Major and rare earth elements in rainwaters from Japan and East China Sea: Natural and anthropogenic sources

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Abstract

Rainwater samples collected from Tokyo and nearby locations in Japan as well as from two locations over the East China Sea have been analyzed for their rare earth elements (REEs) and major ions. The major ion compositions of these samples show the contributions of oceanic, crustal, and anthropogenic sources, and suggest the relative importance of these sources. Rainwater samples collected in Tokyo and Chofu (a town about 8 km from metropolitan Tokyo) have distinctly higher SO_4^{2-} and NO_3^- content than in rainwater samples from the coastal area and the East China Sea, whereas the major ion compositions of the latter two areas are dominated by sea salt.

The rainwater samples also have variable REE compositions, with various enrichment of light REEs over heavy REEs. Rainwater samples from Chofu are significantly enriched in light REEs, whereas those collected in Tokyo have loess or shale-like REE composition. Rainwater from both places, however, has similar major ion compositions. The enrichment of light REEs in the Chofu rainwater samples corresponds to the typical signature of an anthropogenic source. The Y/Ho ratios in these samples are all higher than average crustal values, and in general, increase with increasing enrichment of light REEs. This indicates that physical mixing of crustal and oceanic sources of the REEs cannot account for the variations of the Y/Ho ratios. Furthermore, although the anthropogenic source of the REEs is generally characterized by a high Y/Ho ratio, factors such as particle/rainwater interactions, pH, and speciation of REEs may also be responsible for the variable abundance and fractionation of REEs and Y/Ho in these rainwaters.
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1. Introduction

It has recently been recognized that atmospheric inputs of particles (dry deposition) and rainwater (wet deposition) result in significant fluxes of the rare earth elements (REEs) and other trace metals to the oceans. These inputs are frequently even more significant than riverine inputs (e.g. Sholknovitz et al., 1993; Greaves et al., 1994; Duce et al., 1991; Halstead et al., 2000; Spokes et al., 2001). To our knowledge, however, there has been no data obtained for the dissolved phases of REEs in rainwater since the work of Sholknovitz et al. (1993). Heaton et al. (1990) first reported the concentration of REEs in rainwater, but the REEs in their samples were below the instrumental detection limit of their neutron activation analysis (INAA) method. Freydier et al. (1998) measured the total REE concentration of precipitation from Lamto (Niger) and Kollo (Ivory Coast), but did not separate the dissolved from the particulate phases. Needless to say, the dissolution of the REEs from particles in rainwater and their subsequent introduction of dissolved REEs into seawater may be important, but has not been well documented. With this as motivation, we measured the REEs together with major ion composition of rainwater samples in order to understand the behavior of the REEs during rain-formation processes, as well as the significance of this input to the oceans.

The REEs form a chemically "coherent" group of elements. Because of the systematic variation of their behavior due to the "lanthanide contraction", the relative abundances of the REEs are widely used to study geochemical processes. In addition, the REEs have also been found to be a potential indicator of environmental pollution (Olmez and Gordon, 1985; Olmez et al., 1991; Chiarenzelli et al., 2001; Zhang et al., 2001), because anthropogenic inputs show characteristic signatures of REE composition. Olmez and Gordon (1985) studied the REE compositions of particles released by coal-fired plants and refineries, and recognized that the particles released from these sources were strongly enriched in light REEs (LREEs) due to the zeolite cracking catalysts. Fly ash, bottom ash, and waste waters from oil-fired power plants also show enrichment of the LREEs over heavy REEs (HREEs) (Olmez, 1989). Olmez et al. (1991) were the first to report the anthropogenic REE signal of oil-

refined petroleum products in aquatic sediments, and they reported that the sources of the LREE enrichment were petroleum-cracking catalysts and their products. Zhang et al. (2001) found that distribution of REEs in various waste ashes from Japan differ significantly. Although these studies did not involve the measurement of REEs in rainwater, rainwaters contaminated by certain industries such as the oil-fired power plants and refineries are expected to show dissolved REE signatures of contaminants because of water-or cloud-particle interactions. In addition to achieving a better understanding of the distribution of the major ions and REEs in rainwater, the compositions of the major ions and REEs in samples collected from urban and non-urban areas have been studied.

2. Sampling and analytical procedure

Rainwater samples were collected from five locations, two over the East China Sea (28°N, 126°E) and three in eastern Japan, as shown in Fig. 1. The sampling locations over land, namely Chofu, Tokyo, and Nakaminato, are located respectively 18 km, 9 km and 40 m from the nearest coast. The rainwater samples of Chofu and Nakaminato were collected on the same dates or during the same rain event. The rest of these samples were collected from different rain events.

Fig. 1 also shows the forward trajectories of the rainfalls. The trajectories show the movement of clouds at different heights (500, 1000 and 2000 m) above ground level during the 12 h before the rainfall. From these trajectories, it can be seen that the raining clouds at different elevations came from different directions or had different sources. These rainfalls, especially those at low altitudes at Chofu, had inland sources. For the rainfalls at Nakaminato, three rain events had very similar origin, while those at Tokyo had different sources, with one event originating over the open sea. Two rainfalls over the East China Sea also had different origins, one of which (EC-960925) originated near the main land of China, while the other (EC-960901) was from the open sea.

The rainwater samples were collected manually from the beginning of each event on a roof of a building with a Teflon funnel that was located approximately 1 m above the roof. The roof-top

sampling locations were chosen to avoid contamination from local sources. Two rainwater samples over the East China Sea were collected on the board of the R/V *Kaiyo* (Japan Marine Science and Technology Center) during its K96-08 cruise (22 August to 30 September 1996). Prior to use, the sampler was cleaned with acid (2–3N HCl), rinsed with Milli-Q water, and dried. To prevent contamination from dry deposition, the sampler was set up just prior to the onset of each rain event. Within 4 h after collection,

all samples were filtered through 0.22 ìm membrane filters. An aliquot of about 50 ml was used to measure major ion compositions, and the remainder (about 1 l) was acidified to pH=1.5 for REE determination. Major cations were determined with an ICP-AES (Inductively Coupled Plasma-Association Emission Spectrometer), and the major anions were measured by ion chromatograph. The method for determining REEs was the same as that of Shabani et al. (1990) and Zhang and Nozaki (1996), using an ICP-MS
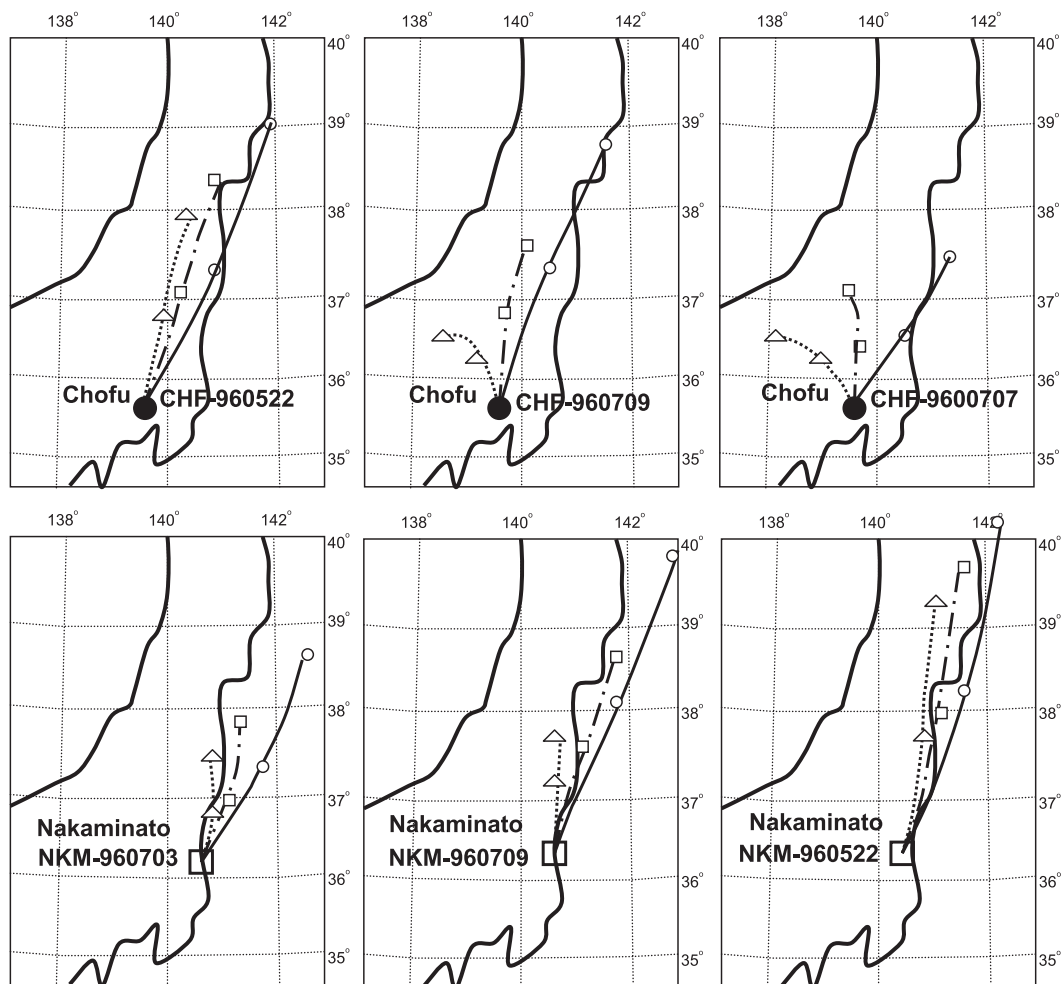

Fig. 1. Maps showing the sampling locations and the forward trajectories of the sampled rainfalls. Sampling locations include Chofu (CHF), Nakaminato (NKM), and Tokyo (TK) in eastern Japan and two sites over the East China Sea (EC). The three locations in eastern Japan are 40 m, 9 km and 18 km from the nearest coast, respectively. The forward trajectories of each rainfall were modified from those supplied by the National Oceanic and Atmospheric Administration of USA, which indicate the routes of the raining clouds at, respectively, 500, 1000 and 2000 m above the ground 6 and 12 h (during 6, 12, 18, and 24 h for EC-960925 and TK-960226) before arriving at the collection sites (website: http://www.arl.noaa.gov/ready/hasplit4.html).
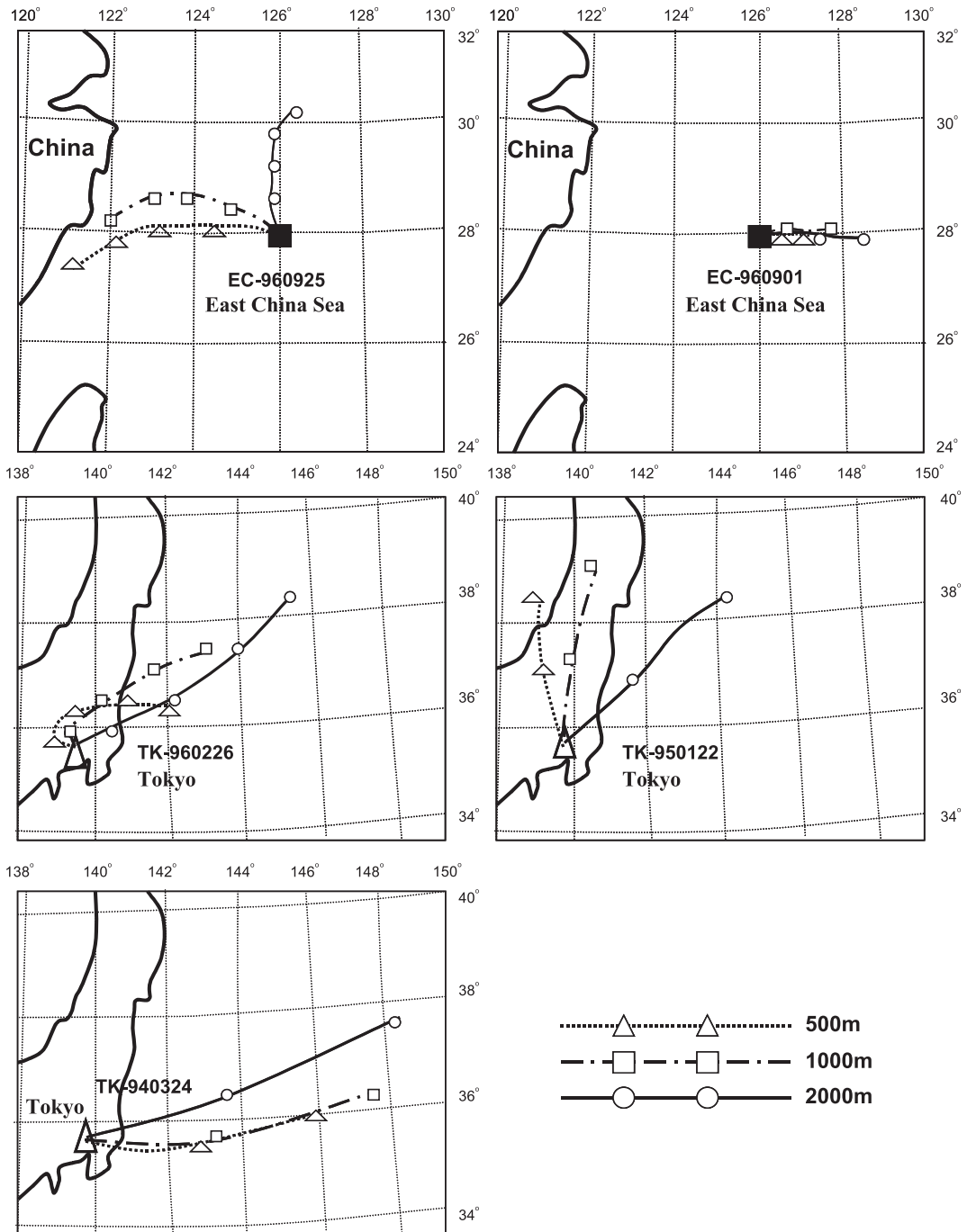
Fig. 1 (*continued*).

(Inductively Coupled Plasma-Mass Spectrometer, PMS2000 quadrupole mass spectrometer, Yokogawa Analytical Systems). Before measurement, samples were concentrated by using solvent extraction and back extraction with a mixture of 65% HDEHP (2-etheylhexyl hydrogen phosphate) and 35% H_2MEHP

(2-ethylhexyl dihydrogen phosphate) in heptane. By using this pre-concentration method, the concentrations of the REEs and Y in solution for the ICP-MS can be made about 200 times higher than in rainwater. The internal standard, indium, was added to the rainwater samples to control the recovery rate of the REEs during the solvent extraction/back extraction procedure, whereas the internal standard, cadmium, was added as a monitor of the equipment stability before ICP-MS analysis.

The concentration and purification procedures are accurate to $99 \pm 0.3\%$ for all REEs, yttrium, and indium (Shabani et al., 1990). The standard solutions provided by SPEX Industries, Inc. are accurate to $\pm 0.5\%$ for each REE. Replicate analysis (five times) of a surface seawater sample from the Pacific Ocean gave relative standard deviations of about 8% for Ce, <5% for LREEs, and <3% for HREEs.

3. Results and discussion

3.1. Variations in pH and major ion concentrations

The pH values range from 5.5 to 6.1, slightly higher than the annual mean values of between 4.5 and 5.8 at each site in Japan from 1989 to 1993 (Hara et al., 1995). Seven major ions were measured. However, since NH_4^+ and HCO_3^- were not been determined, it is not possible to assess electroneutrality (Hara et al., 1995; Sanusi et al., 1996; Noguchi et al., 1995). The HCO_3^- can be neglected at <pH 5.5, but it may be significant at pH>5.5 (Noguchi et al., 1995). The measured total dissolved solids (TDS) are most abundant in the rainwater samples collected near the coastline (Nakaminato) and over the East China Sea. These samples, unlike those collected over land (Sanusi et al., 1996; Tuncel and Ungor, 1996), are characterized by high concentrations of Na^+ and K^+, with remarkably high Na^+/Ca^{2+} and K^+/Ca^{2+} ratios. For anions, Cl^- and NO_3^- dominate in most samples.

3.2. Origins of major ions in rainwaters

There are, in general, three main origins for dissolved solids in rainwaters: marine, anthropogenic, and terrigenic (e.g., mineral dust). The presence of nitrate can be attributed to an input of various gaseous nitrogen oxides (NO_x), and be used as a tracer of anthropogenic pollution (Ezcurra et al., 1988; Colin et al., 1989; Sanusi et al., 1996). However, the source of sulphate is complicated, as it also has a marine origin. Na is generally considered as a tracer of the marine source, although a small contribution of terrigenic origin arises due to the input of crustal aerosols. Consequently, these elements are used to identify the sources of the dissolved solids in the rainwater samples.

Equivalent ratios of none sea salt (nss-) SO_4^{2-}/Na^+ are plotted against Cl^-/Na^+ in Fig. 2. As can be seen from this figure, rainwater samples collected from Chofu and Tokyo have higher nss-SO_4^{2-}/Na^+ ratios, but the Cl^-/Na^+ ratios bracket the average seawater value of 1.17. Three rain events from Nakaminato had similar raining-cloud trajectories with rainwater samples most similar to seawater, with Cl^-/Na^+ ratios close to 1.17, and nss-SO_4^{2-}/Na^+ ratios (Fig. 2). One of the two rainwater samples from the East China Sea is evidently depleted in Cl^- or enriched in Na^+, as compared with the average seawater. This rain can be traced to China (Fig. 1) and the lower Cl^-/Na^+ ratio (Fig. 2, the black square on the left) can be explained by the presence of terrigenic Na^+. The alternative interpretation is that Cl^- has been replaced by SO_4^{2-} or NO_3^- (Keene et al., 1990; Clegg and Brimblecombe, 1985). The calculated percent sea salt (PSS) values (Table 1) for these rain water samples vary with the distance from the nearest coastline.

Differences in chemical composition of the rainwater samples suggest different sources of the major ions, which can be better understood in terms of the trajectories of the rain clouds (Fig. 1). The raining
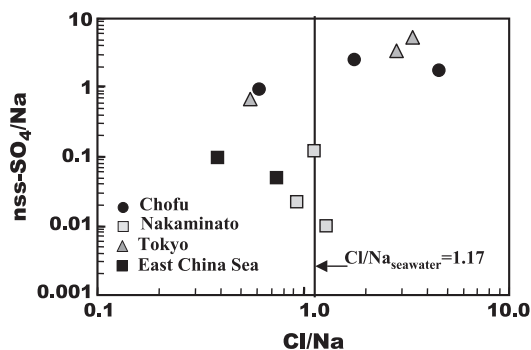

Fig. 2. Variations of nss-SO_4/Na vs. Cl/Na equivalent ratios of the rainwaters.

Table 1
Major components (μeq/kg) of rainwaters

Sample	pH	Sr	Ca	Mg	Na	K	Cl	Br	NO_2	NO_3	SO_4	PSS%	nss-SO_4
CHF960522	5.5	0.016	13.49	4.20	6.48	5.88	3.95	nd	0.59	7.37	6.60	6.17	6.18
CHF960707	5.5	0.016	6.41	4.61	6.66	8.34	11.91	nd	0.46	14.3	17.1	4.67	16.3
CHF960709	5.8	0.011	3.32	2.80	2.44	7.47	11.19	nd	0.48	3.35	4.54	6.42	4.25
NKM960522	5.8	0.064	30.5	26.3	117	14.0	109	0.200	nd	9.93	14.07	79.7	2.54
NKM960703	5.5	0.126	25.6	68.3	243	38.2	275	0.588	nd	58. 7	58.6	48.4	29.4
NKM960709	6.1	0.237	28.1	136	563	15.6	734	0.939	nd	3.93	72.5	92.8	5.51
TK940324	6.0	0.018	2.83	12. 7	17.1	31.5	9.41	nd	nd	14.4	12.8	7.60	11.8
TK950122	6.0	0.016	6.59	4.44	6.48	3.38	22.1	nd	0.33	32.5	35.2	2.20	34.5
TK950226	5.8	0.018	6.98	4.85	6.48	7.52	18.3	nd	nd	28.2	23.1	3.36	22.3
EC960901	5.7	0.582	24.0	6.17	3143	17.4	234	nd	nd	21.6	40.3	59.9	15.5
EC960925	5.7	0.605	22.5	14.4	259	23.4	100	nd	nd	19.5	35.7	28.9	25.1

nd, no data. Sample names reflect the sampling locations and sampling dates. CHF stands for Chofu, NKM for Nakaminato, TK for Tokyo, and EC for the East China Sea. The sampling dates are expressed as year, followed by month and day. None sea salt sulfate (nss-SO_4) and percent sea salt (PSS) values were calculated based on equations as follows: if Cl/Na equivalent ratio>1.17, nss-SO_4=[SO_4]$_{sample}$−[Na]$_{sample}$×[SO_4/Na]$_{seawater}$, PSS%=100×(SO_4/Na)$_{seawater}$/(SO_4/Na)$_{sample}$; if Cl/Na equivalent ratio<1.17, nss-SO_4=[SO_4]$_{sample}$−[Cl]$_{sample}$×[SO_4/Cl]$_{seawater}$, PSS%=100×(SO_4/Cl)$_{seawater}$/(SO_4/Cl)$_{sample}$. In the equations, [SO_4/Na] stands for the equivalent ratio, whereas (SO_4/Cl) is for a weight ratio.

clouds, especially those at 500 and 1000 m in elevation, for the two rain events at Chofu and Tokyo had clearly land-derived sources. Samples from these events show high nss-SO_4^{2-}/Na^+ and Cl^-/Na^+ ratios (the two dots and two triangles in the upper right corner of Fig. 2), suggesting the existence of abundant nss-SO_4^{2-} and Cl^-. Two samples, one from Chofu and the other from Tokyo, are from clouds located over the sea, and hence show lower nss-SO_4^{2-}/Na^+ and Cl^-/Na^+ ratios. Taken all together, the Cl^-/Na^+ ratio generally increases with increasing nss-SO_4^{2-}/Na^+ ratio. Since the existence of the abundant nss-SO_4^{2-} indicates an anthropogenic origin, rainwaters with a Cl^-/Na^+ ratio larger than 1.17 may have not only marine but also anthropogenic origins. If the latter case, it may be from refuse incineration gases, especially the combustion of organochlorine compounds such as polyvinyl chloride.

Noteworthy is that K^+ does not vary with Na^+ in these samples, suggesting a different origin. However, K^+ is correlated with NO_3^- and SO_4^{2-}, as is observed from the co-variations of NO_3^-/Na^+ and nss-SO_4^{2-}/Na^+ when plotted against K^+/Na^+ (Fig. 3). NO_3^-/Na^+ and nss-SO_4^{2-}/Na^+ both increase with increasing K^+/Na^+, and this suggests the same or similar origin of K^+, SO_4^{2-} and NO_3^-. Accordingly, K^+ in these rainwater samples, like NO_3^- and SO_4^{2-}, may originate from human activity. Rainwaters from Chofu and Tokyo show the highest NO_3^-/Na^+, nss-SO_4^{2-}/Na^+ and K^+/Na^+ ratios. This is a clear

indication of atmospheric pollution over these densely populated areas.

3.3. REE distribution in rainwaters

The REEs in rainwater from different rain events show significant differences in composition (Table 2). The contents of total REEs are the highest in the
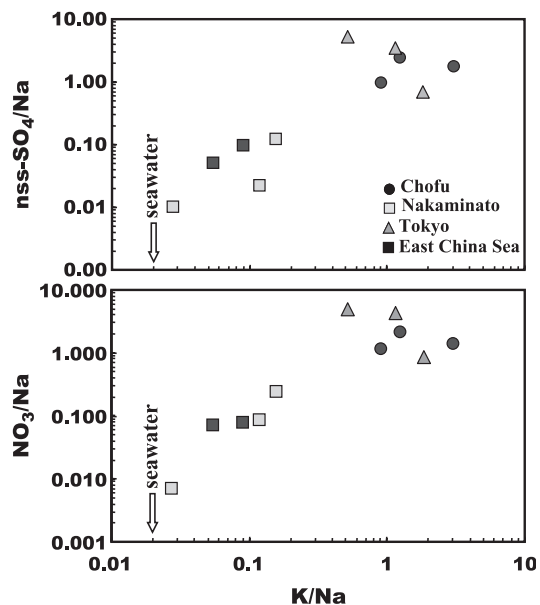

Fig. 3. Variations of NO_3/Na, nss-SO_4/Na vs. K/Na equivalent ratios of the rainwaters.

Table 2
Rare earth element concentrations (pmol/kg) of rainwaters

	CHF 960522	CHF 960707	CHF 960709	NKM 960522	NKM 960703	NKM 960707	NKM 960709	TK 940324	TK 950122	TK 950223	EC 960901	EC 960925
Y	40.55	65.51	31.48	29.60	145.36	76.73	46.05	41.87	18.37	80.74	47.60	16.48
La	386.3	402.5	381.2	84.62	259.1	88.19	83.00	25.29	11.46	55.98	45.94	29.76
Ce	1043	986.3	1056	205.9	571.1	192.0	190.9	28.95	24.57	81.79	130.0	120.1
Pr	61.87	62.53	57.28	13.98	41.65	16.35	13.47	3.74	2.86	11.19	10.76	7.48
Nd	159.0	170.8	147.09	41.16	137.03	60.33	42.57	13.96	11.79	40.94	33.43	24.10
Sm	23.28	24.94	19.91	6.17	22.97	10.95	7.38	2.89	2.36	7.55	4.46	2.28
Eu	3.40	3.84	2.68	1.32	4.64	2.48	1.74	0.73	0.41	1.72	1.03	0.41
Gd	14.97	15.83	11.85	4.97	18.29	9.68	6.52	3.45	2.18	9.30	3.89	1.67
Tb	1.22	1.40	0.80	0.54	2.35	1.44	0.86	0.44	0.31	1.13	0.59	0.23
Dy	4.25	5.86	2.41	2.57	11.84	7.45	4.51	2.57	1.72	6.26	3.61	1.14
Ho	0.75	1.06	0.42	0.50	2.19	1.30	0.79	0.54	0.33	1.27	0.89	0.24
Er	2.41	3.34	1.36	1.63	7.12	4.10	2.51	1.46	0.96	3.39	2.94	0.72
Tm	0.33	0.48	0.17	0.25	0.99	0.59	0.34	0.20	0.14	0.48	0.49	0.09
Yb	2.22	3.21	1.08	1.60	6.68	3.87	2.21	1.16	0.92	3.21	3.73	0.60
Lu	0.37	0.55	0.18	0.28	1.09	0.58	0.33	0.16	0.14	0.46	0.54	0.09
SUM	1703	1683	1683	365.5	1087	399.3	357.2	85.53	60.16	224. 7	242.3	188.9
Y/Ho	53.83	61.72	74.68	59.32	66.48	59.14	58.01	78.26	55.00	63.83	53.27	69.15
Nd/Yb	71.78	53.21	135.7	25.66	20.51	15.60	19.24	12.02	12.80	12.77	8.95	40.08
La/Yb	174.4	125.4	351.5	52.76	38.77	22.80	37.51	21.76	12.45	17.47	12.30	49.50

rainwater samples from Chofu (>1600 pmol/kg), and lowest in samples from the East China Sea and Tokyo (between 60 and 242 pmol/kg). These rainwater samples have similar HREE but clearly higher LREE concentrations compared with the surface seawaters of the Pacific and Indian Oceans. Except for those of Tokyo, samples from different events at the same location have variable HREE contents, but the LREE concentrations are relatively constant. On the other hand, samples from different locations exhibit an order of magnitude variation in LREE concentrations yet the variations in HREE concentrations are smaller.

The shale-normalized REE patterns (Fig. 4) reflect this behavior. In addition, rainwater samples collected in Tokyo have flat REE patterns, indicating a shale-like composition, whereas samples from Chofu have the highest enrichment of LREEs. Two East China Sea samples collected from a squall rain event and a rain front transferred from the Korean Peninsula have different compositions: one shows a LREE-enrichment (EC960925, Fig. 4) and the other a slightly middle-REE-depleted pattern (EC960921). As compared with rainwaters studied by Sholknovitz et al. (1993), which are the only high-precision data available for comparison, our rainwaters show sig-

nificantly larger variations in REE composition. Particularly noteworthy is the significant LREE enrichment in most of the samples studied in this work.

Several main factors may account for the REE compositional variations in these rainwaters, such as the source region, pH of precipitation, speciation of REEs in particles, and particle/rainwater interactions. Sholknovitz et al. (1993) measured the REE concentrations in the dissolved and particulate phases of rainwater and have shown that there is large fractionation of the REEs between the continents, atmosphere and oceans. These fractionations provide information about the aerosol/precipitation ratios and the sources of continentally derived dust particles. Since we have not studied the REEs in the aerosols and there are not many data available on the dissolved and particulate phases of rainwater, the discussion below will focus on the controlling factors other than speciation of REEs in particles and particle/rainwater interactions.

3.3.1. Sources

The REEs in rainwater are most likely derived from the washout or dissolution of aerosols. Like trace metals such as Cu, Zn, and Pb (Chester et al., 1994;
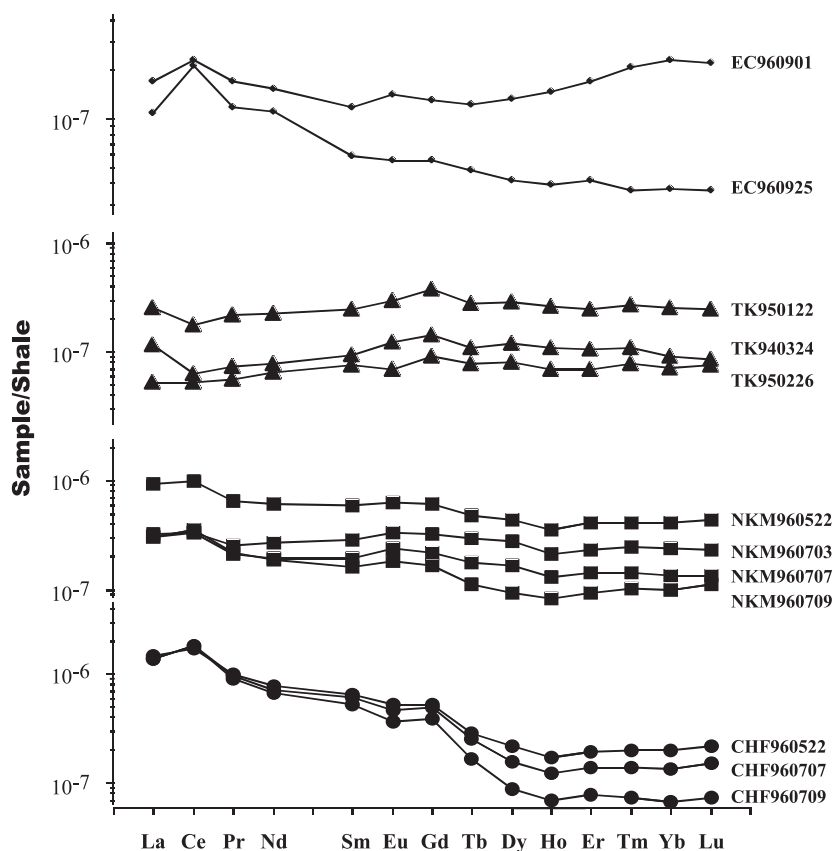
Fig. 4. Patterns of shale-normalized REEs in rainwaters.

Lim and Jickells, 1994; Halstead et al., 2000; Roy and Negrel, 2001), the REEs in aerosols may also have three main sources, which are low temperature crustal weathering (crustal sources), a variety of high temperature anthropogenic processes (anthropogenic sources) and sea-salt or sea-spray generation (oceanic sources).

Rainwaters from Tokyo and Chofu all have high concentrations of anthropogenic components such as NO_3^- and nss-SO_4^{2-} but different shale-normalized REE patterns: the former is loess-like, whereas the latter is LREE-enriched. This suggests that major ions and REEs in rainwaters may originate from different sources. Anthropogenic sources of the REEs to the atmosphere include particles produced during crude oil cracking, combustion of oil and gasoline products, which are highly enriched in the LREEs (Olmez and Gordon, 1985; Olmez et al., 1991; Kitto et al., 1992; Brown et al., 1991). The anthropogenic sources of

REEs in different areas have not been identified, and very little is known of their composition in the atmosphere. Rainwaters of Chofu and one sample from the East China Sea have significant enrichment of LREEs over HREEs. According to the forward trajectories of the rainfalls (Fig. 1), it could be concluded that rainwater originating over land have high LREEs, and the enrichment of LREEs is due to anthropogenic inputs. This is because REEs of anthropogenic sources are characterized by LREE-enrichment (e.g. Koeppenkastrop et al., 1991).

Particle/cloud water interactions may also be a control over the fractionation between LREEs and HREEs in rainwater, but we have not analyzed particulate materials in rainwaters. In the study of dissolved and particulate REEs in the precipitation and aerosols, Sholknovitz et al. (1993) found that the exchangeable (HCl (1.75 N)-dissolved) phase generally exhibit slightly higher LREE concentrations

accompanied by high Nd/Yb ratios, or a larger depletion in HREEs than the residual phase (HF/HNO$_3$-dissolved) in bomb digestion. This implies that the LREEs are more soluble than the HREEs in aerosols or more LREEs relative to HREEs exist in the exchangeable phase because the particle-absorbed phase is often significantly enriched in the LREEs. As there is both an airport located only 1.6 km from Chofu, and a major highway very close to the city, Chofu rainwaters probably contain more anthropogenic REEs than samples collected elsewhere. This is consistent with the high NO$_3^-$/Na$^+$ and nss-SO$_4^{2-}$/Na$^+$ ratios found in rainwaters of Chofu. The large percentage of sea spray (PSS) in the rainwaters of Nakaminato and the East China Sea indicates the importance of this contribution to major ion concentrations, but their REE compositions are not directly comparable with those of surface seawater. With respect to LREE enrichment, these rainwaters fall between those of Tokyo and Chofu. However one sample, EC960925, is enriched in light REEs, but the other, EC960901 collected in a squall rain event, shows HREE enrichment and similar Nd/Yb ratio with surface seawater. We think that the REE composition of the former is related to the land origin and that of the latter to a sea origin, although Halstead et al. (2000) reported negligible seawater contribution to rainwater trace metals.

The discrepancy between major ion and REE compositions for Tokyo rainwaters indicates that trace elements in rainwater may have different sources from those of major ions, and that a simple mixing between different sources cannot explain variations of the REEs. In addition to differences in the sources, other controlling factors such as the solid state speciation of major ions and REEs in aerosols could play an important role in controlling the REE compositions of rainwaters.

3.3.2. Acidity of rainwaters

Adsorption of trace metals on aerosols of various soil components shows strong pH dependence, and the scavenging rate of the REEs in aerosols by rainwater is considered to be largely dependent on its pH (Davis and Kent, 1990; Lim and Jickells, 1994; Spokes et al., 1994; Herut et al., 2000). However, rainwaters often have a complex pH history. Cloudwaters can be very acidic because of oxidation of SO$_2$ and uptakes of H$_2$SO$_4$ and HNO$_3$. During a raining event, the pH of rainwater is often higher at the beginning due to interactions with alkaline dust (Chen et al., 1994). The pH values measured for rainwaters, therefore, may not reflect the pH condition to which the aerosols were exposed prior to its removal. Our measured pH values do not show significant difference among the different samples. However, the Tokyo and Chofu rainwater samples do have significantly higher NO$_3^-$ and SO$_4^{2+}$ concentrations and the highest NO$_3^-$/Na$^+$ and nss-SO$_4^{2+}$/Na$^+$ ratios, indicating that these rainwaters have absorbed more H$_2$SO$_4$ and HNO$_3$ during their earlier stages of rain-formation processes. The high H$_2$SO$_4$ and HNO$_3$ concentrations, if given enough time for the rain/aerosol interaction to occur, may result in a release of more REEs from the crystalline matrix of aerosols, and lead to a shale-like REE pattern as observed from rainwaters over Tokyo. However, since we have no knowledge of the pH dependence of fractionation between REEs, it is not yet possible to assess the effect of pH on the REE composition of rainwater.

3.4. Y/Ho ratios in rainwaters

Fractionation between Ho and Y in the oceanic basin and during water/rock interaction has intrigued many researchers in recent years (e.g. Kawabe et al., 1991; Byrne and Lee, 1993; Zhang et al., 1994; Bau et al., 1995; Nozaki et al., 1997; Takahashi et al., 2002; Möller et al., 2003). Y has a similar chemistry as the lanthanides, especially that of Ho, because these two elements have almost the same ionic radius and valences. These two elements behave geochemically similar in most magmatic systems, and hence the Y/Ho ratio is very constant in the lithosphere of the Earth, and even in planetary materials. However, there is much evidence to show that these two elements are significantly fractionated in aqueous systems (Zhang et al., 1994), indicating that Y has a different aqueous chemistry than that of the lanthanides. However, the mechanism that fractionates these two elements has not yet been well documented.

The Y/Ho molar ratios in these rainwaters range from 53 to 78, all higher than the average value (Y/Ho=52) of the continental crust, but significantly lower than the average ratio of seawater (Y/Ho=105). We are not aware of any report on the factors
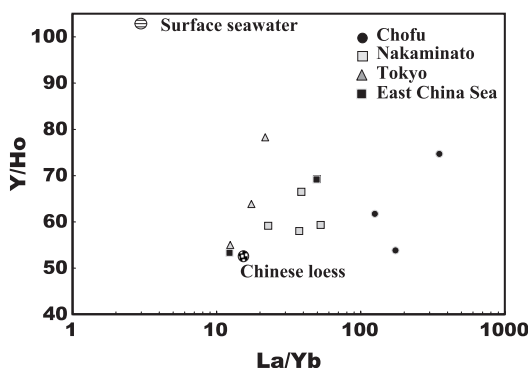
Fig. 5. Variations of La/Yb vs. Y/Ho molar ratios of rainwaters, the average surface seawater, as well as the Chinese loess (Data of the Chinese loess are those from Liu et al., 1993).

controlling the fractionation mechanism of these two elements in rainwater. However, the high Y/Ho ratios in rainwater compared with that of the crust may be inherited from anthropogenic and/or oceanic sources, and may suggest the fractionation between these two elements due to aerosol/rain interactions. If Y/Ho fractionation does take place during aerosol/rain interaction, the particulate-scavenging mechanism suggested by several authors (e.g., Zhang et al., 1994; Nozaki et al., 1997) may also account for this fractionation in rainwaters. It should be noted that, although mixing of sea spray characterized by high Y/Ho ratios in these rainwaters could have resulted in the Y enrichment over Ho, generally, an increase of Y/Ho with increasing La/Yb ratio does not support this interpretation because surface seawaters have a very low La/Yb ratio (Fig. 5). Accordingly, we conclude that the high Y/Ho ratio in rainwaters most likely is the result of anthropogenic input of the REEs in addition to the Y/Ho fractionation during the rain-formation processes.

4. Conclusions

Rainwater samples collected in Japan and the East China Sea show large differences in major ion compositions. Variations in anion and cation compositions reflect mixing of oceanic, crustal, and anthropogenic sources. Rainwaters of Chofu and Tokyo contain more anthropogenic anions such as NO_3^- and SO_4^{2-}, as well as more cations from crustal sources.

Major ions of rainwaters collected over Nakaminato and the East China Sea are dominated by oceanic sources from sea sprays or sea salts.

The REE compositions in these rainwaters are highly variable, and are characterized by various degrees of LREE enrichment, which cannot be accounted for by mixing with oceanic or crustal sources. The largest LREE enrichment is in rainwater of Chofu. When coupled with the highest NO_3^-/Na^+ and nss-SO_4^{2+}/Na^+ ratios, it implies that anthropogenic sources of the REEs may be enriched in LREEs. Rainwater of Tokyo, though exhibiting high concentrations of NO_3^- and nss-SO_4^{2-}, shows loess-like REE patterns, which indicates that the source of REEs might be different from that of NO_3^- and nss-SO_4^{2-}, or that intensive mineral particle/cloud water interaction under low pH conditions has led to a larger contribution of crustal REEs into these rainwaters. Accordingly, the relationship between major ion and the REE compositions cannot be explained simply by mixing of different sources. Rainwater/particle (aerosol) reaction, in addition to mixing of various sources, may also be responsible for the discrepancy between major ion and the REE compositions.

The Y/Ho ratios in these rainwaters are all higher than those of the crust, and, in general, increase with increasing LREE enrichment. Physical mixing of crustal and oceanic sources of the REEs cannot account for these variations. Although the fractionation of these two elements during the rain/particle reaction cannot be ruled out, we favor the conclusion that the anthropogenic REE input is generally characterized by a high Y/Ho ratio.

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