

Seasonal variations of major ionic concentration levels in drifting-snow samples obtained from east Dronning Maud Land, East Antarctica

KAZUO OSADA

Solar-Terrestrial Environment Laboratory, Nagoya University, Nagoya 464-01, Japan

ABSTRACT. Drifting-snow samples were collected at Mizuho Station (74°42' S, 44°20' E, 2230 m a.s.l.) from February to October 1986 and along traverse routes in east Dronning Maud Land (1800–3000 m a.s.l.), East Antarctica, from October 1986 to January 1987. The typical sampling interval was about once a week but two sets of intensive sampling were made at the end of February and November at between 2 h and 1 d intervals.

Measurements for Cl^- , NO_3^- , SO_4^{2-} and Na^+ were made on the drifting-snow samples by ion chromatography. Oxygen-isotope ratios were also measured on the samples. Concentration levels of NO_3^- and SO_4^{2-} show distinctive seasonal variations: high in summer (4.6 neq g^{-1} for NO_3^- and 3.3 neq g^{-1} for SO_4^{2-}) and low in winter during mid-March to mid-November (1.0 neq g^{-1} for NO_3^- and 0.5 neq g^{-1} for SO_4^{2-}). Results obtained at Mizuho Station show that the transition from the summer high values to winter low values takes about 20 d for NO_3^- and SO_4^{2-} . The variations in Cl^- and Na^+ concentration levels are small in both autumn and spring (averages are about 1 neq g^{-1}) with greater variability throughout the rest of the year. The intensive-sampling data set shows that there is considerable variability within a day with NO_3^- and SO_4^{2-} concentration levels up to about a factor of 4 associated with a 10‰ change in $\delta^{18}\text{O}$ ratios.

1. INTRODUCTION

Studies on the chemical constituents of ice cores obtained from polar ice sheets have provided information on the past atmospheric environment (see reviews: Clausen and Langway, 1989; Delmas, 1992). Seasonal variations in concentration levels of chemical constituents recorded in snow deposits and ice cores have been used to identify annual layers of snow or ice and to investigate sources of constituents (Herron, 1982; Legrand and Delmas, 1984). Studies on fallen and drifting-snow samples are essential to understand the chemical stratigraphy of seasonal variations at the concentration levels of constituents in deposited snow. However, reports on the chemistry of fallen and drifting-snow samples are very limited for (1) the number of samples measured (Maupetit and Delmas, 1992) and (2) the period of sampling (Kamiyama and others, 1989).

Even under clear-sky conditions, drifting- or blowing-snow phenomena are observed at Mizuho Station due to strong katabatic winds. Drifting-snow particles originate from the snow surface by wind erosion. Under precipitating conditions, newly fallen snow particles are mixed with the drifting-snow particles. These mixed snow particles, as well as aged drifting-snow particles, again deposit on to the snow surface. In other words, deposited snow in a katabatic-wind region consists of a mixture of newly fallen and aged drifting-snow particles. Since such settled snow

is called "snowdrift", in the same manner, snow trapped in a sampling bottle in a small pit is defined as "snowdrift trapped" in this paper.

The purpose of this study is to extend the preliminary chemical data (Osada and others, 1989) of trapped snowdrift samples obtained from east Dronning Maud Land, East Antarctica, and to investigate the detailed seasonal and short-term (time-scale of a few hours to a day) variation of major soluble constituents (Cl^- , NO_3^- , SO_4^{2-} , Na^+) of the trapped snowdrift samples.

2. SAMPLING AND ANALYSIS

Samples of drifting snow were taken at Mizuho Station (70°42' S, 44°20' E, 2230 m a.s.l.) from February to September 1986, and along oversnow traverse routes in east Dronning Maud Land (1800–3000 m a.s.l.) from October 1986 to January 1987. Figure 1 is a location map of Mizuho Station and the traverse routes. In Figure 1, thick lines indicate the traverse routes where snow-trap sampling was made. The observed area in this study is categorized as a cold katabatic region (Dalrymple, 1966), where drifting and blowing snow conditions are frequently observed (see details for drifting-snow conditions at Mizuho Station in Kobayashi (1978) and Takahashi (1985)).

Snow-trap sampling was carried out with special care to avoid contamination from snow vehicles, station and

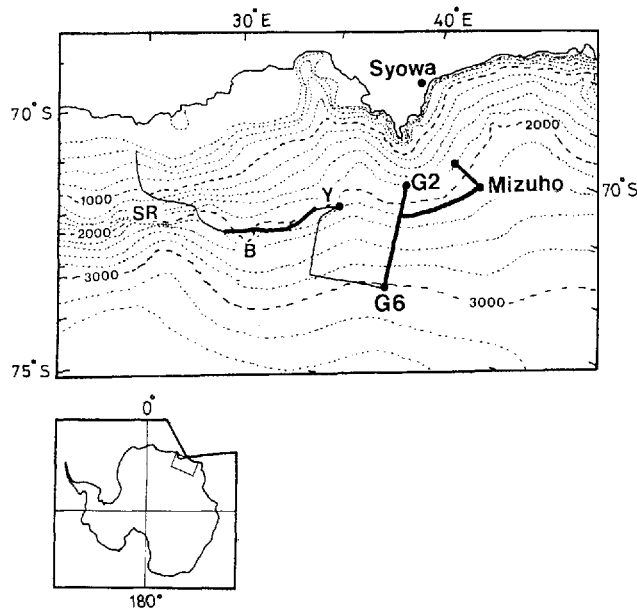


Fig. 1. Map of traverse routes in east Dronning Maud Land, Antarctica. Trap sampling of drifting snow was conducted along the routes shown by the thick lines. G2 and G6: glaciological observation sites, Y: Yamato Mountains, B: Belgica fjella and SR: Sor-Rondane mountains.

human activities, wearing clean clothing, clean mask and powder-free clean PVC gloves. Since the direction of katabatic winds is stable at a given location, all sampling pits were set in a position at least 100 m upwind of station and field-camp activities. Sampling personnel were always kept in their position downwind of the prevailing

katabatic wind direction against the sampling bottles and equipment.

Polypropylene (PP) sampling bottles (1 l) were pre-cleaned as reported by Kanamori and others (1987). About 100–300 g of snow sample drifting just above the snow surface was directly trapped into the wide-mouth 1 l PP bottle. The weight of trapped snow depends on type of drifting-snow particles: a lighter weight for mixed drifting snow with newly fallen snow particles and a heavier weight for aged drifting-snow particles. The sampling duration is typically between 1 h and a few hours until a full sampling-bottle set was obtained in a small pit which is as deep as the height of the bottle (Osada and others, 1989). Then they were sealed in double PE bags and kept frozen until analysis in the laboratory in Japan.

Polyethylene (PE) sampling bottles (250 ml) were pre-cleaned only by deionized water without the use of acids. Some duplicate snow samples using both the PP and the PE bottles were made for comparison of bottle-cleaning procedures.

As described in a previous paper (Osada and others, 1989), snow samples were melted at room temperature in the laboratory and immediately filtered through a membrane filter (Nuclepore filter with a 0.22 μm pore size). In this study, concentrations of Na^+ , Cl^- , NO_3^- and SO_4^{2-} in non-filtered meltwater samples from both the 1 l PP and the 250 ml PE bottles were measured by an ion chromatograph (Dionex 2000i/SP) in the laboratory of the National Institute of Polar Research in Tokyo. Comparison of duplicate samples for bottle-cleaning procedures and filtered/non-filtered samples show an insignificant difference for ions measured, within an error of ion-chromatographic measurements (typically <10%).

Table 1. Concentration levels of major ionic constituents in snowdrift

	NO_3^-	SO_4^{2-}	Cl^-	Na^+	exSO_4^{2-}	exCl^-
	neq g^{-1}					
<i>Summer: 26 Jan–17 Mar and 13 Nov–18 Jan (49 samples)</i>						
Average	4.63	3.29	1.94	1.48	3.10	0.25
STD	2.37	2.46	1.32	1.91	2.35	1.55
Minimum	1.69	0.50	0.31	0.09	0.25	-8.28
Maximum	11.66	11.28	8.99	9.52	10.14	2.85
<i>Winter: 18 Mar–12 Nov (55 samples)</i>						
Average	0.97	0.50	1.72	1.13	0.37	0.39
STD	0.40	0.19	1.38	0.96	0.19	0.39
Minimum	0.21	0.17	0.17	0.04	-0.12	-0.37
Maximum	2.15	0.94	7.46	4.39	0.81	2.34
<i>Year 1986: 26 Jan 1986–18 Jan 1987 (104 samples)</i>						
Average	2.69	1.81	1.83	1.30	1.66	0.37
STD	2.47	2.19	1.35	1.52	2.12	1.13
Minimum	0.21	0.17	0.17	0.04	-0.12	8.28
Maximum	11.66	11.28	8.99	9.52	10.14	2.85

STD, Standard deviation.

The isotopic composition of the meltwater was obtained by analyses with a MAT 250 mass spectrometer at the Water Research Institute, Nagoya, on CO₂ equilibrated with the meltwater of the samples. The analytical error was less than 0.2‰ in δ¹⁸O.

3. RESULTS AND DISCUSSION

Figure 2 shows the variation of δ¹⁸O values measured on the snowdrift samples trapped and the elevation of the sampling points. Variation of the δ¹⁸O values includes short-term variations during a precipitation event (sampled at Mizuho Station until early October) and changes in the sampling-site elevation as well as distance from the coast. Temporal and spatial variations in the δ¹⁸O values for this region have been described by Watanabe and others (1981, 1988) and Ageta (1993).

Figure 3 shows results of chemical analyses of the snowdrift samples that were trapped. In Figure 3, triangles represent snow samples containing newly fallen snow and open circles represent drifting-snow samples without falling snow. No samples were obtained for the

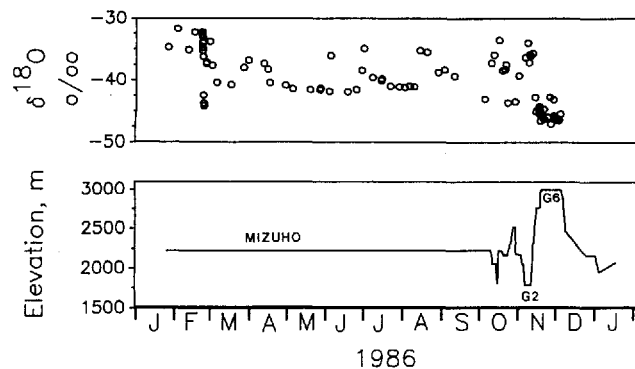


Fig. 2. Oxygen-isotope ratio of drifting-snow samples trapped (upper) and elevation (m.a.s.l.) of sampling points (lower). Station names of longer duration of stay are indicated for Mizuho Station, G2 and G6 sites.

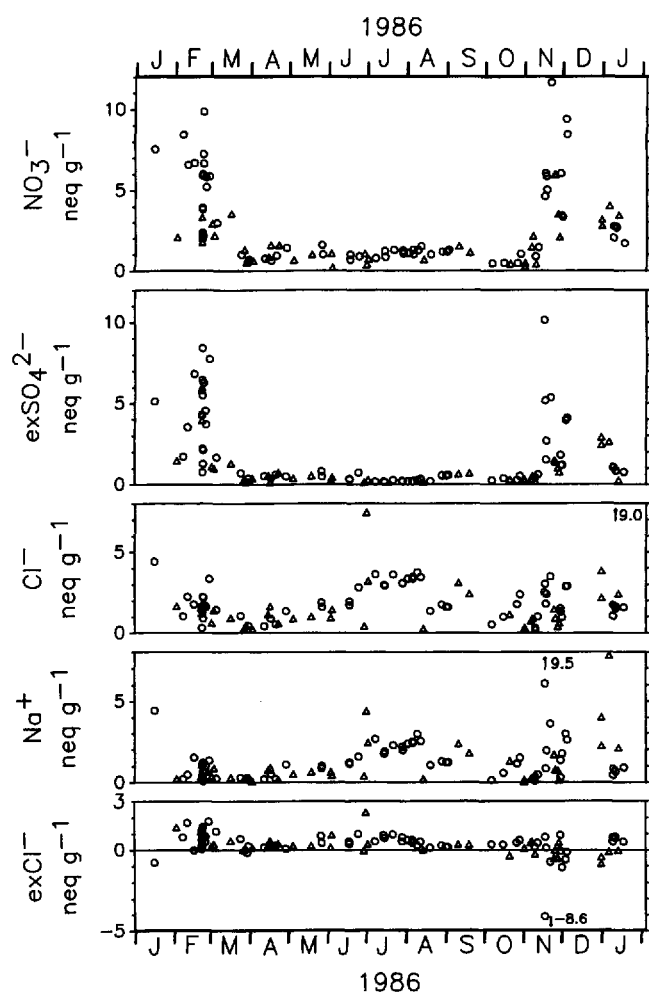


Fig. 3. Variations in concentration levels of ionic constituents in trapped snowdrift samples obtained from east Dronning Maud Land. Triangles represent snow samples containing fresh falling-snow particles. Open circles represent snow samples without falling-snow particles.

gaps in December in the figure, because of the traverse of the bare icefield in the Yamato Mountains area. The results are summarized in Table 1. Excess SO₄²⁻ concentrations (abbreviated as exSO₄²⁻ hereafter) are the non-sea-salt part of the total SO₄²⁻ content measured. The exSO₄²⁻ concentrations are calculated from the measured SO₄²⁻ and Na⁺ contents of the samples using the SO₄²⁻/Na⁺ ratio in sea water (0.12 in equivalent units).

The seasonal variations in the concentrations of NO₃⁻ and exSO₄²⁻ in the snowdrift trapped show distinctive maxima in summer and minima in winter. Concentration levels for NO₃⁻ and exSO₄²⁻ show low variabilities in winter relative to variations in summer. The amplitudes of the concentration levels between summer and winter averages (Table 1) are 4.8 times for NO₃⁻ (summer, 4.63 ~ winter, 0.97 neq g⁻¹) and 8.4 times for exSO₄²⁻ (summer, 3.10 ~ winter, 0.37 neq g⁻¹). These seasonal amplitudes are close to the results of atmospheric aerosols collected at Mawson (Savoie and others, 1992): about 5 times (summer maximum: October–December; winter minimum: April–May) for NO₃⁻ and about 7.6 times (maximum: October–March; minimum: April–September) for exSO₄²⁻.

On the other hand, detailed seasonal variations for NO₃⁻ and exSO₄²⁻ are different from those of aerosol data collected at the coastal stations (at Georg von Neumayer: Wagenbach and others, 1988; at Mawson: Savoie and others, 1992); (1) a small winter peak of NO₃⁻ concentration in aerosols does not appear in the snowdrift trapped, (2) a sharp transition from summer to winter of exSO₄²⁻ in the snowdrift took only about 20 d instead of a sinusoidal smooth curve for the results of the aerosols.

The seasonal variations in the Na⁺ and Cl⁻ concentrations show a similar trend except for a few points of significant excess or a depleted amount for the Cl⁻ concentration levels (Fig. 3). Excess Cl⁻ concentration levels (exCl⁻) with respect to the sea-water composition are calculated from the Cl and Na⁺ contents of the samples using the Cl⁻/Na⁺ ratio in sea water (1.17 in equivalent units). The seasonal variation of exCl⁻ is not significant but it shows excess values about 0.4 neq g⁻¹ for most of the year, except for some summer depletion points. Because sampling locations were moved from Mizuho Station after early October to the inland plateau,

the exCl profile includes changes in fractionation conditions such as the transport distance of sea salts from the coast.

Legrand and Delmas (1985, 1988) reported that the Cl/Na ratio in deposited snow increases with distance inland from the coast. They suggested HCl-formation processes as follows: HCl is formed in the coastal area where sea-salt particles are abundant and then subsequently HCl is transported inland and deposited on the Antarctic Plateau. As opposed to the geographical variation of Cl/Na in deposited snow in Terre Adélie (Legrand and Delmas, 1985), the exCl profile in this study shows negative values with a high sea-salt concentration at the most distant location (G6) from the coast.

Figure 4 shows the short-term variations of $\delta^{18}\text{O}$ and major ionic constituents measured on the snowdrift samples trapped at Mizuho Station in February 1986. The beginning of the intensive sampling set corresponds to a snow-precipitation event. This fallen-snow condition (triangles in Figure 4) continued until the late afternoon of 22 February (Ohmae and others, 1987). The $\delta^{18}\text{O}$ profile shows a decreasing trend (about 10–12‰ decrease) associated with a cooling trend in the air

temperature (about 7°C decrease) within a day. After precipitation stopped, concentration levels of NO_3^- showed an increasing trend but exSO_4^{2-} increased until after noon then decreased at once. The sea-salt components (Cl^- and Na^+) show a similar trend to each other but show different trends with NO_3^- and exSO_4^{2-} . An excess amount of Cl (not shown in Figure 4) always exists during this period (0.06–1.43 neq g^{-1}). Synoptic meteorological charts during this period indicate that a cyclone passed off the coast from 21 to 22 February, then subsequently, a ridge of high pressure came over this region on 23 February.

Figure 5 shows another set of an intensive sampling period of a 16 d stay from 21 November to 5 December 1986 at a glaciological strain-grid station: G6 (73°07' S, 39°46' E, 3005 m a.s.l.; Nishio and others, 1986). During this period, intermittent precipitation events were observed from 24 to 28 November (Nishio and others, 1988). Cloudy sky conditions extended from 28 to 30 November and clear-sky conditions persisted for the rest of the period. No significant trend in the $\delta^{18}\text{O}$ profile is seen in the figure, whereas major ionic contents measured show parallel trends in their variations: low concentration levels during intermittent precipitation events and cloudy

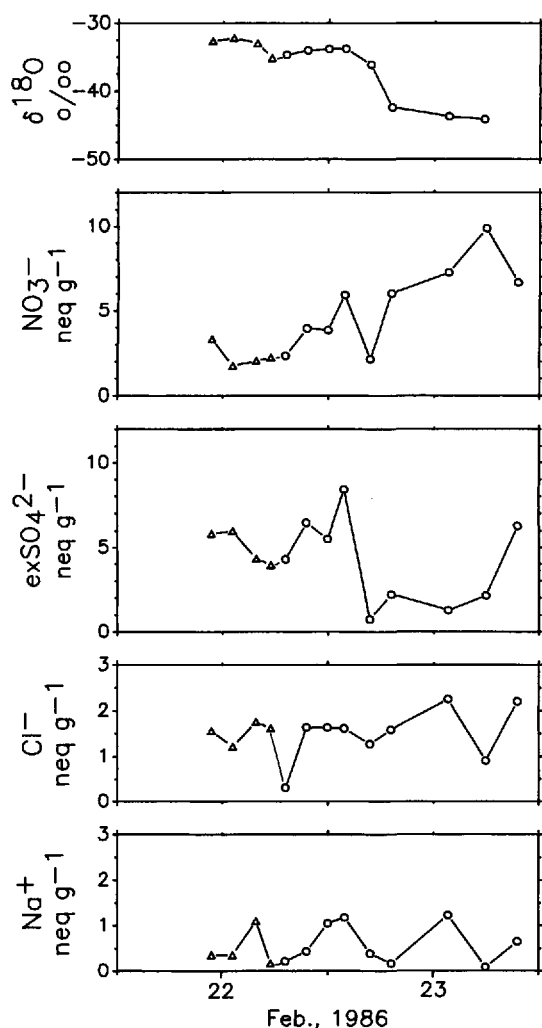


Fig. 4. Short-term variations of oxygen-isotope ratio and ionic concentration levels in snowdrift samples trapped at Mizuho Station. Triangles and circles represent the same as in Figure 3.

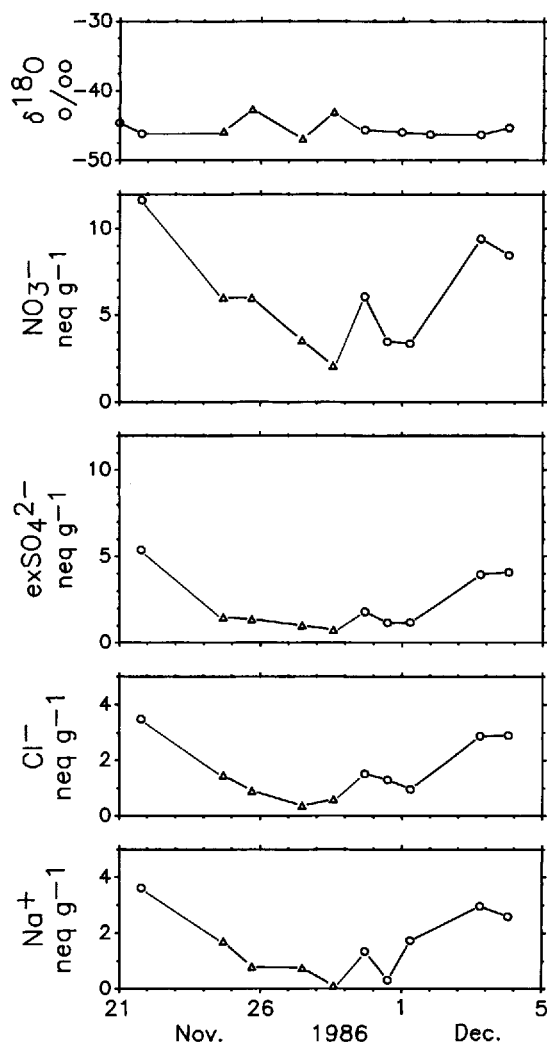


Fig. 5. Same as Figure 4 but collected at G6 glaciological strain-grid station. Triangles and circles represent the same as in Figure 3.

days. Synoptic meteorological charts do not show a passing significant ridge of high pressure over this region before or after the precipitation events.

4. CONCLUDING REMARKS

Despite moving sample locations from Mizuho Station after October, this study shows distinctive seasonal variations for NO_3^- and excess SO_4^{2-} in drifting-snow samples trapped over east Dronning Maud Land. General trends and seasonal amplitudes of NO_3^- and excess SO_4^{2-} are similar to those of reported aerosol studies made at other Antarctic stations near the coast. Details of seasonal variations in NO_3^- and excess SO_4^{2-} concentrations are different from those found in aerosols at the coastal stations: no small peak in winter for NO_3^- and a sharp seasonal transition from summer to winter for excess SO_4^{2-} in this study. The reason for the differences remains unexplained but the differences might have resulted from differences in transport processes of atmospheric aerosols and perhaps acidic gases at different regions, and rapid aerosol scavenging by drifting snow.

Short-term (at a time-scale of a few hours to 1 d) variations of ionic concentration levels in the drifting-snow samples trapped have also been studied for the summer season. The results show high variability, especially for NO_3^- and excess SO_4^{2-} within the short-term periods studied. Sampling strategy of drifting and falling snow particles, as well as atmospheric aerosols, needs to consider these significant short-term variations.

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