

Determination of Rare Earth Elements (REEs) in Airborne Particulate Matter (APM) Collected in Tokyo, Japan, and a Positive Anomaly of Europium and Terbium

Yoshinari SUZUKI, Tatsunosuke SUZUKI, and Naoki FURUTA[†]

Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University, 1-13-27 Kasuga, Bunkyo, Tokyo 112-8551, Japan

The determination of rare earth elements (REEs) in airborne particulate matter (APM) was conducted, and the distribution pattern of atmospheric REEs was evaluated in this study. The APM was collected in the center of Tokyo, Japan, where serious air pollution is always of concern. A cellulose acetate membrane filter was used to collect the APM because Ba and REEs contamination is lower than that in a quartz glass fiber filter. The REEs measurement was conducted by ICP-MS after the digestion of the APM by a microwave acid digestion procedure. The standard reference material (SRM) of NIST 1648 urban particulate matter was used to validate the accuracy of the analytical method. The analytical results for SRM well agreed with those of the reference and reported values. Consequently, the analytical method established in this study was applied to the determination of REEs in APM collected in Tokyo, Japan. The obtained REEs distribution pattern in the APM showed a positive anomaly of Tb and Eu. The La/Sm ratio, which is considered to be as a good indicator of the anthropogenic effect, in size-classified APM showed a high degree of the anthropogenic effect in fine APM with a diameter of <1.1 μm . Emission sources of Tb, Eu and other REEs are discussed.

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Introduction

In recent years, the pollution of the atmosphere, particularly in urban areas, is considered to be serious problems for human health, because enormous amounts of substances are emitted into the atmosphere. Since humans are always breathing air, toxic substances are also being taken up through inhalation. Therefore, it is of concern that toxic substances may cause serious problems for human health. From this point of view, the anthropogenic emission of elements into the atmosphere has been investigated. Many elements in airborne particulate matter (APM), including toxic elements, such as As, Cd, Cr, Pb and Hg, have been reported so far;¹⁻¹⁰ in addition, platinum-group elements (PGEs), such as Pt, Pd and Rh, were also focused on concerning anthropogenic emission from automobiles.¹⁰⁻¹⁵ However, reports of rare earth elements (REEs) in APM are few.¹⁶⁻¹⁹ Because REEs are used for industrial and medical materials, such as ceramics as superconductors, catalysts for automobiles (Ce), lasers (Nd), permanent magnets (Sm, Nd), fluorescent for color TVs (Eu, Y), fluorescent lamps (Eu), contrast medium for MRI (Gd) and so on, it can be considered that large amounts of REEs are consumed and emitted into the atmosphere.¹⁹ Therefore, atmospheric REEs should be determined in order to evaluate atmospheric pollution regarding human health.

In this study, an analytical method for the determination of REEs in APM was established. The standard reference material

(SRM) of NIST 1648 urban particulate matter was used to validate the analytical method for REEs determination, and the atmospheric REEs collected in Tokyo, Japan were determined, and its REEs distribution pattern was evaluated.

Experimental

APM sampling procedure

Table 1 summarizes the sampling conditions of a high-volume air sampler (Model-120V; Kimoto, Tokyo, Japan) used for collecting APM samples. The high-volume air sampler was installed at 45 m above the ground level at the center of Tokyo (at the top of the building in the campus of Chuo University).

Table 1 Sampling volume, amount and APM concentration collected by a high-volume air sampler in this study

Sampling period	Sampling volume/m ³	Collected amount of APM ^a /mg	APM concentration/ $\mu\text{g m}^{-3}$
Jun. 3rd - 5th	2460	93.3	37.9
Jul. 13th - 16th	3010	109	36.1
Aug. 24th - 28th	4020	78.2	19.5
Sep. 28th - 30th	2020	89.8	44.5
Oct. 28th - 30th	2020	105	51.8
Dec. 2nd - 9th	7120	178	24.9

a. APM amount collected on a cellulose acetate membrane filter with the size of 203 × 254 mm.

[†] To whom correspondence should be addressed.
E-mail: nfuruta@chem.chuo-u.ac.jp

Table 2 REEs blank in both quartz glass fiber and cellulose acetate filters

Element	Filter		Cellulose acetate/ quartz glass fiber
	Quartz glass fiber/pg g ⁻¹	Cellulose acetate/pg g ⁻¹	
Ba	20100	187	0.009
La	814	252	0.310
Ce	1420	252	0.177
Pr	401	258	0.644
Nd	795	175	0.221
Sm	487	201	0.414
Eu	287	232	0.808
Gd	704	170	0.242
Tb	391	272	0.698
Dy	919	215	0.234
Ho	391	283	0.724
Er	477	220	0.461
Tm	315	285	0.904
Yb	375	185	0.493
Lu	312	286	0.917

A cellulose acetate membrane filter (0.8 μm , 203 \times 254 mm, Advantech Co. Ltd., Tokyo, Japan) was used to collect the APM, because of its lower contamination of REEs compared to a quartz glass fiber filter, which is generally used for APM collection. Table 2 indicates the analytical results of REEs in both quartz glass fiber and cellulose acetate membrane filters obtained in this study. As can be seen in Table 2, the Ba concomitants in the cellulose acetate membrane filter are about 0.9% compared to those in the quartz glass fiber filter, and REEs concomitants in the cellulose acetate membrane filter are lower than those in the quartz glass fiber filter. Spectral interferences with BaO and BaOH are big problem for REEs determination; therefore, accurate analytical results can be expected for REEs measurement when the cellulose acetate membrane filter is used. The sampling flow rate of the high-volume air sampler was set at 700 L min⁻¹. Six APM samples were collected in different periods, as described in Table 1. The amounts of APM collected and APM concentrations are also indicated in Table 1. A part of the collected APM (approximately 10 – 20 mg) was used for the determination of REEs.

Moreover, we classified APM into six fractions with aerodynamic diameter D_p <0.43, 0.43 – 0.65, 0.65 – 1.1, 1.1 – 2.1, 2.1 – 11 and >11 μm on cellulose acetate membrane filters using an Andersen low-volume air sampler (Model AN-200; Tokyo Dylec Co., Tokyo, Japan). The sampling flow rate of the low volume air sampler was set at 28.3 L min⁻¹. The amount and concentration of size-classified APM are given in Table 3.

Reagents

XSTC-1 Custom Assurance Standards of a mixed REEs standard solution (10 $\mu\text{g mL}^{-1}$; SPEX Certiprep Inc., USA) was used. Appropriate concentrations of REEs for calibration curves were prepared by diluting with 0.1 mol L⁻¹ HNO₃. The 0.1 mol L⁻¹ HNO₃ was prepared by diluting electronic-grade HNO₃ (70%, Kanto Chemical Co., Tokyo, Japan) with Milli-Q purified water (Milli-Q Element, Millipore, Tokyo, Japan). Two elements of In and Re were used as internal standard elements. HNO₃ (70%) and H₂O₂ (30%) acids used for the digestion procedures were of electronic-grade (Kanto Chemical Co.,

Table 3 Size classified APM amount and concentration collected during Dec. 2nd to 25th, 2009 by using a low-volume air sampler

Diameter/ μm	Collected amount of APM ^a /mg	APM concentration ^b / $\mu\text{g m}^{-3}$
>11	1.61	1.80
2.1 – 11	4.53	5.05
1.1 – 2.1	0.670	0.747
0.65 – 1.1	2.37	2.64
0.43 – 0.65	3.98	4.44
<0.43	5.21	5.81

a. APM amount on a cellulose acetate membrane filter with the diameter of 80 mm.

b. Sampling volume was 897 m³.

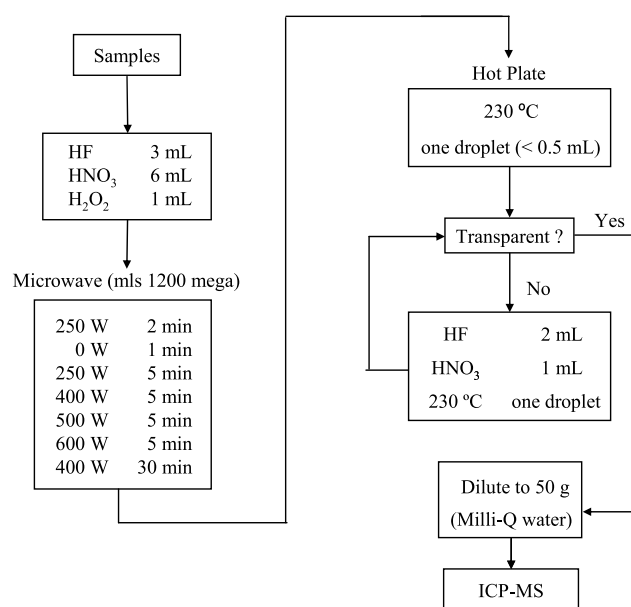


Fig. 1 Sample-preparation procedures.

Japan). HF (50%) acid for semiconductor grade (Daikin Industries Co. Ltd., Tokyo, Japan) was also used for the sample-digestion procedures.

Sample preparation procedures

Four APM samples (in the case of APM sample collected in June, the sample number is two) were circularly clipped with a diameter of 80 mm from the APM collected on the cellulose acetate membrane filter; then, clipped samples were digested into the solution by sample preparation procedures, as shown in Fig. 1. Following a previously reported method,¹ acids of 6 mL of 70% HNO₃, 3 mL of 30% HF and 1 mL of 50% H₂O₂ acids were added to the samples; the samples were then digested into the solutions by using a microwave digestion system (MLS 1200, Milestone, Italy). The digestion programs are shown in Fig. 1. After microwave digestion, HF was evaporated by using a hot plate at 230°C. When the solution became one droplet (ca. 0.5 mL) with transparency, it was diluted to 50 g with Milli-Q water. The internal-standard elements (In, Re) were added during dilution. In addition, 30 mg of SRM of NIST 1648 urban particulate matter (National Institute of Science and Technology, USA) was also digested by the same procedures,

and this was used to validate the accuracy of the analytical method from sample preparation to REEs determinations. A good agreement of the analytical results of major-to-trace elements in the NIST 1648 was reported in a previous paper.¹

Instrumentation

The analytical instrument used in this study was an HP 4500 ICP-MS (Yokogawa Analytical Systems, Tokyo, Japan) with a conventional glass concentric nebulizer. ICP-MS operation was conducted under the following conditions; RF power, 1400 W; plasma gas flow rate, 15.0 L min⁻¹; auxiliary gas flow rate, 1.00 L min⁻¹; carrier gas flow rate, 1.00 L min⁻¹. When the determination of REEs is conducted, spectroscopic interferences of oxide and hydroxide species from the constituent elements particularly, Ba and light REEs, have to be eliminated. In this study, the formation yields of oxide and hydroxide species listed in Table 4 were obtained using 100 ng mL⁻¹ standard solutions of Ba and REEs; then, a numerical correction was carried out to eliminate interferences for obtaining accurate analytical results from total ion counts (TIC) as the equations shown in Scheme 1.

In the case of NIST1648, the analytical results of Eu, Gd and Tb were 15.4, 20.8 and 7.9% overestimated, respectively, if spectral interferences were not corrected.

Table 4 Formation yield (%) of oxide and hydroxide species from Ba and REEs in ICP

Element	MO	MOH
Ba	0.074	0.076
La	0.075	0.001
Ce	0.91	0.063
Pr	0.86	0.045
Nd	0.78	0.074
Sm	0.15	0.033
Eu	0.062	0.023
Gd	0.38	0.055
Tb	0.35	0.041
Dy	0.19	0.017
Ho	0.17	0.015
Er	0.17	0.018
Tm	0.082	0.010
Yb	0.020	0.002
Lu	0.15	0.031

Results and Discussion

Firstly, we validated the analytical method from the sample pretreatment to the REEs determination using SRM of NIST 1648 urban particulate matter. Table 5 lists the obtained analytical results of REEs for SRM. Three individual samples were analyzed; then, the standard deviation (SD) and relative standard deviation (% RSD) were calculated, as also listed in Table 5. Reference values in the certificate of NIST 1648 urban particulate matter and the reported analytical results^{20,21} are also listed in Table 5. As can be seen in Table 5, the obtained analytical results were close to those of the reported and reference values, and our analytical result showed good reproducibility compared to these reported in Refs. 20 and 21. From these facts, it could be evaluated that accurate REEs determinations were performed. Consequently, the determination of REEs in APM samples was conducted by the same analytical method established in this study.

The analytical results of atmospheric REEs collected in Tokyo, Japan are listed in Table 6. As can be seen in Table 6, REEs were found in the APM and the concentration was in the range from 0.055 (Lu) to 20.3 µg g⁻¹ (Ce). These REEs originated from both natural sources, such as soil, crust, marine *etc.*, and anthropogenic emission, which is due to industrial activities, such as oil-fired power plant, refinery of oil and petroleum, and fertilizers plants, fly ash from incinerators, traffic *etc.*¹⁶⁻¹⁸

In order to discuss the emission source of atmospheric REEs collected in Tokyo, the distribution patterns of REEs were evaluated in this study. Figure 2 shows the distribution patterns of REEs in APMs and SRM. The REEs distribution pattern of continental crust²² is also shown in Fig. 2. These REEs distribution patterns were obtained using the analytical results listed in Tables 5 and 6 with C1 chondrite normalization. The standard deviations (SD) for SRM and APMs listed in Tables 5 and 6 are also indicated in Fig. 2, but almost all of the error bars were within the size of the dot. The REEs distribution pattern of NIST 1648 urban particulate matter showed a similar trend compared to that of the continental crust. The concentrations of REEs in NIST 1648 are similar to those in the continental crust, and it was surprising that the patterns were very close to each other. As can be seen in the distribution patterns, concentrations of REEs in the APM samples were about 5 fold and one order of magnitude lower than those in NIST 1648 and continental

$$\begin{pmatrix}
 {}^{139}\text{La} \\
 {}^{140}\text{Ce} \\
 {}^{141}\text{Pr} \\
 {}^{146}\text{Nd} \\
 {}^{147}\text{Sm} \\
 {}^{151}\text{Eu} \\
 {}^{157}\text{Gd} \\
 {}^{159}\text{Tb} \\
 {}^{163}\text{Dy} \\
 {}^{165}\text{Ho} \\
 {}^{166}\text{Er} \\
 {}^{169}\text{Tm} \\
 {}^{172}\text{Yb} \\
 {}^{175}\text{Lu}
 \end{pmatrix}
 =
 \begin{pmatrix}
 {}^{139}\text{TIC} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
 {}^{140}\text{TIC} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
 {}^{141}\text{TIC} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
 {}^{146}\text{TIC} & {}^{130}\text{Ba} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
 {}^{147}\text{TIC} & 0 & {}^{130}\text{Ba} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
 {}^{151}\text{TIC} & {}^{135}\text{Ba} & {}^{134}\text{Ba} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
 {}^{157}\text{TIC} & 0 & 0 & {}^{140}\text{Ce} & {}^{141}\text{Pr} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
 {}^{159}\text{TIC} & 0 & 0 & {}^{142}\text{Ce} & 0 & {}^{143}\text{Nd} & {}^{142}\text{Nd} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
 {}^{163}\text{TIC} & 0 & 0 & 0 & 0 & 0 & {}^{146}\text{Nd} & {}^{147}\text{Sm} & 0 & 0 & 0 & 0 & 0 & 0 \\
 {}^{165}\text{TIC} & 0 & 0 & 0 & 0 & 0 & {}^{148}\text{Nd} & {}^{149}\text{Sm} & {}^{148}\text{Sm} & 0 & 0 & 0 & 0 & 0 \\
 {}^{166}\text{TIC} & 0 & 0 & 0 & 0 & {}^{150}\text{Nd} & 0 & {}^{150}\text{Sm} & {}^{149}\text{Sm} & 0 & 0 & 0 & 0 & 0 \\
 {}^{169}\text{TIC} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & {}^{152}\text{Sm} & {}^{153}\text{Eu} & 0 & {}^{152}\text{Gd} & 0 & 0 \\
 {}^{172}\text{TIC} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & {}^{156}\text{Gd} & {}^{155}\text{Gd} & 0 & {}^{156}\text{Dy} \\
 {}^{175}\text{TIC} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & {}^{158}\text{Gd} & {}^{159}\text{Tb} & 0 & {}^{158}\text{Dy}
 \end{pmatrix}
 \times
 \begin{pmatrix}
 1 \\
 -0.00074 \\
 -0.00076 \\
 -0.00063 \\
 -0.0086 \\
 -0.0078 \\
 -0.00074 \\
 -0.0015 \\
 -0.00033 \\
 -0.00062 \\
 -0.0038 \\
 -0.00055 \\
 -0.0035 \\
 -0.0019 \\
 -0.00017
 \end{pmatrix}$$

Scheme 1 Equation for interference correction.

Table 5 Analytical results of REEs in NIST 1648 urban particulate matter

Element	This study ^a		Lee <i>et al.</i> ²⁰	Chung <i>et al.</i> ²¹		Reference value
	Mean \pm SD/ $\mu\text{g g}^{-1}$	% RSD	Mean \pm SD/ $\mu\text{g g}^{-1}$	Mean/ $\mu\text{g g}^{-1}$	% RSD	
La	31.9 \pm 0.34	(1.1)	37.1 \pm 0.06	34.77	(3.7)	42
Ce	45.4 \pm 0.30	(0.7)	18.5 \pm 0.47	44.86	(1.94)	55
Pr	6.70 \pm 0.53	(7.9)	3.4 \pm 0.16			
Nd	23.5 \pm 0.13	(0.6)	21.6 \pm 0.30	27.96	(9.4)	
Sm	4.08 \pm 0.04	(1.0)	3.32 \pm 0.32	5.085	(4.1)	4.4
Eu	0.797 \pm 0.004	(0.5)	0.51 \pm 0.04	0.49	(10.2)	0.8
Gd	3.11 \pm 0.23	(7.3)	2.40 \pm 0.21			
Tb	0.484 \pm 0.005	(1.0)				
Dy	3.03 \pm 0.04	(1.3)	1.7 \pm 0.25	3.25	(16.8)	
Ho	0.596 \pm 0.022	(3.7)	0.27 \pm 0.04			
Er	1.77 \pm 0.04	(2.3)	0.97 \pm 0.13			
Tm	0.248 \pm 0.004	(1.6)	0.20 \pm 0.015			
Yb	1.66 \pm 0.01	(0.6)	1.02 \pm 0.028			
Lu	0.248 \pm 0.006	(2.4)	1.70 \pm 0.00	0.51	(10.5)	

a. SD and % RSD were calculated by the measurements of three individual samples.

Table 6 Analytical results of REEs in APM collected in Tokyo, in Jun. - Dec., 2009 by using a high-volume air sampler

Element	Sampling period					
	Jun. 3rd - 5th	Jul. 13th - 16th	Aug. 24th - 28th	Sep. 28th - 30th	Oct. 28th - 30th	Dec. 2nd - 9th
Sample number	2	4	4	4	4	4
La	11.3	13.6 \pm 0.35	16.2 \pm 0.17	10.9 \pm 0.17	16.9 \pm 1.39	9.90 \pm 0.59
Ce	17.9	14.5 \pm 0.47	20.3 \pm 0.29	14.1 \pm 0.13	21.7 \pm 0.34	15.9 \pm 0.35
Pr	1.57	1.33 \pm 0.04	1.87 \pm 0.04	1.30 \pm 0.02	1.83 \pm 0.04	1.40 \pm 0.04
Nd	5.69	4.88 \pm 0.11	6.81 \pm 0.04	4.77 \pm 0.04	6.51 \pm 0.29	5.05 \pm 0.21
Sm	0.976	0.946 \pm 0.036	1.23 \pm 0.055	0.799 \pm 0.027	0.945 \pm 0.021	0.694 \pm 0.050
Eu	0.476	0.300 \pm 0.017	0.694 \pm 0.022	0.256 \pm 0.016	0.344 \pm 0.021	0.307 \pm 0.013
Gd	0.846	0.841 \pm 0.013	1.12 \pm 0.075	0.665 \pm 0.029	0.805 \pm 0.042	0.648 \pm 0.058
Tb	0.337	0.199 \pm 0.011	0.430 \pm 0.013	0.169 \pm 0.013	0.204 \pm 0.006	0.152 \pm 0.006
Dy	0.790	0.792 \pm 0.046	1.05 \pm 0.046	0.681 \pm 0.044	0.822 \pm 0.022	0.653 \pm 0.023
Ho	0.149	0.153 \pm 0.007	0.210 \pm 0.013	0.128 \pm 0.008	0.157 \pm 0.0004	0.122 \pm 0.010
Er	0.460	0.473 \pm 0.017	0.647 \pm 0.020	0.413 \pm 0.032	0.462 \pm 0.009	0.378 \pm 0.013
Tm	0.063	0.063 \pm 0.004	0.089 \pm 0.002	0.055 \pm 0.004	0.068 \pm 0.004	0.054 \pm 0.002
Yb	0.410	0.428 \pm 0.015	0.600 \pm 0.019	0.372 \pm 0.038	0.454 \pm 0.011	0.358 \pm 0.007
Lu	0.063	0.063 \pm 0.005	0.090 \pm 0.002	0.055 \pm 0.009	0.070 \pm 0.002	0.057 \pm 0.001
La/Sm	11.5	14.3 \pm 0.7	13.2 \pm 0.6	13.6 \pm 0.5	17.9 \pm 1.5	14.3 \pm 1.3

Analytical results are expressed by $\mu\text{g g}^{-1}$.

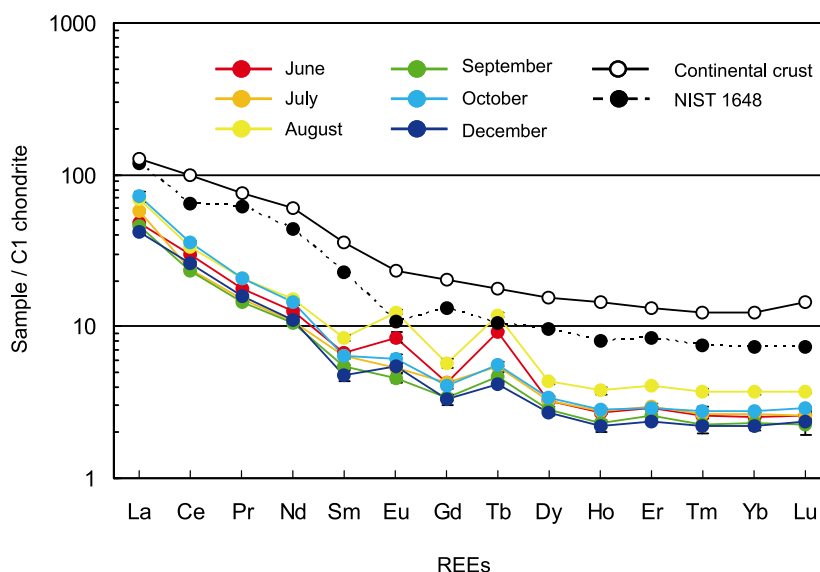


Fig. 2 Distribution patterns of REEs in APM collected in Tokyo, Jun. - Dec., 2009, normalized with C1 chondrite.

crust, respectively. The lower REE concentrations obtained in the APM compared to those of the continental crust can be explained as REEs, which are emitted into the atmosphere, are diluted by other sources of APM. It should be noticed that positive anomalies of Eu and Tb were found in the REEs distribution patterns in APM samples collected in Tokyo, Japan.

The plots of Tb showed significant differences from Gd and Dy with consideration of the error bars of APMs. Moreover, higher Tb/Nd ($0.030 \pm 0.002 - 0.063 \pm 0.002$) and Tb/Sm ($0.21 \pm 0.01 - 0.35 \pm 0.02$) ratios of APM were observed compared to that of the crust (Tb/Nd, 0.024; Tb/Sm, 0.12). Therefore, it can be evaluated that the positive anomaly of Tb could be obtained significantly for all sampling periods. Higher

Eu/Nd ratios ($0.053 \pm 0.004 - 0.102 \pm 0.003$) were observed compared to that of the crust (0.048). Also, a positive anomaly of Eu could be obtained in June and August. Some authors reported Eu anomalies in the water environment²³⁻²⁵ and a negative Eu anomaly in dust aerosol collected in Eastern Pamirs was reported by Wu *et al.*²⁶ As far as the author's knowledge, Tb and Eu positive anomalies have not yet been reported for APM. REE anomalies are often observed for Ce and Eu.²⁷ These anomalies are caused by the fact that these two elements can form different valencies in nature (Ce^{4+} and Eu^{2+}), besides the trivalent ions occurring for all REEs. Therefore, the sources of Eu should be both anthropogenic and natural. Eu is used for a fluorescent substance of a lamp, cathode-ray tube, plasma display panel and phosphorescence. On the other hand, anthropogenic emission can be estimated as an origin of Tb rather than the natural source. Tb is used for a magnet-optical disk, such as MO and MD, and is also used for a cathode-ray tube, as well as Eu. The positive anomaly of Tb in APM may be caused by the large consumption of Tb, which is due to the wide-spread use of the magnet-optical disk and the recent changes of TV devices in Japan from cathode-ray tube to plasma display panel. From these observed results, it is considered that a high concentration level of Tb and Eu are emitted into the atmosphere in Tokyo.

As can be seen in Refs. 16 - 18, the main anthropogenic emission sources of REEs are industrial activities and traffic. The ratio of La/Sm is one of the indicators from industrial activities, such as refinery and fertilizer plants, and the traffic. High values, such as 27 ± 7 , were reported as the originated values from oil-fired plants and processes of oil refineries.¹⁶ Values of 20, 5.2 and 28 were reported as the origin from petroleum-refining, a coal-fired plant and an oil-fired power plant, respectively.²⁸ La/Sm values are listed at the bottom row of Table 6. In this study, La/Sm values were about 11.5 - 17.9 in APMs. On the other hand, La/Sm values were 7.8 and 5.7 in NIST 1648 and the continental crust. Similar values of 6 - 8 reported by Wang *et al.*^{17,18} were considered to have originated from industry and traffic. From these results, industrial activities and traffic should be one of the main factors for the atmospheric

Table 7 Analytical results of REEs in size-classified APM collected in Tokyo, Dec. 2nd - 25th in 2009 by using a low-volume air sampler

Element	Aerodynamic diameter of APM/ μm					
	<0.43	0.43 - 0.65	0.65 - 1.1	1.1 - 2.1	2.1 - 11	>11
La	8.50	5.89	6.65	34.5	19.5	8.36
Ce	18.2	11.9	11.6	47.6	28.9	16.9
Pr	1.58	1.00	0.884	3.46	4.59	1.56
Nd	4.75	3.13	2.78	12.6	9.65	6.01
Sm	0.125	0.070	0.187	2.18	1.77	1.41
Eu	0.042	0.042	0.100	0.925	0.822	0.486
Gd	0.109	0.025	0.137	1.99	1.56	1.21
Tb	0.026	0.012	0.065	0.552	0.490	0.246
Dy	0.108	0.055	0.198	2.21	1.76	1.21
Ho	0.016	0.006	0.027	0.384	0.320	0.255
Er	0.067	ND	0.059	1.26	1.13	0.792
Tm	0.004	ND	0.013	0.147	0.140	0.095
Yb	0.072	ND	0.092	1.14	0.997	0.611
Lu	ND	ND	0.030	0.135	0.163	0.150
La/Sm	68.0	84.1	35.6	15.8	11.0	5.93

Analytical results are expressed by $\mu g g^{-1}$.

ND: not detected.

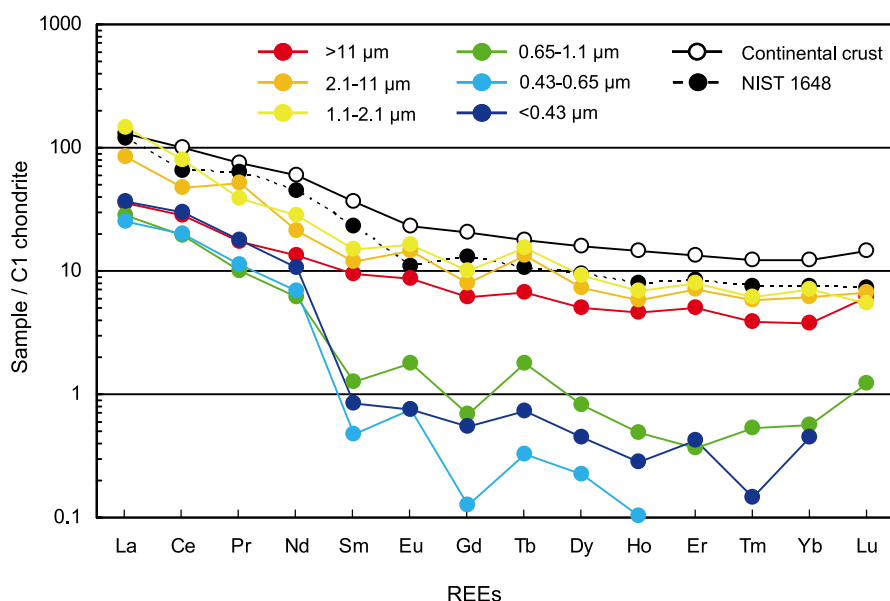


Fig. 3 Distribution patterns of REEs in size-classified APM collected in Tokyo, Dec. 2nd - 25th, 2009, normalized with C1 chondrite.

REEs in Tokyo, Japan.

Analytical results of size-classified APM are shown in Table 7. For almost all REEs, the highest concentrations were observed in APM with diameters of 1.1 – 2.1 μm , and the concentration was in the range from 0.135 (Lu) to 47.6 $\mu\text{g g}^{-1}$ (Ce). On the other hand, the lowest concentrations were observed in APM with diameters of 0.43 – 0.65 μm , and the concentrations were in the range from below the detection limit (Er, Tm, Yb and Lu) to 11.9 $\mu\text{g g}^{-1}$ (Ce). In order to discuss the emission source of atmospheric REEs collected in Tokyo, distribution patterns of REEs were evaluated in this study. The distribution patterns of REEs in size-classified APMs were plotted in Fig. 3 by using the data listed in Table 7. The distribution patterns of REEs in APM with diameter of $>1.1 \mu\text{m}$ showed similar trends compared to those in the continental crust and NIST 1648. In the case of APM with a diameter of $<1.1 \mu\text{m}$, the distribution patterns of Sm-Lu were lower compared to those of the continental crust and NIST 1648. The positive anomalies of Eu and Tb could be observed in APM with diameters of 0.43 – 0.65, 0.65 – 1.1, 1.1 – 2.1 and 2.1 – 11 μm .

The La/Sm value in the APM with diameters of $>11 \mu\text{m}$ was 5.93. This value was similar to that of the continental crust (5.7), and therefore it is considered to have originated from natural sources. The La/Sm values in APM with diameters of 2.1 – 11 and 1.1 – 2.1 μm were 11.0 and 15.8, respectively. These values were higher than that of NIST 1648 urban airborne particulate matter (7.8), but lower than those of petroleum-refining (20) and an oil-fired power plant (28).²⁸ Therefore, it is considered to have originated from both natural sources and anthropogenic sources. The La/Sm values in APM with diameters of 0.65 – 1.1, 0.43 – 0.65, $<0.43 \mu\text{m}$ were 35.6, 84.1 and 68.0, respectively. These values were more than 1.3 – 4.2 times higher than those of petroleum-refining (20) and oil-fired power plants (28).²⁸ On the other hand, high La/Sm values were observed in some areas with high traffic density.²⁹ In that report, the La/Sm values in tailpipe soot of automobiles, equipped with “three-way” catalytic converters, ranged from 10 to 16000. From these results, industrial activities and traffic should be one of the main factors for REEs in nano-sized APM in Tokyo, Japan.

From these results, it is considered that large amounts of REEs are emitted into the atmosphere. Emitted REEs were distributed into the fine APM with diameters of $<1.1 \mu\text{m}$ compared to the coarse APM with diameter of $>1.1 \mu\text{m}$, and then the natural distribution pattern of REEs was disturbed by human activities. The distribution pattern of REEs in size-classified APM showed a higher degree of the anthropogenic effect in fine APM than those in coarse APM.

Conclusions

Atmospheric REEs determination was performed and the REEs distribution pattern was evaluated in this study. Since the concentration of REEs is relatively low, a cellulose acetate membrane filter is suitable for the accurate determination of REEs in APM collected in Tokyo. A numerical correction is useful to eliminate the spectroscopic interferences of oxides and hydroxide species from Ba and light REEs to improve the accuracy of the REEs determination. The analytical procedures from sample preparation to ICP-MS measurement were validated using NIST 1648 urban particulate matter. Consequently, the analytical procedures were applied to the determination of REEs in APM collected in Tokyo, Japan. The distribution pattern of REEs was also evaluated, and Eu and Tb

positive anomalies could be discovered in the APM samples. From these results, a large amount of REEs emission may affect the atmospheric environment. From the distribution pattern of size-classified APM, emitted REEs were distributed into fine APM with diameters of $<1.1 \mu\text{m}$ compared to coarse APM with diameters of $>1.1 \mu\text{m}$, and thus the natural distribution pattern of REEs was disturbed by human activities.

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