Hydrogen and oxygen isotopic characteristics of precipitation in coastal areas of Japan determined by observations for 23 years at Akita and for 1–2 years at other several localities

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The hydrogen and oxygen isotopic characteristics of precipitation in coastal areas of Japan were explained on the basis of a long period (23 years) observation of hydrogen and oxygen isotopic ratios (δD and δ^{18}O) of precipitation collected monthly at Akita as well as a short period (1 or 2 years) observation at other localities. Coastal precipitation is characterized by a high *d*-value (=δD–8δ^{18}O) in winter and a low *d*-value in spring to fall, and the *d*-value of annual mean precipitation depends on the mixing ratio of these two types and is generally higher (15–18) on the Japan Sea side and lower (11–12) on the Pacific Ocean side. The average values of δD and δ^{18}O of monthly precipitation in winter are in ranges of –50 to –30‰ in δD and –9.0 to –6.5‰ in δ^{18}O from northern Honshu to southern Kyushu, and the values in spring to fall are in the ranges of –55 to –45‰ in δD and –8.0 to –7.0‰ in δ^{18}O. These variations seem to be mainly due to differences in sea surface temperature of the Japan Sea or Pacific Ocean where source vapor of precipitation is supplied. The values of δD and δ^{18}O of annual mean precipitation are in the ranges of –55 to –40‰ and –8.6 to –6.7‰, respectively, between northern Honshu to southern Kyushu. The slopes of the δD and δ^{18}O relationship are almost the same in winter and spring to fall and are close to 8 of Craig's meteoric line. This suggests that δD and δ^{18}O in these two seasons are controlled by the same isotopic fractionation processes in source vapor supply except for the kinetic effect and in cloud forming processes. Therefore, if the kinetic effect is eliminated, δD and δ^{18}O show similar seasonal variation patterns.

Keywords: Japanese meteoric water, precipitation, hydrogen isotopic ratio, oxygen isotopic ratio, *d*-value

INTRODUCTION

Hydrogen and oxygen isotopic ratios of meteoric water such as precipitation, ground water and river water are used in meteorological and hydrological studies. These isotopic ratios are also useful in studies on geothermal water, ore-forming fluid, and water related to water-rock interaction, and isotopic ratios of meteoric water in the study area, or so-called local meteoric water, must be known in such studies. Since ground water, river water and other meteoric water originate from precipitation, the hydrogen and oxygen isotopic characteristics of precipitation are important to understand the isotopic characteristics of meteoric water. The hydrogen and oxygen isotopic ratios of such meteoric water have been extensively studied since the beginning of the 1960's with some review papers (e.g., Gat, 1980; Fontes, 1980; Jouzel, 1986; Gat *et al*., 2001). In early period of those studies, one of the important characteristics of meteoric water was found

by Craig (1961), that is, variations in the hydrogen and oxygen isotopic ratios of meteoric water are correlated, and their relationship is described as

$$\delta D = 8\delta^{18}O + 10. \qquad (1)$$

Dansgaard (1964) found another important characteristics of meteoric water, that is, the hydrogen and oxygen isotopic ratios of meteoric water both correlate to annual mean air temperature. Dansgaard (1964) also investigated processes regulating the isotopic ratios of precipitation and reported that variations in the isotopic ratios of precipitation are caused by isotopic fractionation occurring in source vapor supplying and cloud forming processes and that their global features are caused by succession of those isotopic fractionations from low to high latitudes. Jouzel *et al*. (1987) explained such a global distribution of the isotopic ratios of precipitation by results obtained by computer simulation based on an atmospheric general circulation model, and such of computer simulation has since been applied to explain various problems about isotopic ratios of precipitation (e.g., Yoshimura, 2009). Regarding hydrological problems, many studies have been carried out to explain the origin of ground water, runoff

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processes, penetration of precipitation, and characteristics of soil water (e.g., Kendall and McDonnell, 1998). A relatively large number of studies have also been carried out in Japan, though most of those studies were limited to local problems. Waseda and Nakai (1983) studied meteoric water in a relatively large area of central Honshu. Mizota and Kusakabe (1994) reported the spatial distribution of isotopic ratios of surface water and shallow ground water in all of Japan. Regarding precipitation, results of observations over one year were reported by Agata *et al.* (2006) for Ishigaki Island and by Nakamura *et al.* (2008) for Kofu. The International Atomic Energy Agency (IAEA) continuously monitored isotopic ratios of precipitation collected monthly at Tokyo from 1961 to 1979 and has continuously monitored the ratios of precipitation collected at Ryori up to the present time with intermittence from 1986–1997 (IAEA, 2009).

Despite of many studies on isotopic characteristics of meteoric water, those studies have not yet been sufficient to understand the isotopic characteristics of meteoric water in some limited areas. The aim of this study, therefore, is to clarify the characteristics of precipitation in a coastal area of Japan based on results of limited observations and to determine possible processes causing common characteristics revealed by those observations.

METHODS

To clarify the hydrogen and oxygen isotopic characteristics of precipitation in coastal areas, precipitation was collected monthly at Akita for a long period from 1982 to 2004. An attempt was made to estimate the isotopic characteristics of precipitation in the whole coastal area of Japan by means of comparison of the results of long-term observations at Akita and the results of short-term (1–2 years) observations at several other localities. The localities of short-term observations were chosen as follows, taking into account contrast with Akita located on the coast of the Japan Sea in northern Honshu: Misasa, on the coast of the Japan Sea in south-western Honshu; Shirahama, on the coast of the Pacific Ocean in south-western Honshu; Ibusuki, at the southern end of Kyushu; and Satsuma-Iwojima, a small island south of Kyushu. Information for a locality on the coast of the Pacific Ocean in northern Honshu was obtained from results of observations at Ryori by IAEA (2009). These 6 localities of observation are shown in Fig. 1.

Monthly precipitation was collected by the following methods. Rain water was collected with a polyethylene funnel (20 cmø) of which the outlet was extended by flexible tubing to the bottom of a reservoir tank (20 l) equipped with a vent (0.2 cmø, *ca.* 6 cm in length). These devices minimized exposure of the water surface to outside air. In the case of snow, snow that accumulated in a

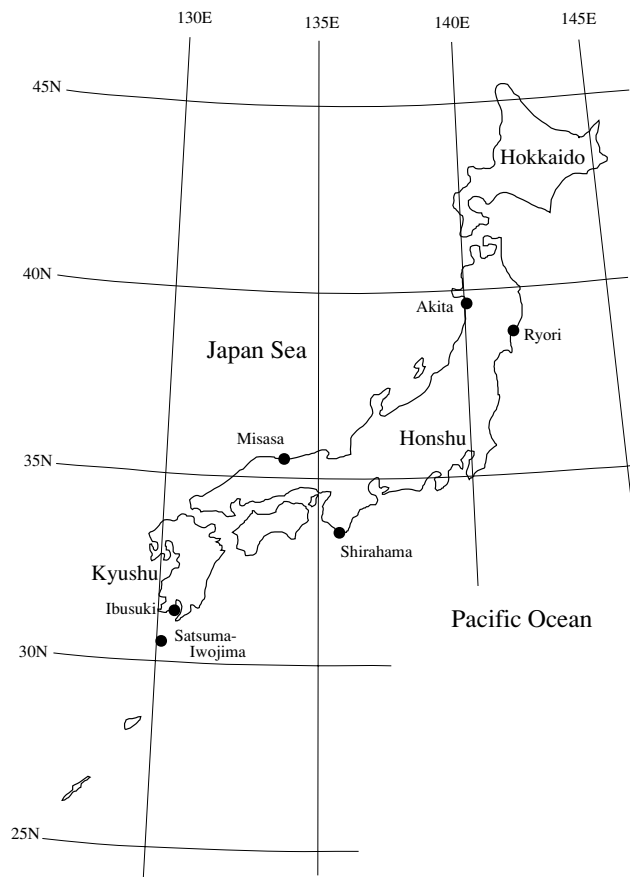*Fig. 1. Map of Japan island, showing the localities of precipitation observation.*

stainless steel can (20 cmø) was collected twice in one day, in morning and evening, and melted in a sealed bottle.

The hydrogen and oxygen isotopic ratios were analyzed by mass spectrometry with gas sample preparation by uranium or zinc reduction for hydrogen isotopes and by CO_2–H_2O equilibration for oxygen isotopes at the Institute for Thermal Spring Research, Okayama University and at the Research Institute of Underground Resources, Mining College, Akita University (currently the Center for Geo-Environment Science, Faculty of Engineering and Resource Science). The results are presented as δD and $\delta^{18}O$ values relative to the SMOW standard. The reproducibilities of repeat analyses were ±1‰ for δD and ±0.1‰ for $\delta^{18}O$ as standard deviations, and the measurement of a sample was mostly a single measurement. The measurements in these two laboratories were consistent. Annual mean air temperature and sea surface temperature are cited from the Rika Nenpyo (Chronological Scientific Table, National Astronomical Observatory, 2009).
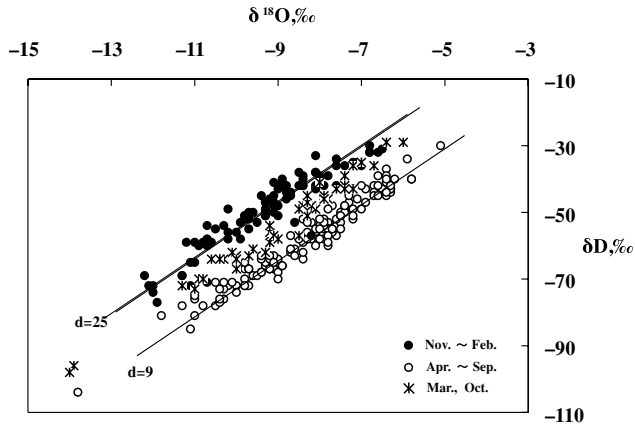
Fig. 2. δD and δ¹⁸O relationship of precipitation collected monthly at Akita from 1982 to 2004. Two linear lines are slope 8 lines fitted to the measured relationship from November to February and from April to September, respectively. The d stands for δD–8δ¹⁸O.

RESULTS AND DISCUSSION

Annual variations in δD and δ¹⁸O of precipitation at Akita

δD and δ^{18}O values of precipitation collected monthly at Akita are shown in Fig. 2 and also in Supplementary Table S1. The values of δD and δ^{18}O show large fluctuations in the ranges of -30 to $-85‰$ and -6 to $-12‰$, respectively, and the fluctuations are rather uniform in these ranges. Also, a linear relationship is observed between δD and δ^{18}O, of which the slope is about 8. The linear relationship with a slope of 8 shown by Eq. (1) can be approximately explained by a simplified model of the isotopic fractionation in the precipitation forming process (e.g., Dansgaard, 1964; Miyake *et al.*, 1968). When an air mass containing water vapor is cooled and the vapor is condensed (cloud droplet, liquid or solid), isotopic fractionation occurs between the condensed water and the residual vapor. If such a cooling of air mass progresses with immediate removal of the condensed water as precipitation, the variation in isotopic ratio of the residual vapor is expressed by the Rayleigh distillation equation (e.g., Matsubaya and Matsuo, 1982) as follows:

$$\ln \frac{R}{R_0} = (\alpha - 1)\ln F, \qquad (2)$$

where R, α and F stand for the isotopic ratio (D/H or ^{18}O/^{16}O), the fractionation factor, and the residual rate of vapor, respectively, and the suffix $_0$ means the initial value. The fractionation factor means the ratio of the isotopic ratio (D/H or ^{18}O/^{16}O) between water (or ice) and vapor. Although the fractionation factor changes with change in temperature, it is assumed to be constant in Eq. (2). If the

δ value (δD or δ^{18}O) is approximately substituted for the term of $\ln R/R_0$ and if $(\alpha - 1) \times 10^3$ is expressed by Δ, Eq. (2) is written as

$$\delta = \Delta \ln F + \delta_0 \qquad (3)$$

and the isotopic ratio of newly formed condensate (δ_c) is expressed as

$$\delta_c = \Delta \ln F + \delta_0 + \Delta. \qquad (4)$$

From two equations of Eq. (4) for hydrogen and oxygen isotopic ratios, then relationship between δD and δ^{18}O of the newly formed condensate is expressed as

$$\delta D = \frac{\Delta(H)}{\Delta(O)} \delta^{18}O + \delta D_0 - \frac{\Delta(H)}{\Delta(O)} \delta^{18}O_0. \qquad (5)$$

The meaning of this linear relationship may be basically the same as the meaning of Eq. (1). However, the slope of the relationship, or $\Delta(H)/\Delta(O)$, changes with change in temperature; for instance, it is 8.6, 9.1 and 9.5 at 20, 10 and 0°C, respectively, and it is 8 at about 35°C (Horita and Wesolowski, 1994). Moreover, the model of a constant fractionation factor in not rational because the condensation of vapor is caused by lowering of air mass temperature.

The constant term of 10 in Eq. (1) corresponds to the difference between δD_0 and $\Delta(H)/\Delta(O) \, \delta^{18}O_0$ in Eq. (5). If δD_0 and $\delta^{18}O_0$ are both in equilibrium with water of which δD and δ^{18}O are 0‰, which is close to most of the sea water, this constant term is zero. Even though the source vapor evaporates from water of which δD and δ^{18}O are 0‰, if the isotopic fractionation in the evaporation includes a non-equilibrium effect (kinetic effect), the constant term is not zero. If the slope of Eq. (5) is fixed at 8 according to Craig's global equation, Eq. (1), the constant term is expressed as follows and is called *d*-value or *d*-excess value:

$$d = \delta D - 8\delta^{18}O. \qquad (6)$$

In evaporation under dry condition, kinetic isotopic fractionation caused by water molecule transportation in air is added to equilibrium fractionation in evaporation and the fractionation degree is expressed as

$$\Delta = \Delta_e + \Delta_k, \qquad (7)$$

where Δ_e stands for the equilibrium fractionation and Δ_k stands for kinetic fractionation (Craig and Gordon, 1965). In such a case, the kinetic effect influences the oxygen isotopic ratio more efficiently than the hydrogen isotopic

ratio because the kinetic effect depends on the mass difference between $H_2^{18}O$ (20) or $HD^{16}O$ (19) and $H_2^{16}O$ (18) and the effect for hydrogen isotopes is half of the effect for oxygen isotopes, while the equilibrium effect for hydrogen isotopes is about 8-times larger than that for oxygen isotopes. Therefore, δD_0 and $\delta^{18}O_0$ are shifted in a decreasing direction in both δD and $\delta^{18}O$ from the equilibrium values on the δD vs. $\delta^{18}O$ plot, and the shift of $\delta^{18}O$ is 2-times larger than the shift of δD. Consequently, the linear relationship of slope 8 passing on the shifted δD_0 and $\delta^{18}O_0$ has a positive d-value, and the d-value is in proportion to Δ_k. In the case of $d = 10$, Δ_k is 1.3‰ in $\delta^{18}O$ and about 15% of the equilibrium fractionation (8–9‰). In an actual case, however, air contains a significant amount of vapor, and δD and $\delta^{18}O$ of vapor evaporating are affected by both the isotopic ratios and the amount of vapor (humidity) in the air.

As mentioned above, Craig's global relationship (Eq. (1)) may be able to be roughly explained on the basis of a simplified model of isotopic fractionation in evaporation and condensation through the precipitation formation process. However, the slope of 8 and the d-value of 10 have not yet been correctly explained, and some modification of the Rayleigh distillation model is required for application to an actual precipitation forming process. Nevertheless, as shown in Fig. 2, δD and $\delta^{18}O$ of precipitation collected monthly at Akita show a good linear relationship of slope 8 in a wide range and also show an obvious difference in the d-value between winter and spring to fall. Therefore, the following discussions are based on the assumption that the variation in δD and $\delta^{18}O$ along the slope 8 line is caused by difference in the progress of Rayleigh-type fractionation (Eq. (2) or Eq. (4)) in the precipitation formation process and also by the difference with temperature in the equilibrium fractionation (Δ_e in Eq. (7)) in source vapor evaporation and the assumption that the difference in the d-value is caused by difference in the kinetic effect in source vapor evaporation (Δ_k in Eq. (7)).

In Fig. 2, if the difference in season is taken note of, precipitation from November to February is plotted in the upper range of the figure, while that from April to September is plotted in the lower range, and that in March and October is plotted between the ranges of these two seasons. If the slope of these two linear relationships are fixed at 8, which is the same as the slope of Craig's global relationship (Eq. (1)), the relationship from Nov. to Feb. is expressed as

$$\delta D = 8\delta^{18}O + 25 \qquad (8)$$

and that from Apr. to Sep. is expressed as
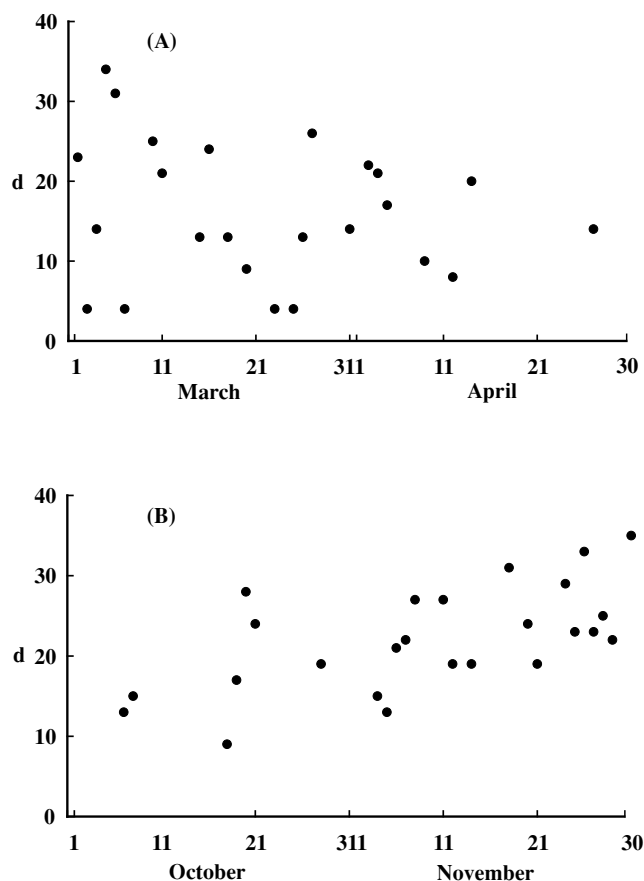
$$\delta D = 8\delta^{18}O + 9. \qquad (9)$$

Fig. 3. Variations in the d-values of every precipitation from March to April (A) and from October to November (B), 1987, at Akita.

Precipitation in Nov. to Feb. and that in Apr. to Sep. are hereafter called winter-type precipitation and summer-type precipitation, respectively. The intermediate relationship between δD and $\delta^{18}O$ in Mar. and Oct. is due to mixing of the winter-type precipitation and summer-type precipitation. March and October are transitional periods from one season to another, and precipitation with low d-values and that with high d-values both occur, an example in 1987 being shown in Fig. 3. Therefore, March and October can be rationally excluded from the discussion about contribution of winter-type precipitation and summer-type precipitation to annual mean precipitation. The difference between d-values of winter-type precipitation and summer-type precipitation is due to the difference in evaporation condition of the source vapor. In winter, cold and dry air mass blowing out from the Eurasian continent is supplied with vapor and heat from the Japan Sea, and convective cloud occurs. The winter-type precipitation is mostly from such convective cloud. On the other hand, the summer-type precipitation is mostly from stratiform cloud formed by an ascending air mass in which
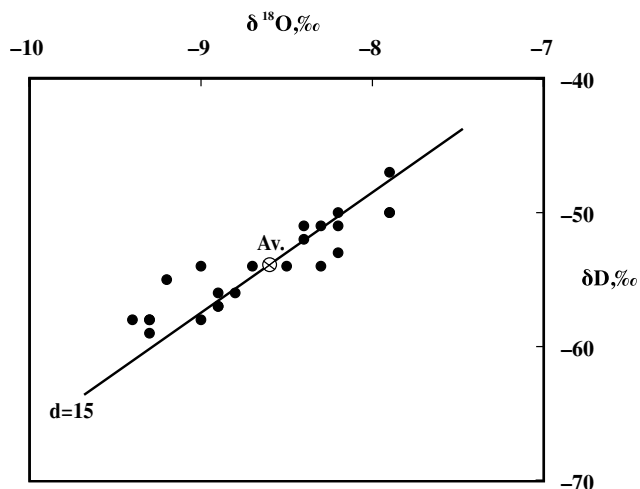
Fig. 4. δD and $\delta^{18}O$ relationship of annual mean precipitation at Akita from 1982 to 2004. Av shows the average.
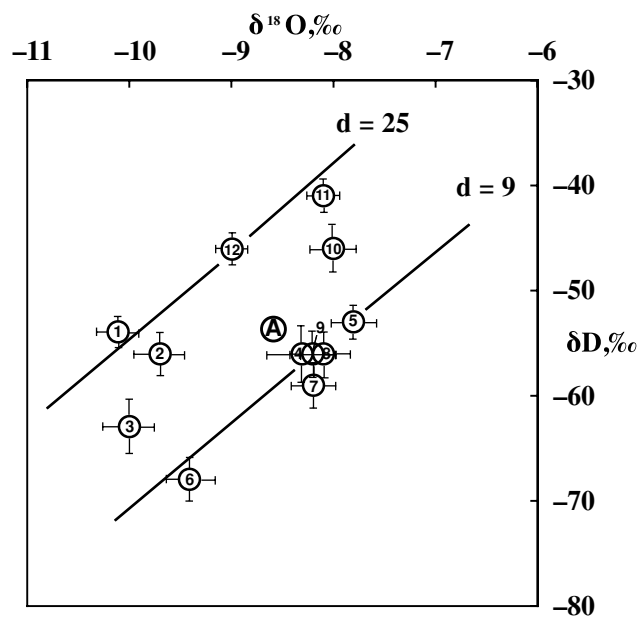

Fig. 5. δD and $\delta^{18}O$ relationship of each month precipitation averaged during 1982 and 2004 at Akita. The numbers in circles stand for months. A is the average of 12 months. Error bars show 95% confidence intervals.

vapor is supplied from the Pacific Ocean. Therefore, in the case of winter-type precipitation, the source vapor evaporates under a dry condition and suffers a greater kinetic evaporation effect, while in the case of summer-type precipitation, the source vapor evaporates under a rather humid condition and suffers less kinetic evaporation effect.

Annual mean values of individual years were obtained as average of each monthly value weighted with amount of precipitation in each month, as shown in Fig. 4. The annual mean values of individual years show relatively even fluctuations in ranges from –47 to –59‰ in δD and –7.9 to –9.4‰ in $\delta^{18}O$, and they do not correlate with the annual precipitation amounts, which vary in the range of 1630 to 2720 mm in the observation period, or with the annual mean air temperature in the range of 10.6–12.7°C (Japan Meteorological Agency, 2012). Also, no systematic trend of temporal variation was observed throughout the observation period. Averages of these annual mean values are –54‰ in δD and –8.6‰ in $\delta^{18}O$ as shown by the symbol Av. The d-value of this average value is 15, which is rather close to the value of summer-type precipitation of 9. This is due to the difference between the amounts of winter-type precipitation and summer-type precipitation, i.e., the former is 58% of the latter. The fluctuation of annual mean values is due to variation in the contribution of winter-type precipitation and summer-type precipitation among the years and also unusual precipitation amount and/or isotopic ratios in some months. For instance, the highest d-value of 19 ($\delta D = -55‰$, $\delta^{18}O = -9.2‰$) in 1996 is due to rather even contributions of winter-type and summer-type precipitation, i.e., the former is 92% of the latter, and also unusual low δD (–62‰) and $\delta^{18}O$ (–9.1‰) of summer-type precipitation,

which consequently reduce the annual mean value. The lowest d-value of 12 ($\delta D = -54‰$, $\delta^{18}O = -8.3‰$) in 1990 is due to the small contribution of winter-type precipitation being only 47% of summer-type precipitation, while δD and $\delta^{18}O$ of the annual mean are rather close to the average (Av) because of usual δD and $\delta^{18}O$ values of summer-type pracipitation.

Seasonal variation in δD and $\delta^{18}O$ of precipitation at Akita

The average values of each month throughout the observation period are shown in Fig. 5. The months from spring to fall except for June have similar values of δD and $\delta^{18}O$, while June has a value lower by about 10‰ in δD and 1‰ in $\delta^{18}O$ than those in the other 5 months. In winter, on the other hand, δD and $\delta^{18}O$ decrease greatly from November to January. A similar difference is also observed between October and March. These average values of monthly precipitation are averages of individual year values, which fluctuate greatly. Therefore, standard deviations of these average values are relatively large, i.e., 7 to 14‰ in δD and 0.9 to 1.7‰ in $\delta^{18}O$. These large fluctuations are due to such a character of monthly precipitation that the monthly precipitation is accumulation of every precipitation in the month, and that δD and $\delta^{18}O$ as well as amount of the each precipitation in the month are various. In Fig. 6, an example of such variety is shown for every precipitation in Nov. 1987, of which d-values
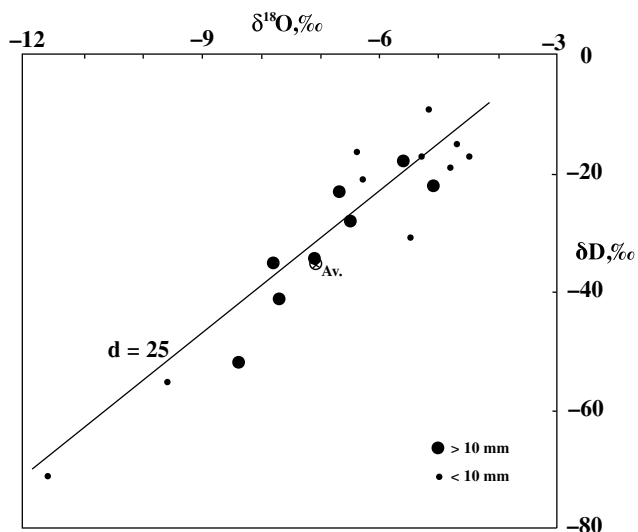
Fig. 6. Variation in δD and δ¹⁸O of every precipitation in November, 1987, of which the d-values are shown in Fig. 3(B). Large and small circles stand for precipitation more than 10 mm and less than 10 mm, respectively. Av stands for the average weighted by precipitation amount, and is the same as the value of monthly precipitation.

are shown in Fig. 3. In this month, there were 18 precipitations and the total amount of precipitation was 220 mm. The average values of δD and $\delta^{18}O$, i.e., the monthly values, are –35‰ in δD and –7.1‰ in $\delta^{18}O$, and they are different from the average values throughout the observation period, –41‰ in δD and –8.1‰ in $\delta^{18}O$ as shown in Fig. 5. The reason for this difference is as follows. Eight of the 18 precipitations were large precipitations of which the amount was more than 10 mm, and the total amount of the 8 precipitations was about 80% of the monthly precipitation. Therefore, the isotopic ratios of monthly precipitation are mostly determined by the isotopic ratios and the amounts of the 8 precipitations. As this example shows, the isotopic ratios of monthly precipitation depend mostly on the isotopic ratios of large amount precipitations in the month, and the isotopic ratios and the amount and number of precipitations vary among each years. This causes a relatively large difference in the isotopic ratios of monthly precipitations. Also, δD and $\delta^{18}O$ of individual precipitation usually vary with time in various manner, as an example is shown in Fig. 7. This precipitation occurred in July 1985, and total precipitation amount, δD and $\delta^{18}O$ were 85 mm, –82‰, and –11.2‰, respectively. This precipitation amount is one third of the total precipitation in July 1985 (260 mm), and δD and $\delta^{18}O$ are lower by 15‰ and 2.0‰, respectively, than the monthly average value (Table S1). This kind variety of individual precipitation causes variation
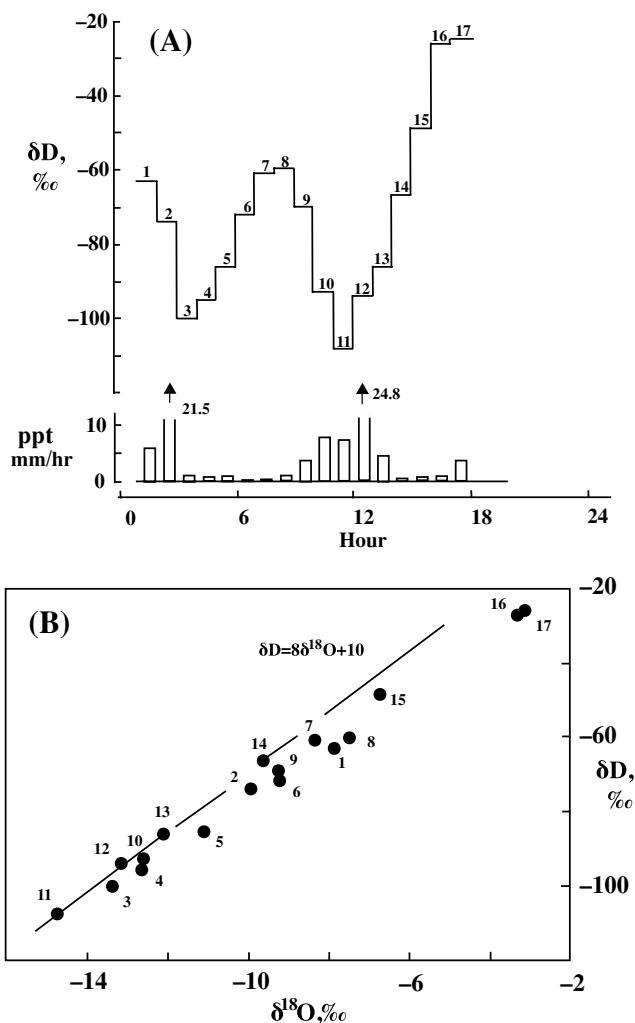

Fig. 7. Time variation in δD and intensity (A) and δD vs. δ¹⁸O relationship (B) of a series of precipitation for 18 hours, in Jul. 11, 1985 at Akita, of which amount is 85 mm.

in monthly values as shown in Fig. 6. Nevertheless, the values shown in Fig. 5 are averages for the 23-year observation period, and the differences among months are available to explain the characteristics of seasonal variation. If the confidence of these average values is expressed by the 95% confidence interval, it is 0.36 times the standard deviation.

On the basis of the average δD and $\delta^{18}O$ values of each month in Fig. 5, variation patterns with season (month) are also represented as shown in Fig. 8. An obvious difference is observed between the two patterns of δD and $\delta^{18}O$ during the period from October to March. As shown in Figs. 2 and 5, a difference between winter and summer-types is observed only in the d-values, and no difference is observed in slopes, both of which are 8. Therefore, the difference between the two patterns of δD
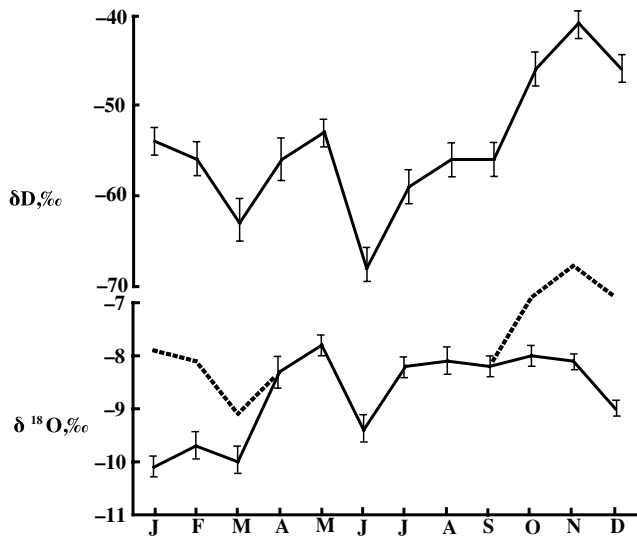
Fig. 8. Seasonal variations in δD and δ¹⁸O of precipitation collected monthly at Akita which correspond to the values shown in Fig. 5. Error bars show 95% confidence intervals. The broken line shows the values corrected for the difference in the d-value between the winter-type and the summer-type precipitation (see the text).

Fig. 9. δD vs. δ¹⁸O relationship of daily heavy snow in January and February, in 1975 to 1977, at Misasa.

and $\delta^{18}O$ in Fig. 8 is thought to be caused by the difference in d-values. Actually, if the extent of $\delta^{18}O$ corresponding to the difference in d-values is eliminated from $\delta^{18}O$ values from October to March by addition of δ_{ex} obtained by the following equation, i.e., conversion of the d-value difference between the d-value (di) of individual months and 9 of the average values of summer-type into the difference of $\delta^{18}O$,

$$\delta_{ex} = (di - 9)/8, \qquad (10)$$

the modified $\delta^{18}O$ pattern is quite similar to the δD pattern, as shown by the broken line in Fig. 8. Because of the same slopes in winter and summer-types in Fig. 5 or the similar seasonal variation patterns of δD and $\delta^{18}O$ (Fig. 8), the seasonal variation in δD and in modified $\delta^{18}O$ is caused by the same isotopic fractionation in precipitation forming processes, and one of δD and $\delta^{18}O$ is enough to discuss the processes regulating the seasonal variation of the isotopic ratios, except for the kinetic effect in source vapor evaporation. In such a case, δD is adequate because the contribution of the kinetic effect in evaporation is much smaller in δD than in $\delta^{18}O$ as mentioned above about Eq. (7).

In the 6 months of summer-type, only June has lower δD. June and July are rainy season, "Baiu" in Japanese, and most of precipitations are caused by stratiform clouds ascending from the south-east to north-west on a discon-
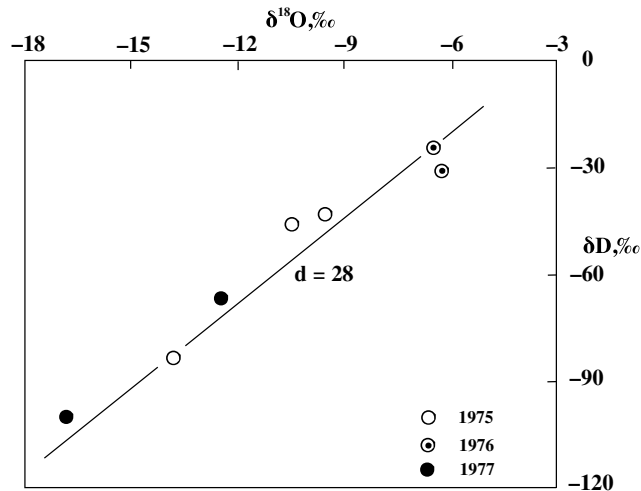
tinuous plain between a lower cold air mass and an upper warm air mass, or frontal surface. The front of the discontinuous plain is generally situated in the south part of Honshu, *ca.* 30°N in May, and then gradually goes north and disappears slightly north of Akita, *ca.* 40°N in late July or early August. In the case of precipitation from stratiform clouds, vapor condensation progresses continuously from low to high altitudes according with the ascending of air mass on the discontinuous plain, and if cloud droplets fall as precipitation soon after condensation, the precipitation at a lower position of the stratiform cloud has higher isotopic ratios, as expressed by the Rayleigh-type fractionation. Therefore, the precipitation near the front has higher δD, while it has lower δD far from the front (Dansgaard, 1964; Miyake *et al.*, 1968). The difference between June and July is thought to be due to the difference in average distance from the front, which means June has more contribution of precipitation far from the front, while July has that near the front.

In winter, the δD values in the latter half of the season (Jan.–Mar.) are significantly lower (*ca.* 15‰ in δD and 2‰ in $\delta^{18}O$) than those in the first half (Oct.–Dec.). At the Japan Sea side in winter, most of the precipitation is caused by convective clouds formed near the Japan Sea coast. In such a case, in general, the precipitation forming process progresses vertically from the lower to upper parts of the cloud with isotopic fractionation, which is basically the same as the Rayleigh-type fractionation. This kind of convective cloud causes showers ("Shigure" in Japanese) during movement from the coast to inland. The difference between the first and second halves may be caused by two factors: one is the difference in the sea surface temperature at which the source vapor evaporates,
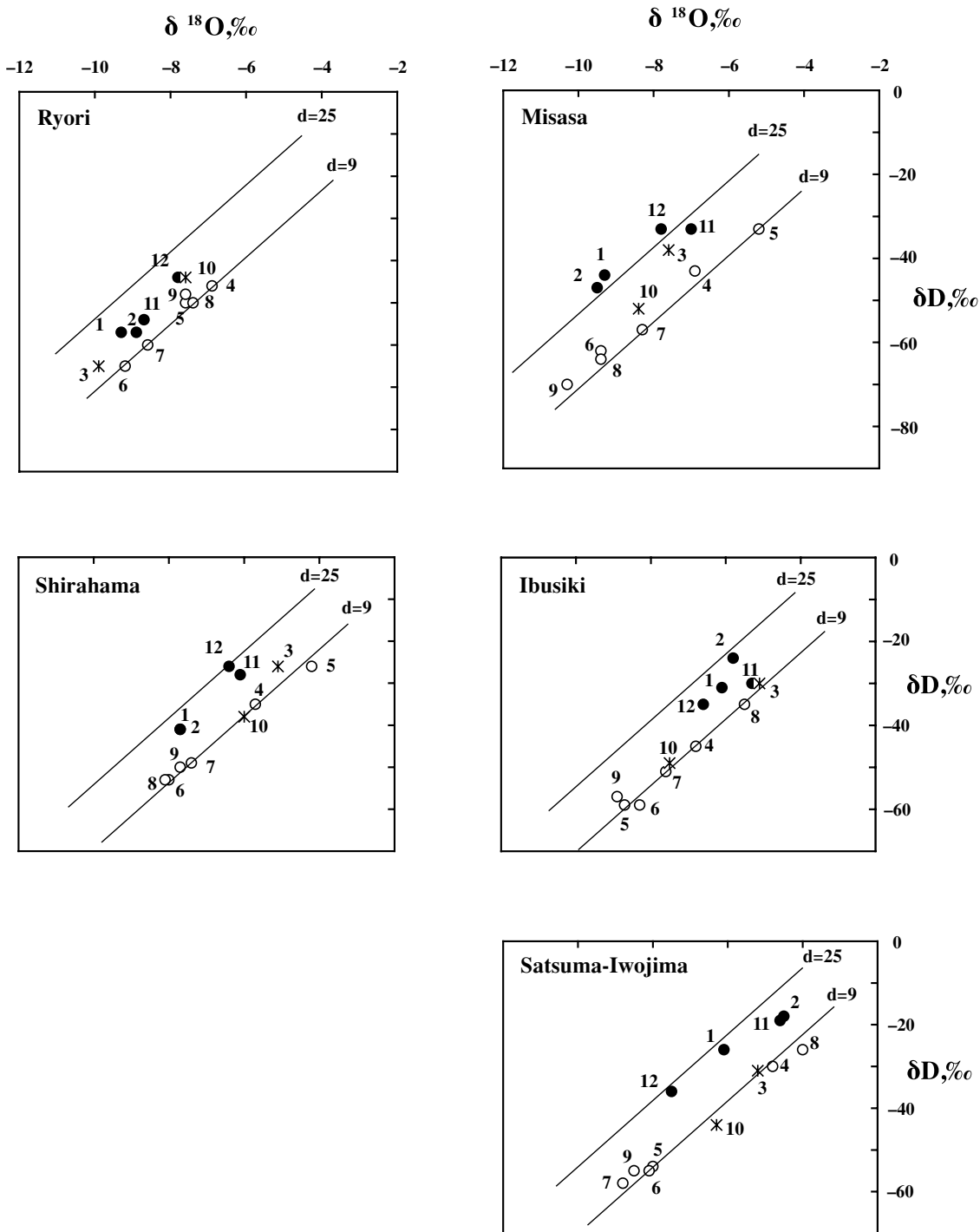
Fig. 10.   δD and δ^{18}O relationships of precipitation collected monthly at Ryori, Misasa, Shirahama, Ibushuki and Satsuma-Iwojima.

and the other is the difference in the progress of Rayleigh-type fractionation (difference of F in Eq. (4)). Regarding the difference in evaporation temperature, if the evaporation temperature is lower, δD of the source vapor decreases. However, the difference in equilibrium fractionation at 0 and 10°C is 13‰ (Horita and Wesolowski, 1994), and the difference in sea surface temperature in the Japan Sea offshore from Akita may be not sufficient to fully explain the difference between δD in the first half and that in the second half.

Locality	Annual mean			Winter-type			Summer-type			ppt-w/ppt-s	Observation period
	δD	$\delta^{18}O$	d	δD	$\delta^{18}O$	d	δD	$\delta^{18}O$	d	(%)	
Akita	−54	−8.6	15	−49	−9.2	25	−58	−8.3	9	58	1982–2004
Ryori	−54	−8.1	11	−53	−8.7	17	−53	−7.9	10	22	1979–1985, 1998–2005
Misasa	−51	−8.6	18	−39	−8.4	28	−55	−8.3	11	65	1975–1977
Shirahama	−45	−7.1	12	−34	−7.0	22	−44	−6.9	11	19	1973–1975
Ibusuki	−42	−6.8	12	−30	−6.0	18	−51	−7.6	10	59	1974–1975
Satsuma-Iwojima	−40	−6.7	14	−25	−5.7	21	−46	−7.0	10	55	1974–1975

Regarding the difference in the progress of Rayleigh-type fractionation, even in the case of vertical progress of isotopic fractionation in a convective cloud, large variation in δD as well as $\delta^{18}O$ is observed at the ground, for instance, several ‰ change in $\delta^{18}O$ of precipitation from the beginning to the end of a shower (Miyake *et al.*, 1968; Sugimoto and Higuchi, 1989) or significant decreases in δD (10–30‰) and $\delta^{18}O$ (2–3‰) of precipitation from a single air mass during movement inland of about 8 km (Sugimoto *et al.*, 1988). As another example, Fig. 9 shows large amounts of daily precipitation (snow) in January and February, 1975–1977 at Misasa. δD and $\delta^{18}O$ of these precipitations vary in wide ranges of −24 to −100‰ and −6.3 to −16.9‰, respectively. The d-values are in the range of 19 to 38, and no correlation is found between d-value and isotopic ratios. These large variations in isotopic ratios may be caused by several processes such as precipitation particle growth by cloud droplet capture at different stages of Rayleigh-type fractionation (different values of F in Eq. (4)), separation of precipitation particles from the convective cloud at different positions (heights) of the cloud, and difference in falling speed of precipitation particles depending on particle size. In a convective cloud or an air mass, if a small convective cell occurs locally and disappears after a certain amount of precipitation falling, repetition of such a process may lower the isotopic ratios of vapor in the convective cloud with time, and consequently the isotopic ratios of precipitation decrease with time. The difference in the effects of these processes may cause the difference of δD between the first and second halves.

δD and $\delta^{18}O$ characteristics of precipitation in coastal areas of Japan estimated from characteristics at Akita

At the 5 localities in this study, δD and $\delta^{18}O$ of precipitation collected monthly show two relationships similar to those of the winter-type and summer-type precipitations at Akita, as shown in Fig. 10 and in Table S1. Also, seasonal variation patterns at the 5 localities
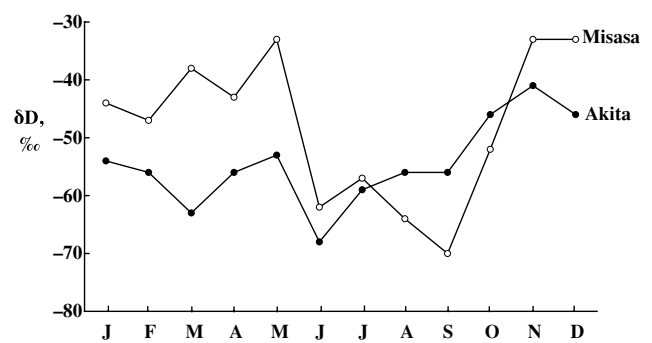

Fig. 11. Comparison of seasonal variation in δD of precipitation collected monthly between Misasa and Akita.

are similar to that at Akita. As an example, comparison between Akita and Misasa is shown in Fig. 11. The patterns in Misasa and Akita are similar, though an obvious difference is observed in August and September. This difference may be due to a fluctuation accidentally occurring in the observation year rather than to a particular characteristic at Misasa, because the lower δD values of −64‰ in Aug. and −70‰ in Sep. are actually averages of −76‰ and −51‰ in Aug. and −74‰ and −66‰ in Sep., respectively, in the two-year observation at Misasa. Therefore, it is rationally inferred that the isotopic characteristics of precipitation in a coastal area of Japan are basically regulated by processes similar to those at Akita. Several interesting characteristics can be deduced from comparison of the δD values and d-values of the annual mean, winter-type and summer-type precipitations at Akita to those of the other 5 localities, which are shown in Table 1.

Regarding the winter-type precipitation at the Japan Sea side, Misasa shows differences in δD and $\delta^{18}O$ between the first and second halves that are similar to those at Akita, while δD is 10‰ higher and the d-value higher by 3 than those at Akita. It may be possible to explain

these differences by difference in sea surface temperature at which the source vapor evaporates. The sea surface temperature off the shore of Misasa is about 5–10°C in winter, while it is about 0–5°C off the shore of Akita. This difference of 5°C corresponds to about 7‰ in δD of source vapor equilibrating with sea water. Also, if the sea surface temperature is higher, it yields a drier condition and consequently a greater kinetic effect, causing a higher d-value. At the Pacific Ocean side, the difference between Ryori and Shirahama is much greater than that between Akita and Misasa. The d-values are 17 and 22 at Ryori and Shirahama, respectively, and higher than those of the summer-type precipitation. The winter is generally dry season on the Pacific Ocean side, and it is unusual for a convective cloud occurring on the Japan Sea to cause precipitation as on the Japan Sea side. Therefore, these higher d-values may be due to such possible cases that the evaporation of source vapor from the Pacific Ocean includes a greater kinetic effect than the evaporation in summer, that the source vapor includes vapor coming over the central mountainous area from the Japan Sea side, or other cases. Although it is not clear at present which of these possibilities are facts, winter-type precipitation is about 20% of summer-type precipitation, and the annual mean values are mostly the same as the summer-type precipitation. In the southern part of Japan, or Ibusuki and Satsuma-Iwojima, the δD values are higher than those at Misasa and Akita, while the d-values are lower. Contributions of winter-type are almost the same as those on the Japan Sea side. The higher δD is certainly due to higher sea surface temperature in the East China Sea (15–20°C) at which the source vapor evaporates and possibly due to the higher temperature of an air mass blowing out from the Eurasian continent resulting in less kinetic effect in the source vapor evaporation.

Regarding the summer-type precipitation, the d-values of the 6 localities are almost the same, suggesting that the evaporation processes of source vapor are similar. The seasonal variation pattern at Ryori is similar to the pattern at Akita (Fig. 10), while the patterns at Misasa as well as the other 3 locations are different from the pattern at Akita. These differences may be mainly due to the difference in distance from the Baiu-zensen (front) during May to July at each localities and also the difference in the contribution of precipitation by typhoons. The δD values are 5–11‰ lower on the Japan Sea side than on the Pacific Ocean side both in northern Honshu (Akita and Ryori) and in south-western Honshu (Misasa and Shirahama). This difference seems due to the difference in progress of Rayleigh-type fractionation when an air mass is ascending on a discontinuous plain. Such an ascent of an air mass occurs mostly in the south-east to north-west direction in northern Honshu and in the south to north direction in south-western Honshu. Therefore,

in both cases from Ryori to Akita and from Shirahama to Misasa, the Pacific Ocean side has a greater contribution of precipitation near the front, of which δD is higher, while the Japan Sea side has a greater contribution of precipitation far from the front, of which δD is lower.

Differences of 2–9‰ in δD of summer-type precipitation were observed on the Pacific Ocean side among Ryori, Shirahama, Ibusuki and Satsuma-Iwojima. These difference may be attributed to difference in evaporation temperature of source vapor from the Pacific Ocean. However, δD at Shirahama was the highest, suggesting the contribution of some other factor, for instance, different formation process of precipitation.

Regarding the annual mean, isotopic ratios are determined by the combination of winter-type and summer-type values as well as March and October values. Therefore, the d-value is higher on the Japan Sea side owing to a greater contribution of winter-type precipitation, while it is lower on the Pacific Ocean side owing to less contribution of winter-type precipitation. The difference between δD in northern Honshu (ca. 40°N) and that in the southern part of Honshu and Kyushu (ca. 30°N) is 12–14‰. In individual areas in Japan, however, the annual mean seems to depend on the contribution ratio of winter-type precipitation and summer-type precipitation. For instance, the annual mean value at Akita (–54‰) is a combination of about 40% winter-type precipitation (–49‰) and about 60% summer-type precipitation (–58‰), while the annual mean at Shirahama (–45‰) is a combination of about 20% winter-type precipitation (–34‰) and about 80% summer-type precipitation (–44‰). Based on weather statistical information provided by the Japan Meteorological Agency (National Astronomical Observatory, 2009), the amount ratio of these two types varies greatly. On the Japan Sea side, the ratio is higher in central Honshu than at Akita (0.58) or Misasa (0.65), e.g., 0.88 at Niigata and 0.89 at Kanazawa, and becomes smaller in the west direction, e.g., 0.39 at Hamada and 0.24 at Fukuoka, while it becomes larger in northern Honshu, e.g., 0.94 at Aomori, and in Hokkaido, e.g., 0.84 at Rumoi. In Kyushu, the ratio is about 0.2 at both the Pacific Ocean and East China Sea coasts. The higher values observed at Ibusuki (0.59) and Satsuma-Iwojima (0.55) in this study may be an unusual case as mentioned about Akita (Fig. 4). At the Pacific Ocean coast of Honshu, the ratios are mostly in the range of 0.2–0.3. At the Okhotsk Sea coast, the ratio is 0.46 at Abashiri. Therefore, in order to explain the isotopic characterstics of precipitation in coastal areas of Japan, a survey at several localities selected from different local climates is needed. In such a survey, 5-year observation may bring an average being close to the average of a much longer observation period, as judged from the results of observation at Akita.

SUMMARY

The hydrogen and oxygen isotopic ratios of annual mean precipitation at Akita vary in the ranges of –47 to –59‰ in δD and –7.9 to –9.4‰ in $\delta^{18}O$, respectively, in observations from 1982 to 2004, and no systematic temporal trend was observed. The precipitation collected monthly was grouped into two types according to the δD vs. $\delta^{18}O$ relationship. One type is precipitation caued by an air mass blowing out from the Eurasian continent in winter that is characterized by a d-value ($\delta D - 8\delta^{18}O$) in the range of 21–29, which is much higher than the value of 10 in Craig's global relationship. The other type is precipitation caused by an air mass from the Pacific Ocean during the period from spring to fall, of which the d-value is in the range of 5–13 and is similar to Craig's global value. This difference in the d-value is due to the difference in the degree of kinetic isotopic fractionation in evaporation of the source vapor of precipitation. On the other hand, the slopes of the δD and $\delta^{18}O$ relationship are almost the same in these two groups. Therefore, if the difference in the kinetic isotopic fractionation is eliminated by normalization to a definite d-value, δD and $\delta^{18}O$ show almost the same patterns of seasonal variation. These facts suggest that δD and $\delta^{18}O$ are controlled by the same isotopic fractionation processes in the equilibrium process of source vapor supply and the cloud forming process, and those processes are able to explain by discussion about one of δD and $\delta^{18}O$. In that case, δD is adequate because the kinetic effect is much smaller in δD than in $\delta^{18}O$.

Comparison of the characteristics mentioned above for Akita with characteristics obtained from observations at the other 5 localities suggests that the isotopic characteristics of coastal precipitation in the whole of Japan are regulated by processes similar to those at Akita. In winter, δD of precipitation on the Japan Sea side varies from –50‰ to –30‰ between northern Honshu and southern Kyushu, and this variation is explained by difference in the sea surface temperature at which source vapor of precipitation evaporates. From spring to fall, on the other hand, only a small difference is observed between northern Honshu and southern Kyushu on the Pacific Ocean side, because of the small difference in sea surface temperature between areas of the Pacific Ocean off the shore of these two areas. However, an obvious difference of 5–10‰ is observed between the Pacific Ocean side and the Japan Sea side. This difference is due to Rayleigh distillation type isotopic fractionation in the precipitation forming process progressing from the Pacific Ocean side to the Japan Sea side.

The annual mean precipitation is a combination of winter precipitation and spring to fall precipitation. The contribution of the former type is larger on the Japan Sea side than on the Pacific Ocean side, and the d-value is therefore higher on the Japan Sea side (15–18) than on the Pacific Ocean side (11–12). δD and $\delta^{18}O$ of the annual mean precipitation vary mostly in the ranges of –55 to –40‰ and –8.6 to –6.7‰, respectively, between northern Honshu and southern Kyushu. However, the mixing ratios of winter precipitation and spring to fall precipitations are vary greatly in individual coastal areas. It is thought that the d-value as well as δD and $\delta^{18}O$ values of annual mean precipitation vary distinctly depending on local climate.

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SUPPLEMENTARY MATERIALS

URL (http://www.terrapub.co.jp/journals/GJ/archives/data/48/MS314.pdf)
Table S1