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Long-range transportation of contaminants from the Asian Continent to The Northern Japan Alps, recorded in snow cover on Mt. Nishi-Hodaka-Dake

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Abstract

Vertical profiles of chemical components in snow cover at Mt. Nishi-Hodaka-dake, the Northern Japan Alps, were obtained over three consecutive winters (2001/02, 2002/03 and 2003/04) for the investigation of long-range transportation of chemical substances from the Asian continent to high mountainous areas in Japan. The δ^{34}S value of non sea-salt (NSS) SO_4^{2-} ions in 2002/03 snow was also measured. Concentrations of anthropogenic components such as NSS-SO_4^{2-} and NO_3^- in snow range from almost 0 to over 100 μeq l^{-1}. Soil derived components (NSS-Ca^{2+} and NSS-Mg^{2+}) were also observed in snow, especially in dirt layers, suggesting the transportation of Asian continental desert dust. The NSS-SO_4^{2-}/NO_3^- (S/N) ratio in snow typically ranges from 0.3 to 6.3. A considerable number of samples had higher S/N ratios than those found in Tokyo, Japan (about 2), while some samples had a much higher ratio (about 4–6), more akin to values found in Beijing, China (about 4). Snowfalls at Mt. Nishi-Hodaka-Dake are considered to include acid contaminants transported from both the Asian continent and the industrial areas of Japan, with a variable proportion depending on weather conditions. High S/N ratios seem to be caused by severe winter pressure patterns. The NSS-δ^{34}S values range from +3‰ to +7‰. These ratios are evidently higher than that afforded by petroleum usage in Japan (−1‰), and is in accord with that of coal used in both northern China (+7.4‰) and the Russian Far East (+3.4‰). These δ^{34}S values also suggest the occurrence of long-range transportation of NSS-SO_4^{2-} from the Asian continent, independent of chemical composition.

1. Introduction

The mountainous area known as the Northern Japan Alps is located in the northern central part of Honshu Island, Japan. In this area, heavy snowfalls frequently occur during the winter season, and this remains as snow cover until the spring. This is possible because the air temperature in this high mountainous area stays well below 0℃ throughout the entire winter season. Therefore, this snow cover can be regarded as a continuous precipitation sample for the period between late autumn and early spring.

In high mountainous areas, the lack of a local pollution source means that the snowfall provides a good sample to study the general trend of the atmospheric environment indicative of the winter period. It is well known that during winter, chemical substances including acidic components (*e.g.* SO_4^{2-}), are transported in the atmosphere from the Asian continent to Japan's coastal area along the Sea of Japan (*e.g.* Satake and Yamane, 1992). These pollutants may also be transported to the mountainous regions set back from the coastal area, and may influence the high mountain environment. Therefore, the investigations of these possibilities are important subjects.

Nakagawa *et al.* (1976) performed the first studies of the physical properties of snow cover at Mt. Tateyama, in the Northern Japan Alps. This was followed a few years later by a second investigation in the same area on the chemical analysis of snow cover performed by Kusakabe and Satake (1983). Since the 1990's, detailed chemical observations have been repeatedly performed at Mt. Tateyama (*e.g.* Osada *et al.*, 2000; Kido *et al.,* 2001; Osada *et al.,* 2004; Watanabe *et al.* 2005). However, chemical investigations of the snow cover in the Northern Japan Alps reveals that except for the Mt. Tateyama area, the overall results for this mountainous region are still insufficient to provide a detailed chemical analysis of the snow covers.

We investigated the chemical and isotopic compositions of the snow cover at Mt. Nishi-Hodaka-dake (located 50 km inland from Mt. Tateyama) in order to clarify whether anthropogenic substances are transported inland to the high mountainous areas of this region, and ultimately, the origin of these pollutants. Tsushima and Hirata (1999) previously measured the chemical composition of various snow cover samples at Mt. Nishi-Hodaka-dake. However, these measurements were performed intermittently, and as such, this investigation may miss the existence of anthropogenic substances. The uninterrupted results collected by Toyama *et al.* (2003) are considered a better representation of the chemical composition of the 2002/03 winter snow samples collected at Mt. Nishi-Hodaka-dake. The authors report however, that these results only represent one winter season, and therefore cannot be regarded as representative of this area.

In this study, the chemical components in snow samples from three consecutive winter seasons (2001/02, 2002/03 and 2003/04) were measured in order to investigate how the long-range transportation of chemical substances from the Asian continent to Mt. Nishi-hodaka-dake varies from year to year, depending on the weather conditions. Further, the sulfur isotope ratio of the 2002/03 snow cover was also measured to clarify the source areas of the SO_4^{2-} ions, through independent methods of chemical composition.

2. Method

Snow samples for chemical analyses were collected (20th March 2002, 10th March 2003 and 22nd March 2004) at a sampling point 250 m east of the Nishi-Hodaka-Guchi station of the Shin-Hodaka Ropeway, Sengoku Ridge of Mt. Nishi-Hotaka-Dake (2200 m A.M.S.L.; Fig. 1). The topography around the sampling point was flat, such that the snow depth at the sampling point is considered representative of the snow depth in this area. Further, sheltering by neighboring trees and buildings, and public contamination are necessarily avoided around the sampling point, such that the obtained results are representative of a contamination-free region. A snow pit was dug, where the walls of the pit were carefully smoothed to leave the stratigraphy of the snow layer undisturbed. The conditions of the snow layer (*e.g.* snow type and particle size) in the pit were then studied. Snow samples (width of 5.8 cm, depth of 5.8 cm and height of 3 cm) were then collected from the surface of the wall using a snow sampler. These snow samples were collected continuously from the lower section of the pit to the snow surface. Samples were then packed into plastic bags, and sealed and stored below 0℃ to keep the samples in the solid state and to prevent alternation of the chemical composition by microbial activity.

The samples were melted under laboratory conditions, and their chemical compositions (anions: F^-, Cl^-, NO_3^- and SO_4^{2-}; cations: Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) analyzed by ion chromatography (anions: Metrohm Compact IC 761, cations: TOSO IC-8010). The accuracy of the measured values was around ±5%.

For the measurement of the sulfur isotope ratio ($\delta^{34}S$), another series of samples were collected at the same sampling point used for chemical analysis, taken 9 days earlier (10th March 2003). The snow depth on 19th March 2003 was 366 cm, which was slightly shallower than the snow depth, 420 cm, measurement taken on 10th March 2003. This decrease in snow depth is considered to be due to compaction of the snow cover, resulting from a slight melting of the snow layer over the 9-day period.

Snow samples obtained from mountainous regions generally have a very low SO_4^{2-} concentration around 1 mgl^{-1} (*e.g.* Tsushima and Hirata, 1999; Osada *et al.,* 2000), such that a quantity of SO_4^{2-} of more than 1 mg is needed in order to obtain meaningful $\delta^{34}S$ measurements. Therefore, a large volume of each snow sample more than 2 l in water equivalent is required for one $\delta^{34}S$ datum. Snow samples for $\delta^{34}S$ analysis were collected from a single homogeneous snow stratum. Since a homogeneous snow stratum can be regarded to pile up during a single snowfall event resulting in a homogeneous $\delta^{34}S$ value, 12 separate samples were collected continuously from the lower section of the pit to the snow surface. Samples

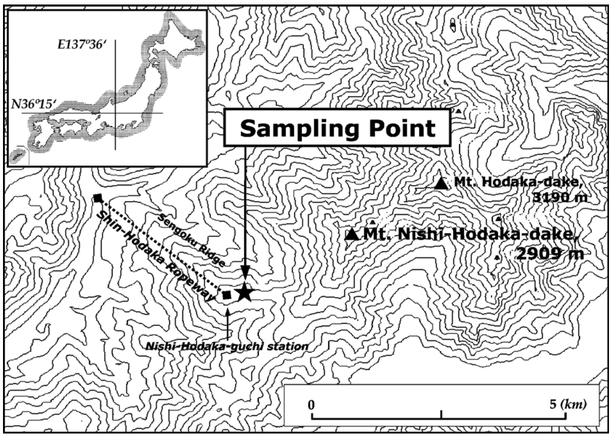

Fig. 1. Location map of Mt. Nishi-Hodaka-dake where snow samples were collected. The sampling point (2200 m A.M.S.L.) is located 250 m east of the Nishi-Hodaka-Guchi station of the Shin-Hodaka Ropeway, at the Sengoku Ridge of Mt. Nishi-Hotaka-Dake.

were sealed into plastic bags, and then transported to the laboratory and stored below 0℃. The samples were then melted under room temperature conditions, filtered, and then concentrated the samples to about 7 times using a rotary evaporator. A $BaCl_2$ solution was added to the concentrated aqueous sample solution to induce the formation of sulfate ions, recovered as $BaSO_4$. The recovered $BaSO_4$ was then mixed with V_2O_5 and heated to form SO_2 gas (Yanagisawa and Sakai, 1983).

The $\delta^{34}S$ value of the SO_2 gas was measured using a mass spectrometer (Micromass PRISM model). The $\delta^{34}S$ value is expressed as the following equation using Canyon Diablo Troilito (CDT) as a standard material:

$$\delta^{34}S=[(^{34}S/^{32}S)_{sample}/(^{34}S/^{32}S)_{CDT}-1]\times10^3 \qquad (1)$$

To obtain the non sea-salt (NSS) $\delta^{34}S$ values, the concentrations of Na^+, Cl^- and SO_4^{2-} ions in the snow samples were also measured.

3. Results and discussion

3.1 *Condition of snow layers*

An outline of the stratigraphies of snow cover in each year is shown in Fig. 2. Here, most of the layers were composed of compacted snow or solid-type depth-hoar, where no melted water was detected. Therefore, it can be regarded that the snow layers maintained their original chemical and isotopic compositions at the time of snowfall. The observations of granular snow suggests that the occurrence of melted water were exceptionally detected at the height of 155–212 cm and 313–327 cm in the 2002/03 snow cover and 285–300 cm in the 2003/04 snow cover.

3.2 *Vertical profile of chemical composition*

To evaluate the contributions of anthropogenic or soil contamination to the snow chemistry, it is important to determine the calculation of NSS-components. The non sea-salt component can be obtained from the following equation using chemical compositions in snow samples and seawater (Berner and Berner, 1987):

$$[NSS-A]_{snow}=[A]_{snow}-[A/Na^+]_{seawater}\times[Na^+]_{snow} \qquad (2)$$

A: SO_4^{2-}, Mg^{2+}, Ca^{2+} and F^-

In this study, the non sea-salt components were calculated for SO_4^{2-}, Mg^{2+}, Ca^{2+} and F^- ions. All the NO_3^- components can be regarded as NSS-components, because the concentration of NO_3^- ions in surface seawater is very low. In all the snow samples, more than 99% of the F^- ions were of NSS-origin, such that all of the F^- ions in snow can also be regarded as NSS-components.

In Fig. 3, the vertical profiles of chemical compositions taken during the 2001/02, 2002/03 and 2003/04 snow covers are shown. The maximum, minimum and mean concentrations of each snow cover are

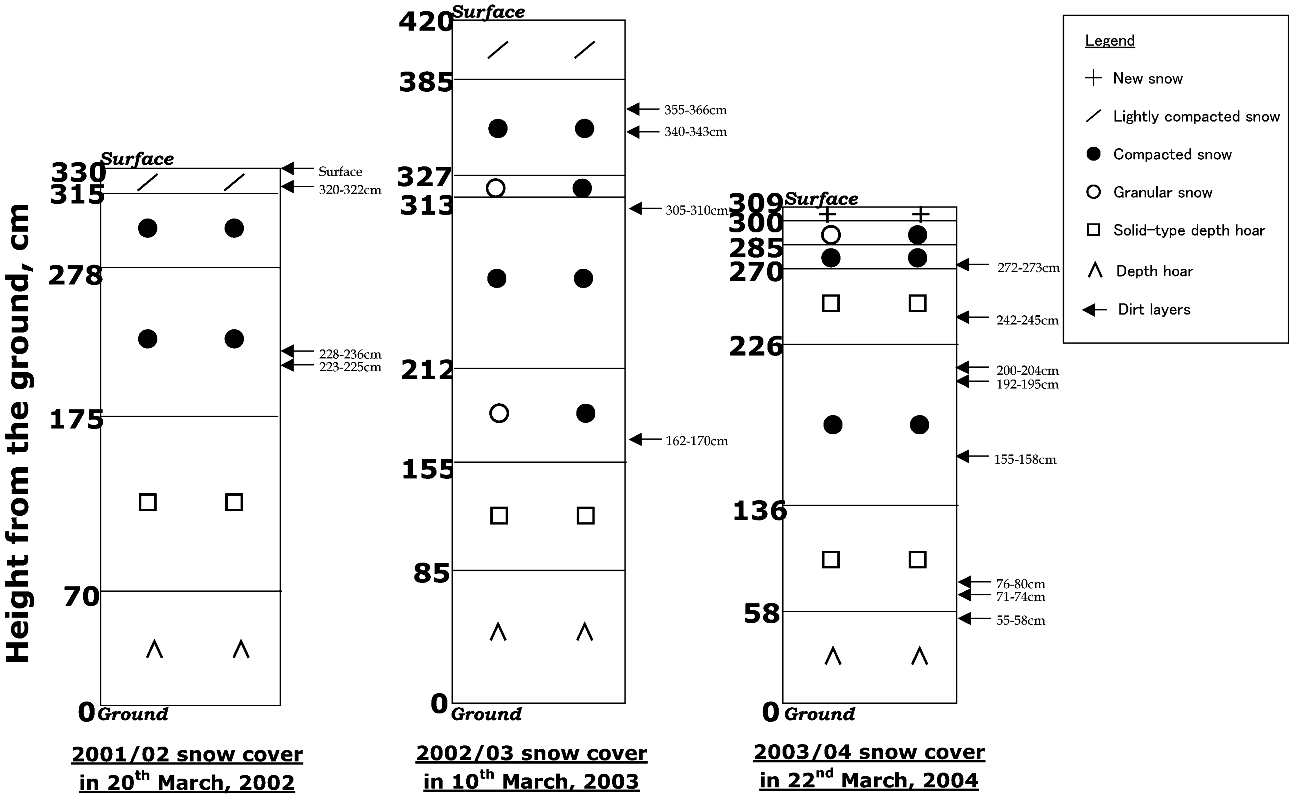

Fig. 2. The stratigraphies of snow cover at the sampling point observed on 20th March 2002, 10th March 2003 and 22nd March 2004. Arrows on the right side of each stratigraphic plot show dirt layers caused by Asian dust (KOSA).

shown in Table 1. The concentration of individual components changes about 100 times depending on the layer studied. In each of the vertical profiles shown in Fig. 3, there are several peaks that represent high concentration. In the NSS-SO_4^{2-} and NO_3^- profiles, for example, such peaks are found at 162 cm, 249 cm and 327 cm during the 2001/02 period, 165 cm and 309 cm during the 2002/03 period, and 72cm and 198cm during the 2003/04 period. From Fig. 3, it is also found that several chemical components are presented simultaneously.

In general, the source of the chemical components in snow can be classified into three origins: 1) sea-salt components, 2) soil components and 3) anthropogenic components. The characteristics of each component are as follows.

3.2.1 Sea-salt components

As shown in the Cl^- versus Na^+ plot diagram in Fig. 4, most snow samples are closely distributed

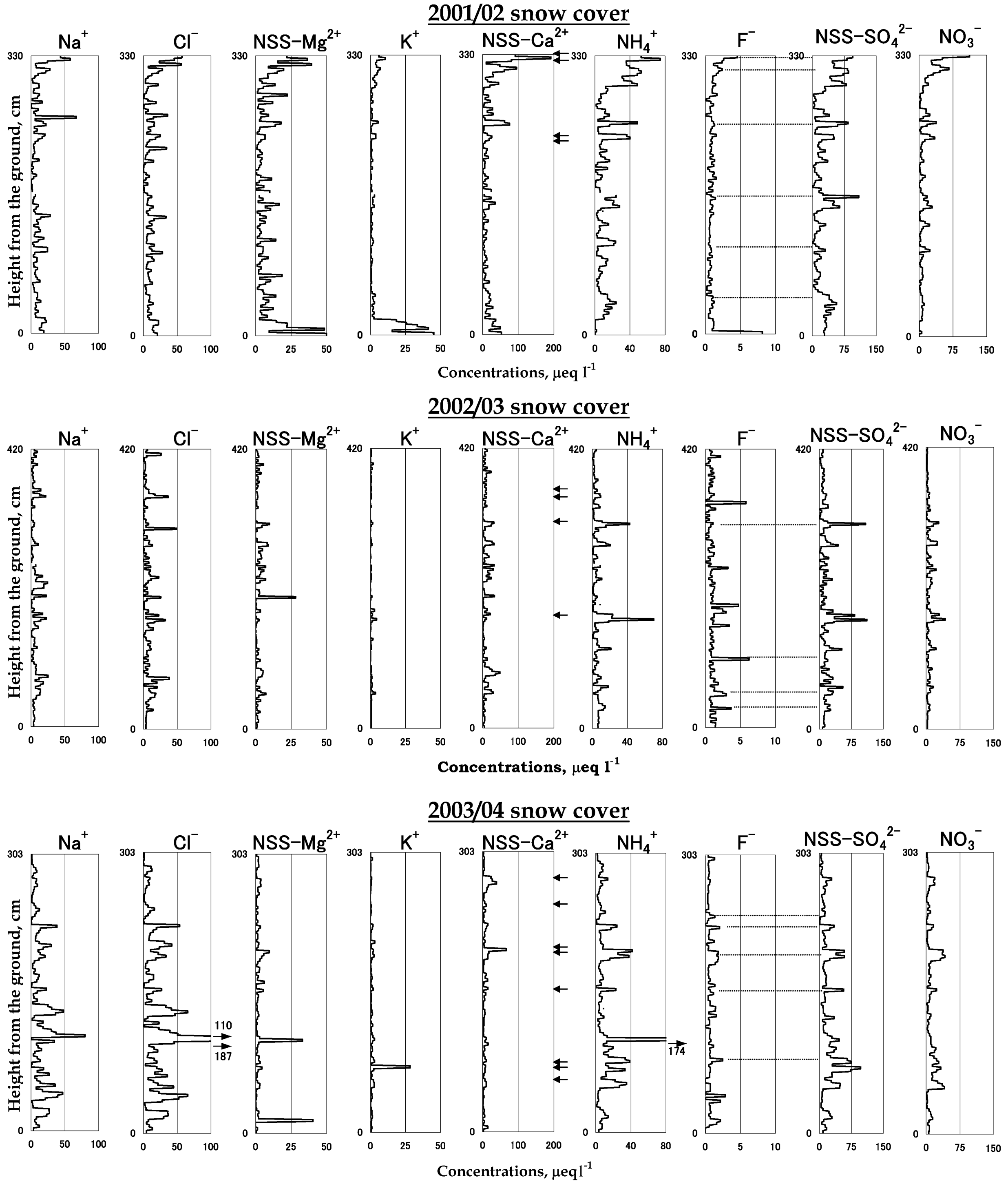

Fig. 3. Vertical profiles representing chemical components in the snow cover samples taken from Mt. Nishi-Hodaka-dake, during the winters of 2001/02, 2002/03 and 2003/04. Profiles of NSS-SO_4^{2-}, NSS-Mg^{2+} and NSS-Ca^{2+} represent the non sea-salt (NSS) compositions in each component. Arrows on the right side of NSS-Ca^{2+} profile reveal the dirt layers.

along the line showing a Cl^-/Na^+ ratio in seawater. Therefore, the Na^+ and Cl^- ions can be regarded to be of seawater origin. The concentrations of Na^+ and Cl^- ions in snow were 0–80μeq l^{-1} and 0–187μeq l^{-1}, respectively. These values are extremely low in comparison with the mean concentration of winter precipitation taken from 29 cities along the Sea of Japan (Na^+ : 282μeq l^{-1}, Cl^- : 331.3μeq l^{-1}; Fukuzaki *et al.,* 1996). It is known that the Cl^- ion concentration in precipitations exponentially decreases with increasing distance from the seashore (Tsunogai, 1975; Suzuki, 1987). Therefore, the greater part of these two components in cloud probably fell in coastal areas, with very little arriving in the high mountainous areas.

As described above, most snow samples are distributed along the seawater line in the Cl^- versus Na^+ diagram (Fig. 4). However, the snow samples with Cl^- ion concentrations greater than 20μeq l^{-1} are plotted slightly above the seawater line. This suggests that such snow samples also contain small amounts of Cl^- ions of non sea-salt origin. It is reported that anthropogenic or volcanic Cl^- ions occur in the atmosphere (Okita *et al.,* 1974). Anthropogenic Cl^- ions are exhausted from inclination facilities for household and industrial wastes in the form of HCl (Tsuruta, 1989).

3.2.2 Soil components

The concentration of NSS-Ca^{2+} ions is represented by peaks corresponding to the dirt layers (see Fig. 3). These dirt layers in the snow cover are thought to be caused by Asian dust (KOSA) blown over from the deserts of northwestern China (Kido *et al.,* 1997). This suggests that high NSS-Ca^{2+} ion concentrations in the dirt layers were caused by the dissolution of calcium carbonate ($CaCO_3$), which is a major component of Asian dust. Moreover, NSS-Ca^{2+} ions are constantly detected in samples extracted from the dirt layers. Kumai (1951) and Ishizaka (1973) pointed out that in the case of winter precipitation in the coastal area along the Sea of Japan, most of the ice nuclei are soil particles transported from the Asian continent. Further, Iwasaka *et al.* (1988) reported that a background amount of Asian dust always exists in the troposphere over Japan. Therefore, the lower concentration of NSS-Ca^{2+} ions observed in

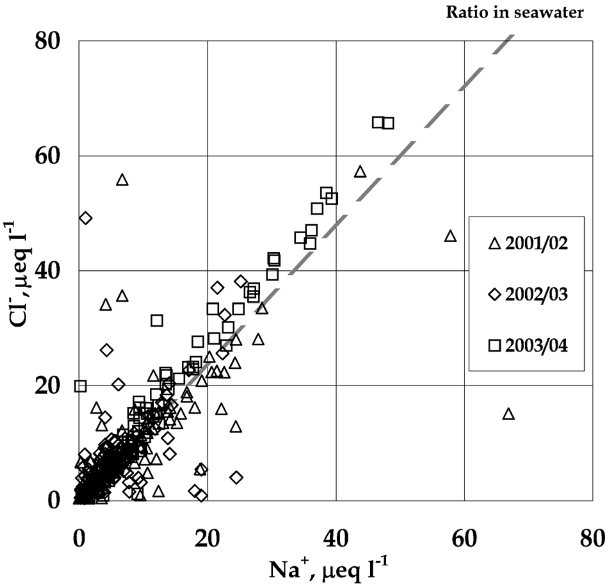

Fig. 4. Cl^- versus Na^+ plot of snow samples taken over three winters (2001/02, 2002/03 and 2003/04). The dashed line represents the ratio of concentrations in seawater. Most of the snow samples are closely distributed near the seawater line.

Table. 1. Maximum, minimum, and average concentrations, and total deposition of chemical components in the 2001/02, 2002/03 and 2003/04 snow cover samples taken at Mt. Nishi-Hodaka-dake.

		Na^+	Cl^-	NSS-Mg^{2+}	K^+	NSS-Ca^{2+}	F^-	NH_4^+	NO_3^-	NSS-SO_4^{2-}
2001/01 winter	Max., μeq l^{-1}	67	57	46	45	189	8	75	112	109
	Min., μeq l^{-1}	0	0	0	0	0	0	0	0	2
	Ave., μeq l^{-1}	10	11	5	3	17	1	13	11	27
	Total deposition, g m^{-2}	**0.30**	**0.52**	**0.09**	**0.16**	**0.45**	**0.03**	**0.30**	**0.90**	**1.69**
2002/03 winter	Max., μeq l^{-1}	25	49	28	4	48	6	70	42	112
	Min., μeq l^{-1}	0	0	0	0	0	0	1	0	0
	Ave., μeq l^{-1}	6	7	2	1	8	1	6	6	15
	Total deposition, g m^{-2}	**0.20**	**0.39**	**0.03**	**0.03**	**0.26**	**0.03**	**0.17**	**0.58**	**1.12**
2003/04 winter	Max., μeq l^{-1}	80	187	40	28	66	3	174	42	97
	Min., μeq l^{-1}	0	0	0	0	0	0	0	1	1
	Ave., μeq l^{-1}	12	18	2	1	7	1	11	10	19
	Total deposition, g m^{-2}	**0.34**	**0.79**	**0.03**	**0.05**	**0.17**	**0.02**	**0.23**	**0.74**	**1.09**

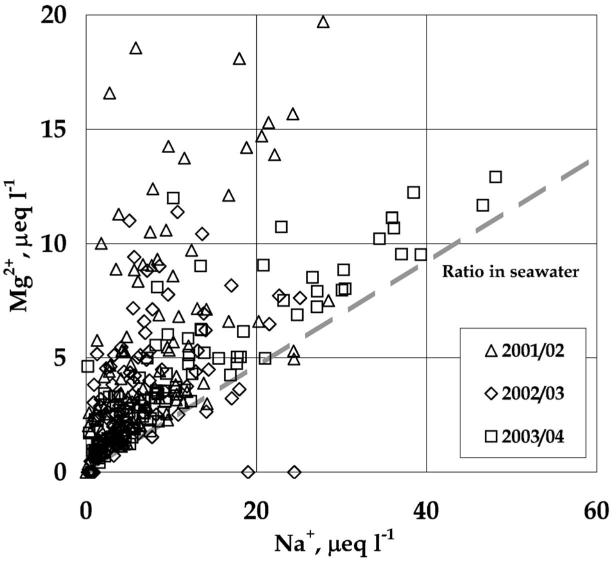

Fig. 5. Na^{+} versus Mg^{2+} (bulk) plot of snow samples taken over three winters (2001/02, 2002/03 and 2003/04). The dashed line represents the ratio of concentrations in seawater. Most of the snow samples are plotted above the seawater line.

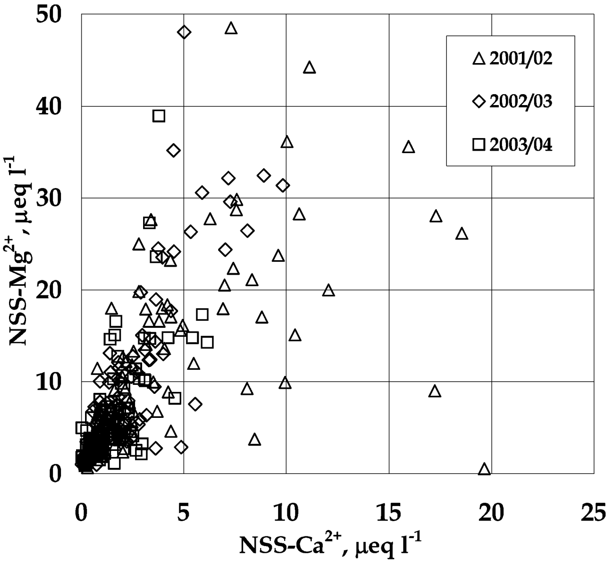

Fig. 6. NSS-Ca^{2+} versus NSS-Mg^{2+} plot of snow samples taken over three winters (2001/02, 2002/03 and 2003/04). A high positive correlation was found between the two parameters.

non-dirt layers can also be regarded as derived from Asian dust.

Most of the snow samples are plotted above the seawater line in a plot of Mg^{2+} versus Na^{+} (Fig. 5). Further, in snow samples, a positive correlation ($R = 0.6$) was found between the NSS-Ca^{2+} and NSS-Mg^{2+} ions (Fig. 6). This suggests that the Mg^{2+} ions in snow are mostly composed of soil-derived and sea-salt components; although in coastal areas most Mg^{2+} ions in precipitation are of sea-salt origin. The soil transported from the Asian continent can be regarded as a dominant source of NSS-Mg^{2+} and NSS-Ca^{2+} ions in the snow cover found at Mt. Nishi-Hodaka-dake.

3.2.3 Anthropogenic components

NSS-SO$_4^{2-}$ values of 0 to 112 μeq l^{-1} and NO$_3^-$ values of 0 to 112 μeq l^{-1} are observed in the snowfall at Mt. Nishi-Hodaka-dake. The maximum concentrations of NSS-SO$_4^{2-}$ and NO$_3^-$ ions in Mt. Nishi-Hodaka-dake snowfalls are comparable to those found in precipitations in urban areas (*e.g.*, Fukuzaki *et al.*, 1996). Osada *et al.* (2000) also observed similar concentrations of acid components in snow samples taken at Murodo-daira (2450 m), an area in Mt. Tateyama of similar altitude and located much closer to the Sea of Japan. The NSS-SO$_4^{2-}$ and NO$_3^-$ ions are typical anthropogenic components derived from exhaust gas or industrial activity. These ions are major acidifying materials found in precipitation. As Mt. Nishi-Hodaka-dake is surrounded by forest, there are no local sources of acid contaminants. Therefore, it is suggested that these acid components were transported from distant sources. It is well known that acid contaminants originating from the Asian continent are transported to the coastal area along the Sea of Japan by winter seasonal winds (*e.g.* Satake and Yamane, 1992). In this respect, we must examine the possibility that these long-range transported acid components may arrive at inland mountainous areas, such as Mt. Nishi-Hodaka-dake.

The high concentration peaks of the NSS-SO$_4^{2-}$ and NO$_3^-$ ions are often accompanied by peaks associated with NSS-Ca^{2+} ions (*e.g.* 249 cm and 327 cm taken from snowfalls in 2001/02, 165 cm, respectively, and 309 cm from snowfalls in 2002/03; see Fig. 3). This observation does not contradict the possibility that acid components exhausted in China are transported simultaneously with Asian dust, although another possibility that SO$_4^{2-}$ ions discharged from the coastal area along the Sea of Japan were transported with Asian dust cannot be excluded. Moreover, F$^-$ ions were also detected in snow samples. The concentration of F$^-$ ions is 0–8 μeq l^{-1} with an average of about 1 μeq l^{-1}, which is much lower than the NSS-SO$_4^{2-}$ and NO$_3^-$ ion concentrations. However, as shown in Fig. 3, the vertical profiles of F$^-$ ions were partially similar to those of the NSS-SO$_4^{2-}$ ions. Sakamoto (1994a) pointed out that F$^-$ ions are discharged as HF as a result of coal combustion in China. So, it may be regarded that the detected F$^-$ ions were probably includes anthropogenic F$^-$ ions that transported from the Asian continent.

3.3 NSS-SO$_4^{2-}$/NO$_3^-$ *ratio in snow*

To investigate the source of anthropogenic NSS-SO$_4^{2-}$ and NO$_3^-$ ions in snow cover, the relation between NSS-SO$_4^{2-}$ and NO$_3^-$ ions will be considered in this section. NSS-SO$_4^{2-}$ versus NO$_3^-$ plot of samples is shown in Fig. 7, and the corresponding histogram of NSS-SO_4^{2-}/NO_3^- ratio in eq l^{-1} units (S/N ratio) is shown in Fig. 8. The S/N ratios in Beijing, China (in 1985–86; Sakamoto, 1994b) and Tokyo, Japan (in 1984–88; Mori *et al.,* 1991) are also shown in Figs. 7 and 8, respectively. Most of the snow samples obtained during 2001/02 and 2002/03, and half of the snow samples taken in 2003/04, are distributed between the lines showing S/N ratios in Beijing and Tokyo (Fig. 7 and Fig. 8).

In China, the principal energy source coal accounts for 65% of the total energy, while petroleum accounts for 24% in 2001 (National Bureau of Statistics of China, 2004). On the other hand, in Japan, 50% of the total energy is supplied by petroleum, while coal accounts for just 20% in 2001 (Statistics Bureau, Ministry of Internal Affairs and Communications, Japan, 2006). In comparison with petroleum, coal has a somewhat higher content of sulfur. So, in China, the total discharges of sulfur dioxide and nitrogen oxide are 20.0 and 7.4 million tons in 1987 (Kato *et al.* 1992), discharge of sulfur dioxide is relatively higher than that of nitrogen oxide. In Japan, as described above, the major energy source is petroleum. Furthermore, desulfurization equipment is installed in power plants and large-scale factories in Japan. As a result, the amounts of sulfur dioxide and nitrogen oxide exhausted are 0.9 and 2.0 million tons, respectively in 2002 (OECD, 2005). So, the S/N ratio, in equivalent, in China (about 4) is much higher than that in Japan (about 2).

Consequently, the results in Fig. 7 and Fig. 8 suggested that acid contaminants in the snow cover at Mt. Nishi-Hodaka-Dake comprised a mixture of contaminants from both China and Japan with variable ratio. Thus, it is clear that the acid components transported from the Asian continent reached Japan's

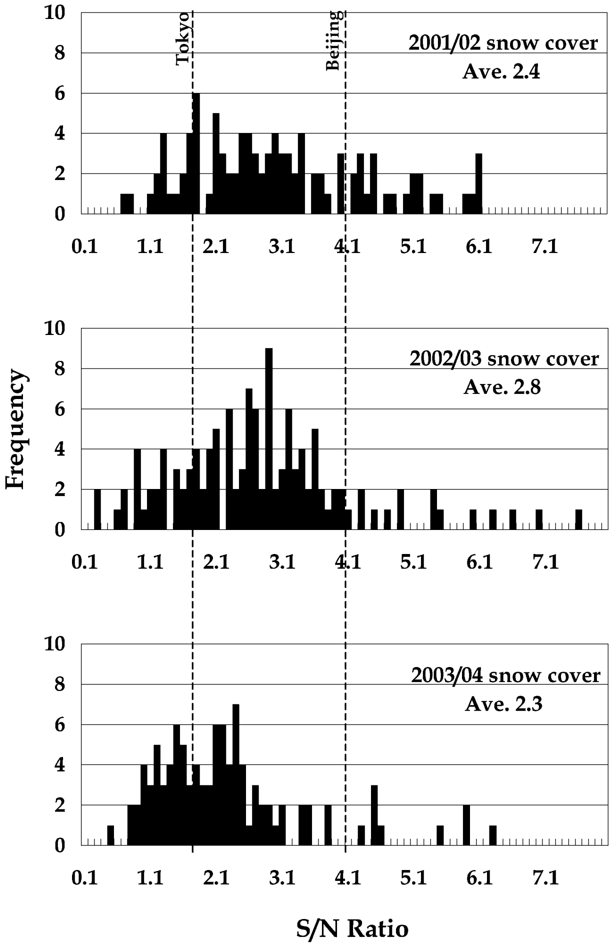

Fig. 8. The histograms of NSS-SO_4^{2-}/NO_3^- (S/N) ratios in the 2001/02, 2002/03 and 2003/04 snow cover samples taken at Mt. Nishi-Hodaka-dake. The S/N ratios in precipitations taken at Beijing, China in 1985–86 (Sakamoto, 1994b) and Tokyo, Japan in 1984–88 (Mori *et al.,* 1991) are also shown in the diagram.

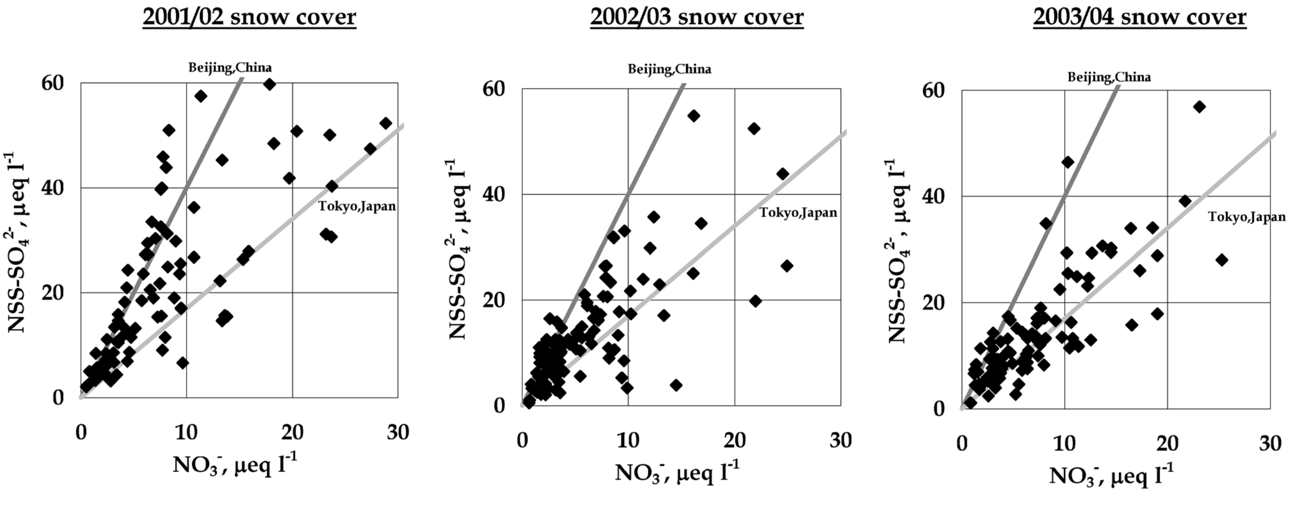

Fig. 7. NSS-SO_4^{2-} versus NO_3^- plot of snow samples taken over three winters (2001/02, 2002/03 and 2003/04). The dashed lines showing the SO_4^{2-}/NO_3^- ratios in precipitations taken at Beijing, China in 1985–86 (Sakamoto, 1994b) and Tokyo, Japan in 1984–88 (Mori *et al.,* 1991) are also shown in the figures.

inland high mountainous areas, such as Mt. Nishi-Hodaka-Dake, located 70 km inland from the coastline of the Sea of Japan.

However, from a comparison of snowfall data taken over a period of three years, the situation of long-range transportation seems to be different from year to year. The total depositions of NSS-SO_4^{2-} and NO_3^- ions in snowfalls in 2001/02 are 1.69 g m^{-2} and 0.90 g m^{-2}, respectively. The depositions observed in 2001/02 are systematically larger than those in snowfall samples in 2002/03 (NSS-SO_4^{2-}: 1.12 g m^{-2} and NO_3^-: 0.58 g m^{-2}) and in 2003/04 (NSS-SO_4^{2-}: 1.09 g m^{-2} and NO_3^-: 0.74 g m^{-2}). From Fig. 7, it is observed that in the snow sample of 2001/02, the S/N ratio is widely distributed from 1 to 6, although a weak peak is observed at 1.8. On the contrary, in the snowfall samples of 2002/03 and 2003/04, there are conspicuous peaks around 3 and 2, respectively. This fluctuation among three winter seasons may be caused by changes in the transportation situation of acid components, which may depend on the weather condition observed during each winter season. Figure 9 shows the vertical profiles of S/N ratios, which consider a five point moving average value, in snow cover. The temporal variation in the S/N ratio, and the general weather conditions experienced in each of the years (Japan Meteorological Agency, 2006), may control the long-range transportation of NSS-SO_4^{2-} ions, as follows.

3.3.1 2001/02 winter season

A series of typical winter pressure patterns, characterized by high-pressure in the west and low-pressure in the east, were frequently observed during December 2001. The transportation of substances from the Asian continent can be considered active during this period. As such, the lower section of snow cover (0–50 cm), which was observed to have higher S/N ratios (4.0–6.0), may correspond to this period. During the period between January 2002 and March 2002, the weather condition changed repeatedly from severe winter pressure patterns to southern coast low-pressure patterns, which are characterized by low-pressure areas moving along the southern coast of the Japan Islands. The S/N ratio in the 50–330 cm range of the snow cover samples fluctuated from 0.7 to 6.1. This fluctuation in the S/N ratio seems to be induced by the repeated weather condition changes during January-March 2002. The total deposition of NSS-SO_4^{2-} ions (see Table 1) in the 2001/02 snow season is among the highest of the three winter seasons. Therefore, it is considered that the transportation of contaminants from the Asian continent during the 2001/02 winter period was the most active among the three winter seasons.

3.3.2 2002/03 winter season

From December 2002 to February 2003, the winter pressure pattern and southern coast low-pressure pattern appeared alternately. The S/N ratio in 0–300 cm of contaminants changes periodically from 0.3 to 6.3, which may be a reflection of the weather situation. In March 2003, the winter pressure pattern intensified. The S/N ratio in the upper part of the snow cover (320–400 cm) is relatively high (3–4). This high S/N ratio may reflect the severe winter which occurred in March 2003. The concentration of chemical components in the snow cover that fell during the 2002/03 period is low relative to the snowfall periods in 2001/02 and 2003/04. This may be the result of dilution by the large accumulation of snow (420 cm), which is the highest among the three periods of snowfall (2001/02: 330 cm and 2003/04: 309 cm).

3.3.3 2003/04 winter season

The winter pressure pattern from December 2003 to February 2004 was found to be weak. The observed low S/N ratio (around 2) in 0–200 cm may be a reflection of this weak winter pressure pattern, which was observed to intensify in the early part of March 2004. A high S/N ratio (over 4) observed in 200–220 cm and 250–260 cm may be induced by the intensified winter pressure pattern. The total deposition of NSS-SO_4^{2-} (1.09 g m^{-2}) ions was the lowest among three winter seasons (2001/02: 1.69 g m^{-2} and 2002/03: 1.12 g m^{-2}). This suggests that the transportation of contaminants from the Asian continent was not active during the 2003/04 winter.

Through the observation of three snow seasons, it is revealed that the long-range transportation of chemical substances from the Asian continent is closely related to the winter weather conditions. The combination of detailed dating of the snow layers (*e.g.* Toyama *et al.,* 2005) with the corresponding chemical analyses of snow may remarkably improve the investigation of the long-range transportation of anthropogenic contaminants from the Asian continent.

3.4 Sulfur isotope ratio (δ^{34}S)

The δ^{34}S values of the 2002/03 snow samples were measured for the independent evidence for determining the origin of NSS-SO_4^{2-} ions. As described previously, snow contains SO_4^{2-} with sea-salt origin, although most of the SO_4^{2-} (about 90%) ions are of non sea-salt origin. To determine the δ^{34}S value of NSS-SO_4^{2-} in snow, we must calculate the NSS-δ^{34}S values using the following equation:

$$\mathrm{NSS}-\delta^{34}\mathrm{S}=(\delta^{34}\mathrm{S}_{\mathrm{sample}}\times[\mathrm{SO_4}^{2-}{}_{\mathrm{sample}}]-\delta^{34}\mathrm{S}_{\mathrm{sea}}\times[\mathrm{SO_4}^{2-}{}_{\mathrm{sea}}])/[\mathrm{SO_4}^{2-}{}_{\mathrm{NSS}}] \quad (3)$$

δ^{34}S value of SO_4^{2-} in seawater ($\delta^{34}S_{sea}$) is reported to be +20.0‰ (Rees *et al.,* 1978).

Vertical profiles of the NSS-δ^{34}S value and the S/N ratio are shown in Fig.10. The profile of the S/N ratio for snow collected in 19th March 2003 was obtained by reducing the height of the S/N ratio profile of the 2002/03 snow collected on the 10th March 2003. Since the snow cover collected on the 19th March 2003 can be regarded as a homogeneously-compressed version of the snow collected on 10th March 2003.

The NSS-δ^{34}S values range from +3.1 to +6.8‰ with an average of +4.9‰. The highest NSS-δ^{34}S value in the 0–300 cm section of snow cover fluctuated periodically from +4.5 to +5.5‰, although the highest value, +6.8‰, is found in the section 110–160 cm. In the upper part, 300cm to the surface, the NSS-δ^{34}S value gradually decreased from +4.0‰ to +3.0‰ with increasing height.

In winter, the northwest wind blows from the Asian continent to the Japan Islands. So it is expected that a considerable amount of NSS-SO_4^{2-} ions was transported from the northern part of China and the far eastern part of Russia. Maruyama *et al.* (2000) measured the δ^{34}S values of coals used in East Asia. They obtained δ^{34}S values of +7.8±11.0‰ in northern China and +4.5±4.8‰ in the Russian Far East. Furthermore, Maruyama *et al.* (2000) pointed out that the δ^{34}S value of petroleum used in Japan is about −1‰. The NSS-δ^{34}S value of snow at Mt. Nishi-Hodaka-dake is around +5‰, and was obviously higher than that of domestic petroleum (−1‰), and much closer to the value of coals mined in northern China. Thus, the NSS-SO_4^{2-} ion contribution from the Asian continent to Mt. Nishi-Hodaka-dake is also observed, based on the sulfur isotope ratio.

In the major part of the snow, the S/N ratio and NSS-δ^{34}S value seem to fluctuate in parallel. These two parameters show weak positive correlation (R=0.2). This suggests that in the periods of higher S/N ratios (*e.g.* samples No. 4, 5, 6, 10 and 12 in Fig. 9), the transportation of contaminants from the Asian continent is active; NSS-SO_4^{2-} with high NSS-δ^{34}S were transported from northern China. There is a possibility that sample No.10 with the highest NSS-δ^{34}S value, contains NSS-SO_4^{2-} ions derived from around Beijing; an area known to have the highest δ^{34}S value (av.: +9.6±10.8‰; Motoyama *et al.,* 2002) in China. On the contrary, in the periods with lower S/N ratios, the transportation of contaminants from the Asian continent is not active, and the observation of domestic NSS-SO_4^{2-} ions with low NSS-δ^{34}S values is dominant in the snow samples. Samples No. 2, 3 and 11 are representative of this period.

However, sample No.1 has a high S/N ratio (2.8) and the lowest NSS-δ^{34}S value (+3.1‰). Maruyama *et al.* (2000) described that the average δ^{34}S value of coal in southern China is −7‰, and the sulphur concentration of coals in southern China is higher than that of coals in northern China. There is a possibility that NSS-SO_4^{2-} ions in sample No.1 with a high S/N ratio (2.8) and low δ^{34}S value (+3.1‰) may include NSS-SO_4^{2-} ions derived from southern China. On the contrary, samples No.7 and 8 have low S/N ratios (2.3 and 2.5), although its NSS-δ^{34}S value is high (+5.6‰). The major energy sources in the Russian Far East (Russian Academy of Sciences Far East Branch, 2001)

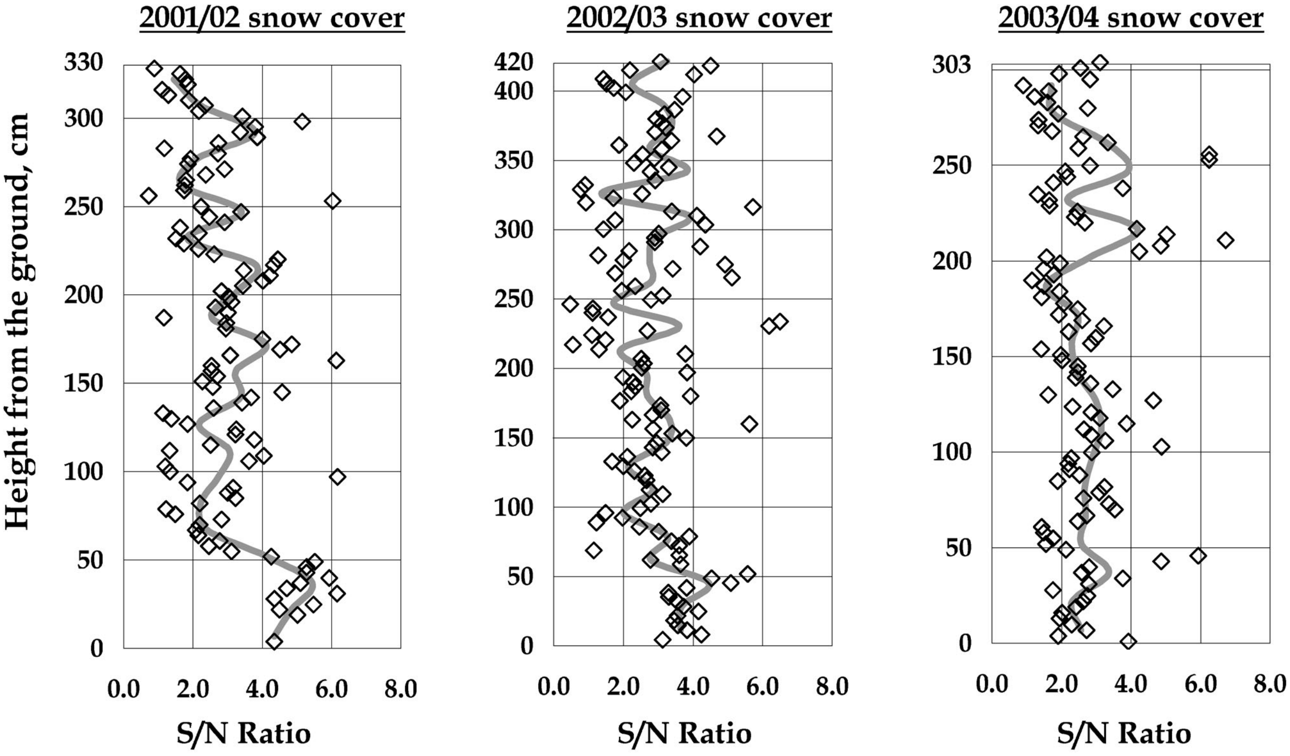

Fig. 9. Vertical profiles of the S/N ratio (five points moving average) in the 2001/02, 2002/03 and 2003/04 snow cover samples taken at Mt. Nishi-Hodaka-dake.

are coal (ca. 45%), petroleum (ca. 34%) and natural gas (ca. 10%). Therefore, the S/N ratio of the Russian Far East can be considered to be intermediate between China and Japan. Further, the NSS-δ^{34}S value in the Russian Far East (av.: +4.5±4.8‰) is lower than that in northern China, but much higher than that in Japan. Considering these facts, NSS-SO_4^{2-} ions in samples No.7 and 8 with low S/N ratios and high NSS-δ^{34}S values may include NSS-SO_4^{2-} ions derived from the Russian Far East.

The relationship between S/N ratio and NSS-δ^{34}S value in each sample is shown in Fig.11. From this figure, NSS-SO_4^{2-} ion in snow seems to be transported from four areas, that is, northern China, southern China, Russian Far East and Japan. Then NSS-SO_4^{2-} from thesse four areas was mixed with variable proportion depending on weather condition, and was transported to Mt. Nishi-Hodaka-Dake. Dense NSS-δ^{34}S measurement by short sampling interval may make the origin of acid contaminants clear.

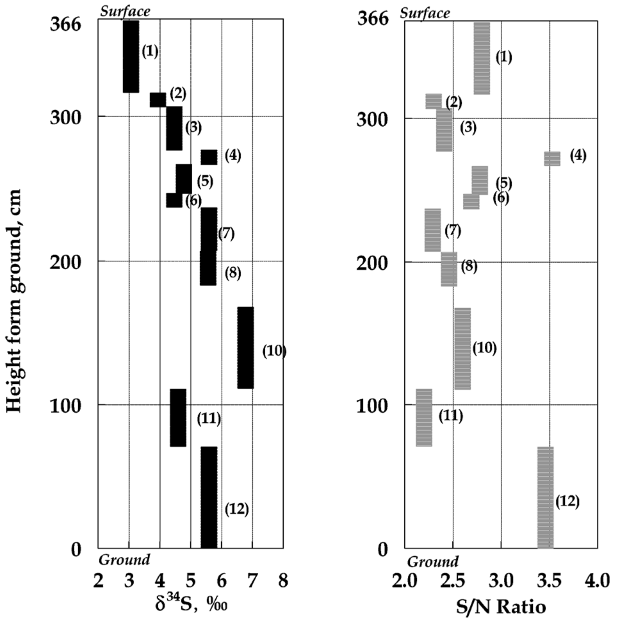

Fig. 10. Vertical profiles of the NSS-δ^{34}S and S/N ratios in the snow cover samples taken at Mt. Nishi-Hodaka-dake, collected in 19th March 2003.

4. Conclusions

(1) The chemical components in snow cover at Mt. Nishi-Hodaka-dake in the Northern Japan Alps were measured over a period of three consecutive (2001/02, 2002/03/ and 2003/04) winter seasons. The concentrations of NSS-SO_4^{2-} and NO_3^- ions in this snow cover ranged from almost 0μeq l^{-1} to over 100μeq l^{-1}. The maximum concentrations over 100μeq l^{-1} are comparable to concentrations in precipitations monitored in urban areas.

(2) A considerable number of snow samples taken from this region had higher S/N ratios than that of Tokyo, Japan (about 2). Some samples had much higher S/N ratios (about 4 to 6), which is the same as the S/N ratio of Beijing, China. This suggests that the snow cover at Mt. Nishi-Hodaka-Dake includes acid contaminants transported from the Asian continent, as well as those of domestic origin with variable proportion depending on weather conditions. Through the observation of three snow seasons, it is revealed that the long-range transportation of chemical substances from the Asian continent is closely related to the winter weather conditions.

(3) The NSS-δ^{34}S values range from +3‰ to +7‰ (average: +4.9‰). These ratios are evidently higher than those associated with the amount of petroleum used in Japan (−1‰). The NSS-δ^{34}S values in snow samples are in accord with the δ^{34}S values of coal used in northern China (+7.8‰), which are located on the windward side of the winter seasonal winds. This sulfur isotopic result also shows the long-range trans-

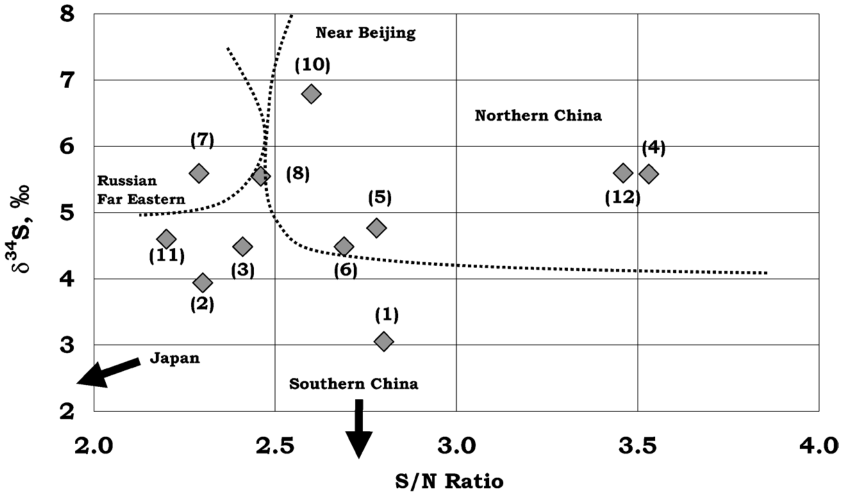

Fig. 11. S/N ratio versus NSS-δ^{34}S plot of snow cover sample collected from Mt. Nishi-Hodaka-dake, on 19th March 2003.

portation of NSS-SO_4^{2-} ions from the Asian continent, independently of the S/N ratio.

(4) The NSS-δ^{34}S value in snow cover shows positive correlation with the S/N ratio, suggesting a contribution of NSS-SO_4^{2-} ions from northern China. However, there were some exceptional cases, which seem to suggest the transportation of NSS-SO_4^{2-} ions from southern China and the Russian Far East.

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References

Berner, K. B. and Berner, R. A. (1987): The global water cycle: Geochemistry and environment. Prentice-Hall, New Jersey, 397 pp.

Fukuzaki, N., Oshio, T., Noguchi, I., Matsumoto, M., Morisaki, S., Oohara, M., Tamaki, M. and Hiraki, T. (1996): Chemical features of major constituents in winter-precipitation along the Sea of Japan on Honshu Island, Japan. *Nippon Kagaku Kaishi,* **8**, 726–733. (In Japanese with English abstract)

Ishizaka, Y. (1973): On materials of solid particles contained in snow and rain water: Part 2. *J. Meteor. Soc. Japan,* **51**, 325–336.

Iwasaka, Y., Yamato, M., Imasu, R. and Ono, A. (1988): Transport of Asian dust (KOSA) particles: importance of weak Kosa events on the geochemical cycle of soil particles. *Tellus,* **40B**, 494–503.

Japan Meteorological Agency (2006): Weather statistics information. http://www.jma.go.jp/jma/menu/report.html. (In Japanese)

Kato, N. and Akimoto, H. (1992): Anthropogenic Emissions of SO_2 and NO_x in Asia: Emissions Inventories (plus errata). *Atmos. Env.* **26a,** 2997–3017.

Kido, M., Osada, K., Yabuki, H. and IIDA, H. (1997): Dating of seasonal layers at Murodo, Mt.Tateyama, Japan. *Seppyo,* **59**, 181–188. (In Japanese with English abstract)

Kido, M., Osada, K., Matsunaga, K. and Iwasaka, Y. (2001): Temporal change in ammonium/sulfate ratios for free tropospheric aerosols from early winter to spring at high elevation site in the Japanese Alps. *J. Env. Chem.,* **11**, 33–41.

Kumai, M. (1951): Electron-microscope study of snow-crystal nuclei. *J. Meteor.,* **8**, 151–156.

Kusakabe, M. and Satake, H. (1983): Satble isotope ratio and tritium concentration of Kuranosuke snow patch, Northern Japan Alps. *Abstracts of the annual meeting in 1983, The Geochem. Soc. of Japan,* 55. (In Japanese)

Maruyama, T., Ohizumi, T., Taneoka, Y., Minami, N., Fukuzaki, N., Mukai, H., Murano, K. and Kusakabe, M. (2000): Sulfur isotope ratios of coals and oils used in China and Japan. *Nippon Kagaku Kaishi,* **1**, 45–51. (In Japanese with English abstract)

Mori, A., Ohara, M., Wakamatsu, S., Murano, K., Taguchi, K., Sekiguchi, K., Tamaki, M., Kato, H., Kitamura, M., Okita, T., Yamanaka, Y and Hara, H. (1991): Studies on equivalent ratio of Nitrate to sulfate in acid precipitation. *Nippon Kagaku Kaishi,* **6**, 920–929. (In Japanese with English abstract)

Motoyama, R., Yanagisawa, F., Akita, N., Suzuki, Y., Kanai, Y., Kojima, T. and Ueda, A. (2002): Sulfur isotope ratios of coals used in East Asia. *Seppyo,* **64**, 49–58. (In Japanese with English abstract)

Nakagawa, M., Kawada, K., Okabe, T., Shimizu and H. and Akitaya, E. (1976): Physical properties of the snow cover on Mt.Tateyama in central Honshu, Japan. *Seppyo,* **38**, 157–164. (In Japanese with English abstract)

National Bureau of Statistics of China (2004): China statistical yearbook 2004. China Statistics Press, Beijing, 1011 pp. (In Chinese)

OECD (2005): OECD Environmental data compendium 2004. Organization for Economic Co-operation and Development, Paris, 320 pp.

Okita, T., Kaneda, K., Yanaka, T. and Sugai, R. (1974): Determination of gaseous and particulate chloride and fluoride in the atmosphere. *Atmos. Environ.,* **8**, 927–936.

Osada, K., Kido, M., Iida, H., Yabuki, H., Kohshima, S., Kawada, K. and Nakawo, M. (2000): Chemical stratigraphy of water soluble constituents in spring snow cover at Murododaira, Tateyama Mts., Japan. *Seppyo,* **62**, 3–14. (In Japanese with English abstract)

Osada, K., Iida, H., Kido, M., Matsunaga, K., and Iwasaka, Y. (2004): Mineral dust layers in snow at Mount Tateyama, Central Japan: formation processes and characteristics. *Tellus,* **56B**, 382–392.

Rees, C. E., Jenkins, W. J. and Monster, J. (1978): The sulphur isotopic composition of ocean water sulphate. *Geochem. et Cosmochem. Acta,* **42**, 377–381.

Russian Academy of Sciences Far East Branch (2001): The strategy of the development of fuel and energy potential in the Russian Far East economic region up to 2020. Dalnauka, Vladivostok, 111 pp. (In Russian)

Sakamoto, K. (1994a): The present situation of acid rain in the world — East Asia. *Meteor. Study Note,* **182**, 15–32. (In Japanese)

Sakamoto, K. (1994b): Science and prevention of acid rain. T. Mizoguchi, Maruzen, Tokyo, 321 pp. (In Japanese)

Satake, H., and Yamane, T. (1992): Deposition of non-sea salt sulphate observed at Toyama facing the Sea of Japan for the period of 1981–1991. *Geochem. J.,* **26**, 299–305.

Statistics Bureau, Ministry of Internal Affairs and Communications, Japan (2006): Japan statistical yearbook 2006. Japan Statistical Association, Tokyo, 935 pp.

Suzuki, K. (1987): Spatial distribution of chloride and sulfate in the snow cover in Sapporo, Japan. *Atomos. Env.,* **8**, 927–936.

Toyama, K., Tsuruta, M., Satake, H., Takai, G. and Kawada, K. (2003): Long-distance transportation of contaminants from the Asian Continent in snow cover of central Japan high mountain region. *Geochem. et Cosmochem. Acta,* Special Supplement — Abstracts of the 13th V. M. Goldschmidt Conference, 488.

Toyama, K., Suzuki, G., Satake, H., Kawada, K. and Iida, H. (2005): Dating of snow layers in the mountain area based on the variation of oxygen isotope ratio. *Seppyo,* **67**, 319–330. (In Japanese with English abstract)

Tsunogai, S. (1975): Sea salt particles transported to the land. Tellus, 27, 51–58.

Tsuruta, H. (1989): Acid rain in East Asia. *Kagaku,* **59**, No. 5, 305–315. (In Japanese)

Tsushima, K. and Hirata, K. (1999): Comparison of chemical properties in deposited snow between Mt.Shinhodaka-ropeway, Gifu Toga-village, Toyama. *Cold region technology conference '99,* 816–823. (In Japanese)

Watanabe, K., Iwai, A., Takeda, N., and Takebe, Y. (2005): Measurements of peroxide concentrations in precipitation in Toyama and in the snow pit at Murododaira, near the summit of Mt. Tateyama. *Bulletin of Glaciol. Res.,* **22**, 51–55.

Yanagisawa, F. and Sakai, H. (1983): Thermal decomposition of barium sulfate-vanadium pentaoxide-silica glass mixture for preparation of sulfur dioxide in sulfur isotope ratio measurement. *Anal. Chem.,* **55**, 985–987.