979; Masuda *et al.*, 1987; Masuda and Akagi, 1989; Kawabe *et al.*, 1991; Akagi *et al.*, 1993; Lee *et al.*, 1944).

The tetrad effect (or double-double effect) itself has originally been proposed for the characteristic variations of logarithmic distribution coefficients of trivalent lanthanide ions (Ln^{3+}) in experimental studies of mutual separation of Ln^{3+} by phase partition chromatography (Fidelis and Siekierski, 1966) and liquid-liquid extraction of lanthanide and actinide ions (Peppard *et al.*, 1969, 1970). This experimental proposal has been interpreted immediately by the refined spin-pairing energy theory (RSPET) for $(4f)^n$ electronic configurations of Ln^{3+} (Jørgensen, 1970; Nugent, 1970).

Recently, Kawabe (1992) re-examined the theoretical basis of RSPET in relation to the tetrad effect in Ln^{3+} ionic radii, and proposed a newly improved RSPET equation: The tetrad effect variation in the ionic radii of Ln^{3+} for CN = 6 is conspicuous in contrast to a rather smooth variation of the ionic radii for Ln^{3+} with CN = 8. The ionic radii of Ln^{3+} with CN = 6 and 8 are determined mainly from Ln-O distances in $\text{LnO}_{1.5}$ and Ln-F ones in LnF_3 , respectively. The tetrad effect in the ionic radii with CN = 6 is related to the tetrad effect in the variation of lattice energies of $\text{LnO}_{1.5}$. The Racah parameters for gaseous free Ln^{3+} are significantly larger than those for $\text{LnO}_{1.5}$. Hence, the lattice energies of $\text{LnO}_{1.5}$ exhibit a convex tetrad effect variation of M-type. The smooth variation of Ln^{3+} radii with CN = 8 is related to a negligible tetrad effect variation in the lattice energies of LnF_3 . This means that Racah parameters are not significantly different between gaseous free Ln^{3+} and LnF_3 . Applying the newly improved RSPET to lattice energies of $\text{LnO}_{1.5}$ and

LnF_3 and the enthalpy difference of $\Delta H_f(\text{LnF}_3) - \Delta H_f(\text{LnO}_{1.5})$, Kawabe (1992) analyzed relative differences of the Racah parameters among $\text{LnO}_{1.5}$, LnF_3 , and gaseous free Ln^{3+} . The results are quite consistent with careful spectroscopic determinations of Racah parameters for NdF_3 and $\text{NdO}_{1.5}$.

Apart from theoretical aspects of the tetrad effect and RSPET, however, McLennan (1994) addressed objections against the reported tetrad effects in the chondrite-normalized REE patterns for geochemical samples. The main reason of McLennan's objection is that the reported tetrad effect variations are likely to be analytical artifacts due to difficulties in REE determinations. Behind such suspicion of the analytical artifacts, there is a prevailing perception that REE abundance patterns for geochemical samples normalized by an appropriate reference material like chondrite or average shale are to be so smooth. This perception, in fact, has grown in many geochemists as the analytical accuracy of REE analyses has improved over more than two decades. In particular, it is well-known that REE abundances in volcanic rocks when normalized by chondrite usually display simple linear patterns with or without breaks or smoothly curved ones. In this context, the reported tetrad effects in chondrite-normalized patterns particularly for leuco-granitic rocks and gneisses (Masuda *et al.*, 1987; Masuda and Akagi, 1989; Lee *et al.*, 1994) are indeed challenging the paradigm in the present stage of REE geochemistry.

In the course of our REE study, we have analyzed REE and Y in the Geological Survey of Japan (GSJ) carbonate reference rocks by ICP-AES with a pre-concentration technique (Kawabe *et al.*, 1994). We showed that chondrite-normalized REE patterns for the carbonate reference rocks are characterized commonly by concave tetrad effects of the W-type. We applied our method to determinations of all REE and Y in other GSJ reference rocks including granitic and rhyolitic samples. The purpose of this paper is to describe the analytical results and to discuss their geochemical meanings in relation to the lanthanide tetrad effect in igneous rocks. We believe that REE analyses for the GSJ

reference rocks provide us a good opportunity to respond to the suspicion that the reported tetrad effects in geochemical samples are analytical artifacts.

SAMPLES AND EXPERIMENTAL

REE and Y in eight GSJ reference rocks of JB-1, JG-1, JG-1a, JG-2, JG-3, JR-1, JR-2, and

Table 1. ICP-AES analyses of REE and Y in GSJ reference rocks*

	JB-1	JG-1	JG-1a	JG-2	JG-3	JLk-1	JR-1	JR-2
La	38.6 ±3.2	20.9 ±.5	20.8 ±.01	18.6 ±.9	19.7 ±.6	37.6 ±.8	20.4 ±1.1	15.2 ±.7
Ce	64.7 ±4.1	42.7 ±1.7	42.7 ±.9	44.9 ±1.9	37.8 ±1.1	79.2 ±.7	46.6 ±2.9	36.8 ±1.1
Pr	6.97 ±.53	4.76 ±.05	4.44 ±.20	5.61 ±.24	4.19 ±.29	8.73 ±.46	5.77 ±.32	4.69 ±.14
Nd	26.6 ±1.5	19.2 ±.9	18.9 ±.1	23.9 ±.4	16.6 ±.3	34.3 ±.7	23.1 ±1.4	18.5 ±.4
Sm	5.05 ±.35	4.21 ±.14	4.13 ±.04	7.62 ±.29	3.04 ±.16	7.27 ±.25	5.42 ±.27	5.14 ±.16
Eu	1.42 ±.07	0.629 ±.021	0.626 ±.010	0.0917 ±.0079	0.763 ±.015	1.16 ±.02	0.233 ±.006	0.067 ±.009
Gd	4.37 ±.11	4.16 ±.16	4.11 ±.05	8.88 ±.19	2.66 ±.09	6.73 ±.13	5.30 ±.25	5.38 ±.06
Tb	0.669 ±.085	0.686 ±.015	0.693 ±.02	1.71 ±.10	0.389 ±.027	1.12 ±.07	0.896 ±.007	0.979 ±.023
Dy	3.99 ±.18	4.44 ±.16	4.60 ±.11	11.6 ±.5	2.50 ±.07	6.80 ±.13	6.01 ±.17	6.53 ±.10
Ho	0.776 ±.037	0.876 ±.022	0.909 ±.041	2.48 ±.18	0.487 ±.009	1.32 ±.08	1.23 ±.06	1.35 ±.04
Er	2.21 ±.06	2.73 ±.06	2.84 ±.05	7.75 ±.51	1.55 ±.03	3.97 ±.09	3.85 ±.09	4.35 ±.07
Tm	0.283 ±.007	0.375 ±.014	0.398 ±.010	1.12 ±.07	0.209 ±.008	0.547 ±.028	0.582 ±.009	0.687 ±.024
Yb	1.93 ±.03	2.72 ±.09	2.89 ±.10	8.00 ±.49	1.58 ±.01	3.82 ±.03	4.29 ±.02	5.06 ±.08
Lu	0.273 ±.005	0.396 ±.025	0.416 ±.008	1.15 ±.07	0.239 ±.005	0.544 ±.012	0.632 ±.005	0.762 ±.008
Y	20.3 ±.8	25.8 ±1.0	26.0 ±.6	71.2 ±4.6	13.9 ±.4	35.7 ±1.1	37.6 ±2.4	41.9 ±1.8
	(n = 6)	(n = 4)	(n = 3)	(n = 4)	(n = 4)	(n = 3)	(n = 3)	(n = 3)

*Averages and 1- σ errors calculated from replicate analyses are listed in ppm. The number of analyses is listed in the last row.

JLk-1 have been analysed by ICP-AES with a pre-concentration method similar to Kawabe *et al.* (1994). The analytical procedures of our method are described in Appendix. According to Ando *et al.* (1987), JB-1 is an alkali basalt, JG-1 and JG-3 are granodiorites, and JG-2 is a granite. Both JR-1 and JR-2 are rhyolites. JLk-1 is not an igneous rock but a fresh-water lake sediment (Ando *et al.*, 1990).

RESULTS

Each GSJ reference rock sample other than JB-1 has been analyzed three to four times. JB-1 has been analyzed six times. Table 1 lists the averages and one σ errors for individual analyses calculated from the replicate analyses of all REE and Y in the eight GSJ reference rocks. Figures 1, 2, and 3 compare our results with the compilation by Itoh

Fig. 1. REE and Y abundance patterns for JG-1, JG-2, and JG-3 by ICP-AES analyses (filled circles) compared with the compilation values (open circles) by Itoh *et al.* (1992). Error bars indicate $\pm 1\sigma$ errors. The errors not greater than the symbols are not shown. The C1 chondrite values for normalization are from Anders and Grevesse (1989).

et al. (1992) in their abundance patterns normalized by C1 chondrite. The REE and Y values for C1 chondrite are cited from Anders and Grevesse (1989). Precision of our ICP-AES data for the elements is on the average $(4 \pm 1)\%$, and the averaged accuracy is estimated to be about 4% from the comparison of our results with reported analyses by MS-ID, ICP-MS, and HPIC. In Appendix, we have summarized the evaluation of the accuracy and precision of our ICP-AES analyses, together with our comments.

DISCUSSION

Step-like irregularities in heavy REE and tetrad effects in chondrite-normalized REE patterns

The chondrite-normalized REE patterns of the eight GSJ samples shown in Figs. 1, 2, and 3 exhibit irregularities more or less. In particular, step-like irregularities between Er and Tm are commonly seen in all cases. Their Tm, Yb, and Lu abundances appear to be lowered constantly from their Er abundances. This is clearly seen in the

Fig. 2. REE and Y abundance patterns for JB-1, JG-1a, and JLK-1 by ICP-AES analyses (filled circles) compared with the compilation values (open circles) by Itoh *et al.* (1992). Error bars indicate $\pm 1\sigma$ errors. The errors not greater than the symbols are not shown. The C1 chondrite values for normalization are from Anders and Grevesse (1989).

Fig. 3. REE and Y abundance patterns for JR-1 and JR-2 by ICP-AES analyses (filled circles) compared with the compilation values (open circles) by Itoh *et al.* (1992). Error bars indicate $\pm 1\sigma$ errors. The errors not greater than the symbols are not shown. The C1 chondrite values for normalization are from Anders and Grevesse (1989).

pattern of JB-1 in Fig. 2. The REE analyses for JB-1 not only by our ICP-AES but also by ICP-MS by Hirata *et al.* (1988) indicate a step-like irregularity in heavy REE in its chondrite-normalized REE pattern (Fig. A1 in Appendix). Hence, this irregularity is not an analytical artifact. The choice of C1 chondrite values may be a possible cause of the irregularity, but it is too large to be explained by the ambiguity for REE values of C1 chondrite.

The step-like irregularity in heavy REE of JB-1 seems to give us an important implication to understanding apparently irregular chondrite-normalized REE patterns for granitic and rhyolitic GSJ samples. If we assume that similar step-like irregularities are also present in the chondrite-normalized patterns for the GSJ samples other than

JB-1, then the apparently irregular patterns become quite regular patterns in view of tetrad effect variations. We illustrate this interpretation in Fig. 4, where the chondrite-normalized patterns for JG-2 and JR-1 are used as examples. We assumed that the observed abundances for the last three REE in JG-2 and JR-1 are constantly lowered relative to the respective Er abundances as is seen in the pattern of JB-1. In Fig. 4, by taking this assumption, we corrected the observed relative abundances of Tm, Yb, and Lu in JR-1 and JG-2 by +12% and +17%, respectively, and then draw the four tetrad curves. The correction values have been estimated in a trial and error manner in reference to the points described below. The first and third tetrad curves can be shown unequivocally. We assumed that the cusp of the third and fourth

Fig. 4. Convex tetrad effects of the M-type in the chondrite-normalized REE patterns for JR-1 and JG-2 with correction for their step-like irregularities in Tm, Yb, and Lu. The open circles indicate that the observed abundances of the three HREE in JR-1 and JR-2 are increased uniformly by +12% and +17%, respectively.

tetrad curves is located at the mid-point between Ho and Er. Although second tetrad curves may not be well defined because of the large Eu anomalies and the absence of Pm values, we draw them in such a way that the first and second tetrad curves intersect at the mid-point between Nd and Pm.

The corrected REE abundance patterns for JG-2 and JR-1 show distinctly convex tetrad effect variations of the M-type. From the spin-pairing energy theory for the tetrad effect (Jørgensen, 1979; Kawabe, 1992), the tetrad effect is a quantum-chemical effect originating from small differences in Racah parameters and the spin-orbit

interaction parameters for the partly filled (4f)^q electronic configurations among Ln(III) compounds and complexes. Hence, such a quantum-chemical effect is not expected for La³⁺ or Lu³⁺, since La³⁺ has no 4f electron and Lu³⁺ has the closed 4f subshell. The contribution of the differences in the spin-orbit interaction parameter is usually very small relative to that of the differences in Racah parameters (Kawabe, 1992), so that Ce³⁺ and Yb³⁺ are virtually unrelated to the quantum-chemical effect. Therefore, by connecting the four points for La³⁺, Ce³⁺, Yb³⁺, and Lu³⁺, we have drawn a smooth curve for each example in Fig. 4. The difference between each "smooth"

curve and the observed variation curve with corrections for Tm, Yb, and Lu is strikingly similar to the ideal tetrad variation with the convex polarity of the M-type.

The examples of Fig. 4 clearly illustrate that the chondrite normalized REE patterns for the granitic and rhyolitic rocks indicate convex tetrad effect variations slightly modified by step-like irregularities in the three heaviest REE. The irregularities cannot be related to the tetrad effects, because an analogous irregularity is seen in the chondrite-normalized pattern of the basalt sample (JB-1) which appears to be smoothly curved without significant tetrad effects except for the last three REE.

Tetrad effects in REE patterns normalized by JB-1

If our inference as to step-like irregularities in the chondrite-normalized REE patterns is correct, their step-like irregularities in heavy REE may disappear when the REE analyses for the granitic and rhyolitic rocks are normalized by JB-1. This normalization is a simple practice without any assumptions like the corrections we made for the Tm, Yb, and Lu data in Fig. 4. The normalization of REE data for one sample by another, both of which are obtained by the same method and analyst, may remove possible systematic errors in the original analytical data from the normalized results. This is another merit of the normalization by JB-1.

Fig. 5. Convex tetrad effect variations in the REE patterns for JG-2, JR-1, and JR-2 normalized by JB-1. Error bars indicate $\pm 1\sigma$ (mean) for the respective ratios. The errors not greater than the symbols are not shown.

The results normalized by JB-1 are shown in Figs. 5 and 6. The irregularities observed in heavy REE of the chondrite-normalized patterns indeed disappear in those normalized by JB-1. As a result, the convex tetrad effect variations of the M-type are clearly seen in the REE patterns for JG-2, JR-1, and JR-2 (Fig. 5). The first, third, and fourth tetrad curves can be well defined by the normalized analyses alone. The second tetrad curves cannot be determined only by the two points for Gd and Sm. We used, however, such constraint that the first and second tetrad curves intersect at the mid-point between Nd and Pm. This makes it possible to draw the second tetrad curves. The

REE patterns for JG-1, JG-1a, and JLk-1, when normalized by JB-1, also show similar but less marked tetrad effect variations (Fig. 6). Only the pattern for JG-3 appears to show a linear variation with a break at Ho, although the first tetrad is slightly curved. JLk-1 is a fresh-water sediment sampled from Lake Biwa, central Japan. The REE pattern of JLk-1 resembles those of JG-1 and JG-1a. Many granodioritic rock bodies distribute around Lake Biwa. The REE pattern of JLk-1, therefore, represents the average REE pattern for such rocks in its provenance.

The characteristic variations of relative REE abundances in the GSJ granitic and rhyolitic rocks

Fig. 6. REE patterns for JG-1, JG-1a, JG-3, and JLk-1 normalized by JB-1. Error bars indicate $\pm 1\sigma$ (mean) for the respective ratios. The errors not greater than the symbols are not shown.

in Fig. 5 are a strong line of evidence for the tetrad effect operating in magmatic processes. We like to emphasize that the GSJ rock samples are by no means exceptional rocks: JG-2 is a representative Japanese granite from Naegi, Gifu Pref., central Japan; JR-1 and JR-2 are also well-known rhyolite obsidians sampled respectively from the north and south of Wada-Toge, Nagano Pref., central Japan (Ando *et al.*, 1987).

It seems interesting that the fine structures of step-like irregularities in the chondrite-normalized REE patterns are so similar between the basalt of JB-1 and the GSJ acidic rocks. There is no direct genetic relationship between JB-1 and each acidic rock or the sediment. The fine structures may be common signature corresponding to some general characteristics in magmatic systems. They are conceivably independent of the mechanism to originate the tetrad effect variations.

Petrochemical features correlating with the convex tetrad effect

In search for possible correlations between the convex tetrad effect and petrochemical features, the reported analytical data of the GSJ rocks (Ando *et al.*, 1987, 1990) as well as our present ones have been examined. As a result, the tetrad effect appears to correlate with negative Eu anomaly and F content. This may be a clue to interpret the observed tetrad effects. Large negative Eu anomalies are commonly seen in the chondrite-normalized patterns for JG-2, JR-1, and JR-2 (Figs. 1 and 3), and they all show distinct convex tetrad effects when normalized by JB-1 (Fig. 5). In contrast, JG-1 (JG-1a) and JLk-1 having moderate negative Eu anomalies in their chondrite-normalized patterns, show less marked convex tetrad effects (Fig. 6). In the case of JG-3, its negative Eu anomaly is the smallest, and no tetrad effect is seen in its REE pattern normalized by JB-1 (Fig. 6). Thus the magnitude of negative Eu anomalies appears to correspond to the visible degree of convex tetrad effects after the JB-1 normalization. The reported fluorine contents of the GSJ samples (Ando *et al.*, 1987, 1990) also appear to be related to the REE characteristics. JG-2, JR-1, and JR-2

have high F contents of about 1,000 ppm, but JG-1 (JG-1a) and JLk-1 have much lower F contents of 496 ppm and 650 ppm, respectively. JG-3 shows the smallest F content of 335 ppm.

Eu anomaly suggesting high temperature aqueous fluid

Large positive Eu anomalies have been found in hydrothermal fluids (Michard, 1989), and the thermodynamic properties of aqueous Eu^{2+} and Eu^{3+} (Sverjensky, 1984) strongly suggest the dominance of $\text{Eu}^{2+}(\text{aq})$ in hydrothermal or aqueous magmatic fluids at high temperatures even greater than 250°C. Therefore, the large negative Eu anomalies of the GSJ acidic rocks indicate the preferential dissolution of Eu^{2+} from silicates into coexisting aqueous fluids during intensive interactions between them. The high F contents also may be the trace of such interactions. According to Ishihara (1981), JG-3 is a typical Sanin granitoid of the magnetite series, and JG-2 and JG-1 (JG-1a) are classified into the ilmenite series granitoids. The redox conditions of the ilmenite series granitoids are more reducing than those of the magnetite series ones (Ishihara, 1981), which is consistent with the magnitude of negative Eu anomalies we discussed here.

In a strict sense, however, the tetrad effects appeared in the chondrite-normalized REE patterns are attributed to the integral processes to have produced the samples in reference to chondritic materials. When the normalizing material is JB-1, the resultant patterns indicate how the integral processes to have produced the samples and JB-1 are different. The integral processes, of course, include even the processes that their source materials experienced. As a matter of fact, it is difficult to distinguish the source effects in the observed results. In this context, the reported Ce and Nd isotopic compositions of JR-1 (Tanaka *et al.*, 1987) is interesting, because the isotopic data strongly suggest that JR-1 is a differentiation product of mantle-derived magma with little contamination by crustal REE. Hence, the observed convex tetrad effect of JR-1 is originated from the magmatic differentiation process, not from

such an effect of its source material. The convex tetrad effect of JR-1 can be attributed to its magmatic differentiation process in which some aqueous fluid participated, and to REE partitioning between the aqueous fluid and silicates.

Geochemical meanings of convex tetrad effects

Aqueous fluids associated with silicate magmas are important in view of lanthanide tetrad effects in igneous rocks from the two reasons; (1) Water can decrease melting points of silicate systems greatly. In such hydrous systems, silicate melts can survive at temperatures down to 600–700°C (Burnham, 1979). Lower temperature conditions, as discussed below, are favored to make the tetrad effect visible through partitioning reactions of Ln^{3+} ions. (2) Aqueous fluids can dissolve Ln^{3+} ions as silicate melts can do. The bondings of Ln^{3+} ions with water, F^- , and Cl^- in aqueous fluids are expected to be less covalent than those in silicate minerals or melts. This contrast in the bondings of Ln^{3+} is another necessary condition to produce the tetrad effect (Kawabe, 1992). We will briefly discuss partitioning of Ln^{3+} ions in hydrous felsic magmas in relation to the convex tetrad effect of the M-type.

In a late stage of a magmatic differentiation process, Ln^{3+} can be partitioned between felsic silicate melt and aqueous fluid in a hydrous magmatic system:

where X and Y denote ligands bonding to Ln^{3+} ions in fluid and silicate melt, respectively. From the equilibrium constant for the reaction (1), we can write the following equation;

$$\begin{aligned} &RT \ln[\text{Ln-Y}/\text{Ln-X}] \\ &= \Delta G_f[\text{Ln-X}(\text{fluid})] - \Delta G_f[\text{Ln-Y}(\text{melt})] \\ &\quad + \text{constant}, \end{aligned} \quad (2)$$

where $\Delta G_f[\text{Ln-X}(\text{fluid})]$ and $\Delta G_f[\text{Ln-Y}(\text{melt})]$ are the Gibbs free energies of formation for the respective Ln^{3+} species in the silicate melt and

aqueous fluid at the temperature and pressure. The left hand side of Eq. (2) is derived from the mixing entropy terms for the reaction (1). The quotient in the brackets denotes the Ln^{3+} concentration ratio between two phases. This is originally the activity ratio, but we bring the activity coefficients associated with them into the constant term on the right hand side of Eq. (2).

The reaction (1) is analogous to the ligand-exchange reaction between $\text{LnO}_{1.5}$ and LnF_3 discussed by Kawabe (1992). It is conceivable that the bonding of Ln^{3+} ions in silicate melt with oxygen-ion ligands is more covalent than the bonding of Ln^{3+} ions in the fluid with water, F^- , or Cl^- . In other words, the Racah parameters for the $(4f)^q$ electronic configuration in $\text{Ln-X}(\text{fluid})$ are greater than those in $\text{Ln-Y}(\text{melt})$. The electronic configuration energy difference due to the different Racah parameters is the internal energy difference, and then it is included in the enthalpy difference between the two Ln^{3+} species. Hence, the term $\{\Delta G_f[\text{Ln-X}(\text{fluid})] - \Delta G_f[\text{Ln-Y}(\text{melt})]\}$ on the right hand side of Eq. (2) includes the enthalpy difference. The enthalpy difference shows the convex tetrad effect of the M type, since the Racah parameters for $\text{Ln-X}(\text{fluid})$ are greater than those for $\text{Ln-Y}(\text{melt})$.

As discussed elsewhere (Kawabe, 1995a, b), when the tetrad effect variation is seen in the enthalpy changes for ligand-exchange reactions between a pair of $\text{Ln}(\text{III})$ complex or compound series, a similar tetrad effect variation with the same polarity (concave or convex) is also recognized in the entropy changes for the same reactions. Since $\Delta G = \Delta H - T\Delta S$, the enthalpy contribution to the tetrad effect in ΔG is more likely to be canceled out by the entropy contribution with the same polarity at higher temperatures. Therefore, at moderate temperature conditions where the enthalpy contribution with the convex tetrad effect variation is only partly canceled by the similar convex tetrad effect variation in the entropy contribution, the term $\{\Delta G_f[\text{Ln-X}(\text{fluid})] - \Delta G_f[\text{Ln-Y}(\text{melt})]\}$ can retain the convex tetrad effect variation. As a result, the logarithmic concentration ratio on the left hand side of Eq. (2), namely,

the logarithmic partition coefficient,

$$RT \ln[\text{Ln-Y(melt)/Ln-X(fluid)}] = \ln K_d(\text{Ln}), \quad (3)$$

shows the convex tetrad effect variation of the M-type. The presence of aqueous fluid is necessary not only to make bonding of Ln^{3+} ions less covalent than in the silicate phase, but also to keep the magmatic system at a moderately high temperature condition.

We assume that the initial hydrous magma before the phase separation does not have any tetrad effect variation in reference to the chondritic REE abundances like many basaltic samples. As far as the $\ln K_d(\text{Ln})$ with the convex tetrad effect variation controls the REE fractionation due to preferential escape of the aqueous fluid once equilibrated with the silicate melt, the REE abundances in the silicate melt relative to the initial abundances before the phase separation become to show a convex tetrad effect variation similar to that of $K_d(\text{Ln})$. How the convex tetrad effect in $\ln K_d(\text{Ln})$ is reflected in the relative REE abundances in the residual silicate melt depends on the modes of phase separation, a continuous Rayleigh type or one-step separation, and the quantity of escaping aqueous fluid relative to silicate melt. Although we do not refer to the details here, it is essential that the convex tetrad effect similar to that in $\ln K_d(\text{Ln})$ is expected more or less in the REE abundances in the residual silicate separated from the aqueous fluid.

Finally we like to comment on the experimental results for partitioning Ln^{3+} ions between rhyolitic silicate melts and aqueous fluids (Cullers *et al.*, 1973; Flynn and Burnham, 1978; London *et al.*, 1988; Webster *et al.*, 1989). Most of the experimental $K_d(\text{Ln})$ -values are reported for limited numbers of Ln^{3+} , and their accuracy and precision are insufficient for our discussion about fine structures of $\ln K_d(\text{Ln})$. However, the set of $K_d(\text{Ln})$ -values for eight Ln^{3+} reported by Cullers *et al.* (1973) indicate that the experimental $K_d(\text{Gd})$ is slightly smaller than an interpolated $K_d(\text{Gd})$ value from the experimental K_d -values for La, Ce, Yb, and Lu. This characteristic of $K_d(\text{Gd})$ appears to be

consistent with the convex tetrad effect variation in $\ln K_d(\text{Ln})$ we expected.

CONCLUSIONS

ICP-AES with a pre-concentration technique enabled us to determine all fourteen REE plus Y in silicate rocks. Applying this method to eight GSJ reference rocks including granitic and rhyolitic samples, REE and Y can be determined with the precision of $(4 \pm 1)\%$. From a comparison of our ICP-AES analyses with those reported by MS-ID, ICP-MS, and HPIC, the accuracy of our ICP-AES analyses is evaluated to be about 4% on the average. The precision and accuracy of our ICP-AES data made it possible to discuss the fine structures of REE abundance patterns for the GSJ reference rocks:

(1) Two rhyolites (JR-1 and JR-2) and one granite (JG-2) show convex tetrad effects of the M-type even in their chondrite-normalized patterns, but they accompany some irregularities in heavy REE from Tm to Lu.

(2) Similar irregularities in the heavy REE are also seen in the cases of granodiorites (JG-1, JG-1a, and JG-3), a lake sediment (JLk-1), and even an alkali basalt (JB-1).

(3) When we normalize the REE analyses for JR-1, JR-2, and JG-2 by those for JB-1, the resultant REE patterns for the three GSJ acidic rocks exhibit quite regular tetrad effects with the convex polarity. The other GSJ samples except JG-3, when normalized by JB-1, also display analogous but less marked convex tetrad effects.

(4) Negative Eu anomalies and F contents appear to correlate with magnitudes of the convex tetrad effects in the basalt-normalized patterns.

These observations are strong evidence for the tetrad effect in igneous rocks. They are also important clues to understanding the nature of tetrad effect variations of REE abundances in igneous rocks. We suggest that the convex tetrad effects in REE patterns of the silicic rocks are originated from REE fractionations between aqueous fluids and silicic melts in late stage differentiations of hydrous magmas. In order to explain the observed

convex tetrad effects of the silicic rocks, the presence of aqueous fluids in magmatic systems is so important from the following two reasons: Water as well as F^- and Cl^- in such fluids is the ligand making the bonding of Ln^{3+} ions less covalent in fluids than in silicate phases. Such aqueous fluids also play an important role to keep the magmatic system at moderately high temperature conditions.

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APPENDIX

(1) Analytical procedures for pre-concentration of REE and Y

An aliquot of each sample weighing 1 to 2 g is digested by HF, HNO₃, and HClO₃ in a Teflon beaker with a Teflon lid on a hot plate. After removing the lid, it is evaporated to dryness under infrared lamps. This cycle is repeated at least twice. The final evaporation residue is dissolved in HCl, and then filtered with Toyo No. 5C filter paper (equivalent to Whatman No. 42). The filtered insoluble materials, after being ignited in a Pt crucible, is mixed with Na₂CO₃ (400 mg) plus H₃BO₃ (200 mg) and then fused. The fusion product is dissolved in HCl and combined with the first filtrate. This sample solution is used in the following co-precipitation and cation-exchange procedure for the group separation of REE and Y.

By adding ammonia water to the sample solution and adjusting its pH value to be 6.5, REE and Y co-precipitate with Fe(OH)₃ and other hydroxides. The precipitates are filtered with Toyo

No. 5A filter paper (equivalent to Whatman No. 41). Fe^{3+} of 14 mg is added to the filtrate, and residual REE and Y in the solution are further coprecipitated with $\text{Fe}(\text{OH})_3$ at pH = 6.5 in order to make their recoveries satisfactory. The first and second precipitates are dissolved in HCl and combined into a single sample solution. This HCl solution is evaporated to dryness, and then dissolved in 1.76 M HCl solution, which is used in the cation-exchange purification of REE and Y in the next. The cation-exchange columns (1 cm $\times$ 11 cm) of Bio-Rad AG 50WX8 (200–400 mesh) resin are used. For loading the sample solution and eluting Fe^{3+} and other major cations, 60 ml of 1.76 M HCl is used. REE and Y are eluted by 120 ml of 6 M HCl. After evaporating the HCl solution containing REE and Y to dryness, it is dissolved by HCl and transferred into volumetric flask. Finally it is made up to 15 or 20 ml with 0.34 M HCl, and then used for ICP-AES determinations of REE and Y.

(2) ICP-AES for REE and Y

An ICP-AES spectrometer of Seiko SPS-1500R is used for all the runs. This spectrometer has a computer-controlled sequential Czerny-Turner scanning monochromator with the focal length of 1.0 m and the holographic grating of 3,600 grooves/mm. From the emission intensity data for the sample and standard solutions, the concentrations of REE and Y in the sample solutions are first calculated, and then they are corrected for spectral interferences among REE and Y using predetermined linear correction factors for the spectral interferences. Table A1 lists the wavelengths of the emission lines used in our ICP-AES measurements. The blank corrections have been found to be unnecessary. The recovery tests indicate that $(98 \pm 3)\%$ of REE and Y can be recovered by our method.

The standard solutions are prepared from the standard solutions for atomic absorption spectrometry purchased from Wako Chem. Corp. In addition, the standard solutions for La, Tm, Lu, and Y have been prepared by us from the respective oxides with high purity of 99.99%. They are

standardized by gravimetrically and complexometrically. The results by the two standardization methods agreed within 1%. The two sets of standard solutions prepared from pure oxides and purchased AA standard solutions for La, Tm, Lu, and Y have been cross-checked by ICP-AES. There were no significant differences greater than the experimental uncertainty of 1 to 2% between them.

(3) Precision and accuracy of ICP-AES analyses

The average coefficients of variation for REE and Y have been calculated from the replicate analyses of the eight GSJ samples of Table 1. They are listed in Table A2. The minimum and maximum C. V. values are 2.5% for Yb and 6.5% for Tb, respectively. The average for C.V. values of all REE and Y is calculated to be $(4 \pm 1)\%$. The agreements of our results with the consensus values compiled by Itoh *et al.* (1992) are generally good not only for JB-1 but also for JG-3, JG-1a, JR-1 and JR-2. However, the compiled average values for Er in JG-1 and Ho, Er, and Tm in JG-2 are significantly lower than ours (Figs. 1, 2, and 3). It is well-known that some minerals enriched in heavy REE like zircon are less soluble in conventional open sample digestions with HF plus mineral acids (Gromet *et al.*, 1984; Sholkovitz, 1990). The compilation averages for Er in JG-1 and Ho, Er, and Tm in JG-2 may have been influenced by the reported values based on analyses with incomplete sample digestions.

Watkins and le Roex (1992) reported REE analyses by HPIC for the GSJ reference samples, in which they prepared sample solutions by open digestion with HF plus HClO_4 and then they fused the filtered insoluble residues with KHF_2 according to Walsh *et al.* (1981). We have compared our ICP-AES results with their HPIC analyses for evaluating the accuracy of our results. Table A3 lists the average deviations of our ICP-AES values for respective REE from the HPIC values. The maximum and minimum deviations are +5.2% for La and +0.70% for Yb, respectively. The grand average for the deviations over the 11 REE is calculated to be $(-0.8 \pm 3.4)\%$, suggesting a good

average accuracy of about 4% for our ICP-AES data. The fusion of insoluble materials after HF-mineral acid digestion with Na₂CO₃ plus H₃BO₃ or KHF₂ is effective for complete dissolutions of silicate rock samples.

Our ICP-AES method combined with a pre-concentration technique enables us to determined all 14 REE plus Y in silicate rock samples with the average precision and accuracy of about 4%. Crocks *et al.* (1984) reported similar results using a multi-channel polychromator ICP spectrometer. However, when ICP spectrometers were used (Walsh *et al.*, 1981; Jarvis, I. and Jarvis, K. E., 1985; Roelandts, 1988; Sholkovitz, 1990), Pr, Tb, Ho, and Tm or some of them were not determined because of their lower abundances in samples and their lower sensitivities in ICP-AES. The four REE are all monoisotopic elements with odd Z. Accurate MS-ID data for them are not available usually.

Accurate determinations of all REE including Pr, Tb, Ho, and Tm are important for the discussion of tetrad effects in geochemical samples. In this context, the HPIC technique (le Roex and Watkins, 1990; Watkins and le Roex, 1992) is not satisfactory, since Ho, Tm, and Lu data are not reported by their HPIC method due to analytical difficulties caused by the co-elution of Y with Ho and detection limits for Tm and Lu. ICP-MS is currently one of the most sensitive techniques to analyze all REE. We will make a comparison of our results for JB-1 with those by ICP-AES and MS-ID reported by Hirata *et al.* (1988) for further evaluation of the accuracy of our ICP-AES data.

(4) ICP-AES analyses compared with ICP-MS and MS-ID values

Hirata *et al.* (1988) reported their ICP-MS analyses of all REE and Y in several GSJ refer-

Table A1. Wavelengths (nm) of emission lines used in ICP-AES*

La(II)	398.852	Ce(II)	413.380	Pr(II)	417.939
Nd(II)	430.358	Sm(II)	442.434	Eu(II)	381.967
Gd(II)	342.247	Tb(II)	350.917	Dy(II)	353.170
Ho(II)	345.600	Er(II)	369.265	Tm(II)	313.126
Yb(II)	328.937	Lu(II)	261.542	Y(II)	371.030

*II denotes a singly charged ion emission line.

Table A2. Averaged values of coefficient of variation (%) for REE and Y analyses for eight GSJ reference rocks*

La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
3.9	4.1	5.1	3.5	4.4	4.7	3.1	6.5	4.1	4.4	2.9	4.3	2.5	2.7	4.2

*C.V. values for the analyses for GSJ samples listed in Table 1 are averaged with respect to each element.

Table A3. Averaged deviations of ICP-AES analyses of REE from the HPIC analyses reported by Watkins and le Roex (1992)*

La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Er	Yb
+5.2	+3.3	-3.1	+1.8	-3.8	-2.1	-3.5	-4.8	-1.9	+1.3	+0.7

*Deviations (%) of our results in Table 1 from the reported HPIC values for seven GSJ reference samples (JB-1, JG-1, JG-1a, JG-2, JG-3, JR-1, and JR-2) are averaged, except for the case of Eu. Because of large negative Eu anomalies in JG-2, JR-1, and JR-2, the HPIC values of Eu for the three samples involve rather large uncertainty compared with those in other GSJ samples. We have averaged the deviations for Eu with respect to the four GSJ samples of JB-1, JG-1, JG-1a, and JG-3.

ence rocks (JA-1, JB-1, JB-2, and JB-3). They evaluated the accuracy of their ICP-MS data by comparing them with those by their thermal-ionization MS-ID data. They concluded that their ICP-MS data are in excellent agreement with the MS-ID ones within differences of about 5%. Figure A1(A) shows our ICP-AES results for JB-1 compared with the ICP-MS and MS-ID ones reported by Hirata *et al.* (1988). In Fig. A1(B), the deviations of our ICP-AES values from the MS-ID data are shown together with $\pm 2\sigma$ (mean) for ours. Similar deviations of the ICP-MS values by Hirata *et al.* (1988) are also plotted in Fig. A1(B) for comparison. Since the MS-ID data set as the ref-

erence for calculating the deviations in Fig. A1(B) do not include Pr, Tb, Ho, and Tm values, the HPIC values for Pr and Tb (Watkins and le Roex, 1992) and the MS-ID value for Ho using ^{163}Ho with $T_{1/2} = 6,000$ y (Kawakami and Masuda, 1984) were tentatively used as the reference values. For the Tm data, however, we did not make such calculations, since we cannot select any acceptable Tm value for JB-1 except for our ICP-AES value and the ICP-MS one by Hirata *et al.* (1988).

From the results of Fig. A1, we conclude the followings:

(i) Our ICP-AES analyses are in very good agreements with the MS-ID values. The average

Fig. A1. Comparison of REE analyses for JB-1 by ICP-AES with those by ICP-MS and MS-ID reported by Hirata *et al.* (1988). (A): Chondrite-normalized REE patterns for JB-1 by ICP-AES, ICP-MS, and MS-ID data. (B): The deviations of ICP-AES analyses (open circles) from the reported MS-ID data by Hirata *et al.* (1988). Error bars indicate $\pm 2\sigma$ (mean) of the ICP-AES values. Similar deviations of ICP-MS analyses (crosses) from the MS-ID data are cited from Hirata *et al.* (1988). Since Pr, Tb, Ho, and Tm values are lacking in the MS-ID data set, the HPIC data for Pr and Tb (Watkins and le Roex, 1992) and the MS-ID value for Ho using ^{163}Ho with $T_{1/2} = 6,000$ y (Kawakami and Masuda, 1984) are tentatively used as the reference values for calculating the deviations for the monoisotopic REE. Since there seems to be no reliable reference value for Tm except for our ICP-AES value and the ICP-MS one by Hirata *et al.* (1988), we do not calculate the deviations for Tm.

deviation of our ICP-AES values from the MS-ID ones for ten polyisotopic REE is $(-1.7 \pm 4.5)\%$. For the thirteen REE including three monoisotopic Pr, Tb, and Ho, their average deviation is $(-1.9 \pm 4.2)\%$. In the case of the ICP-MS values by Hirata *et al.* (1988), similar average deviations for the ten and thirteen REE are $(+3.8 \pm 4.0)\%$ and $(+3.0 \pm 5.9)\%$, respectively. Thus our ICP-AES data have the accuracy comparable to the ICP-MS analyses.

(ii) Our ICP-AES analyses agree with the MS-ID and HPIC data within 4% on the average, but only our Lu value is lower than the MS-ID value by 10%. The coefficient of variation for our Lu analysis for JB-1 is 1.8%, and the average of C. V. values for Lu analyses in Table 1 is 2.7%. Hence, the difference of 10% from the MS-ID value of Lu in JB-1 may represent a possible sys-

tematic error in our Lu analyses as far as the MS-ID value is correct. Although we cannot judge whether the discrepancy is limited in our analysis of Lu in JB-1 or not, we must keep in mind the possible bias in our Lu data.

(iii) As shown in Fig. A1(A), the ICP-MS values by Hirata *et al.* (1988) for heavy REE from Gd to Lu appear to be systematically higher than the MS-ID and our ICP-AES values by 5–10%. However, the abundance pattern for the heavy REE based on the ICP-MS analyses is in parallel with our ICP-AES results and their MS-ID as well. The step-like irregularity between Er and the three heaviest REE is recognized in our ICP-AES data and the ICP-MS ones in common. This coincidence strongly suggests that the small irregularity in the chondrite-normalized pattern of JB-1 is real.