

CHEMICAL COMPOSITION OF SNOW DRIFT ON MIZUHO PLATEAU

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Abstract: The chemical composition was determined on snow drift which was sampled at Mizuho Station (2230 m a.s.l.) and Mizuho Plateau (1800-3000 m a.s.l.), East Antarctica, in 1986. Na^+ , Cl^- , NO_3^- and SO_4^{2-} were determined by ion chromatography on 44 samples. Electroconductivity and H^+ concentration were also measured on 85 samples. The concentrations of NO_3^- and SO_4^{2-} of snow drift showed maximum values in summer. It is considered that the concentrations of both Na^+ and Cl^- of snow drift during winter are dependent on not only the amount of sea-salt in the atmosphere but also on the dilution effect through mixing with falling snow. It is pointed out that increase in their concentrations of snow drift in late summer results from aerosol scavenged by drifting snow particles rather than sublimation of drifting snow particles.

1. Introduction

It has been considered that aerosol in the Antarctic atmosphere is supplied with snow fall and as dry-fallout to deposited snow. At the surface of deposited snow, sublimation and condensation of water vapor cause metamorphism of deposited snow (FUJII and KUSUNOKI, 1982), and wind erosion of deposited snow and deposition process cause re-distribution of snow particles (WATANABE, 1978), because drifting snow particles are settled again behind obstacles such as sastrugi. During snow falls, drifting snow particles mix with falling snow particles, and also they settle behind the obstacles. Since such settled snow is called "snow drift", in the same manner, trapped snow in a small pit is defined as "snow drift" in the present paper.

Drifting snow contributes to the surface mass balance in a strong katabatic wind region such as Mizuho Plateau. Therefore, from the viewpoint of the material cycle, drifting snow particles play an important role in transport of materials as well as surface mass balance. Therefore, snow drift samples were taken by some of the authors during the 27th Japanese Antarctic Research Expedition (JARE), and the chemical composition of the snow drift was determined in the laboratories of the Water Research Institute and the National Institute of Polar Research in Tokyo.

The purpose of the present study is to obtain chemical data of snow drift on

Mizuho Plateau, to know the seasonal variation of major soluble constituents of the snow drift, and to find the relation between the seasonal variation and material transport process which is related to drifting snow.

2. Sampling and Analysis

2.1. Snow drift samples

Snow drift samples were taken at Mizuho Station ($70^{\circ}42'S$, $44^{\circ}20'E$ 2230 m a.s.l.) from February to September, and along oversnow traverse routes on Mizuho Plateau ($70^{\circ}42'S$ – $73^{\circ}07'S$, $39^{\circ}45'E$ – $44^{\circ}20'E$ 1800–3000 m a.s.l.) from October to December in 1986, as shown by the hatched area in Fig. 1. Samplings were carried out with special care to avoid contamination from snow vehicles, wearing clean cloth, clean cap, clean mask and powder-free clean PVC gloves in downwind position against the sampling sites.

The polypropylene (PP) sampling bottles (1 l) were precleaned as reported by KANAMORI *et al.* (1987). But polyethylene (PE) sampling bottles (250 ml) for some of the anion analyses, electroconductivity measurements and pH measurements were

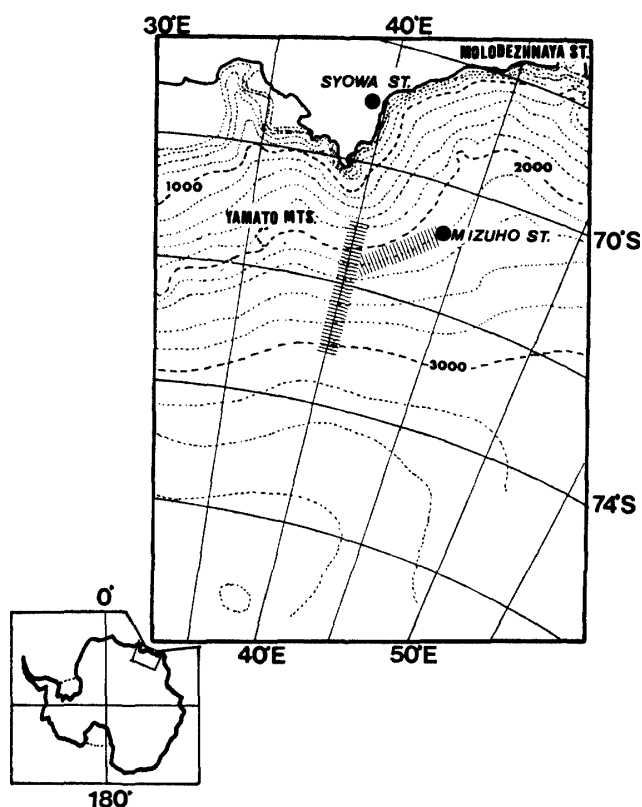


Fig. 1. Location map of snow drift sampling. Sampling was carried out at Mizuho Station (2230 m a.s.l.) from February to September, 1986, and in the hatched area (1800–3000 m a.s.l.) during the oversnow traverse of Mizuho Plateau from October to December, 1986.

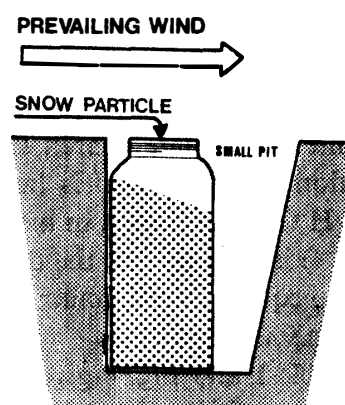


Fig. 2. Schematic depiction of snow drift sampling.

precleaned only by deionized water without the use of acids. In the same manner, PE sampling bottles (500 ml) were prepared for *in-situ* measurement of electroconductivity. About 100 to 300 g of snow drift samples were taken in 1 l PP bottles directly just above the snow surface into a sampling bottle set in a small pit as shown in Fig. 2. Then they were sealed in PE bags and kept frozen until analysis in the laboratory.

2.2. Analysis

2.2.1. *In situ* measurement of electroconductivity

After melting of snow drift samples at room temperature in Mizuho Station or a snow vehicle during the inland glaciological traverse, the electroconductivity of the sample was measured *in-situ* by a conductivity meter, TOA Model CM-50AT equipped with CG-7001PL electrode under aerated condition (water temperature was about 14–20°C).

2.2.2. Laboratory measurement

Melt water of frozen samples at room temperature in the laboratory was filtered through a membrane filter (Nuclepore filter with 0.22 μm pore size). Concentrations of Na^+ , Cl^- , NO_3^- , and SO_4^{2-} in the filtrate were measured by an ion chromatograph, Dionex Model 10 and 2000 i/SP. Electroconductivity and pH of samples were measured by a conductivity meter, CM-50AT set and a pH meter, Iwaki Glass Model M-225 equipped with IW-050 combination glass electrode, respectively, under CO_2 -free condition (CRAGIN *et al.*, 1984) in a temperature controlled water bath (25°C). The reproducibility of the pH and electroconductivity measurements in the laboratory is ± 0.05 pH and $\pm 0.1 \mu\text{S}\cdot\text{cm}^{-1}$, respectively.

3. Results and Discussion

3.1. Seasonal variation of chemical composition of snow drift

Electroconductivity is an index of total ionic concentration of a solution. Figure 3 shows electroconductivity and pH values of melt samples of snow drift collected on Mizuho Plateau. They do not contain CO_2 . As seen from the figure, both values show maxima in summer (from late November to early March; 29 samples) and minima in winter (from late March to early November; 56 samples). For both values, the variation in one season is large in summer and small in winter. The difference in mean H^+ concentration in melt samples between summer ($5.2 \mu\text{eq}\cdot\text{l}^{-1}$) and winter ($1.7 \mu\text{eq}\cdot\text{l}^{-1}$) is $3.5 \mu\text{eq}\cdot\text{l}^{-1}$, the difference is larger than that of deposited snow ($1 \mu\text{eq}\cdot\text{l}^{-1}$) with $4 \mu\text{eq}\cdot\text{l}^{-1}$ in maximum and $3 \mu\text{eq}\cdot\text{l}^{-1}$ in minimum at the South Pole (LEGRAND and DELMAS, 1984).

Table 1 and Fig. 4 give results of chemical analyses of snow drift samples. The ionic compositions listed in Table 1 show a good balance in winter and unbalance in summer between cations and anions. Since concentrations of major cations except Na^+ and H^+ are not determined, detailed discussion of such unbalance is impossible.

The seasonal variations in concentrations of both NO_3^- and SO_4^{2-} of snow drift show a trend of summer maximum and winter minimum similar to the above mentioned trend for H^+ concentration and electroconductivity. The variations of mean con-

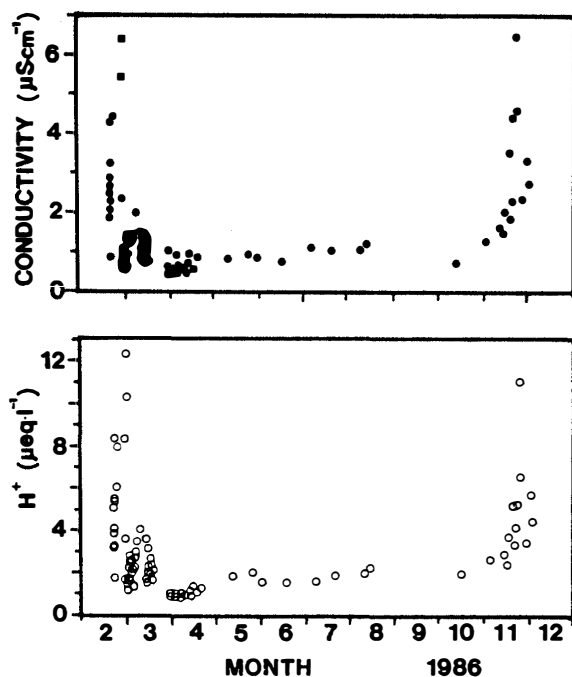


Fig. 3. Seasonal variations of electroconductivity and H^+ concentration.

Table 1. Chemical composition of snow drift on Mizuho Plateau ($\mu\text{eq}\cdot\text{l}^{-1}$).

Element	Summer $n=26$ 1986/2/2-3/4 11/17-12/4	Winter $n=18$ 1986/3/4-11/12	Annual mean $n=44$ 1986/2/2-12/4
Na^+	1.14 (1.28)	1.06 (0.84)	1.11 (1.12)
Cl^-	1.76 (0.78)	1.77 (1.11)	1.76 (0.93)
NO_3^-	4.92 (2.37)	1.03 (0.67)	3.33 (2.68)
SO_4^{2-}	4.15 (2.27)	0.60 (0.37)	2.70 (2.48)
H^+	5.17 (2.67)	1.65 (0.78)	2.85 (2.37)
Conductivity*	3.04 (1.51)	0.92 (0.35)	1.64 (1.37)

() ; Standard deviation.

*; $\mu\text{S}\cdot\text{cm}^{-1}$.

centration between summer and winter are $3.9 \mu\text{eq}\cdot\text{l}^{-1}$ for NO_3^- and $3.5 \mu\text{eq}\cdot\text{l}^{-1}$ for SO_4^{2-} . Furthermore, NO_3^- concentration reached its maximum before appearance of that for SO_4^{2-} in Fig. 4. Such a trend is different from the reports on deposited snow obtained by HERRON (1982) and LEGRAND and DELMAS (1984) at the South Pole that concentration of SO_4^{2-} reached its maximum before appearance of that for NO_3^- .

Such a difference between snow drift and deposited snow is interpreted to be due to that nitric acid vapor migrates more easily than sulfuric acid in the snow layer, because the volatility of nitric acid is higher than that of sulfuric acid. NEUBAUER and HEUMANN (1988) reported that NO_3^- concentration of freshly deposited snow is higher than that of old snow, and they suggested that NO_3^- loss from snow result from both evaporation of nitric acid from surface snow into the atmosphere and photochemical decomposition of nitric acid.

Their result and suggestion support the interpretation that nitric acid in deposited

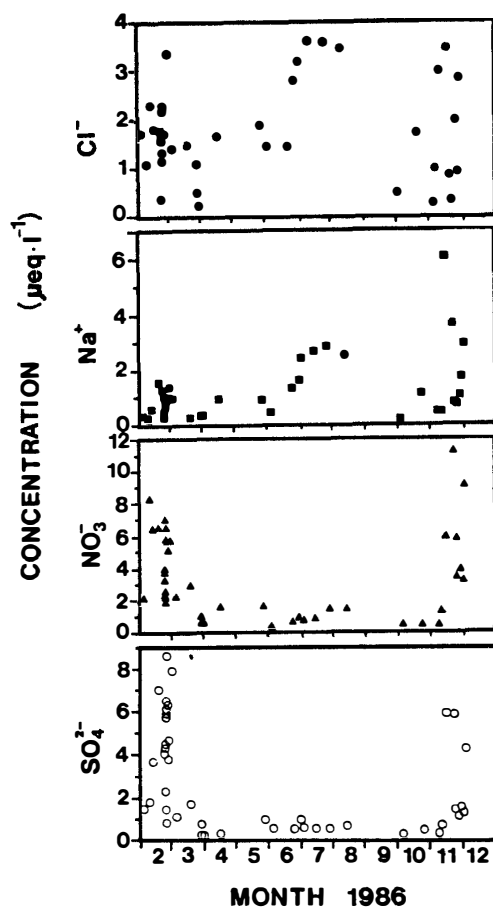


Fig. 4. Seasonal variations in the concentrations ($\mu\text{eq}\cdot\text{l}^{-1}$) of various constituents.

snow migrates into the atmosphere during summer or toward the upper layer in deposited snow during autumn. Therefore, the concentration of NO_3^- in deposited snow should reach its maximum after appearance of that for SO_4^{2-} .

The seasonal variations of Na^+ and Cl^- concentration show a similar trend except in late summer. The variations of Na^+ and Cl^- concentration in winter are different from those at the South Pole (LEGRAND and DELMAS, 1984). Monthly mean concentrations of Na^+ and Cl^- of snow drift increase, in many cases, with increasing storms from the coast into the inland of the Antarctic ice sheet, but their concentrations in snow drift do not always increase during the storm season in the present study. For example, a snow storm accompanied by both blowing snow and snow precipitation occurred 8 days in March and 5 days in July in 1986 (OHMAE *et al.*, 1987), but Na^+ concentration was lower in March than in July. Such an example indicates that sea-salt concentration in snow drift is not proportional to the frequency of storm penetration.

FUJII and OHATA (1982) have also indicated that the low concentration of microparticles in snow drift in March is due to mixing of snow drift with falling snow particles having low microparticle concentration. Their indication can be applicable to the present case. In other words, the Na^+ and Cl^- concentrations in snow drift are dependent on not only the amount of sea-salt in the atmosphere, but also on the dilution

effect through mixing with falling snow. Therefore, it is considered that their concentrations in snow drift do not always increase during the storm season.

As reported by DELMAS *et al.* (1982) and LEGRAND (1987), deposited snow in Antarctica contains sea-salt and three strong mineral acids such as H_2SO_4 , HNO_3 and HCl . Hence, excess SO_4^{2-} and excess Cl^- with respect to sea water constituents are calculated from Na^+ concentration in snow drift:

$$(\text{SO}_4^{2-})_{\text{ex}} = (\text{SO}_4^{2-}) - 0.12(\text{Na}^+) \quad (1)$$

$$(\text{Cl}^-)_{\text{ex}} = (\text{Cl}^-) - 1.17(\text{Na}^+) \quad (2)$$

where (x) denotes the concentration of x species in equivalent per liter, and 0.12 and 1.17 are $(\text{SO}_4^{2-})/(\text{Na}^+)$ and $(\text{Cl}^-)/(\text{Na}^+)$ equivalent ratio in normal seawater, respectively.

Figure 5 indicates the characteristic seasonal variations of these excess values in the samples. The values of excess SO_4^{2-} show a clear seasonal variation, whereas variation of excess Cl^- values is less than that of excess SO_4^{2-} values. This is quite interesting in comparison with the seasonal variations of net concentration (Fig. 4). A similar result on aerosol was reported by BODHAINE *et al.* (1986) at the South Pole.

The SO_4^{2-} concentration is mostly explained by excess SO_4^{2-} . The excess Cl^- values indicate chlorine addition and also chlorine depletion. The excess Cl^- values show such a characteristic of chlorine addition with low Na^+ concentration in autumn and its depletion with high Na^+ concentration in spring. LEGRAND and DELMAS

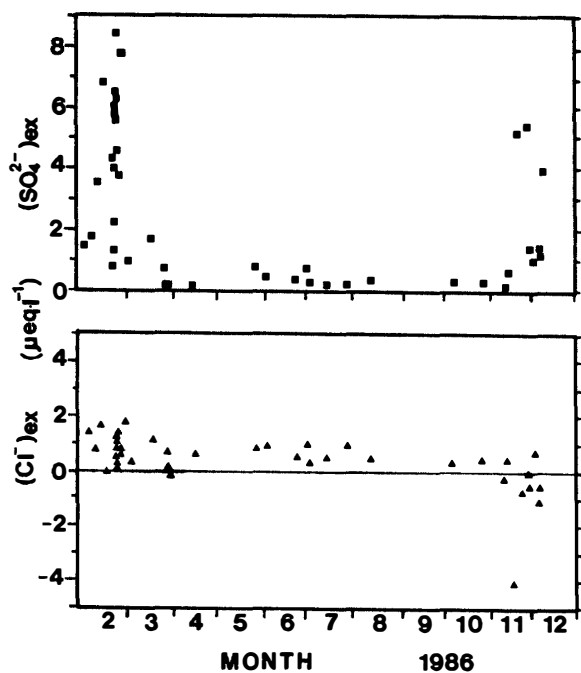


Fig. 5. Seasonal variations of excess SO_4^{2-} and excess Cl^- . Negative values of excess Cl^- indicate chlorine depletion.

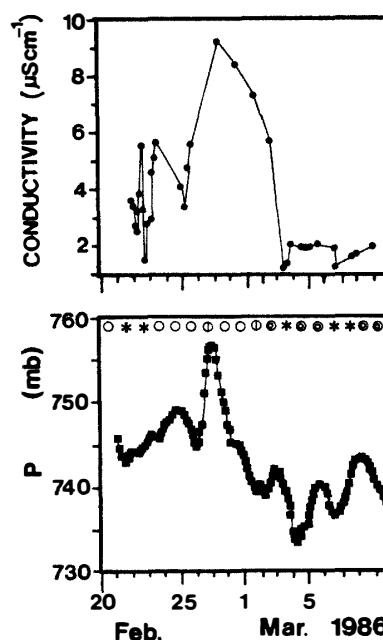


Fig. 6. Short time variations of electroconductivity, weather condition and atmospheric pressure (P) at Mizuho Station. Electroconductivity was measured in situ.

(1985) have mentioned that the Cl/Na ratio in deposited snow increases with distance from the coast to inland, that HCl is formed in the coastal area where sea-salt particles are abundant, and that subsequently HCl is transported inland and deposited preferentially on the Antarctic Plateau. Therefore, it is considered that chlorine depletion of snow drift is caused by incorporation of sea-salt particles which are Cl^- depleted by reaction with sulfuric acid in spring when sea-salt particles are abundant in the atmosphere, as shown in Fig. 4, and subsequently HCl formed by such reaction diffuses into the snow drift.

3.2. Material transport on Mizuho Plateau

Figure 6 shows atmospheric pressure (P) and weather condition at Mizuho Station (OHMAE *et al.*, 1987), and also the results of *in-situ* measurements of electroconductivity from February 20 to March 9. The figure indicates that the variation of electroconductivity shows a maximum value under anticyclonic and clear sky conditions.

Therefore, the following two processes are considered to be the reasons for the maximum electroconductivity of snow drift. The first probable process is scavenging of aerosols by drifting snow particles. Assuming that drifting snow particles in summer are originated by erosion of deposited snow which accumulated from autumn to spring, because seasons of snow layer formation at Mizuho Station are mainly autumn and spring (FUJII and OHATA, 1982), the maximum SO_4^{2-} concentration of snow drift in late summer, C_s , is represented by the following equation:

$$C_s = C_{s_0} + D \cdot S \cdot E \cdot n \quad (3)$$

where C_{s_0} : the initial concentration ($\text{ng} \cdot \text{g}^{-1}$) of SO_4^{2-} of drifting snow particles, D : range (m) where drifting snow particles scavenged aerosols, S : total-cross section (cm^2) of 1 g of drifting snow particles with a diameter of 0.2 mm at 3 cm above the surface (BUDD, 1966), E : collection efficiency (g^{-1}) of aerosol particles by drifting snow particles, n : concentration ($\text{ng} \cdot \text{m}^{-3}$) of aerosol SO_4^{2-} during late summer.

In this case, C_s is $380 \text{ ng} \cdot \text{g}^{-1}$ and C_{s_0} is $30 \text{ ng} \cdot \text{g}^{-1}$ as shown in Fig. 4, S is 82 cm^2 , and n is $150 \text{ ng} \cdot \text{m}^{-3}$ according to preliminary data at Mizuho Station in 1986 (S. KANAMORI *et al.*, unpublished data). Aerosols can be considered as Aitken particles in this case, because HOGAN and BARNARD (1978) and ITO and IWAI (1981) reported sudden increase in the proportion of acidic Aitken particles in the summer atmosphere. Therefore, the radius of Aitken particles is assumed to be $5 \times 10^{-7} \text{ cm}$ in the case of ITO (1985), so E can be assumed to be $3 \times 10^{-2} (\text{g}^{-1})$ according to MURAKAMI *et al.* (1985) based on the collection efficiency of plane type snow crystals with respect to Aitken particles with a radius of $5 \times 10^{-7} \text{ cm}$. By introducing these values into eq. (3), the value of D was calculated to be 9500 m.

Since wind velocity 5 m above the surface is about $12 \text{ m} \cdot \text{s}^{-1}$ during this period (OHMAE *et al.*, 1987), wind velocity at 10 cm above the surface is considered to be $7 \text{ m} \cdot \text{s}^{-1}$ according to the wind profile of BUDD *et al.* (1966). Assuming that drifting snow particles are transported with the wind velocity at 10 cm above the surface, the period of aerosols scavenging by drifting snow particles during the above range is 1400 s. Therefore, the observed SO_4^{2-} value of $380 \text{ ng} \cdot \text{g}^{-1}$ in snow drift is explained

if a drifting snow particle was in the air during 1400 s and 9500 m in scavenging range. It seems reasonable to move a drifting snow particle through a scavenging range of 9500 m, because drifting snow diverges around Mizuho Station (TAKAHASHI, 1988).

The second probable process is due to increase in SO_4^{2-} concentration of drifting snow particles by its sublimation of H_2O . Vapor pressure at the snow surface is usually higher than vapor pressure at 2 m height during summer (FUJII and KUSUNOKI, 1982). Furthermore, they observed that sublimation rate at the snow surface indicates daily periodic variation, being high around 1200 LT and low around 2400 LT.

Therefore, when drifting snow particles are taken from the snow surface with the same vapor pressure as that of the snow surface, it will sublimate in air having low vapor pressure, and the SO_4^{2-} concentration in drifting snow particles will increase during drifting under clear sky in the present case. Also, it should be expected that the concentration of SO_4^{2-} in drifting snow particle around 1200 LT will be larger than that at around 2400 LT.

For example, as shown in Fig. 6, values of electroconductivity of snow drift during February 25 are $3.46 \mu\text{S}\cdot\text{cm}^{-1}$ around 0200 LT and $5.69 \mu\text{S}\cdot\text{cm}^{-1}$ around 1400 LT under clear sky condition similar to February 27 when electroconductivity of snow drift showed a maximum value ($9.31 \mu\text{S}\cdot\text{cm}^{-1}$, 0930 LT).

If the maximum value on February 27 was due to such successive and daily variation of sublimation of H_2O from drifting snow particles, decreases in electroconductivity of samples collected around noontime from February 27 to March 2 should not be explained without accounting for the dilution effect due to snow fall, but snow fall was not observed during such a period (OHMAE *et al.*, 1987).

On the other hand, if the maximum concentration of SO_4^{2-} in snow drift during late summer is due to increase of concentration after sublimation of H_2O , Na^+ concentration in snow drift should also have a maximum through sublimation during late summer. However, Na^+ concentration in snow drift does not show a maximum during late summer, as seen in Fig. 4.

Therefore, it is reasonable that the maximum values of electroconductivity and SO_4^{2-} concentration in snow drift during late summer can be explained by the first process, namely scavenging of aerosols by drifting snow particles, rather than the second process.

4. Concluding Remarks

The present study shows the important role of drifting snow particles in material transport from atmosphere to the ice sheet surface. It is, therefore, necessary to pursue further simultaneous studies on vertical distributions of water vapor pressure, aerosol concentration and drifting snow particles near the surface through a year, in the various parts of the Antarctic ice sheet under different climatic conditions to evaluate the role of drifting snow particles in material transport. These studies will contribute also to interpretations of chemical stratigraphy of snow and ice cores obtained by drilling.

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