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Article

Environmental Characteristics of Precipitations Based on Both Oxygen Stable Isotopic Ratio and Concentrations of Rare Earth Elements (REEs), Thorium (Th), Uranium (U) in Niigata Prefecture

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In order to investigate the characteristics (or the sources) of precipitations in Niigata Prefecture, oxygen stable isotopic ratios (i.e., $\delta^{18}O$) and the concentrations of rare earth elements (REEs), thorium (Th), and uranium (U) in the precipitation samples were measured. The precipitation samples were collected using a filtrating bulk sampler every two weeks at 3 points in Niigata Prefecture during the period from December 2003 to December 2004.

Consequently, the following matters have been mainly clarified. (1) In rainy season, $\delta^{18}O$ value of precipitations was the smallest. (2) In regard to $\delta^{18}O$ value, "Continental effect" and "Amount effect" was generally observed in this work. On the other hand, "Temperature effect" was remarkably found only in winter. (3) The concentrations of trace metallic elements (REEs, Th, U) increased in spring. (4) REEs in precipitations might have been derived from a crustal source as well as oceanic source, while anthropogenic source was not negligible.

Key Words : oxygen stable isotopic ratio, rare earth element, thorium, uranium, precipitation, ICP-MS, stable isotope ratio mass spectrometer, Niigata Prefecture

1. Introduction

Oxygen and hydrogen isotopes serve as useful tool for characterizing the origin of local waters and local hydrological cycle. Hence, isotopic analyses of oxygen and hydrogen (i.e., $\delta^{18}O$, δD) in environmental water samples have been widely performed in the world including Japan[1)-5)].

In addition, rare earth elements (REEs) have received great attention for the understanding of the aqueous chemistry in last decades[6)-8)]. The lanthanides (i.e., La - Lu), particularly, are largely noticed because of their similar chemical behavior, and the behavior allows them to be used as a tracer of a wide variety of geochemical processes. The REE pattern, where the abundance of lanthanide in each sample

Table 1 Sampling lists of precipitations at 3 points in Niigata Prefecture

	Sampling Date	Sado	Amount (mm)	pH	Niigata	Amount (mm)	pH	Shitada	Amount (mm)	pH
	24-Dec-03 – 5-Jan-04	S-1	61.4	4.54	N-1	75.3	4.29	K-1	165	4.25
	5-Jan-04 – 19-Jan-04	S-2	49.4	4.22	N-2	61.8	4.38	K-2	79.3	4.59
I	19-Jan-04 – 2-Feb-04	S-3	23.4	4.49	N-3	98.3	4.46	K-3	135	4.53
	2-Feb-04 – 16-Feb-04	S-4	23.9	4.40	N-4	93.1	4.49	K-4	173	4.50
	16-Feb-04 – 1-Mar-04	S-5	29.6	4.33	N-5	29.0	4.90	K-5	88.5	4.78
	1-Mar-04 – 15-Mar-04	S-6	25.5	4.90	N-6	53.3	5.80	K-6	77.8	6.08
	15-Mar-04 – 29-Mar-04	S-7	34.6	–	N-7	21.7	5.55	K-7	20.0	4.80
II	29-Mar-04 – 12-Apr-04	S-8	38.7	5.37	N-8	35.4	5.49	K-8	49.8	4.89
	12-Apr-04 – 26-Apr-04	S-9	21.9	5.08	N-9	43.0	4.94	K-9	63.9	4.96
	26-Apr-04 – 10-May-04	S-10	78.2	5.74	N-10	98.0	5.09	K-10	123	4.94
	10-May-04 – 24-May-04	S-11	102	6.09	N-11	102	4.84	K-11	178	4.77
	24-May-04 – 7-Jun-04	S-12	150	5.25	N-12	30.9	4.83	K-12	42.0	4.40
	7-Jun-04 – 21-Jun-04	S-13	33.6	6.62	N-13	64.7	5.20	K-13	58.8	4.49
	21-Jun-04 – 5-Jul-04	S-14	57.6	4.88	N-14	69.0	4.94	K-14	41.2	4.32
III	5-Jul-04 – 19-Jul-04	S-15	132	4.74	N-15	167	4.86	K-15	551	4.78
	19-Jul-04 – 2-Aug-04	S-16	0	–	N-16	34.6	4.56	K-16	40.9	4.17
	2-Aug-04 – 16-Aug-04	S-17	3.60	–	N-17	11.2	5.64	K-17	42.2	4.73
	16-Aug-04 – 30-Aug-04	S-18	264	5.98	N-18	114	5.10	K-18	149	4.94
	30-Aug-04 – 13-Sep-04	S-19	61.1	5.35	N-19	28.5	6.39	K-19	61.9	4.57
	13-Sep-04 – 27-Sep-04	S-20	83.6	4.51	N-20	108	4.75	K-20	180	4.60
IV	27-Sep-04 – 11-Oct-04	S-21	102	4.78	N-21	122	4.81	K-21	208	4.91
	11-Oct-04 – 25-Oct-04	S-22	48.9	5.42	N-22	112	4.88	K-22	166	4.75
	25-Oct-04 – 8-Nov-04	S-23	22.4	4.46	N-23	43.2	4.66	K-23	89.2	4.32
	8-Nov-04 – 22-Nov-04	S-24	28.0	4.45	N-24	124	4.48	K-24	166	4.45
	22-Nov-04 – 6-Dec-04	S-25	38.7	4.86	N-25	50.9	4.69	K-25	116	4.41
I	6-Dec-04 – 20-Dec-04	S-26	35.7	–	N-26	102	–	K-26	99.6	–

"—" represents the defect of data

(relative to that of chondrite or shale) is plotted on a logarithmic scale against the atomic number, is therefore regarded as a "fingerprint" of a geological sample[9)–11)].

Niigata Prefecture is located in the geographic position where the monsoon comes from the Continent. Moreover, a large amount of snow falls every year in winter season. Therefore, it is expected that isotopic and chemical investigation of the precipitation samples may bring new knowledge about hydrologic environment in this area.

However, hydrological and environmental investigations using $\delta^{18}O$ and δD (as well as the concentrations of REEs, Th, and U) in the precipitation have been scarcely reported in Niigata Prefecture.

In previous papers[12),13)], we mainly observed $\delta^{18}O$ of precipitation, river water, and some groundwater samples, and consequently obtained some new knowledge about the characteristics of environmental waters in Niigata Prefecture.

In order to investigate the sources of precipitations in addition to the characteristics of precipitations, the concentrations of REEs, Th, and U as well as $\delta^{18}O$ values of the precipitations at 3 points in Niigata Prefecture have been determined in the present work.

2. Experimental

2·1 Samples

Precipitation samples were collected with a filtrating bulk sampler every two weeks at 3 points in Niigata Prefecture. The sampling period was one year, from the end of December 2003 to the end of December 2004. These samples are listed in Table 1 along with the amount of precipitation and pH. The pH of each sample was measured with a pH meter (HORIBA F-24).

The sampling points, namely Sado (38° 14′ N, 138° 24′ E; Altitude 136 m), Niigata (37° 50′ N, 138° 56′ E, Altitude 5 m), and Shitada (37° 38′ N, 138° 58′ E, Altitude 190 m), are located respec-

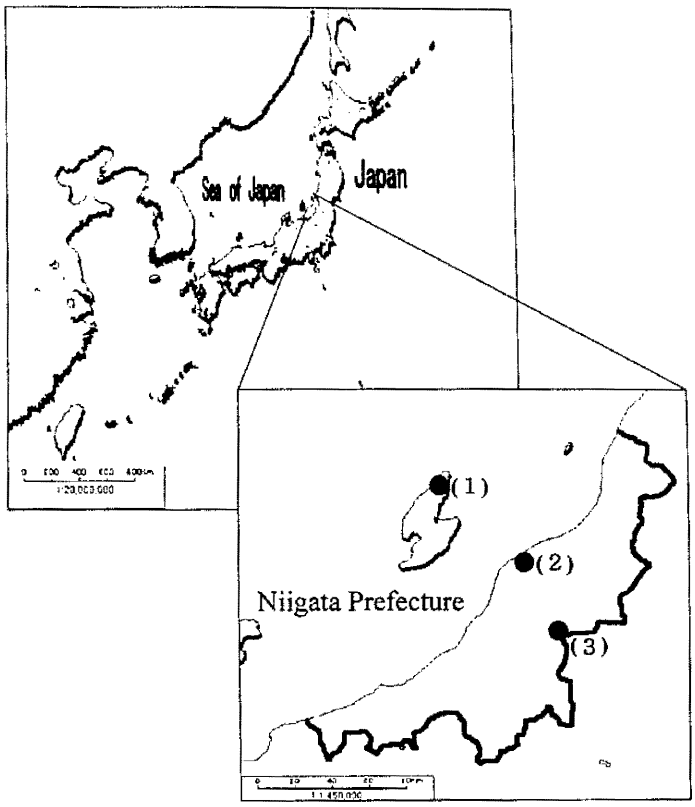

Fig. 1 Location of sampling points in Niigata Prefecture. (1) : Sado, (2) : Niigata, (3) : Shitada.

tively about 0.1 km, 3 km, and 40 km from the nearest coast (Fig. 1).

These samples are classified into the following four classes based on seasons [I : "winter" (Dec., Jan., Feb.), II : "spring" (Mar., Apr., May), III : "summer" (Jun., Jul., Aug.), IV : "autumn" (Sep., Oct., Nov.)]. The wind direction in each season (3 points) is shown in Fig. 2. It indicates that the wind direction varied significantly with both the places and the seasons.

2·2 Analytical method

2·2·1 Oxygen stable isotopic ratios ($\delta^{18}O$)

For the measurement of oxygen isotope ratio, CO_2-H_2O isotope equilibration method was used. The sample preparation procedure based on the method of Watanabe et al.[4] was applied in this work. Isotopic measurements were performed with a stable isotope ratio mass spectrometer (Micromass PRISM).

2·2·2 Determination of REEs, Th, and U

REEs, Th, and U standard solutions used for making the calibration curve were prepared by diluting the standard solution (XSTC-1 for REEs and XSTC-13 for Th, U ; both 10 mg·dm^{-3} 5% HNO_3 solution) purchased from SPEX CertiPrep, Inc. (USA).

Rare earth elements, Th, and U were separated from matrix by the chelate disk (47 ϕ mm) (Empore™ Sumitomo 3M Co.). In the separation procedure, the disk was placed in an ordinary disk holder. Each sample was run through the disk after adjusting pH to 3 by using ammonium acetate (CH_3COONH_4) and nitric acid (HNO_3). Then, REEs, Th, and U on the disk was eluted by 1.5 mol·dm^{-3} nitric acid

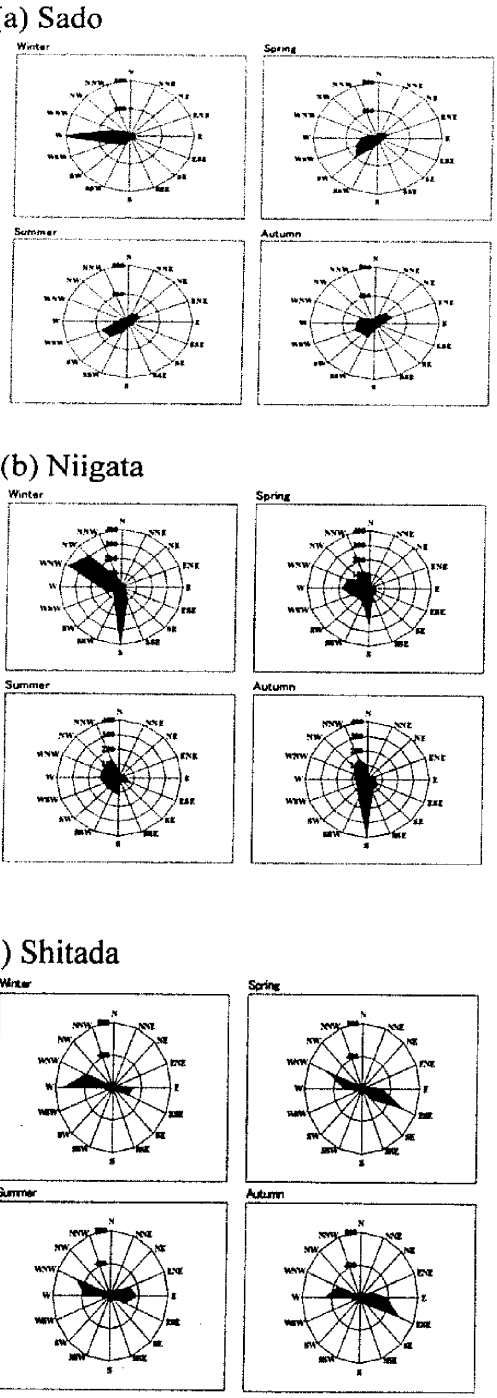

Fig. 2 The wind direction of each season in Niigata Prefecture. (a) : Sado, (b) : Niigata, (c) : Shitada.

(20 cm^3). The preconcentraion of REEs, Th, and U was carried out according to the procedure described in Takaku et al.[15].

Table 2 Operating conditions of ICP-MS

RF power	1150 W
Plasma gas flow	15 L/min
Carrier gas flow	1.2 L/min
Sampling depth	6.5 mm
Sample uptake rate	0.5 mL/min
Measurement point	3 points/peak
Integration time	1.0 sec/point
Measured Isotopes	^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{153}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{172}Yb, ^{175}Lu, ^{232}Th, ^{238}U

After the preconcentraion procedure, the concentrations of REEs, Th, and U in samples were measured with an ICP-MS (HP4500; Yokogawa Analytical systems, Tokyo). The operating condition of ICP-MS (including the measured isotopes) is shown in Table 2.

3. Results and Discussion

3·1 $\delta^{18}O$ values in the precipitation in Niigata Prefecture

The $\delta^{18}O$ values in the precipitation samples obtained at 3 points from the end of December 2003 to the end of December 2004 are shown in Table 3. From this table, it is found that the mean value of $\delta^{18}O$ in Niigata City is more than 1.0‰ larger than that of two other points (Sado City and Shitada Village).

Seasonal variation of $\delta^{18}O$ values in the precipitation samples at 3 points in Niigata Prefecture is shown in Fig. 3. From this figure, the following matters have been found. (1) As for 3 observation points, the seasonal behavior of $\delta^{18}O$ was almost similar to each other. In particular, $\delta^{18}O$ values of precipitation were relatively small in rainy season in all points. (2) $\delta^{18}O$ values in Niigata are generally larger than

Table 3 $\delta^{18}O$ values in precipitations at 3 points in Niigata Prefecture

Sado		Niigata		Shitada	
S-1	-10.80	N-1	-6.10	K-1	-7.06
S-2	-12.47	N-2	-7.63	K-2	-10.26
S-3	-9.88	N-3	-8.25	K-3	-10.03
S-4	-9.90	N-4	-9.37	K-4	-10.70
S-5	-8.79	N-5	-5.31	K-5	-8.70
S-6	-9.37	N-6	-7.82	K-6	-9.96
S-7	-6.13	N-7	-7.69	K-7	-8.45
S-8	—	N-8	—	K-8	—
S-9	-4.23	N-9	-3.78	K-9	-7.34
S-10	-6.81	N-10	-6.38	K-10	-7.36
S-11	-12.78	N-11	-11.95	K-11	-10.86
S-12	-7.90	N-12	-5.67	K-12	-7.07
S-13	-7.54	N-13	-7.64	K-13	-9.20
S-14	-8.73	N-14	-7.54	K-14	-7.57
S-15	-6.92	N-15	-7.08	K-15	-7.81
S-16	—	N-16	-7.63	K-16	-7.78
S-17	—	N-17	-3.50	K-17	-4.36
S-18	-12.27	N-18	-9.90	K-18	-9.22
S-19	-10.29	N-19	-7.54	K-19	-9.58
S-20	-6.65	N-20	-6.39	K-20	-7.33
S-21	-9.43	N-21	-10.81	K-21	-11.30
S-22	—	N-22	—	K-22	—
S-23	-5.74	N-23	-6.49	K-23	-6.69
S-24	-7.42	N-24	-7.65	K-24	-7.57
S-25	-8.67	N-25	-8.39	K-25	-8.79
S-26	-7.08	N-26	-6.11	K-26	-5.71
Mean	-8.70	Mean	-7.41	Mean	-8.48
SD	2.28	SD	1.97	SD	1.64

"— " represents the defect of data due to the lack of sample

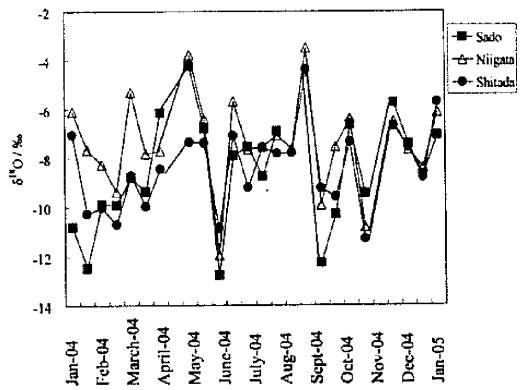

Fig. 3 Seasonal variations of $\delta^{18}O$ values in precipitation at 3 points in Niigata Prefecture.

those in Shitada throughout the year.

For the explanation of the above-mentioned (2), "Continental effect"[12),16)] and/or "Altitude effect"[12),16)] may be presented. However, "Altitude effect" of $\delta^{18}O$ in the precipitation is known as at most $-0.14‰/100\ m$[4)] or $-0.25‰/100\ m$[17)] in central Japan. Therefore, "Continental effect" (i.e., $\delta^{18}O$ in "coastal area" is generally larger than that in "inland area") is considered to be larger in this case.

3·2 Relationship between $\delta^{18}O$ value and weather condition

3·2·1 Relationship between $\delta^{18}O$ and temperature

Relationship between temperature and $\delta^{18}O$ values in precipitation at 3 points in Niigata Prefecture is shown in Fig. 4. In any places, a remarkable correlation between $\delta^{18}O$ values and temperature is not found.

In order to examine the seasonal characteristics of $\delta^{18}O$ in more detail, plot of temperature vs. $\delta^{18}O$ is shown per each season (Fig. 5). In winter, the relationship between the temperature at the sampling points and $\delta^{18}O$ values is relatively good ($r = 0.57$). In other words, "Temperature effect"[12),16)] is remarkably found in

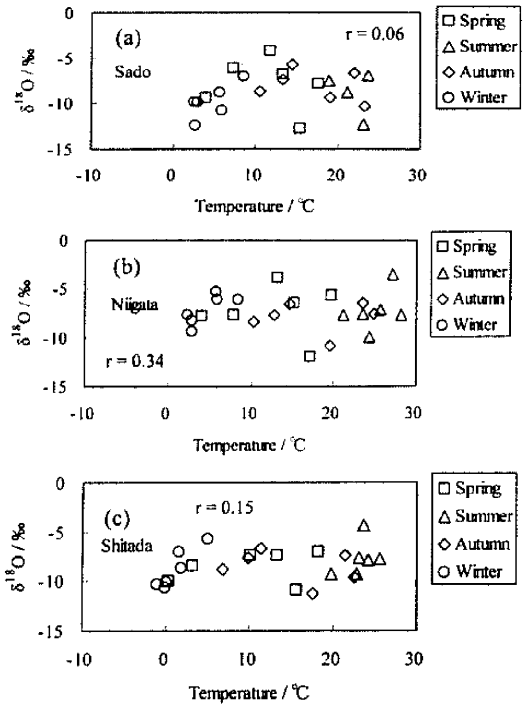

Fig. 4 Relationships between temperature and $\delta^{18}O$ values in precipitation at 3 points. (a) : Sado, (b) : Niigata, (c) : Shitada.

winter. In addition, comparatively high correlation ($r = 0.34$) was seen in summer.

As to the observation that the degree of "Temperature effect" is different among seasons, it is considered that the stability of the air mass, and the wind direction etc. for each season can be greatly related.

3·2·2 Relationship between $\delta^{18}O$ and the amount of precipitation

Relationship between the amount of precipitation and $\delta^{18}O$ values in precipitation at 3 points in Niigata Prefecture is shown in Fig. 6. "Amount effect"[12),16)] is generally found in these places.

In order to examine the seasonal behavior of $\delta^{18}O$ in more detail, the amount of precipitation vs. $\delta^{18}O$ is represented per each season (Fig. 7). Except winter, the relationship between the amount of precipitation at each sampling point and $\delta^{18}O$ values is relatively good. Poor relationship in winter might be attributable to the

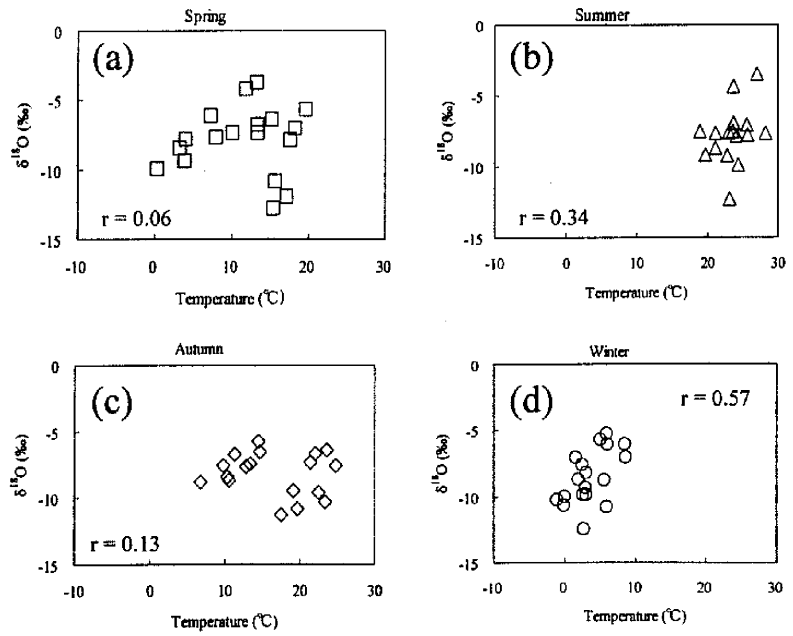

Fig. 5 Relationships between temperature and $\delta^{18}O$ values in precipitation in each season. (a) : Spring, (b) : Summer, (c) : Autumn, (d) : Winter.

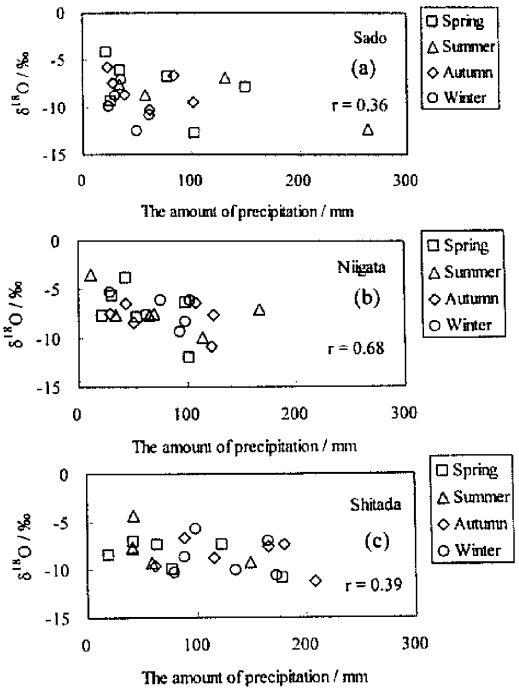

Fig. 6 Relationships between the amount of precipitation and $\delta^{18}O$ values in precipitation at 3 points. (a) : Sado, (b) : Niigata, (c) : Shitada.

difficulty in estimating the amount of precipitation because a large amount of snow falls in Niigata Prefecture area in winter.

3·3 The concentrations of REEs, Th, U in precipitation

The concentrations of REEs, Th, and U in some representative precipitations at 3 points in Niigata Prefecture are shown in Table 4. The relative standard deviation (RSD) of the three replicated analyses of each sample was less than 10%.

The concentrations of REEs, Th, and U in precipitations scarcely show significant differences among different locations. However, the concentrations of REEs, Th, and U are largely varied depending on season in any points. In other words, the concentrations of REEs, Th, and U in winter and/or spring are larger than those of summer and/or autumn.

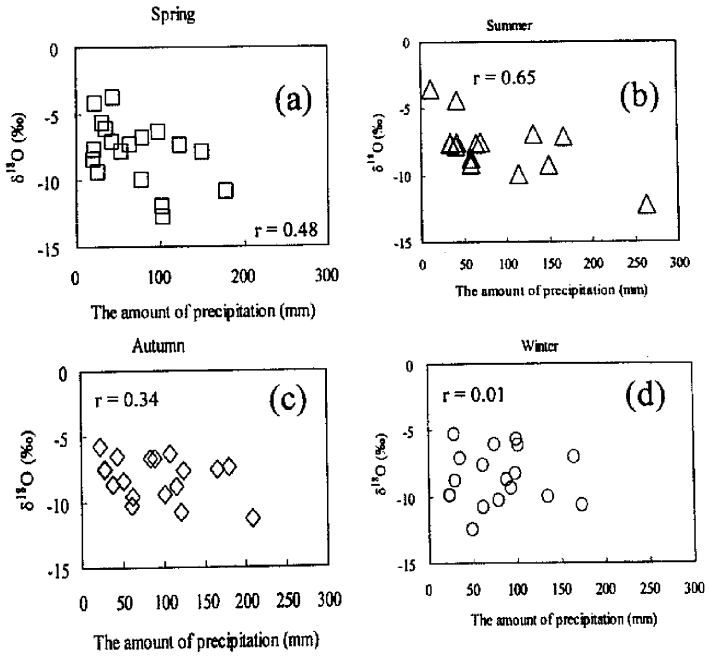

Fig. 7 Relationships between the amount of precipitation and $\delta^{18}O$ values in precipitation in each season. (a) : Spring, (b) : Summer, (c) : Autumn, (d) : Winter.

Table 4 The concentrations of REEs, Th, U ($ng \cdot dm^{-3}$) in some representative precipitations at 3 points in Niigata Prefecture

Sample	N-1	N-6	N-13	N-20	S-1	S-6	S-13	S-20	K-1	K-6	K-13	K-20
Element												
La	95.4	188	21.9	13.2	125	382	99.7	31.5	134	75.3	44.2	16.4
Ce	141	217	26.5	15.5	119	577	133	40.6	171	99.3	76.6	19.9
Pr	15.8	25.1	3.50	2.37	13.3	60.5	15.2	5.08	18.7	13.3	9.61	2.83
Nd	58.0	98.7	14.3	8.48	47.0	229	57.5	18.8	67.1	51.5	38.2	10.5
Sm	12.4	20.8	3.05	1.68	9.28	43.8	11.8	3.70	14.6	10.4	7.68	1.91
Eu	2.91	5.72	0.690	0.467	2.24	10.2	2.62	1.59	3.28	3.08	1.85	0.732
Gd	13.1	22.2	2.77	1.46	10.1	41.5	10.75	3.22	14.6	10.1	7.02	1.90
Tb	2.06	4.16	0.485	0.307	1.53	7.21	1.75	0.721	2.32	2.02	1.20	0.371
Dy	10.1	20.8	2.52	1.39	7.36	37.6	8.60	2.92	10.2	8.28	6.03	1.61
Ho	2.12	4.72	0.517	0.327	1.56	7.79	1.68	0.642	2.28	2.19	1.23	0.354
Er	5.56	12.5	1.48	0.969	3.93	20.3	4.16	1.70	5.47	5.14	3.49	0.917
Tm	0.875	2.31	0.180	0.137	0.614	3.15	0.520	0.310	1.01	1.30	0.446	0.128
Yb	4.81	11.3	1.35	0.926	3.51	17.4	2.96	1.40	4.64	4.65	3.03	0.769
Lu	0.941	2.33	0.229	0.184	0.675	3.11	0.499	0.314	1.08	1.25	0.451	0.161
Th	10.2	19.6	32.7	2.10	7.23	22.4	14.7	2.16	18.4	9.10	7.17	2.00
U	14.3	22.4	3.81	1.68	17.0	44.6	5.80	9.11	13.2	10.5	4.94	1.19

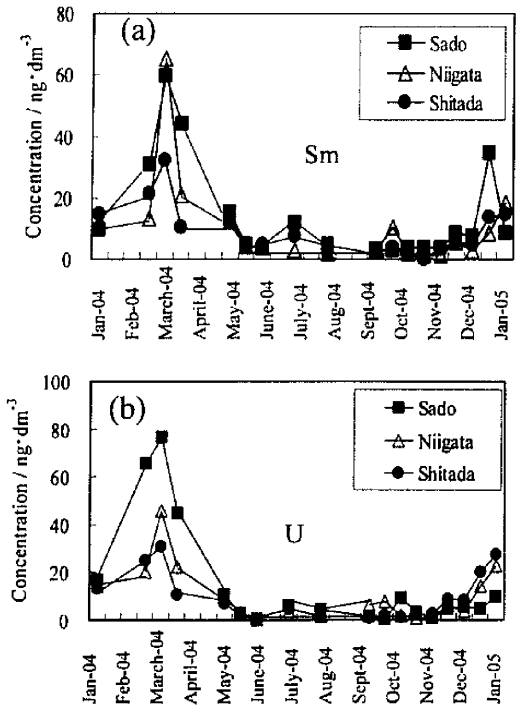

Fig. 8 Seasonal variations of the concentrations of trace metallic elements at 3 points in Niigata Prefecture. (a) : Sm, (b) : U.

The seasonal variations of the concentrations of Sm and U in precipitation at 3 points are shown in Fig. 8. For other REEs and Th, similar seasonal behavior to those of Sm and U was observed.

From this figure, it was found that the concentrations of trace metallic elements (such as REEs, Th, and U) in precipitation in Niigata Prefecture remarkably increase from winter to spring especially in March. It is noteworthy that pH values also remarkably increase in this season as shown in Table 1. Moreover, the concentrations of nss(non-sea salt)-Ca^{2+} in this season also extremely increase at all 3 points. The concentrations of nss-Ca^{2+} is 0.82 – 2.27 $mg \cdot dm^{-3}$ in the samples of Sado (i.e., S5 to S9), 0.88 – 1.64 $mg \cdot dm^{-3}$ in Niigata (i.e., N5 to N9), and 0.71 – 1.72 $mg \cdot dm^{-3}$ in Shitada (i.e., K5 to K9), though the concentrations are almost 0.1 – 0.2 $mg \cdot dm^{-3}$ in other seasons.

It is considered that this must have been due to the yellow sand (so-called "Kosa") from Eur-

asian Continent. We therefore suggest that the trace metallic elements in the precipitation may be carried with the yellow sand.

3·4 "REEs pattern" and sources of REEs in the precipitation

It is generally considered that REEs in the precipitation have three main types of sources[18)-20)] : 1) crustal source, 2) oceanic source, and 3) anthropogenic source.

For the crustal source, the REE composition of shale may be taken as a reference[21),22)]. Further, we determined the REE compositions of seawater taken on the coast in Niigata Prefecture at 4 seasons (i.e., 22nd Apr., 13th Jul., 13th Oct., and 7th Dec.) in 2004 as a reference for the oceanic source. On the other hand, the anthropogenic source is probably characterized by light-REE (LREE) enrichment and low heavy-REE (HREE) concentration[20)].

Shale-normalized REEs patterns in representing precipitation at 3 points in Niigata Prefecture from each season are shown in Fig. 9. The set of normalizing values (i.e., the concentrations of REEs in shale) used in this study was assinged from the values of "Post-Archean Australian average shale" (PAAS)[21)].

From Fig. 9, it is found that these samples in each place (or each season) generally have flat patterns, indicating a shale-like composition. It is suggested that these precipitations are greatly affected by crustal source (i.e., soil origins). However, the concentrations of La are slightly high in most of these samples. Therefore, it is considered that they would be influenced by the component of the artificial origin. As seen from the shale-normalized REEs patterns, the concentrations of REEs in these precipitations are largely variable depending on seasons in all 3 points, although REE patterns

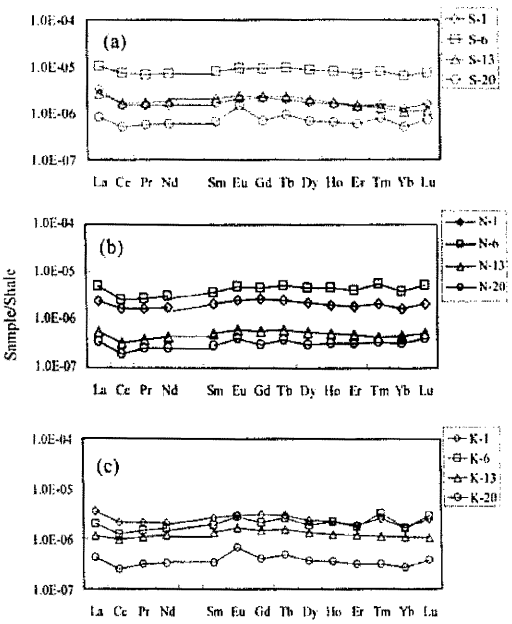

Fig. 9 Shale-normalized REE patterns of the precipitation at 3 points. (a) : Sado, (b) : Niigata, (c) : Shitada.

are not so different among seasons.

In the precipitations of Shitada, which are located less influenced by oceanic source than those of Sado and Niigata, the concentration of REEs or REE patterns are not so much different from other 2 points.

To investigate the sources of the REEs in the precipitation in more detail, plot of Nd/Yb vs. 1/Yb in precipitation at 3 points in Niigata Prefecture is shown in Fig. 10 by applying the method described in Zhang et al.[19)]. The data of seawater analyzed by our laboratory is also shown in the figure as a reference for the oceanic source. The data of Chinese loses (Liu et al.[23)]) are also shown in this figure.

From Fig. 10, a proper portion of mixing between above-mentioned three components (i.e., crustal, oceanic, and anthropogenic source) can account for the REE compositional variations for most of the precipitations. It is considered

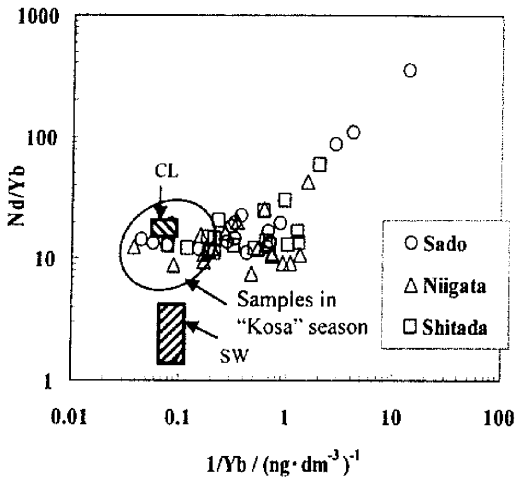

Fig. 10 Plot of Nd/Yb vs. 1/Yb for the precipitation at 3 points in Niigata Prefecture. Data for the seawater analyzed by our laboratory [SW] and for Chinese loses (data from Liu et al., 1993) [CL] are also shown as reference.

that larger 1/Yb values of the precipitations (than those of seawater and/or Chinese loses) might be attributable to the influence of anthropogenic source.

Moreover, it is worth noting that plots of the precipitations in "Kosa" season (shown as the open circle area in Fig. 10) are closely located to the slanting-line area in Chinese loses (CL) area. It is also suggested that these samples at this season are strongly influenced by the yellow sand from the Continent.

From this work, the sources (and the characteristics) of precipitations in Niigata Prefecture could be quantitatively clarified to some extent. The data obtained and the method used in this work can be useful for environmental preservation.

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要　旨

酸素安定同位体比および希土類元素，トリウム，ウラン濃度から見た新潟県における降水の特徴

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新潟県における降水の特徴（あるいは起源）を探求するため，降水試料中の酸素安定同位体比及び微量金属元素（希土類元素，Th，U）濃度を測定した。降水試料は県内3地点において，ろ過式バルクサンプラを用いて，2003年12月から2004年12月の1年間，2週間ごとに採取した。

その結果，主として以下のことが明らかになった。(1) 梅雨期において，降水中の $\delta^{18}O$ 値は最も低くなった。(2) $\delta^{18}O$ 値に関して，本研究において"内陸効果"と"雨量効果"が概して見られた。他方，"温度効果"は冬季においてのみ顕著に見られた。(3) 降水中の微量金属元素の濃度は春季に増加した。(4) 降水中の希土類元素には，人為起源も無視できないものの，海洋起源の他，地殻起源によるところが大きいと考えられる。