

SPRING PEAKS OF MAJOR AND TRACE ELEMENTS IN SNOW AT ASUKA STATION, EAST ANTARCTICA

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Abstract: In the austral spring of 1991, drifting snow samples were collected at Asuka Station (71° 32' S, 24° 08' E, 930 m above sea level) in Queen Maud Land, East Antarctica. A total of 36 elements including Na, Mg, K, Ca, Fe, Al, Li, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, Se, Rb, Sr, Cd, Pb, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Th in snow were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS). Major soluble ions (Cl⁻, NO₃⁻ and SO₄²⁻) of the snow were also determined by ion chromatography. Based on data available for comparison, the concentration ranges of the elements in Antarctic snow are one to four orders of magnitude smaller than those of Arctic snow. Pronounced peak concentrations of most of the elements and non sea salt sulfate were observed in late September to early October at Asuka Station. Before the peak concentration, enrichment factor analysis indicates that Na, Mg, Ca, K and Sr are of sea salt origins and Al, Fe, Mn, Rb, Cr, Ni, Ga, V and all the rare earth elements are of crustal origin. After the peak concentration, sea salt and crustal enrichment factors showed several fold increase. Chloride ion shows a strong correlation with Na. The precipitation of anomalously enriched elements with non sea salt sulfates could be derived from anthropogenic matter and volcanism, possibly from the Mt. Pinatubo eruption (June 1991) or the Mt. Hudson eruption (August 1991).

1. Introduction

The Greenland and Antarctic ice sheets contain a record of precipitation chemistry over time spans of thousands of years. In understanding these unique records of global climatic change, it is necessary to know the processes controlling the spatial and temporal distribution of chemical components at the ice-sheet surface. Chemical constituent concentrations in air and snow in the Arctic show a distinct seasonal pattern caused by the variation of long range atmospheric circulation in high and mid latitude areas (DAVIDSON *et al.*, 1993; HEIDEM *et al.*, 1993). The well known phenomenon of

Arctic haze is caused by springtime peaks of a number of aerosol species (DAVIDSON *et al.*, 1993; HEIDEM *et al.*, 1993), caused by pollution during the winter.

In Antarctica, a seasonal pattern of crustal, marine and sulfate aerosol concentrations has been reported at the South Pole (BODHAINE *et al.*, 1986; CUNNINGHAM and ZOLLER, 1981; WAGENBACH *et al.*, 1988) and the coastal region (LAMBERT *et al.*, 1990). Autumn-spring peaks of lead on the east coast of the Antarctic Peninsula have been reported by SUTTIE and WOLFF (1992) and summer peaks of NO_3^- and SO_4^{2-} concentration in the snow at Mizuho Station by OSADA *et al.* (1989). However, available data sets and the number and the period of sampling are still limited (IKEGAWA *et al.*, 1997).

Previous analyses of trace elements in polar snow have been carried out by graphite furnace atomic absorption following pre-concentration in a clean room (LAMBERT *et al.*, 1990; WOLFF and PEEL, 1985; LANDY and PEEL, 1981; WEISS *et al.*, 1978; BOUTRON and LORIUS, 1979). Since the introduction of inductively coupled plasma-mass spectrometry (ICP-MS), which is a well established powerful technique for the determination of trace elements, it has become possible to determine as many as 40 elements at detection limits of sub ppt order (YAMASAKI *et al.*, 1994). In this study, we present seasonal variations of trace elements of 36 species and major soluble constituents (Cl^- , NO_3^- , SO_4^{2-}) of the trapped snow drift samples obtained at Asuka Station in East Queen Maud Land, East Antarctica.

2. Materials and Methods

2.1. Samples

Samples of drifting snow were taken at Asuka Station ($71^\circ 32'S$, $24^\circ 08'E$, 930 m above sea level) from July to December 1991. Asuka Station is located 120 km from the coast in Queen Maud Land, East Antarctica (Fig. 1). The Sør Rondane Mountains are situated within 100 km south of the station. At the station, katabatic wind prevails with the mean annual wind speed of 12.6 ms^{-1} toward the ESE direction (SUKEGAWA and YAMANOUCHI, 1993). Net deposition of snow over January–November 1991 at the station was estimated as 35 cm by the snow stake method (SUKEGAWA and YAMANOUCHI, 1993). The deviation of the stake measurements was within 10 cm in the period of this study (SUKEGAWA and YAMANOUCHI, 1993).

Snow was obtained by the snow trap method, as reported by OSADA *et al.* (1989). Snow samples were collected in specially prepared polyethylene bottles, which were thoroughly washed with nitric acid and distilled water (Fig. 2).

We also collected Arctic snow samples at Upernavik, Greenland, Ny-Ålesund, Spitzbergen, and Cambridge Bay, Canada between December 1992 and January 1993. The samplings were carried out near manned stations situated near the coast. These locations are given in Table 1.

2.2. Chemical analysis

A total of 36 elements including Na, Mg, K, Ca, Fe, Al, Li, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, Se, Rb, Sr, Cd, Pb, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Th in snow were determined by ICP-MS (ELAN 6000, Perkin Elmer). Pre-concentration or filtration was not performed before measurement. Running

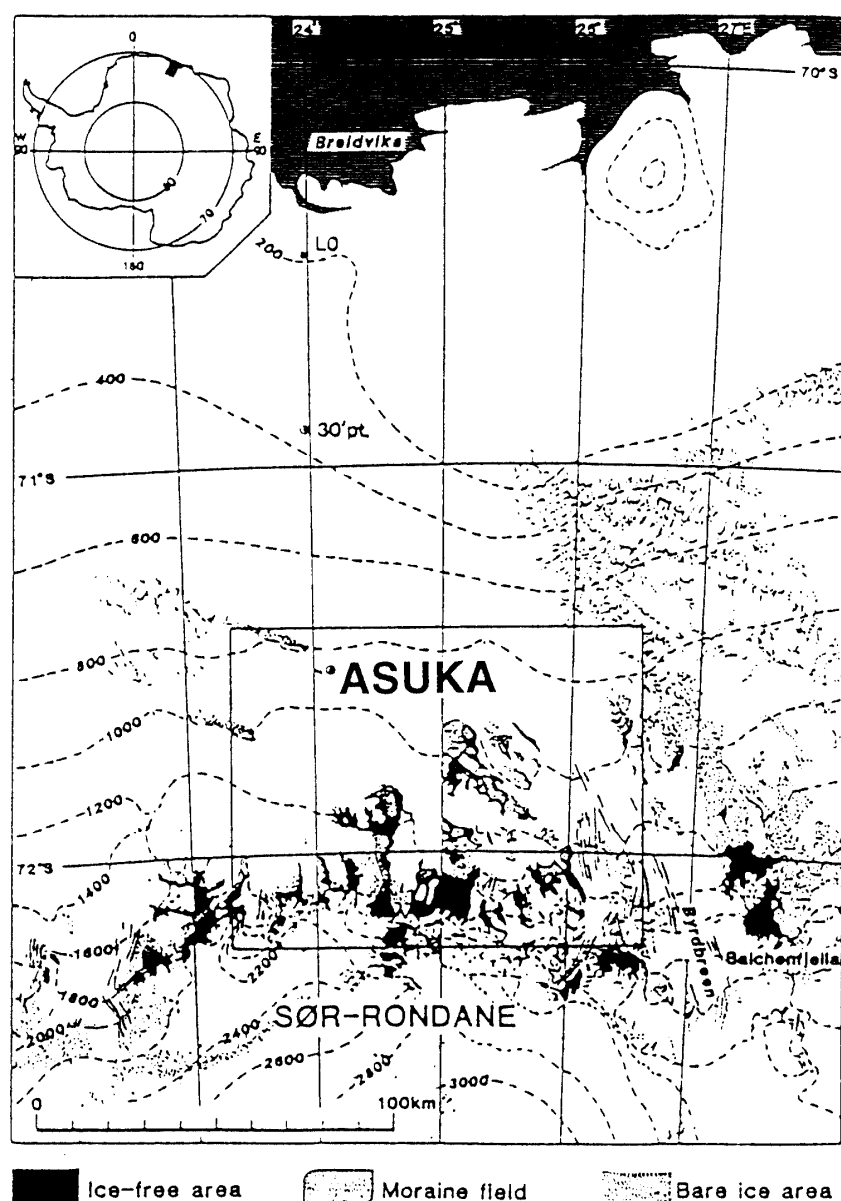


Fig. 1. Asuka Station in Queen Maud Land, East Antarctica.

conditions of the ICP-MS were as follows; RF power is 1000 W for Ca, Mg, K, Al and 600 W for the other elements, nebulizer gas flow rate is 0.725 l min^{-1} for Ca, Mg, K, Al and 1 l min^{-1} for the other elements respectively. The sampling cone and skimmer cone were made of Pt. Ultra pure water (Tama pure-100) and ultrahigh purity nitric acid provided by Tama Chemical Industry Co., Ltd. (Tokyo), as prepared for the semiconductor industry, were used throughout the experiments. Major and trace elements of this water were certified as having concentrations $< 50 \text{ ng l}^{-1}$. Dilution was carried out on a clean bench using teflon-coated volumetric ware.

Prior to the measurements of the Antarctic samples, a test experiment was performed to evaluate approximate concentrations of major and trace elements in the snow by total quant analysis. Detection limits are defined here as the equivalent

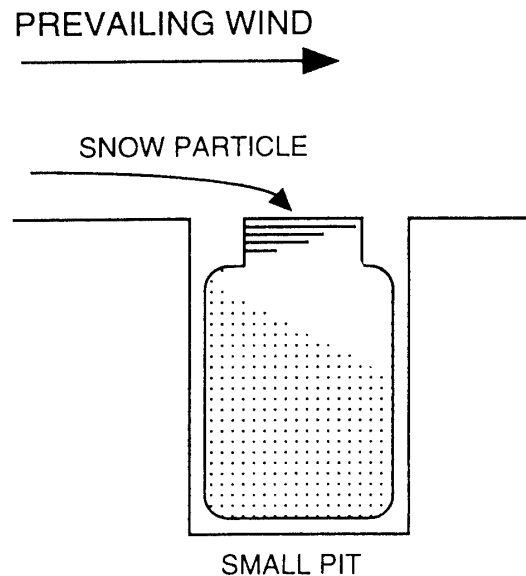


Fig. 2. Schematic depiction of snow trap method.

concentration of three times the standard deviation of the blank response. The standard deviation was calculated from three consecutive measurements.

We analyzed the standard reference material SRM1643c provided by the National Institute of Standards and Technology for the selected elements. Concentration values obtained by this method were in good agreement with the certified values for all the elements examined (NIST, 1991). The contents of the field blank of this study were measured to be lower than detection limits. Cross check analysis for Na in the Antarctic samples was performed by Atomic Absorption Spectrophotometer (SHIMADZU AA-670) and gave good agreement with the present study.

Besides major and trace elements, we measured Cl^- , SO_4^{2-} and NO_3^- concentration in drift snow by ion chromatography (SHIMADZU HIC-6A). Snow samples were melted at room temperature in the laboratory.

3. Results and Discussion

3.1. Comparison of 'background elements' between Arctic and Antarctic snow

The data of concentrations of major and trace elements are shown in Table 1. Concentrations of Na, K, Ca, Mg, Pb, Se, Cd, Mn and Ni measured in Antarctic snow are 1 or 2 orders of magnitude smaller than those observed in Arctic snow. CUNNINGHAM have extensively studied "background" aerosols in Greenland and at the South Pole, which show the tremendous difference in both crustal dust and sea salt between the two glacier-covered areas (CUNNINGHAM and ZOLLER, 1981).

3.2. Seasonal variation and relationship of trace elements and soluble ions

3.2.1. Sea salt origin

Sodium and chloride ions are used as indexes for elements of sea salt origin. The seasonal trend of Na and Cl shows a transient increase in early October, imposed on a

Table 1. Concentrations of major and trace elements in Arctic and Antarctic snow.

| | Na ng/l | Mg μg/l | Al μg/l | K μg/l | Ca μg/l | Fe μg/l | As ng/l |
|---------------|----------------------------|---------------------------|-------------------|--------------------------|---------------------------|------------|--------------------------|
| Greenland | $3.55 \times 10^3 \pm 25$ | $3.72 \times 10^2 \pm 2$ | * 2.20 | $2.07 \times 10^2 \pm 1$ | $1.03 \times 10^2 \pm 11$ | <DL | 65.7 ± 2.2 |
| Arctic | $1.27 \times 10^4 \pm 129$ | $1.19 \times 10^3 \pm 10$ | 0.782 ± 0.037 | $4.88 \times 10^2 \pm 7$ | $6.17 \times 10^2 \pm 9$ | <DL | $1.41 \times 10^2 \pm 2$ |
| Canada | $2.09 \times 10^2 \pm 1$ | 39.1 ± 0.4 | * 0.520 | 36.3 ± 0.1 | 90.2 ± 11 | <DL | 44.8 ± 0.9 |
| S 16 | $3.26 \times 10^2 \pm 23$ | 11.4 ± 0.2 | * 1.30 | 3.23 ± 0.06 | * 9.70 | <DL | 4.50 ± 0.8 |
| Antarctic | 3.83 ± 0.002 | 2.71 ± 0.16 | 2.19 ± 0.07 | 1.60 ± 0.03 | * 6.30 | <DL | * 3.30 |
| Advanced Camp | $2.87 \times 10 \pm 0.5$ | 3.67 ± 0.02 | 1.25 ± 0.02 | 2.33 ± 0.01 | * 5.20 | * 0.210 | 28.4 ± 0.2 |
| Dome Fuji | 0.03 | 0.007 | 0.006 | 0.015 | 0.05 | 0.005 | 0.006 |
| # D.L. | ng/l | | | | | | |

| | Ba ng/l | Cd ng/l | Co ng/l | Cr ng/l | Cu ng/l | Ga ng/l | Li ng/l |
|---------------|--------------------------|--------------------------|-----------------|---------------------------|---------------------------|-----------------|----------------------------|
| Greenland | $1.51 \times 10^3 \pm 9$ | 39.5 ± 1.8 | <DL | $1.45 \times 10^2 \pm 13$ | $3.14 \times 10^2 \pm 3$ | 86.0 ± 1.4 | $1.45 \times 10^2 \pm 4$ |
| Arctic | $7.06 \times 10^2 \pm 2$ | $1.18 \times 10^2 \pm 1$ | <DL | $4.80 \times 10^2 \pm 21$ | $3.03 \times 10^3 \pm 24$ | 55.5 ± 2.1 | $2.15 \times 10^2 \pm 0.3$ |
| Canada | $6.20 \times 10^2 \pm 1$ | 44.0 ± 2.3 | <DL | * 77.0 | $4.62 \times 10^2 \pm 11$ | 53.0 ± 0.5 | 44.7 ± 2.2 |
| S 16 | * 3.00 | * 0.304 | 4.17 ± 0.31 | <DL | * 338 | <DL | <DL |
| Antarctic | 59.1 ± 2.0 | * 1.81 | * 0.520 | 40.0 ± 5.8 | $1.98 \times 10^2 \pm 29$ | 3.46 ± 0.47 | 3.34 ± 0.37 |
| Advanced Camp | 30.9 ± 1.3 | 17.9 ± 0.6 | 4.80 ± 0.33 | <DL | 56.8 ± 0.9 | <DL | * 1.90 |
| Dome Fuji | 0.002 | 0.003 | 0.0009 | 0.02 | 0.003 | 0.001 | 0.0001 |
| # D.L. | ng/l | | | | | | |

| | Mn ng/l | Ni ng/l | Pb ng/l | Se ng/l | Sr ng/l | V ng/l | Zn ng/l |
|---------------|---------------------------|--------------------------|---------------------------|---------------------------|---------------------------|--------------------------|----------------------------|
| Greenland | $2.94 \times 10^3 \pm 33$ | $4.34 \times 10^2 \pm 7$ | $4.19 \times 10^2 \pm 14$ | $1.40 \times 10^2 \pm 8$ | $1.09 \times 10^2 \pm 47$ | 64.3 ± 2 | 7300 ± 40 |
| Arctic | $8.10 \times 10^2 \pm 11$ | $2.34 \times 10^2 \pm 8$ | $4.11 \times 10^2 \pm 20$ | $2.83 \times 10^2 \pm 37$ | $7.81 \times 10^3 \pm 90$ | $1.74 \times 10^2 \pm 4$ | $1.90 \times 10^4 \pm 170$ |
| Canada | $7.55 \times 10^2 \pm 8$ | $2.52 \times 10^2 \pm 8$ | 95.0 ± 1.0 | <DL | $3.14 \times 10^2 \pm 2$ | 28.4 ± 0.2 | $2.01 \times 10^3 \pm 24$ |
| S 16 | 23.2 ± 2.1 | <DL | <DL | <DL | 68.5 ± 2.6 | * 1.66 | 79.3 ± 2.4 |
| Antarctic | 61.7 ± 0.7 | 25.4 ± 1.1 | 90.2 ± 9.3 | <DL | 21.5 ± 1.8 | <DL | 2.85 ± 0.01 |
| Advanced Camp | 36.0 ± 6 | <DL | <DL | <DL | 25.0 ± 1.2 | 2.28 ± 0.24 | $5.57 \times 10^2 \pm 2$ |
| Dome Fuji | 0.002 | 0.005 | 0.001 | 0.06 | 0.008 | 0.002 | 0.003 |
| # D.L. | ng/l | | | | | | |

Greenland: 73°N, 56°W (1992); Spitzbergen: 79°N, 11°E (1992); Canada: 69°N, 105°W (1992); S 16: 69°01'S, 40°03'E (1993); Advanced Camp: 74°12'S, 34°59'E (1992); Dome Fuji: 77°22'S, 39°36'E (1993). mean ± SD. * n = 2.

slowly increasing background from winter to summer (Fig. 3). Previous meteorological studies have clarified that meridional long range air transports from the surrounding oceans become prominent in September to October (FUJII and OHATA, 1982; ITO, 1983). A transient increase in wind speed was also observed in the period of 5–8 October in the present study (ABE *et al.*, 1994). The Na and Cl peak event can be attributed to sea salt spray transported during low pressure disturbances in the austral spring.

The relation between sodium and chloride concentration is shown in Fig. 4. The seasonal trend of chloride ions show good agreement with Na ($[Cl] = 1.71 X [Na]$, $r = 0.993$). The chloride *versus* sodium ratio for 18 samples was calculated as 1.71, which is close to the sea water value of 1.73 (DUCE *et al.*, 1983).

Mg, K, Ca and Sr have peaks in the spring significantly correlated with Na and Al (Table 2). To examine maritime contributions to these elements, enrichment factors

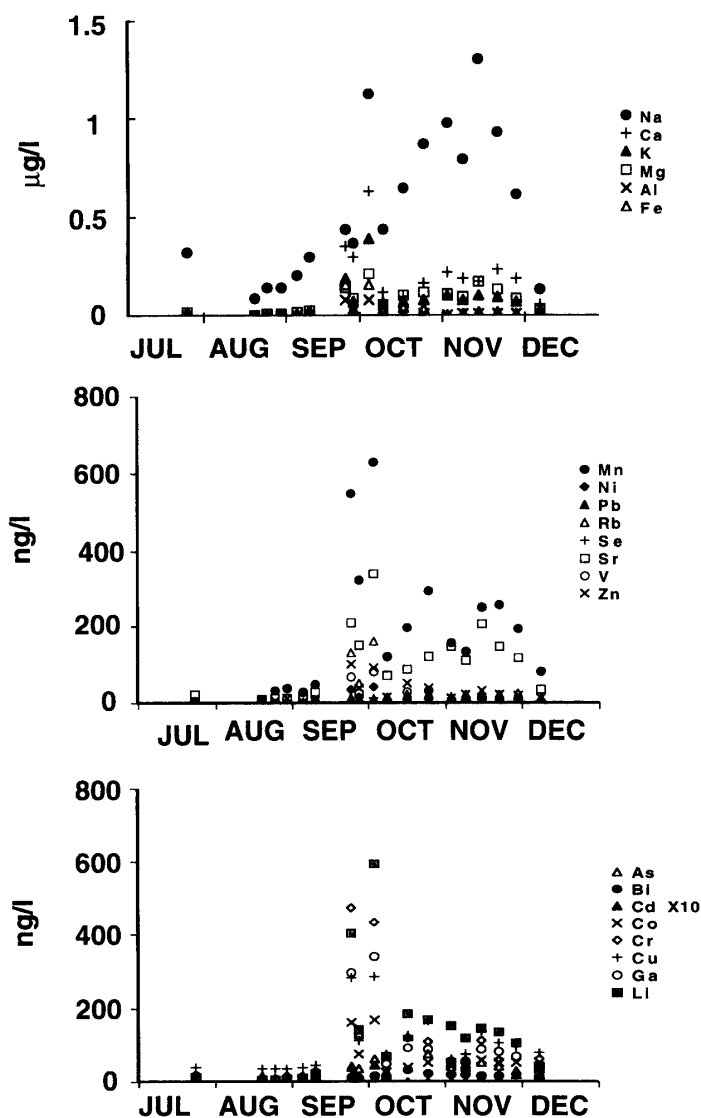


Fig. 3. Seasonal variations of major and trace elements in snow at Asuka Station, 1991.

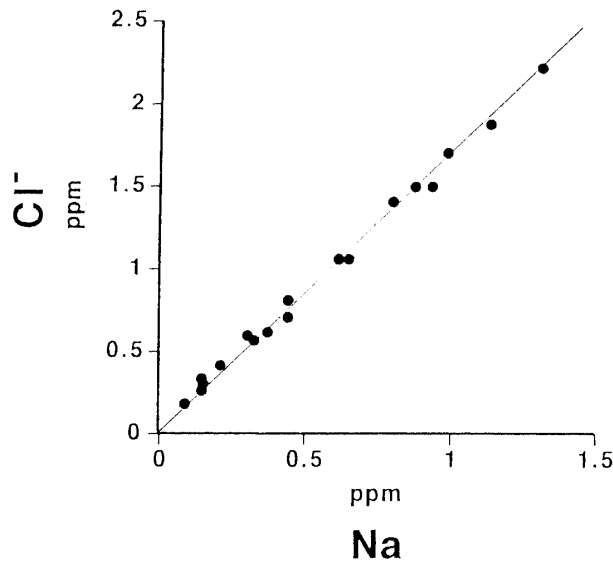


Fig. 4. Relation between sodium and chloride ions in snow at Asuka Station.

for these elements were calculated by applying the following equation (WEISS *et al.*, 1978):

$$EF_{\text{sea salt}} = [X/\text{Na}]_{\text{snow}} / [X/\text{Na}]_{\text{sea salt}},$$

where X refers to the concentrations of the measured elements. Calculated $EF_{\text{sea salt}}$ for Mg, K, Ca and Sr is almost unity except in late September. After the peak concentration, $EF_{\text{sea salt}}$ increased to two to ten fold higher values. They are in the order $\text{Mg} < \text{Sr} < \text{K} < \text{Ca}$ (Fig. 5). Therefore, origins other than sea salt spray such as biological processes, must be considered as a source for these elements.

3.2.2. Crustal origin

Aluminium, a crustal reference element, shows a strong peak in late September and early October (Fig. 3). Except for Na and Se, all the elements examined have a significant correlation with Al (Table 2). Crustal enrichment factors were calculated by the following equation (WEISS *et al.*, 1978; TAYLOR, 1964):

$$EF_{\text{crust}} = [X/\text{Al}]_{\text{snow}} / [X/\text{Al}]_{\text{crust}},$$

EF_{crust} values near unity were obtained for Fe, Mn, Rb, Cr, Ni, V and all the rare earth elements before peak concentrations. So these elements are thought to be of crustal origin. After peak concentrations, crustal enrichment factors were increased several to ten fold (Fig. 6a, b).

Elements such as Mg, K, Ca, Pb and Se have significant correlations with both Al and Na. This raises the possibility that these elements are transported by the same mechanism as sea salt and crust. According to the degree of enrichments, the elements may be grouped as follows:

Table 2. Inter-elemental correlation coefficient.

| (a) Major Elements | | | | | | |
|--------------------|--------|--------|--------|--------|--------|----|
| | Na | Mg | K | Ca | Fe | Al |
| m/z | 23 | 24 | 39 | 44 | 54 | 27 |
| Na | 1 | | | | | |
| Mg | 0.90** | 1 | | | | |
| K | 0.64** | 0.85** | 1 | | | |
| Ca | 0.64** | 0.86** | 0.95** | 1 | | |
| Fe | 0.32 | 0.67** | 0.87** | 0.83** | 1 | |
| Al | 0.34 | 0.70** | 0.87** | 0.85** | 0.99** | 1 |

Correlation coefficient by paired *t*-test.
** p<0.01, * p<0.05.

| (b) Trace Elements | | | | | | | | | | | | | | |
|--------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|-------|--------|--------|--------|--------|
| | Li | V | Cr | Mn | Co | Ni | Cu | Zn | Ga | Se | Rb | Sr | Cd | Pb |
| m/z | 7 | 51 | 52 | 55 | 59 | 58 | 63 | 64 | 69 | 82 | 85 | 88 | 114 | 208 |
| # Na | 0.58* | 0.42 | 0.37 | 0.58* | 0.52* | 0.51* | 0.52* | 0.43 | 0.49* | 0.70* | 0.39 | 0.79* | 0.23 | 0.93** |
| # Al | 0.94** | 0.96** | 0.99** | 0.93** | 0.96** | 0.97** | 0.95** | 0.95** | 0.98** | 0.01 | 0.9849 | 0.80** | 0.96** | 0.64** |

Correlation coefficient with Na and Al by paired *t*-test.
** p<0.01, * p<0.05.

| (c) Rare Earth Elements | | | | | | | | | | | | | | | | |
|-------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|-------|--------|--------|--------|--------|
| | Y | La | Ce | Pr | Nd | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu | Th |
| m/z | 89 | 139 | 140 | 141 | 143 | 147 | 153 | 157 | 159 | 163 | 165 | 167 | 169 | 173 | 175 | 232 |
| # Na | 0.33 | 0.17 | 0.3 | 0.1 | 0.11 | 0.19 | 0.32 | 0.22 | 0.21 | 0.33 | 0.33 | 0.11 | -0.18 | 0.32 | 0.3 | 0.38 |
| # Al | 0.83** | 0.67** | 0.83** | 0.65** | 0.68** | 0.73** | 0.84** | 0.76** | 0.79** | 0.83** | 0.81** | 0.57* | 0.61** | 0.81** | 0.83** | 0.98** |

Correlation coefficient with Na and Al by paired *t*-test.
** p<0.01, * p<0.05.

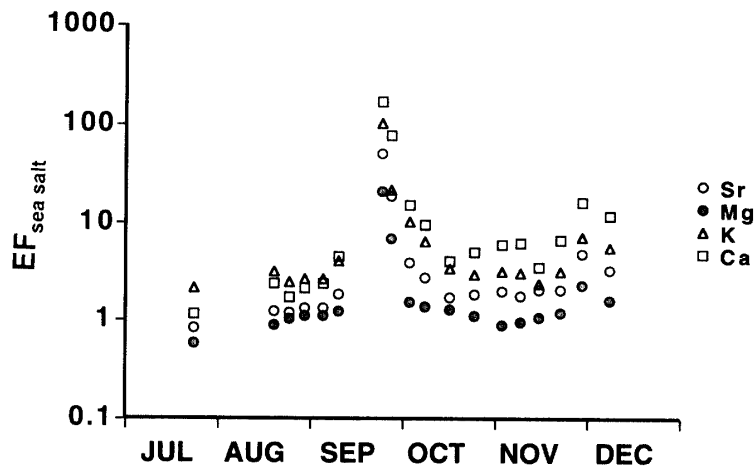


Fig. 5. Seasonal variations of $EF_{\text{sea salt}}$ in snow at Asuka Station.

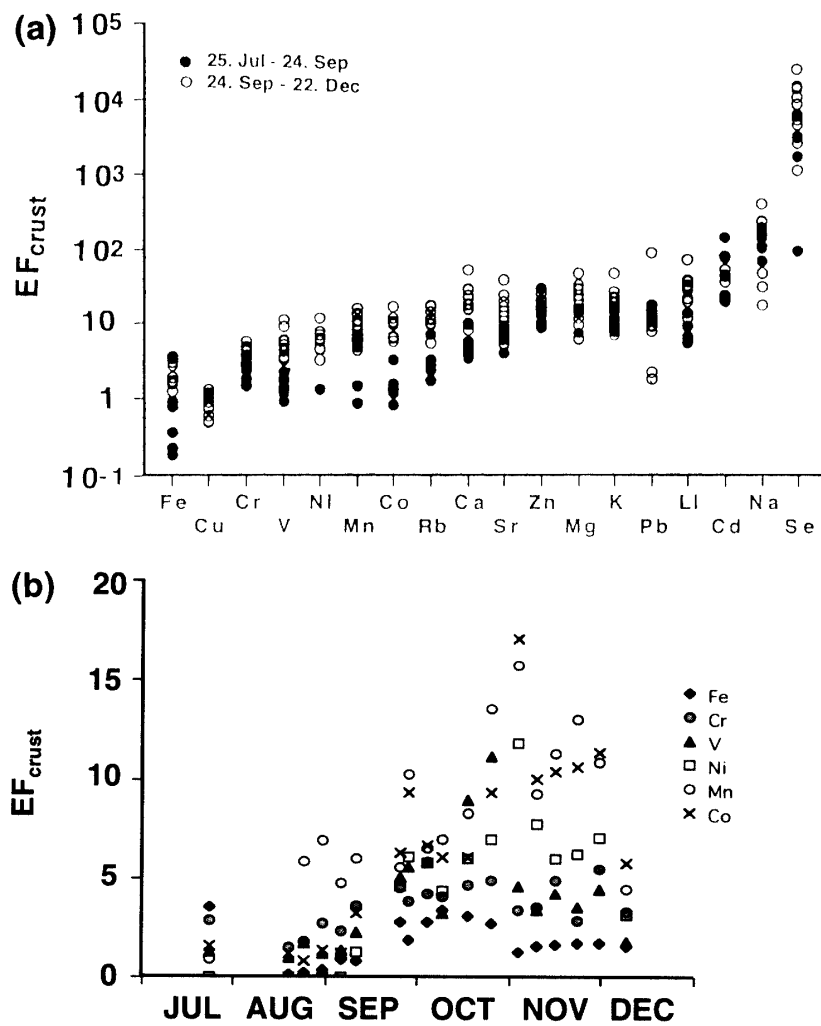


Fig. 6. (a) EF_{crust} in snow at Asuka Station.
(b) Seasonal variations of EF_{crust} in snow at Asuka Station.

- 1) Highly enriched ($EF_{\text{crust}} > 100$): Se, Cd, Pb, As.
- 2) Moderately enriched ($EF_{\text{crust}} = 10-100$): Zn, Ca, Na, Mg, K, Sr, Li, Cu, Ba.
- 3) Less enriched ($EF_{\text{crust}} < 10$): Fe, Rb, Mn, Ni, V, Cr, Co, La, Y, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th.

Lead concentration values for the recent Antarctic surface snow are in the range 2–13 pg g^{-1} (WOLFF and PEEL, 1985; LANDY and PEEL, 1981; WEISS *et al.*, 1978; BOUTRON and PATTERSON, 1987). This is almost the same level as concentrations before peak events (Fig. 3). The subsequent lead peak may be due to volcanism or anthropogenic production transported by long range air transport processes.

In the present study, the general trend of rare earth elements is characterised by bimodal peaks in late September and early October as with Al (Table 2). The crustal enrichment factor for all the rare earth elements is < 5 before the peak events; the EF crust for La, Ce, Pr, Nd, Sm, Gd and Th increased to 5–10 after the peak events. One possible source for the rare earth elements in snow is local emissions from the Sør Rondane Mountains located windward of Asuka Station. The other is long range air transport process from the troposphere, or stratospheric precipitation.

3.2.3. Volcanic origin

The eruption of Mt. Pinatubo (15°N , 120°E , 13–15 June 1991) caused what is believed to be the largest aerosol perturbation to the stratosphere this century (HOFMAN *et al.*, 1992). In addition, in the austral spring of 1991, the Antarctic lower stratosphere was characterized by a layer of volcanic aerosols from the Mt. Hudson eruption (46°S , 73°W , 12–15, August 1991) (McCORMICK *et al.*, 1995). Volcanic eruptions and the atmospheric sulfate budget have been extensively studied by LEGRAND and DELMAS (1987), and sulfuric acid is clearly the most important compound connected with volcanic activity.

It is customary to refer to SO_4^{2-} for polar snow as nss SO_4^{2-} where nss SO_4^{2-} is the non sea salt concentration corrected for the marine contribution (CLAUSEN and LANGWAY, 1989). Non sea salt sulfate was calculated according to the following equation;

$$\begin{aligned} [\text{nss SO}_4^{2-}] &= [\text{SO}_4^{2-}] - 0.14X [\text{Cl}^-] \\ \text{or } [\text{nss SO}_4^{2-}] &= [\text{SO}_4^{2-}] - 0.25X [\text{Na}]. \end{aligned}$$

Apparently, nss SO_4^{2-} shows very low or even negative concentration until 24–27 September and thereafter it increased to as high as 150–650 ng l^{-1} (Fig. 7b). Previous studies have shown that the volcanogenic SO_4^{2-} is the dominant component following major eruptions in Antarctica (LEGRAND *et al.*, 1987). Another possible source for nss SO_4^{2-} is biogenic production in the ocean. Non sea salt sulfate, generally in the form of sulfuric acid or ammonium sulfate, is a precursor that could be dimethylsulfide (DMS) released by the biogenic activity of the marine surface or carbonyl sulfide, as suggested by DELMAS *et al.* (1982). From a study of the composition of volcanic smoke fumes (MROZ and ZOLLER, 1975), Pb, Cd, Cu, Zn and Se have been reported to be derived from volcanoes. Anomolously enriched elements significantly correlated with these elements are also candidates for volcanic origine.

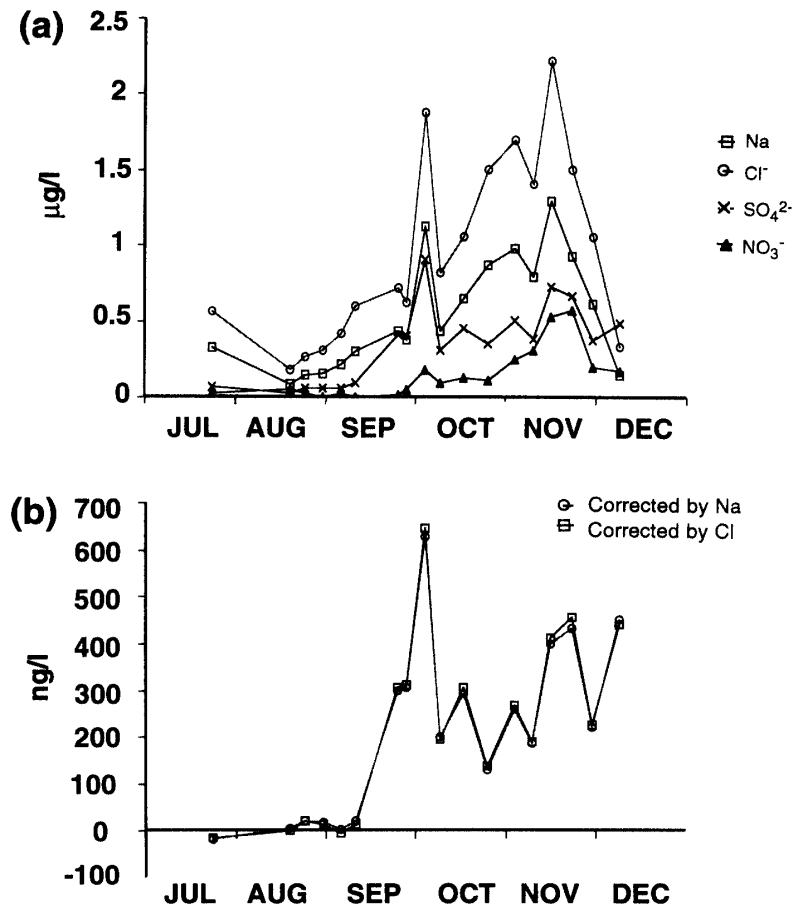


Fig. 7. (a) Seasonal variations of soluble ions in snow at Asuka Station.
(b) Seasonal variations of nss SO_4^{2-} in snow at Asuka Station.

3.2.4. Polar stratospheric precipitation

From July to late September, NO_3^- concentration stayed below 60 ppb; it gradually increased to 570 ppb in mid-November and recovered in December (Fig. 7a). The spring to early summer maximum in nitrate has also been confirmed in South Pole ice cores (MAYEWSKI and LEGRAND, 1990; LEGRAND and KIRCHNER, 1990; MULVANEY and WOLFF, 1993). Sublimation cannot explain this trend well because maximum sublimation is thought to occur in mid to late December, when the daily solar radiation is maximum (FUJII and KUSUNOKI, 1982). NO_3^- versus nss SO_4^{2-} concentration shows positive correlation (Na-corrected nss SO_4^{2-} : $r=0.5903$, $p<0.01$, Cl^- -corrected nss SO_4^{2-} : $r=0.6023$, $p<0.01$) in the present study. Recent work indicates that nitrate can enter the troposphere through stratosphere-troposphere air exchange, or through the subsidence of nitrate laden Polar Stratospheric Clouds (PSCs). Increase of tropospheric HNO_3 level could be reflected in spring polar precipitation during or after October and intensity of this process may be the temperature of the polar vortex (MAYEWSKI and LEGRAND, 1990; LEGRAND and KIRCHNER, 1990; MULVANEY and WOLFF, 1993).

From the meteorological data collected at Syowa Station in 1991 (ABE *et al.*, 1994), lowest value of daily total ozone was observed on 30 September, when peak events in the

various elements were observed in the present observation. This ozone loss in the lower stratosphere is believed to be a new phenomenon peculiar to the 1991 polar vortex and its relationship to volcanic activity has been suggested (HOFMAN *et al.*, 1992). As for lower tropospheric ozone, a prominent seasonal change of winter maximum and summer minimum, which are very close to results of surface ozone measurements (MURAYAMA *et al.*, 1992; SCHNELL *et al.*, 1991; AOKI, 1993) has been reported. This could be also the clues to understand the mechanism of seasonal variations in the chemical composition of the surface snow at Asuka Station.

4. Conclusions

Mass spectroscopy has played a vital role in studies of snow chemistry, allowing determination of pg g^{-1} levels of ultratrace elements. This is the first report on multi-elemental analysis of Antarctic snow by ICP-MS. Where an element displays natural variations in isotopic composition, their variations can be used to characterize different sources of the elements. From a comparison of isotope abundances of Pb in surface snow, ROSMAN *et al.* (1994) have observed the influence of anthropogenic lead on Antarctica. These measurements of isotopic abundances in snow are applicable to our study and this technique appears to be a promising way to establish reference material in understanding polar atmospheric environment.

Springtime peaks of most of the elements and non sea salt sulfate analysed in snow collected at Asuka Station could result from a long range air transport process. The peak concentration of nitrate ion seen in late November may be derived from polar stratospheric clouds, suggesting the existence of a precipitation process from the lower stratosphere to the snow surface. Moreover, the atmospheric peculiarity of austral spring in 1991 characterized by volcanic emissions of Mt. Hudson and Mt. Pinatubo may affect the chemistry of the drift snow at Asuka Station.

Acknowledgments

We thank all the members of 32nd Japanese Antarctic Research Expedition, especially, the wintering-over group at Asuka Station, for their help and encouragement to our research.

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(Received March 5, 1997; Revised manuscript accepted December 18, 1997)