Simultaneous Determination of Lanthanoids and Yttrium in Rock Reference Samples by Inductively Coupled Plasma-Mass Spectrometry Coupled with Cation Exchange Pretreatment

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The amounts of lanthanoids (Ln) and yttrium (Y) in eleven GSJ (Geological Survey of Japan, Tsukuba) rock reference materials have been determined. Fundamental studies on trace analysis of rock samples by inductively coupled plasma-mass spectrometry (ICP-MS) were conducted to obtain accurate contents of rare earth elements. The samples were dissolved using a conventional acid digestion technique, then treated on a cation exchange column for the removal of matrix components. Isobaric interferences from metal oxide ions were corrected based on the results of the experimentally obtained percentages of the metal oxide formation. A long-term stability test of the ICP-MS instrument with multielement standard solutions proved that all data obtained at concentration ranges from 0.01 to 10 $\mathrm{ng\,ml^{-1}}$ were reproducible, the drift of signals were less and the relative standard deviation (RSD) was within ±2.5%. The recoveries of Ln and Y from the cation exchange column were found to be (100±4)%. The results obtained for an igneous rock series showed good agreement with the recommended values given by GSJ, and their chondrite-normalized patterns were smooth.

Recently, rare-earth elements (REEs : lanthanoids, Sc and Y) have been increasingly used in advanced technical fields, such as electronics, semiconductors, superconductors, and supermagnets. On the other hand, the contents and the distribution patterns of REEs in geological samples play a key role in geochemistry for modeling earth's compositions and for dating ages of rocks.[1]

For the determination of REEs in geological samples, neutron activation analysis (NAA),[2] isotope dilution thermal ionization-mass spectrometry (ID-TIMS),[3] inductively coupled plasma-atomic emission spectrometry (ICP-AES)[4,5] and inductively coupled plasma-mass spectrometry (ICP-MS)[6] have been applied. Of these, NAA and ID-TIMS have some disadvantages such as long analysis times, high costs for their instruments, and the need for highly skilled operators. Furthermore, as ID-TIMS requires at least two stable isotopes, monoisotopic elements (Pr, Tb, Ho, Tm) can not be determined. Compared with such methods, ICP-MS seems to be a most promising technique for determining REEs in rocks because of its high sensitivity, short analysis time, simple background spectrum, wide dynamic ranges, simultaneous multielemental detection, and easy choice for analyte isotopes. However, ICP-MS also has several disadvantages: signal drift, or sensitivity change caused by matrix elements and spectral interferences from metal oxides. The formation of metal oxides and the effects of instrumental parameters, such as radiofrequency power, nebulizer flow rate, distance from the load coil and ion lens settings, on their intensities have been discussed in detail by several authors.[7—12] Although the effect of metal oxides on REEs measurement can be minimized by the optimization of the instrumental parameters, it is impossible to eliminate it completely. To compensate for the signal drift and the sensitivity change, some internal standard elements have often been added to the sample solution.[13—16]

ICP-MS has enough sensitivity for the measurement of REEs in rocks without any preconcentration procedures. However, direct introduction of sample solutions containing salts at high concentrations to ICP-MS results in sensitivity deterioration due to changes of physical properties. Therefore, removing matrix substances is required for accurate and precise measurements. Some workers have adopted a column separation method with cation exchange for the elimination of matrices in samples.[17—19] Haraguchi et al. reported the determination of rare earth elements (REEs) by ICP-AES[20—22] and ICP-MS[23—25] coupled with liquid chromatography (LC). Also, Kawabata et al. reported the determination of REEs by ICP-MS coupled with ion chromatography (IC).[26] These methods do not require tedious procedures for removing matrix elements, but need a longer measuring time (about 1 h per one sample) than direct introduction methods. The detection sensitivity obtained by the above LC-ICP-MS for REEs becomes worse by one or two orders of magnitude than that obtained by direct introduction, because of the dispersion of samples in the separation column. Furthermore, introduction of salts at high concentrations into the ICP-MS which is eluted from the column sometimes results in the lowering of the sensitivity and reproducibility. For a while, the procedure with a cation exchange has been established as a reliable method for matrix separation from REEs. So, we adopted an off-line column method in this paper.

The present study shows the application of ICP-MS for accurate analyses of REEs in rock samples. The method consists of acid digestion of rock samples, matrix elimination, and REEs separation with a cation exchange column, and data treatment including accurate evaluation and correction of the isobaric effects of metal oxides and isotopes.

Experimental

Samples. The following eleven geological standard rock samples available from the Geological Survey of Japan (GSJ, Tsukuba) were examined in this work: JA2 (andesite), JA3 (andesite), JB1 (basalt), JB2 (basalt), JB3 (basalt), JG1a (Granodiorite), JG2 (Granite), JG3 (Granodiorite), JGb1 (Gabbro), JR1 (Rhyolite), and JR2 (Rhyolite).

Reagents and Standard Samples. Multielement standard working solutions which contain fourteen lanthanoids, yttrium and barium in 0.1 M (1 M = 1 mol dm^{-3}) nitric acid were prepared by dilution of 1000 µg ml^{-1} standard solutions for atomic absorption spectrometry (Wako Pure Chemicals, Osaka): Each element concentration was in the range from 0.01 to 50 ng ml^{-1}. Internal standard elements were not added to the working solutions. Ultrapure water (18.2 MΩ cm resistivity) was prepared with a Milli-Q Labo (Nihon Millipore, Tokyo). Ultrapure grade nitric acid (60%, density 1.38 g cm^{-3}, Kanto Chemicals, Tokyo) was diluted with the purified water to give a 0.1 M solution. For preparing all solutions used, 0.1 M nitric acid solution was used. Dilution of the solutions was carried out by weight. Pieces of plastic labware made of polyethylene, polypropylene and polytetrafluoroethylene (PTFE) were used after by soaking them for a week in 1 M HNO_3 and rinsing them with purified water. All acids (HF, HNO_3, $HClO_4$, HCl) used for cation column pretreatment were of analytical reagent grade.

Acid Digestion of Rock Standard Samples. A powdered rock sample of 100 mg was weighed in a PTFE vial (PFA jar, volume of 7 ml; Masuda Rika, Osaka, Japan) with a screw cap, into which 1 ml of concd HNO_3 and 3 ml of concd HF were added. Then, the vial was sealed with the cap, and was heated on a sand bath at 100 °C in a draft chamber for 24 h. After confirming that the sample was almost dissolved, we further heated it several times at intervals of 1 min, using a microwave oven to obtain a clear solution. Then, the solution was evaporated to dryness on a sand bath at 140 °C. After 600 mg (about 15 drops) of perchloric acid was added dropwise to the residue, any hydrofluoric acid which remained was completely eliminated by heating on a sand bath at 200 °C. The residue was dissolved in 5 ml of 6 M HCl, and it was again evaporated to dryness to convert all the metals to metal chlorides. After adding 14 ml of 2 M nitric acid containing 0.5 M oxalic acid, the residue was warmed on the water bath in order to dissolve the residual precipitates.

Column Separation of REEs from Other Metals. The experimental conditions of column separation used in this work were those modified by Kusachi et al.[27] on the basis of the elution procedures with nitric acid developed by Cassidy.[28] The AG-50WX-12 Dowex resin (200—400 mesh; Bio-Rad, Richmond, CA), a strong cation exchange resin, was used. Eight ml of the cation exchange resin (suspended in H_2O) was transferred to a 13 mm i.d. × 120 mm plastic column (Muromachi Chemicals, Tokyo). After the resin was washed with 20 ml of 8 M HNO_3 at a flow rate of 2 ml min^{-1} and then 30 ml of H_2O at a flow rate of 2 ml min^{-1}, the resin was preconditioned with 20 ml of 2 M HNO_3 at a flow rate of 2 ml min^{-1}. The rock sample solution (14 ml) was passed at a flow rate of 2 ml min^{-1}. Then, 75 ml of 2 M HNO_3 was flowed at a flow rate of 2 ml min^{-1} for eliminating almost all of the major components, such as Fe, Al, alkali metals, alkaline earth metals, and transition metals. Finally, REEs were eluted with 50 ml of 6 M HNO_3 at a flow rate of 2 ml min^{-1}. The REEs fraction obtained was evaporated to dryness, and the residue was dissolved in 0.1 M HNO_3 to give a 25 ml stock solution. Prior to ICP-MS analysis, the measuring solution was diluted when the concentrations of REEs were too high.

Instrumentation and Measurements. The ICP-MS system used was a Seiko model SPQ 8000H quadrupole mass spectrometer. A NEC model PC9801 BA2 personal computer was used for mulielement mass spectral analysis. The standard operating conditions of ICP-MS system and the data acquisition parameters are summarized in Table 1. The system was daily checked with a 1 ng ml^{-1} of Pb solution to obtain maximum sensitivity. The system was also optimized by using a 10 ng ml^{-1} solution of Pr, which yielded the largest oxide formation, to be the minimum ratio of its metal oxide ion to metal ion before ICP-MS measurement.

The ICP-MS measurements in this work was performed as follows: measurement of (1) a blank solution (0.1 M HNO_3), (2) the series of the standard solutions, (3) the monitoring solutions for metal oxide corrections, (4) the rock sample solutions, (5) the blank solution, and finally (6) the series of the standard solutions. Eight kinds of concentration levels of standard solutions, 0.01, 0.05, 0.1, 0.5, 1, 5, 10, and 50 ng ml^{-1} of each REEs element, were used for the calibration graph. All REEs concentrations in rock samples tested were in the range of the standard solutions. Five kinds of solutions; (a) Ba+Pr+Tb, (b) Ce, (c) Nd, (d) Sm, and (e) Gd, containing 10 ng ml^{-1} of each element, were used for oxide monitoring.

Correction of Isobaric Interferences from Metal Oxides and Isotopes. In order to evaluate the isobaric overlaps, we measured the ratios of MO^+/M^+ for barium and rare earth elements using three kinds of the oxide monitoring solutions, containing 1, 10, and 100 ng ml^{-1} of each metal ion. The values of MO^+/M^+ for all metals examined were almost constant over the concentration ranges of the monitoring solutions. Therefore, the intensities of interfering oxide ions were proportional to the concentrations of the monitoring elements (isotopes). Thus we adopted a simple correction for metal oxide on the basis of an algebraic principle.[12] The analyte elements and monitoring isotopes are summarized in Table 2. La, Ce, Pr,

Table 1. Operating Parameters of ICP-MS System

Plasma conditions :	
Rf frequency	27.12 MHz
ICP radio frequency power	1.1 kW
Plasma gas flow rate	Ar 15 l min^{-1}
Carrier gas flow rate	Ar 0.45 l min^{-1}
Auxiliary gas flow rate	Ar 0.50 l min^{-1}
Sample uptake rate	1.0 ml min^{-1}
Spray chamber	Scott type
Nebulizer	Glass concentric type (Meinhard TR-30-C2)
Sampling condition :	
Distance from the load coil	10 mm
Sampling cone	Copper 1.1 mm ϕ
Skimmer cone	Copper 0.35 mm ϕ
Data acquisition :	Peak hopping mode
Dwell time	100 ms at each *m*/*z*
Data points	3 points per peak[a)]
No. of scans	60

a) Assuming peak center and ±0.125u from the center.

Table 2. Isotopes Selected for Analysis and Main Interferences

Analyte	*m/z*	Oxides /Isotopes Isobaric interferences[b)]	Monitoring isotopes
Y	89[a)]		
La	139[a)]		
Ce	140[a)]		
Pr	141[a)]		
Nd	142	$^{142}\mathrm{Ce}^+$	$^{142}\mathrm{Ce}^+$
Nd	146[a)]	$^{130}\mathrm{BaO}^+$ [c)]	
Sm	147[a)]		
Sm	152	$^{136}\mathrm{BaO}^+$	$^{138}\mathrm{Ba}^+$
Eu	153[a)]	$^{137}\mathrm{BaO}^+$	$^{138}\mathrm{Ba}^+$
Gd	157[a)]	$^{141}\mathrm{PrO}^+$	$^{141}\mathrm{Pr}^+$
Gd	158	$^{142}\mathrm{CeO}^+ + {}^{142}\mathrm{NdO}^+$	$^{140}\mathrm{Ce}^+$ and $^{146}\mathrm{Nd}^+$
Tb	159[a)]	$^{143}\mathrm{NdO}^+$	$^{146}\mathrm{Nd}^+$
Dy	164[a)]	$^{149}\mathrm{NdO}^+ + {}^{149}\mathrm{SmO}^+$	$^{146}\mathrm{Nd}^+$ and $^{147}\mathrm{Sm}^+$
Ho	165[a)]	$^{149}\mathrm{SmO}^+$	$^{147}\mathrm{Sm}^+$
Er	166[a)]	$^{150}\mathrm{NdO}^+ + {}^{150}\mathrm{SmO}^+$	$^{146}\mathrm{Nd}^+$ and $^{147}\mathrm{Sm}^+$
Tm	169[a)]	$^{153}\mathrm{EuO}^+$	$^{153}\mathrm{Eu}^+$
Yb	174[a)]	$^{158}\mathrm{GdO}^+ + {}^{158}\mathrm{DyO}^+$	$^{157}\mathrm{Gd}^+$ and $^{164}\mathrm{Dy}^+$
Lu	175[a)]	$^{159}\mathrm{TbO}^+$	$^{159}\mathrm{Tb}^+$

a) These isotopes were measured. Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu were corrected for oxide isobaric effect. b) This column represents the oxides and isotopes, and their isobaric corrections used to obtain the true ion counts in this work. Interferences from other interfering oxide species can be considered to be negligible. c) $^{146}\mathrm{Nd}^+$ was interfered with $^{130}\mathrm{BaO}^+$, but this could be ignored since the very low natural abundance of $^{130}\mathrm{Ba}$ (0.106%) and for example, relatively high abundance ratio of Nd/Ba (0.05) than those of Sm/Ba (0.008) or Eu/Ba (0.003) in JB-1.

and Y could be determined without any metal oxide correction. Eu through Lu were affected by the isobaric oxide ions. Barium oxide ions gave the isobaric effect on the isotopes of Eu and Sm, as well as Nd, but the isobaric effect on $^{146}\mathrm{Nd}^+$ was negligibly small because of low natural abundance of $^{130}\mathrm{Ba}$ (0.106%). Barium is often present in sample solutions at relatively high concentrations compared to REEs, and the effect of the isobaric overlaps of BaO^+ will be sometimes significant, so that $^{138}\mathrm{Ba}^+$ was always measured in this study.

The determination of $^{157}\mathrm{Gd}^+$ is not easy due to the isobaric effect of $^{141}\mathrm{PrO}^+$, which is easily formed. As $^{158}\mathrm{Gd}^+$ had to be corrected by using the isobaric effect of two oxide species, $^{142}\mathrm{CeO}^+$ and $^{142}\mathrm{NdO}^+$, $^{157}\mathrm{Gd}^+$ was chosen. The calibration graphs of all REEs, whose counts were corrected by the oxide/isotope correction method, showed good linearity (correlation coefficient $\geqq 0.999$) within their concentration ranges from 0.01 to 10 ng ml^{-1}.

Result and Discussion

Stability of ICP-MS System. To test the stability of the system, eight kinds of the multielement standard solutions were used and ion counts of REEs were measured at 2 h intervals over a period of 6 h. One sample throughput was 3 min, and the first measurement was started at 5 min after the plasma was turned on: Four data groups were obtained for the standard solutions during 6 h. The rock sample solutions were also measured between the measurements of the standard solutions. The beginning data obtained within 30 min showed relatively large drift, compared with later runs; a positive deviation of about 6% was seen in the 0.01 ng ml^{-1} standard solution. Thereafter, the signal drifts were lowered to 2%. The deviations of the second runs were within ±2%, those of the third runs within ±2%, and those of fourth runs within ±1%. As a result, the sample solutions free from major elements can be determined by ICP-MS without any spiking internal standard element, if we can accept instrumental variation within about 2%.

Limits of Detection (LOD) of Lanthanoids and Yttrium. Instrumental LODs, which were defined as the concentrations corresponding to three times of the standard deviations (σ) of blank intensities at *m/z* for each analyte, are summarized in Table 3. The average values of blank intensities were obtained from 10 measurements of 0.1 M nitric acid. The LODs for all elements were sub-ppt (pg ml^{-1}) levels, which indicates that the present ICP-MS system is sensitive enough for determining REEs in the rock samples, even after several hundred-fold dilution. $^{146}\mathrm{Nd}^+$ (0.55 pg ml^{-1}) and $^{157}\mathrm{Gd}^+$ (0.60 pg ml^{-1}) provided relatively high detection limits, while $^{169}\mathrm{Tm}^+$ was the lowest detection limit (0.046 pg ml^{-1}).

Validation of Oxide Correction Method. An artificial rock sample, which contains Y, Ba, and lanthanoids in almost the same compositions as the standard rock sample JB1 (Table 6), was prepared. This solution which was used for validation of the proposed correction method, therefore did not contain other matrix elements. The analytical data for the artificial rock sample are shown in Table 4. The corrected data are in good agreement with the expected values (prepared concentrations), while all uncorrected values of $^{157}\mathrm{Gd}^+$, $^{159}\mathrm{Tb}^+$, $^{166}\mathrm{Er}^+$, and $^{174}\mathrm{Yb}^+$ show positive errors. Such large discrepancies were due to some interfering species, such as $^{141}\mathrm{PrO}^+$, $^{143}\mathrm{NdO}^+$, ($^{150}\mathrm{NdO}^+ + {}^{150}\mathrm{SmO}^+$) or $^{158}\mathrm{GdO}^+$.

Table 3. Limits of Detection for Y and Lanthanoids

Analyte	Isotopes selected (*m/z*)	LOD (pg ml^{-1})[a)]
Y	89	0.091
La	139	0.13
Ce	140	0.14
Pr	141	0.069
Nd	142	0.27
Nd	146	0.55
Sm	147	0.33
Sm	152	0.24
Eu	153	0.22
Gd	157	0.60
Gd	158	0.48
Tb	159	0.069
Dy	164	0.092
Ho	165	0.072
Er	166	0.13
Tm	169	0.046
Yb	174	0.092
Lu	175	0.083

Calibration range: 0.01—0.1 ng ml^{-1}. LOD a) limit of detection, corresponding to 3σ, where σ is standard deviation of a blank solution (0.1 M $\mathrm{HNO_3}$, $n = 10$).

Table 4. Analytical Results of Artifitial Rock Standards Obtained with and without Oxide Correction

Element	Ba	Y	La	Ce	Pr	Nd		Sm		Eu	Gd		Tb	Dy	Ho	Er	Tm	Yb	Lu
m/z	138	89	139	140	141	142	146	147	152	153	157	158	159	164	165	166	169	174	175
	Concentration (ng ml^{-1})																		
Expected	60.0	3.00	4.00	7.00	1.00	3.00	3.00	0.500	0.500	0.200	0.500	0.500	0.100	0.500	0.100	0.300	0.040	0.200	0.030
without Oxide correction		2.92	4.10	6.75	1.01	**4.05**	3.01	0.496	**0.550**	**0.227**	**0.695**	**0.898**	**0.115**	**0.510**	**0.100**	**0.321**	0.040	**0.205**	**0.032**
with Oxide correction						2.97			0.492	0.199	0.496	0.459	0.096	0.483	0.099	0.295		0.200	0.030

Sample was an artificial rock sample solution containing Y, Ba, and lanthanoids, whose concentrations are almost the same as composition of JB1. Values in bold letters are the corrected concentrations.

In the present column procedures, Ba was not fully separated from the REEs, and showed somewhat similar elution behavior to that of the REEs. Therefore, barium oxide can produce positive errors for $^{146}Nd^+$, $^{150}Nd^+$, $^{150}Sm^+$, $^{152}Gd^+$, $^{152}Sm^+$, $^{151}Eu^+$, $^{153}Eu^+$, and $^{154}Gd^+$, though BaO^+/Ba^+ was very low. Among these isotopes, the isobaric effects were substantial to $^{152}Sm^+$, $^{151}Eu^+$, $^{153}Eu^+$ (about 0.05%). The abundance ratios of Ba/Sm (120) and Ba/Eu (300) were large in JB1, and the interferences from Ba in the determination of $^{152}Sm^+$ and $^{153}Eu^+$ were about 9 and 14%, respectively.

Recovery of REEs in the Column Pretreatment. The artificial solutions were used to evaluate the recoveries of REEs in the pretreatment with the ion exchange column. The stock solutions were prepared by mixing the REE standard solutions to give nearly the same compositions as JB1, JG2, JGb1, JR2; a solution (100 ng ml^{-1}) of each REE was also prepared. These solutions did not contain other matrix elements. Some aliquots of the artificial solutions were pretreated using three independent columns for each sample. Other aliquots of the artificial solutions were determined directly. As examples, the analytical results for two artificial samples, ART (JB1) and ART (JG2), are shown in Table 5. The recoveries (%) of REEs in five artificial solutions were nearly 100%, and the standard deviations, SD, obtained by the triplicate analysis were 5% or less. From these results, the recovery in the column treatment was found to be very reliable.

Analysis of Geological Standard Rock Samples (GSJ). Analytical results of Y and lanthanoids of the eleven standard rock samples obtained by the present method are summarized in Table 6. Certified values or compilation data are also in-

Table 5. Recoveries of REEs of Artificial Standard Samples with the Ion Exchange Column Pretreatment

Element	ART(JB1)[a)]		ART(JG2)[a)]	
	Expected	Recovery	Expected	Recovery
	ng ml^{-1}	%[b)]	ng ml^{-1}	%[b)]
Y	4.8	101 ±2.2	14.4	101 ±0.5
La	6.4	102 ±0.03	3.2	95.7±1.6
Ce	11.2	101 ±0.3	8.0	97.1±0.5
Pr	1.6	103 ±0.1	0.96	97.2±0.6
Nd	4.8	102 ±1.0	4.0	95.6±0.6
Sm	0.80	102 ±1.7	1.28	94.0±0.3
Eu	0.32	101 ±1.1	0.02	95.1±2.6
Gd	0.80	102 ±1.2	1.3	98.0±0.4
Tb	0.16	98.9±2.0	0.24	95.0±0.5
Dy	0.80	99.1±2.5	1.6	92.0±0.4
Ho	0.16	103 ±2.4	0.24	101 ±0.5
Er	0.48	101 ±2.1	0.96	100 ±1.0
Tm	0.06	102 ±2.0	0.16	95.6±0.8
Yb	0.32	104 ±4.2	1.1	99.0±0.6
Lu	0.05	105 ±4.8	0.16	98.3±0.6

a) ART (JB1) : Artificial sample which contents of REEs are similar to those of JB1; ART (JG2) : Artificial sample which contents of REEs are similar to those of JG2. b) The figures show average values of recovery (*n* = 3), and the figures with ± show standard deviations.

Table 6. Analytical Results of GSJ Geological Standard Rocks by the Present ICP-MS Method

	Found/μg g^{-1}								
	JA-2			JA-3		JB-1			
Element	This study	Certified[c)]	Ref. 31	This study	Certified	This study	Certified	Ref. 30	Ref. 25
Y	16.1[a)] ± 0.1[b)]	18.3	15.9	17.9 ± 0.1	21.2	22.3 ± 0.07	24.3	22.4 ± 0.3	18.9 ± 1.4
La	16.9 ± 0.1	15.8	14.5	9.19 ± 0.06	9.33	37.6 ± 0.2	38.6	39.9 ± 0.3	33.6 ± 1.0
Ce	35.6 ± 0.3	32.7	29.4	22.1 ± 0.2	22.8	64.4 ± 0.4	67.8	66.5 ± 0.6	56.2 ± 0.73
Pr	3.94 ± 0.06	3.84	3.44	2.81 ± 0.02	2.40	6.81 ± 0.04	7.01	7.36 ± 0.05	6.5 ± 0.23
Nd	14.8 ± 0.1	13.9	12.6	12.3 ± 0.1	12.3	26.8 ± 0.1	26.8	26.9 ± 0.2	22.8 ± 0.66
Sm	3.06 ± 0.04	3.11	2.97	2.89 ± 0.08	3.05	5.13 ± 0.09	5.13	5.17 ± 0.03	4.6 ± 0.13
Eu	0.919 ± 0.02	0.930	0.810	0.769 ± 0.008	0.820	1.50 ± 0.03	1.49	1.60 ± 0.03	1.4 ± 0.09
Gd	3.28 ± 0.1	3.06	2.90	3.27 ± 0.04	2.96	4.98 ± 0.09	4.90	5.19 ± 0.25	4.4 ± 0.17
Tb	0.506 ± 0.009	0.440	0.430	0.531 ± 0.004	0.520	0.720 ± 0.01	0.820	0.732 ± 0.022	0.80 ± 0.12
Dy	2.92 ± 0.03	2.80	2.68	3.15 ± 0.02	3.01	4.38 ± 0.07	4.14	4.30 ± 0.12	3.7 ± 0.08
Ho	0.570 ± 0.009	0.500	0.570	0.640 ± 0.01	0.510	0.790 ± 0.009	0.790	0.822 ± 0.020	0.7 ± 0.03
Er	1.66 ± 0.05	1.48	1.65	1.91 ± 0.01	1.57	2.19 ± 0.04	2.27	2.24 ± 0.05	2.3 ± 0.13
Tm	0.269 ± 0.006	0.280	0.250	0.300 ± 0.005	0.280	0.330 ± 0.01	0.350	0.320 ± 0.008	0.30 ± 0.02
Yb	1.74 ± 0.01	1.62	1.59	2.01 ± 0.03	2.16	2.13 ± 0.01	2.13	2.05 ± 0.03	2.1 ± 0.07
Lu	0.269 ± 0.003	0.270	0.240	0.300 ± 0.007	0.320	0.330 ± 0.008	0.310	0.313 ± 0.010	0.32 ± 0.03
	JB-2			JB-3			JG-1a		
Element	This study	Certified[c)]	Ref. 30	This study	Certified	Ref. 30	This study	Certified	Ref. 31
Y	24.8[a)] ± 0.2[b)]	24.9	26.4 ± 0.5	24.9 ± 0.09	26.9	27.4 ± 0.4	19.7 ± 0.1	32.1	—
La	2.19 ± 0.02	2.35	2.67 ± 0.05	8.56 ± 0.05	8.81	9.07 ± 0.19	22.3 ± 0.2	21.3	18.7
Ce	6.60 ± 0.06	6.76	7.03 ± 0.05	22.7 ± 0.2	21.5	22.5 ± 0.4	48.2 ± 0.1	45.0	40.0
Pr	1.13 ± 0.008	1.01	1.27 ± 0.03	3.38 ± 0.02	3.11	3.35 ± 0.07	5.38 ± 0.05	5.63	4.58
Nd	6.25 ± 0.04	6.65	6.62 ± 0.08	16.3 ± 0.09	15.6	16.2 ± 0.3	20.0 ± 0.1	20.4	17.0
Sm	2.48 ± 0.02	2.31	2.41 ± 0.03	4.29 ± 0.08	4.27	4.44 ± 0.15	4.38 ± 0.06	4.53	4.00
Eu	0.925 ± 0.02	0.860	0.949 ± 0.024	1.34 ± 0.02	1.32	1.40 ± 0.05	0.731 ± 0.01	0.700	0.650
Gd	3.71 ± 0.07	3.28	3.43 ± 0.10	4.98 ± 0.09	4.67	5.00 ± 0.40	4.30 ± 0.08	4.08	3.83
Tb	0.669 ± 0.01	0.600	0.603 ± 0.013	0.775 ± 0.01	0.730	0.743 ± 0.026	0.669 ± 0.02	0.810	0.620
Dy	4.36 ± 0.05	3.73	4.12 ± 0.06	4.57 ± 0.05	4.54	4.70 ± 0.18	3.63 ± 0.09	4.44	3.85
Ho	1.00 ± 0.01	0.750	0.886 ± 0.021	0.860 ± 0.01	0.800	0.952 ± 0.028	0.738 ± 0.06	0.820	0.780
Er	2.80 ± 0.04	2.60	2.71 ± 0.08	2.67 ± 0.03	2.49	2.78 ± 0.14	2.77 ± 0.06	2.57	2.22
Tm	0.438 ± 0.01	0.410	0.401 ± 0.014	0.400 ± 0.008	0.420	0.389 ± 0.013	0.425 ± 0.007	0.380	0.330
Yb	2.89 ± 0.01	2.62	2.70 ± 0.06	2.63 ± 0.03	2.55	2.68 ± 0.07	2.73 ± 0.09	2.70	2.26
Lu	0.438 ± 0.006	0.400	0.408 ± 0.022	0.394 ± 0.007	0.390	0.388 ± 0.019	0.408 ± 0.009	0.440	0.330

Table 6. (Continued)

	Found/μg g^{-1}							
	JG-2			JG-3		JGb-1		
Element	This study	Certifiedc)	Ref. 31	This study	Certified	This study	Certified	Ref. 31
Y	74.4a) ± 0.4b)	86.5	—	13.8 ± 0.5	17.3	8.94 ± 0.03	10.4	10.0
La	21.3 ± 0.2	19.9	19.3	20.2 ± 0.6	20.6	3.25 ± 0.05	3.60	3.65
Ce	51.4 ± 0.3	48.3	47.3	41.6 ± 0.9	40.3	8.56 ± 0.07	8.17	8.08
Pr	6.50 ± 0.04	6.20	6.23	4.56 ± 0.1	4.70	1.13 ± 0.02	1.13	1.14
Nd	26.8 ± 0.08	26.4	25.3	16.6 ± 0.2	17.2	5.25 ± 0.06	5.46	4.87
Sm	8.26 ± 0.09	7.78	8.10	3.00 ± 0.04	3.39	1.44 ± 0.02	1.49	1.74
Eu	0.088 ± 0.003	0.100	0.09	0.784 ± 0.01	0.900	0.619 ± 0.007	0.620	0.70
Gd	8.13 ± 0.1	8.01	9.08	3.04 ± 0.05	2.92	1.78 ± 0.04	1.61	1.99
Tb	1.73 ± 0.01	1.62	1.64	0.438 ± 0.006	0.460	0.288 ± 0.004	0.290	0.30
Dy	10.9 ± 0.1	10.5	10.8	2.38 ± 0.03	2.59	1.69 ± 0.04	1.56	1.81
Ho	2.03 ± 0.04	1.67	2.27	0.506 ± 0.008	0.380	0.369 ± 0.01	0.330	0.40
Er	7.16 ± 0.1	6.04	6.90	1.50 ± 0.01	1.52	1.05 ± 0.04	1.04	1.13
Tm	1.00 ± 0.03	1.16	1.02	0.225 ± 0.004	0.240	0.150 ± 0.005	0.160	0.19
Yb	7.26 ± 0.1	6.85	6.93	1.47 ± 0.005	1.77	0.975 ± 0.03	1.06	1.12
Lu	0.988 ± 0.005	1.22	1.02	0.222 ± 0.003	0.260	0.144 ± 0.005	0.150	0.17

	JR-1			JR-2		
Element	This study	Certifiedc)	Ref. 31	This study	Certified	Ref. 31
Y	40.3a) ± 0.2b)	45.1	43.7	49.7 ± 0.3	51.1	50.9
La	19.9 ± 0.3	19.7	18.4	15.6 ± 0.08	16.3	14.5
Ce	48.0 ± 0.3	47.2	44.2	41.2 ± 0.3	38.8	36.3
Pr	6.05 ± 0.08	5.58	5.56	5.42 ± 0.05	4.75	4.69
Nd	23.8 ± 0.4	23.3	21.8	21.5 ± 0.1	20.4	18.6
Sm	5.76 ± 0.1	6.03	5.40	5.92 ± 0.09	5.63	5.14
Eu	0.273 ± 0.007	0.300	0.22	0.104 ± 0.002	0.140	0.06
Gd	5.99 ± 0.1	5.06	5.13	6.54 ± 0.1	5.83	5.50
Tb	1.01 ± 0.02	1.01	0.92	1.15 ± 0.002	1.10	0.98
Dy	6.20 ± 0.1	5.69	5.87	7.30 ± 0.1	6.63	6.46
Ho	1.19 ± 0.02	1.11	1.25	1.60 ± 0.04	1.39	1.40
Er	4.00 ± 0.05	3.61	3.87	5.13 ± 0.09	4.36	4.34
Tm	0.674 ± 0.01	0.670	0.61	0.840 ± 0.03	0.740	0.71
Yb	4.72 ± 0.06	4.55	4.30	5.96 ± 0.07	5.33	5.20
Lu	0.709 ± 0.02	0.710	0.64	0.917 ± 0.01	0.880	0.80

a) Average values of the duplicate sample solutions. b) Standard deviation obtained by five measurements (n = 5, error = 1 σ). c) Recommended values issued from GSJ.

cluded in Table 6 to allow comparison of the accuracy. Our results are in very good agreement with the certified or literature values,[29] most of which were determined by NAA or ID-TIMS methods. The average values were obtained from the duplicate rock sample solutions. The deviations from the certified values were within ±10%, except for Ho, and the relative standard deviations (RSD), which were obtained by using five replicate measurements for one rock sample, were less than 3.5%.

Lanthanoid abundances in geological samples are often discussed with their relative abundances normalized to those in chondrites. In this study, the analytical data were normalized to the Leedey chondrite values. The normalized values are shown in Fig. 1, where the normalized values calculated from the certified values are also plotted for comparison. The lanthanoids exhibit similar behavior to those in geological environments because of the similarity in their chemical properties (ionic radii and oxidation states). The exceptions were Ce and Eu, which can occur in the +4 and +2 oxidation states, respectively. The normalization of the REEs data can show some inconsistencies in the data due to the irregularities appearing in the normalized patterns. JB1, JA2, JG1a, and JG3 exhibit steep LREE-enriched patterns with or without small negative Eu-anomalies, whereas JG2, JR1, and JR2 exhibit flatter patterns with very large negative Eu-anomalies. The Leedey chondrite normalized patterns obtained from the present analytical data are very smooth, and most of the lanthanoid values, except for Ho, are found to be consistent with the certified values within ±10%, as shown in Table 6. In Ho, deviations from the normalized patterns were observed for JB2, JG2, JG3 etc., which deviate by 7 to 25%. Ho concentration in JB2 obtained in this study (1.00

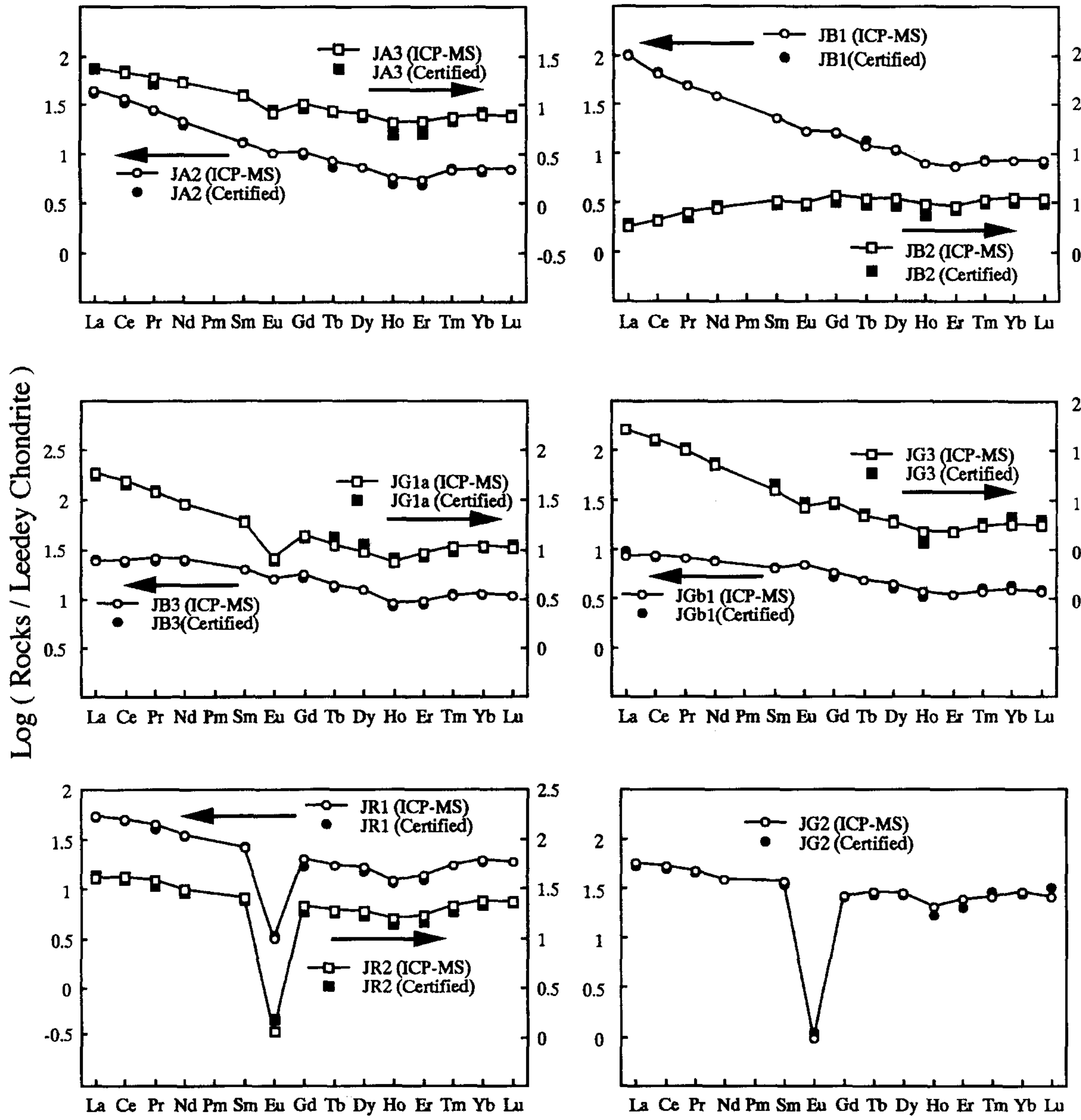

Fig. 1. REE abundances in some GSJ standard rock samples normalized to those of Leedey Chondrite. The ICP-MS data obtained in this study are shown by open symbols. The closed symbols indicate certified values.

$\mu g\,g^{-1}$) is closer to ICP-MS data reported by Shinotsuka et al.[30] (0.886 $\mu g\,g^{-1}$) than to the certified value (0.75 $\mu g\,g^{-1}$). Ho concentration in JG2 obtained in this study (2.03 $\mu g\,g^{-1}$) is closer to ICP-MS data reported by Garbe–Schönberg[31] (2.27 $\mu g\,g^{-1}$) than to the certified value (1.67 $\mu g\,g^{-1}$).

Conclusion. The cation exchange column separation of REEs from matrix substances with ICP-MS was found to be very useful for the determination of REEs in a wide variety of rocks. The wide-range concentrations of standard samples for preparing calibration graphs gave the best choice for the optimal determination ranges of elements, whose concentrations vary from 0.01 to 50 $ng\,ml^{-1}$. The isobaric effect of metal oxide species was necessarily corrected for REEs determination. The author recommends the separation of REEs in rock samples from the matrix elements before measuring by ICP-MS method because of more reliable data, more reproducible signal and less damage to mass spectrometer; matrix-eliminated sample throughput showed excellent long-term instrumental stability, which enabled us to apply ICP-MS to the accurate routine analysis for the determination of REEs in rocks.

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