Approximate estimation of the degree of lanthanide tetrad effect from the data potentially involving all lanthanides

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Here is presented a mathematical method which enables us to evaluate the degrees of lanthanide tetrad effects from the data involving all of REE. Each of the four spans corresponding to four subgroups, La-Nd, Pm-Gd, Gd-Ho, and Er-Lu, is approximately fitted to a quadratic function and the resultant quadratic coefficient is employed as a numerical indicator for the tetrad effect. For the purpose of approximation by a quadratic function, the least-squares method is used under the constraint that the first and second quadratic curves intersect at the middle point between Pm and Sm, and that the third and fourth ones intersect at the middle point between Ho and Er. Since, mathematically, the subject is a problem on the conditional extremum, the method of Lagrange undetermined multipliers should be used. It is noted that the degrees of four tetrad effects can be evaluated simultaneously. This method can lead us to the mathematically well-defined estimation of the tetrad effect.

INTRODUCTION

Increasing attention is being paid to the lanthanide tetrad effect in relation with geochemical problems. This effect was first pointed out by Fidelis and Siekierski (1966) based on their experimental data for the phase partition chromatography. Peppard *et al.* (1969) experimentally disclosed it in liquid-liquid solvent extraction. The tetrad effect divides fifteen lanthanide elements into four subgroups: La to Nd, Pm to Gd, Gd to Ho, and Er to Lu, corresponding to $4f^0$ – $4f^3$, $4f^4$ – $4f^7$, $4f^7$ – $4f^{10}$, and $4f^{11}$ – $4f^{14}$. Each of the four tetrad effects widely observed in chemical systematic perturbation is represented by a distinct smooth curve; the first and second ones, the second and third ones, and the third and fourth ones appear, respectively, to intersect each other at the middle point between Nd and Pm, at Gd, and at the middle point between Ho and Er, corresponding to “one-quarter-filled”, “half-filled” and “three-quarters-filled” 4f electron shell. The tetrad effect can be

theoretically explained in terms of the interelectron repulsion, expressed by the Racah parameters, in the 4f orbital (Jørgensen, 1970). Kawabe (1992) reported that the Racah parameters depend on the effective nuclear charge in his new refined spin-pairing energy theory. Masuda *et al.* (1994) paid attention to possible three-dimensional symmetry of f^3 , f^4 , f^{10} and f^{11} electron clouds, and those of f^7 and f^{14} could have the maximum symmetry in this connection, which was depicted by Masuda (1995a).

Masuda and Ikeuchi (1979) first reported the above tetrad effect in REE patterns for seawaters in nature. Further, Masuda and his co-workers have shown evidence for this effect in geological materials such as groundwaters, leuco-granites, and kimuraite. Two types, “W-type” and “M-type”, of tetrad phenomenon are found out (Masuda *et al.*, 1987). It is indispensable to deeper arguments to indicate quantitatively the tetrad effect in natural samples. Masuda *et al.* (1994) recently proposed a new mathematical method to evaluate the relative

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magnitudes of lanthanide tetrad effects. According to their method, it is assumed that the four observed curves of a given REE pattern can be approximated by four quadratic functions, respectively, and each of the resultant quadratic coefficients is employed as an indicator of the degree of the tetrad effect concerned. The method is applied to REE data obtained by isotope dilution mass spectrometry (ID-MS), with void of data on monoisotopic lanthanides. For the purpose of estimation of the degrees of the third and fourth tetrad effects, first a quadratic function is calculated from abundances for three elements of Er, Yb and Lu and the resultant quadratic coefficient is used as the fourth tetrad effect degree, and then another quadratic function is calculated from two measured values for Gd and Dy combined with the one estimated value for the middle point between Ho and Er on the fourth quadratic curve. For the first and second tetrad effects, both degrees are assumed to be equal because only four members of La, Nd, Sm and Gd can be employed due to the absence of Pm, to the possible anomalous behaviors of Ce and Eu, and to undetermined Pr by isotope dilution.

The method by Masuda *et al.* (1994) is useful for partially void data obtained by ID-MS. In a subsequent paper, Masuda *et al.* (1995) examined the extent of the potential validity of the mathematical hypotheses described above using the data on multi-isotopic lanthanides plus Pr and Ho. Two independent quadratic curves for the third and fourth tetrad effects intersect at almost the middle point between Ho and Er, and likewise the first and second curves are inferred to intersect at the middle point Nd and Pm, in samples of leucogranitic gneiss (Lee *et al.*, 1994), and seawater (Shabani *et al.*, 1990). This confirms the validity of hypothesis about the crossing position. Anyway it is desirable to develop a mathematical method which can be applicable to the case where the abundance data with high and comparable precisions are available for all of lanthanides. The purpose of this study is to advance such a mathematical method.

THE METHOD OF LAGRANGE UNDETERMINED MULTIPLIERS

In order to evaluate the tetrad effect degrees for the first subgroup (La-Pr-Nd), the second one (Sm-Gd), the third one (Gd-Tb-Dy-Ho) and the fourth one (Er-Tm-Yb-Lu), four quadratic curves specifically covering the corresponding four spans are approximated simultaneously by means of the least-squares method under the constraint that the first and second curves intersect at the middle point between Nd and Pm, and that the third and fourth ones intersect at the middle point between Ho and Er. This case is mathematically accordant to a problem on the conditional extremum, and should be treated by the method of Lagrange undetermined multipliers.

Now, x -coordinates for lanthanide elements are employed as $x_i = 0, 1, \dots$, and 14 corresponding to La, Ce, ..., and Lu. Four quadratic functions are estimated by means of the least-squares method under a condition that the first and second curves, the second and third ones, and the third and fourth ones intersect at $x = x' (= 3.5)$, $x'' (= 7)$ and $x''' (= 10.5)$, respectively. Let these four specific quadratic functions be $y = a_1x_i^2 + b_1x_i + c_1$ ($i = 0, 1, 2, 3$), $y = a_2x_i^2 + b_2x_i + c_2$ ($i = 4, 5, 6, 7$), $y = a_3x_i^2 + b_3x_i + c_3$ ($i = 7, 8, 9, 10$) and $y = a_4x_i^2 + b_4x_i + c_4$ ($i = 11, 12, 13, 14$). They intersect each other at $x = x', x''$ and x''' . Namely,

$$a_1(x')^2 + b_1(x') + c_1 = a_2(x')^2 + b_2(x') + c_2,$$

$$a_2(x'')^2 + b_2(x'') + c_2 = a_3(x'')^2 + b_3(x'') + c_3,$$

and

$$a_3(x''')^2 + b_3(x''') + c_3 = a_4(x''')^2 + b_4(x''') + c_4.$$

Under the above condition, we should minimize the sum of squares S , where S is given as

$$S = \sum_{i=0}^3 \left\{ (a_1 x_i^2 + b_1 x_i + c_1) - y_i \right\}^2 \\ + \sum_{i=4}^7 \left\{ (a_2 x_i^2 + b_2 x_i + c_2) - y_i \right\}^2 \\ + \sum_{i=7}^{10} \left\{ (a_3 x_i^2 + b_3 x_i + c_3) - y_i \right\}^2 \\ + \sum_{i=11}^{14} \left\{ (a_4 x_i^2 + b_4 x_i + c_4) - y_i \right\}^2.$$

Here, we should use the method of Lagrange undetermined multipliers. Let us introduce the Lagrangian form L as

$$L = S - \lambda' \{ a_1 (x')^2 + b_1 (x') + c_1 \\ - a_2 (x')^2 - b_2 (x') - c_2 \} \\ - \lambda'' \{ a_2 (x'')^2 + b_2 (x'') + c_2 \\ - a_3 (x'')^2 - b_3 (x'') - c_3 \} \\ - \lambda''' \{ a_3 (x''')^2 + b_3 (x''') + c_3 \\ - a_4 (x''')^2 - b_4 (x''') - c_4 \},$$

where λ' , λ'' and λ''' are the indeterminate coefficients. When L has an extremum, the following equations should be satisfied

$$\partial L / \partial a_1 = 0, \quad \partial L / \partial b_1 = 0, \quad \partial L / \partial c_1 = 0,$$

$$\partial L / \partial a_2 = 0, \quad \partial L / \partial b_2 = 0, \quad \partial L / \partial c_2 = 0,$$

$$\partial L / \partial a_3 = 0, \quad \partial L / \partial b_3 = 0, \quad \partial L / \partial c_3 = 0,$$

$$\partial L / \partial a_4 = 0, \quad \partial L / \partial b_4 = 0, \quad \partial L / \partial c_4 = 0,$$

$$\partial L / \partial \lambda' = 0, \quad \partial L / \partial \lambda'' = 0, \quad \partial L / \partial \lambda''' = 0.$$

These equations are reduced to fifteen linear equations which are written by 15×15 square matrix as

$$\begin{pmatrix} 2 \sum_{i=0}^3 x_i^4 & 2 \sum_{i=0}^3 x_i^3 & 2 \sum_{i=0}^3 x_i^2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -(x')^2 & 0 & 0 \\ 2 \sum_{i=0}^3 x_i^3 & 2 \sum_{i=0}^3 x_i^2 & 2 \sum_{i=0}^3 x_i & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -x' & 0 & 0 \\ 2 \sum_{i=0}^3 x_i^2 & 2 \sum_{i=0}^3 x_i & 2 \sum_{i=0}^3 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 2 \sum_{i=4}^7 x_i^4 & 2 \sum_{i=4}^7 x_i^3 & 2 \sum_{i=4}^7 x_i^2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & (x')^2 & -(x'')^2 & 0 \\ 0 & 0 & 0 & 2 \sum_{i=4}^7 x_i^3 & 2 \sum_{i=4}^7 x_i^2 & 2 \sum_{i=4}^7 x_i & 0 & 0 & 0 & 0 & 0 & 0 & 0 & x' & -x'' & 0 \\ 0 & 0 & 0 & 2 \sum_{i=4}^7 x_i^2 & 2 \sum_{i=4}^7 x_i & 2 \sum_{i=4}^7 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 2 \sum_{i=7}^{10} x_i^4 & 2 \sum_{i=7}^{10} x_i^3 & 2 \sum_{i=7}^{10} x_i^2 & 0 & 0 & 0 & 0 & (x'')^2 & -(x''')^2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 2 \sum_{i=7}^{10} x_i^3 & 2 \sum_{i=7}^{10} x_i^2 & 2 \sum_{i=7}^{10} x_i & 0 & 0 & 0 & 0 & x'' & -x''' & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 2 \sum_{i=7}^{10} x_i^2 & 2 \sum_{i=7}^{10} x_i & 2 \sum_{i=7}^{10} 1 & 0 & 0 & 0 & 0 & 0 & 1 & -1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2 \sum_{i=11}^{14} x_i^4 & 2 \sum_{i=11}^{14} x_i^3 & 2 \sum_{i=11}^{14} x_i^2 & 0 & 0 & (x''')^2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2 \sum_{i=11}^{14} x_i^3 & 2 \sum_{i=11}^{14} x_i^2 & 2 \sum_{i=11}^{14} x_i & 0 & 0 & x''' & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2 \sum_{i=11}^{14} x_i^2 & 2 \sum_{i=11}^{14} x_i & 2 \sum_{i=11}^{14} 1 & 0 & 0 & 1 & 0 \\ -(x')^2 & -x' & -1 & (x')^2 & x' & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -(x')^2 & -x'' & -1 & (x'')^2 & x'' & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -(x'')^2 & -x''' & -1 & (x''')^2 & x''' & 1 & 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} a_1 \\ b_1 \\ c_1 \\ a_2 \\ b_2 \\ c_2 \\ a_3 \\ b_3 \\ c_3 \\ a_4 \\ b_4 \\ c_4 \\ \lambda' \\ \lambda'' \\ \lambda''' \end{pmatrix} = \begin{pmatrix} 2 \sum_{i=0}^3 x_i^2 y_i \\ 2 \sum_{i=0}^3 x_i y_i \\ 2 \sum_{i=0}^3 y_i \\ 2 \sum_{i=4}^7 x_i^2 y_i \\ 2 \sum_{i=4}^7 x_i y_i \\ 2 \sum_{i=4}^7 y_i \\ 2 \sum_{i=7}^{10} x_i^2 y_i \\ 2 \sum_{i=7}^{10} x_i y_i \\ 2 \sum_{i=7}^{10} y_i \\ 2 \sum_{i=11}^{14} x_i^2 y_i \\ 2 \sum_{i=11}^{14} x_i y_i \\ 2 \sum_{i=11}^{14} y_i \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

expressed as a simplified form of $AX = B$. Thus the unknown coefficients are given by $X = A^{-1}B$, where A^{-1} is the inverse matrix of A . If all lan-

thanide elements from La to Lu including Pm are considered, A is shown as

$$A = \begin{pmatrix} 196 & 72 & 28 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -3.5^2 & 0 & 0 \\ 72 & 28 & 12 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -3.5 & 0 & 0 \\ 28 & 12 & 8 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 9156 & 1496 & 252 & 0 & 0 & 0 & 0 & 0 & 0 & 3.5^2 & -7^2 & 0 \\ 0 & 0 & 0 & 1496 & 252 & 44 & 0 & 0 & 0 & 0 & 0 & 0 & 3.5 & -7 & 0 \\ 0 & 0 & 0 & 252 & 44 & 8 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 46116 & 5168 & 588 & 0 & 0 & 0 & 0 & 7^2 & -10.5^2 \\ 0 & 0 & 0 & 0 & 0 & 0 & 5168 & 588 & 68 & 0 & 0 & 0 & 0 & 7 & -10.5 \\ 0 & 0 & 0 & 0 & 0 & 0 & 588 & 68 & 8 & 0 & 0 & 0 & 0 & 1 & -1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 204708 & 16000 & 1260 & 0 & 0 & 10.5^2 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 16000 & 1260 & 100 & 0 & 0 & 10.5 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1260 & 100 & 8 & 0 & 0 & 1 \\ -3.5^2 & -3.5 & -1 & 3.5^2 & 3.5 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -7^2 & -7 & -1 & 7^2 & 7 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -10.5^2 & -10.5 & -1 & 10.5^2 & 10.5 & 1 & 0 & 0 & 0 \end{pmatrix}$$

Kawabe (1992) has proposed that the ionic radii of Ln^{3+} with the six and eight coordination numbers plotted against the atomic number show the tetrad and octad effects, respectively (Fig. 1). As an example of application of the Lagrange method to all lanthanide elements, let us estimate the degrees of the tetrad effects seen in the ionic radii of VILn^{3+} and $\text{VIII}\text{Ln}^{3+}$ by Shannon and Prewitt (1970) and Shannon (1976). The calculated results are shown in Table 1. It draws our attention that the numerical value for the first tetrad is markedly higher than the values for the other three tetrads in 6-fold coordination, while the value for the first tetrad is almost zero, lower than those for the other tetrads in 8-fold coordination. The absolute values of the tetrad degrees in the ionic radii of Ln^{3+} can not be compared with those in REE pattern, but it is possible to estimate mutual trend of a set of four tetrad effects in the same way.

In geochemical samples, the plots of Ce, Pm and Eu should be omitted because of the absence of Pm and the possible anomalous behaviors of Ce and Eu. In this case, the tetrad degrees are also calculated by the same way as above. The degrees of the first, second, third and fourth tetrad effects, in case of omitting Ce, Pm and Eu, are given by

$$a_1 = (16.667 \times y_0 - 50.000 \times y_2 + 33.333 \times y_3) \times 10^{-2},$$

$$a_2 = (2.381 \times y_0 - 16.667 \times y_2 + 33.333 \times y_3 - 33.333 \times y_5 + 13.772 \times y_7 + 1.381 \times y_8 - 1.009 \times y_9 - 0.283 \times y_{10} + 0.653 \times y_{11} - 0.101 \times y_{12} - 0.271 \times y_{13} + 0.143 \times y_{14}) \times 10^{-2},$$

$$a_3 = (21.811 \times y_7 - 19.584 \times y_8 - 20.736 \times y_9 + 7.444 \times y_{10} + 17.011 \times y_{11} - 2.628 \times y_{12} - 7.053 \times y_{13} + 3.734 \times y_{14}) \times 10^{-2},$$

and

$$a_4 = (4.087 \times y_7 - 7.834 \times y_8 - 2.498 \times y_9 + 18.051 \times y_{10} + 6.847 \times y_{11} - 22.196 \times y_{12} - 17.473 \times y_{13} + 21.015 \times y_{14}) \times 10^{-2},$$

where y_i ($i = 0, 2, 3, 5, 7, 8, \dots$, and 14) are given as logarithms of abundances divided by normalizing values for La, Pr, Nd, Sm, Gd, Tb, ..., and Lu in a given REE pattern. Since the absolute values of a_n ($n = 1, 2, 3, 4$) are small for most of geological samples, $T(n)$ defined as $a_n \times 100$ ($n = 1, 2, 3, 4$) are employed as a numerical index for the tetrad effect according to Masuda *et al.* (1994). $T(n) = 0$ indicates that tetrad phenomenon is not

Fig. 1. The ionic radii of 6- and 8-fold coordinations by Shannon and Prewitt (1970) and Shannon (1976) are plotted against the atomic number. This figure is reproduced in modified form from Kawabe (1992).

Table 1. Degrees of the first, second, third and fourth tetrad effects in the ionic radii of 6- and 8-fold coordinations

Coordination number	a_1 $\times 10^3$	a_2 $\times 10^3$	a_3 $\times 10^3$	a_4 $\times 10^3$
6	+3.28	+1.17	+1.01	+0.78
8	-0.06	+0.30	+0.29	+0.46

Table 2. Degrees of the first, second, third and fourth tetrad effects in leuco-granites, leuco-granitic gneisses, rhyolites, kimuraite and seawaters

Sample	T(1)	T(2)	T(3)	T(4)
leuco-granite				
No. 12	-19.7	-9.5	-5.1	-8.7
No. 15	-9.2	-5.0	-4.3	-4.3
leuco-granitic gneiss				
3318WR	-2.6	-6.4	-3.7	-5.0
3321WR	-4.2	-4.0	-4.1	-3.2
rhyolite				
JR-1	-2.2	-0.9	+0.3	-0.8
JR-2	-3.1	-2.0	-0.2	-1.2
kimuraite				
A (middle layer)	+2.8	+2.8	+1.9	+4.8
A (inner layer)	+3.8	+5.5	+3.2	+2.1
B	+1.8	+2.8	+2.4	+3.1
seawater				
1	+2.8	+4.1	+2.3	+0.3
2	+2.6	+3.1	+3.2	+0.4

observed in REE pattern, and $T(n) > 0$ and $T(n) < 0$ indicate that "W-type" and "M-type" tetrad effects are observed, respectively. The stronger the tetrad phenomenon observed in REE pattern is, the larger the absolute value of $T(n)$ becomes.

APPLICATION OF THE LAGRANGE METHOD TO GEOCHEMICAL SAMPLES

We tried to apply this method to REE data for leuco-granites at Linwu, Hunan Province, China (Masuda and Akagi, 1989), leuco-granitic gneisses in the Imweon area in South Korea (Lee *et al.*, 1994), rhyolites of Wada Pass, Nagano, Japan (a geochemical reference rock of Geological Survey of Japan) (Kawabe, 1995), kimuraite (Akagi *et al.*, 1993) and seawaters (Shabani *et al.*, 1990). The kimuraite samples were collected from fissures of alkali basalts occurring at Higashi Matsuura-gun, Saga Prefecture, Japan. The seawater samples were collected from latitude $35^{\circ}40'22''$ N and longitude $133^{\circ}3'33''$ E., Japan Sea, near the Shimane Prefecture (depth 1 m from surface). The chondrite-normalized REE patterns of the leuco-granites, leuco-granitic gneisses and rhyolites exhibit M-type tetrad effects (Figs. 2(a), 2(b) and 2(c)), and those of the kimuraite and seawaters reveal W-type tetrad effects (Figs. 3(a) and 3(b)). For normalization, the Leedeey chondrite (Masuda *et al.*, 1973; Masuda, 1975) was used. The evaluated degrees of the first, second, third, and fourth tetrad effects for the leuco-granites, leuco-granitic gneisses, kimuraite and seawaters are listed in Table 2.

It is worthwhile to note that it is a problem to be studied separately whether the quadratic function can be strictly applicable to any cases. In fact,

Fig. 2. (a) Chondrite-normalized REE patterns of Chinese leuco-granites, excluding Eu. Data from Masuda and Akagi (1989). (b) Chondrite-normalized REE patterns of Korean leuco-granitic gneisses. Data from Lee *et al.* (1994). (c) Chondrite-normalized REE patterns of Japanese rhyolites, excluding Eu. Data from Kawabe (1995). Dotted lines are considered to be original source patterns.

Fig. 2.

Fig. 3. (a) Chondrite-normalized REE patterns of kimurite, excluding Ce. ICP-MS data from Akagi *et al.* (1993). (b) Chondrite-normalized REE patterns of seawaters from the Japan Sea. ICP-MS data from Shabani *et al.* (1990).

the approximation by a simple quadratic function appears invalid (Masuda, 1995b) for the fine-structures of lanthanide tetrad effects estimated from the data exhibited by Peppard *et al.* (1969) for liquid-liquid solvent extraction. In case of partitioning between 11.4M LiBr + 0.5M HBr and di 2-ethylhexyl-chloromethyl phosphate (DEH[CIMP]) in benzene, approximate quadratic curves can not be smoothly fitted to tetrad effect, in contrast with 0.05M HCl vs. 0.3M di *n*-octyl

phosphoric acid (HDOP) system and other phosphoric acid systems (unpublished data). The high concentration of Li in the aqueous phase in DEH[CIMP] system is noteworthy. Masuda (1995b) interpreted that DEH[CIMP] does not form a compound with strong ligand-cation chemical bonding, and that the state of 4f electron configuration is relatively free from the ligand field in DEH[CIMP] system. Therefore, distorted curves could show any other effects than the common tetrad effect. The "quadratic" approximation is expected to serve as a measure to characterize the "non-quadratic" tetrad effect, too, in a versatile use. Further, it is emphasized that highly precise determinations for elements concerned are a prerequisite for any mathematical treatment of the available data. If some data have especially large uncertainties, tetrad curves are subject to erratic distortion and it is required to omit such data in calculation. The method proposed here can be applied to partially void data. Estimation of the tetrad effect degrees in some cases of partially void data is shown in Appendix.

A comment is added here about the systematic definite bias which can result from the choice of the abundance set for normalization. Provided that the logarithmic linearity of chondrite-normalized values holds good strictly for the tetrad span under consideration, any bias does not result from the replacement of the normalizing values by the system other than the chondrite, apart from the problem reflecting the mutual variation of lanthanide abundances within the chondrites. From a simple mathematical consideration, the degrees of quadratic coefficients for four tetrad effects do not change even if a REE pattern slopes linearly from La to Lu, or even if a pattern has bends at the middle point between Nd and Pm, at Gd and at the middle point between Ho and Er, where neighbor quadratic curves intersect each other. However, most of chondrite-normalized REE patterns for continental materials have a sharp break in inclination between two logarithmically linear portions, which cover the light and middle lanthanide span and the heaviest lanthanide span (substantially horizontal in general). The position

of the sharp break can be variable depending on rocks between Tb and Ho as illustrated by Masuda *et al.* (1994). In this case, $T(3)$ can be subject to the variation affected by REE patterns of the original source materials and/or the set of normalizing values. A mathematical bias for $T(3)$ due to this geochemical effect is evaluated to range mostly from 0.8 to 2.5. As an example, the REE patterns of rhyolites are taken to estimate a mathematical bias for $T(3)$ in Figs. 2(c). Supposing that the patterns of rhyolites are originated from a relatively common continental pattern consisting of two straight lines with a sharp break at the middle point of Tb and Dy, the values of $T(3)$ for JR-1 and JR-2 are corrected from +0.3 to -1.7 and from -0.2 to -2.5, respectively. Both $T(1)$ and $T(2)$ are unchanged by the calculation, and $T(4)$ for JR-1 and JR-2 are calculated at -1.0 and -1.4, which are 0.2 lower than the previous values. Therefore, indirect effect on $T(4)$ derived in application of the method presented here is generally negligible.

It is important to consider original or background curves for a REE pattern on evaluation of tetrad effect degrees, but what is original or background curve is obscure in most cases. First of all, it is highly significant to apply estimation of the degree of lanthanide tetrad effect to a REE pattern as it is (Masuda and Shimoda, 1996). Approximation by a quadratic function is quite reasonable. It is noted that four tetrad effect degrees in a REE pattern can be estimated simultaneously with mathematically strict treatment based on this method.

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APPENDIX

The degrees of the first, second, third and fourth tetrad effects for some cases of partially void REE data can be obtained as follows:

(1) In case of omitting only Pm,

$$a_1 = (24.548 \times y_1 - 24.146 \times y_2 - 24.682 \times y_3 + 22.941 \times y_4 + 5.859 \times y_6 - 7.031 \times y_7 + 2.421 \times y_8 + 0.243 \times y_9 - 0.177 \times y_{10} - 0.050 \times y_{11} + 0.115 \times y_{12} - 0.018 \times y_{13} - 0.048 \times y_{14} + 0.025 \times y_{15}) \times 10^{-2},$$

$$a_2 = (5.187 \times y_1 - 9.797 \times y_2 - 3.650 \times y_3 + 23.627 \times y_4 - 17.233 \times y_6 - 19.321 \times y_7 + 20.425 \times y_8 + 2.047 \times y_9 - 1.496 \times y_{10} - 0.420 \times y_{11} + 0.968 \times y_{12} - 0.150 \times y_{13} - 0.401 \times y_{14} + 0.213 \times y_{15}) \times 10^{-2},$$

$$a_3 = (0.134 \times y_1 - 0.254 \times y_2 - 0.095 \times y_3 + 0.612 \times y_4 - 1.743 \times y_6 + 2.091 \times y_7 + 21.091 \times y_8 - 19.655 \times y_9 - 20.684 \times y_{10} + 7.459 \times y_{11} + 16.977 \times y_{12} - 2.622 \times y_{13} - 7.039 \times y_{14} + 3.727 \times y_{15}) \times 10^{-2},$$

and

$$a_4 = (0.025 \times y_1 - 0.048 \times y_2 - 0.018 \times y_3 + 0.115 \times y_4 - 0.327 \times y_6 - 0.392 \times y_7 + 3.952 \times y_8 - 7.847 \times y_9 - 2.488 \times y_{10} + 18.054 \times y_{11} + 6.840 \times y_{12} - 22.195 \times y_{13} - 17.473 \times y_{14} + 21.014 \times y_{15}) \times 10^{-2}.$$

(2) In case of omitting Pm and Eu,

$$a_1 = (25.000 \times y_1 - 25.000 \times y_2 - 25.000 \times y_3 + 25.000 \times y_4) \times 10^{-2},$$

$$a_2 = (6.429 \times y_1 - 12.143 \times y_2 - 4.524 \times y_3 + 29.286 \times y_4 - 33.333 \times y_6 + 13.772 \times y_8 + 1.381 \times y_9 - 1.009 \times y_{10} - 0.283 \times y_{11} + 0.653 \times y_{12} - 0.101 \times y_{13} - 0.271 \times y_{14} + 0.143 \times y_{15}) \times 10^{-2},$$

$$a_3 = (21.811 \times y_8 - 19.583 \times y_9 - 20.736 \times y_{10} + 7.444 \times y_{11} + 17.011 \times y_{12} - 2.628 \times y_{13} - 7.053 \times y_{14} + 3.734 \times y_{15}) \times 10^{-2},$$

and

$$a_4 = (4.087 \times y_8 - 7.833 \times y_9 - 2.498 \times y_{10} + 18.051 \times y_{11} + 6.847 \times y_{12} - 22.196 \times y_{13} - 17.473 \times y_{14} + 21.015 \times y_{15}) \times 10^{-2}.$$

(3) In case of omitting Pm, Eu and monoisotopic elements,

$$a_1 = (33.333 \times y_1 - 50.000 \times y_2 + 16.667 \times y_4) \times 10^{-2},$$

$$a_2 = (7.936 \times y_1 - 16.667 \times y_2 + 27.778 \times y_4 - 33.333 \times y_6 + 14.286 \times y_8) \times 10^{-2},$$

$$a_3 = (14.286 \times y_8 - 33.333 \times y_{10} + 27.778 \times y_{12} - 16.667 \times y_{14} + 7.937 \times y_{15}) \times 10^{-2},$$

and

$$a_4 = (16.667 \times y_{12} - 50.000 \times y_{14} + 33.333 \times y_{15}) \times 10^{-2}.$$

y_i ($i = 1, 2, 3, \dots$, and 15) are given as logarithms of abundances divided by normalizing values for La, Ce, Pr, ..., and Lu in a given REE pattern.