

## DISTRIBUTION OF CHEMICAL ELEMENTS IN THE SNOW AT THE SITE S25 IN ANTARCTICA

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**Abstract:** The firn block samples, being 50 cm deep and covering nearly one-year formation, were taken at the site S25 on Antarctic ice sheet near Syowa Station. The vertical distribution of Cl, Na, and SO<sub>4</sub> showed high and nearly constant level in the upper 37.5 cm (766 ppb, 425 ppb, and 119 ppb, respectively) which accumulated within the period from the autumn of 1985 (based on the distribution of major elements) to early summer of 1986 when high influence of marine air is expected. On the other hand, very low concentration levels of these species (219 ppb, 117 ppb, and 64 ppb, respectively), but with high SO<sub>4</sub>/Na ratio, were found in the lower 12.5 cm layer which accumulated in the late summer of 1985 when concentration of SO<sub>4</sub> aerosols is high. NO<sub>3</sub> showed several peaks in the upper 37.5 cm and K and NH<sub>4</sub> low level.

The mean concentrations of Al, Fe, Zn, and Cu were 323 ppt, 251 ppt, 435 ppt, and 118 ppt, respectively. These concentration levels are much higher than those reported for snow and ice from inland area but comparable with those measured at the Syowa Station and the site S16 near the site S25.

The metal organic compounds of these heavy metal elements were firstly determined in the Antarctic snow and their contributions to the total amounts were significant. This new finding, in association with the observation that the organic heavy metal compounds has also been found in atmospheric aerosols collected in the Antarctic air as well as in the marine air, suggests their new possible origin and path to the Antarctica.

### 1. Introduction

The Antarctic ice and snow are interesting as they retain historical records on accumulation of chemical elements from other continents and oceans through atmosphere and also on global environmental change in the past. However, only limited chance has been given to those who are interested in trace element study due to the difficulty to get Antarctic ice and snow samples which are clean enough to be processed by ultra-microanalysis. The reported chemical analyses of snow at the Syowa Station or inland area not so far from there are mostly restricted to the major species in the surface snow and only a few reports on trace constituents (NISHIKAWA *et al.*,

1985). The observation of vertical distribution of chemical elements is also rare (KOYAMA 1986).

The authors had a chance to take samples of firn block with special care to avoid any contamination at the site S25 near the Syowa Station and sent them back to a clean laboratory in Nagoya University. The vertical distributions of Cl, SO<sub>4</sub>, NO<sub>3</sub>, Na, K, and NH<sub>4</sub> were observed for samples in the upper 50 cm from the surface which covers nearly a 1-year time sequence. The average contents of Al, Fe, Cu, and Zn were also measured and their chemical state was studied.

## 2. Samples

The site S25 is located at *ca.* 35 km inland from the sea coast, to the east of the Syowa Station (Fig. 1); both are close enough to be covered under single low-pressure air mass. The deposited snow at the site S25 is expected to accept high contribution of sea salt aerosols and moisture, especially in the winter (March–October) when occurrence of storm from the sea side is frequent as reflected in the significantly high number of blizzards at the Syowa Station (KAWAGUCHI and KANZAWA, 1988). At the same time, the site S25 is located on the ice sheet at the altitude of approximately 1000 m and the meteorological condition at the ground level is similar to that at the inland area where katabatic wind prevails. The deposited snow at the site S25 is expected to accompany SO<sub>4</sub> aerosols which are characteristic in the Antarctic summer atmosphere and may include some drifted snow.

Sampling of firn blocks was carried out by F. NISHIO and others of the JARE-27 on Feb. 1, 1986, with special care to avoid any contamination of samples according to the procedure given in the previous work (KANAMORI *et al.*, 1987). The sample consists of two successive blocks of 45 cm × 35 cm × 25 cm covering 50 cm from snow surface and almost 1-year formation according to the observation by the JARE-26 (Table 1) by the use of snow stick.

The sample has thin ice layers at the depths of 17 cm, 27 cm, and 36 cm; the lower-

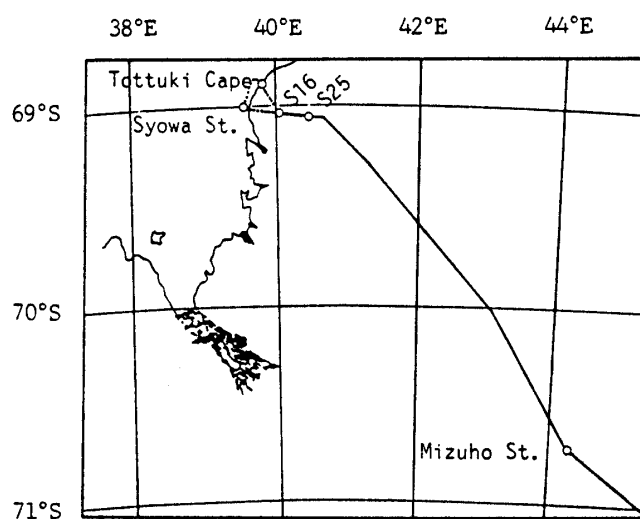


Fig. 1. Map of sampling locality.

Table 1. Data on the snow accumulation at the site S25 by the use of snow stick (JARE-26).

Date of measurement	Snow accumulation (cm)
End of Jan., 1986	64.4
3-5 Nov., 1985	55.0
20-30 Aug., 1985	52.5
20-27 March, 1985	34.0
14-18 Jan., 1985	0.0

most 15 cm is of compacted snow. The three ice layers indicate the time when snowfall ceases and, therefore, the sample consists of at least four snowfalls.

### 3. Methods of Chemical Analysis

The four vertical faces of sample block were cut off at 5 cm inside the surface to remove the possibly contaminated part, and the remaining sample was divided into 20 subsamples by slicing it every *ca.* 20 mm from the surface to the bottom (Fig. 2).

The procedures for pretreatments and the analytical methods of Cl, SO<sub>4</sub>, NO<sub>3</sub>, Na, K, NH<sub>4</sub>, Al, Fe, Zn, and Cu are exactly the same as those given in the previous paper (KANAMORI *et al.*, 1987).

To distinguish each chemical state of heavy metal elements (Al, Fe, Cu, and Zn) contained in snow firn, the following procedure was used. Each melted subsample was first filtered through 0.2 μm Nucleopore filter and the filtered residue was analyzed

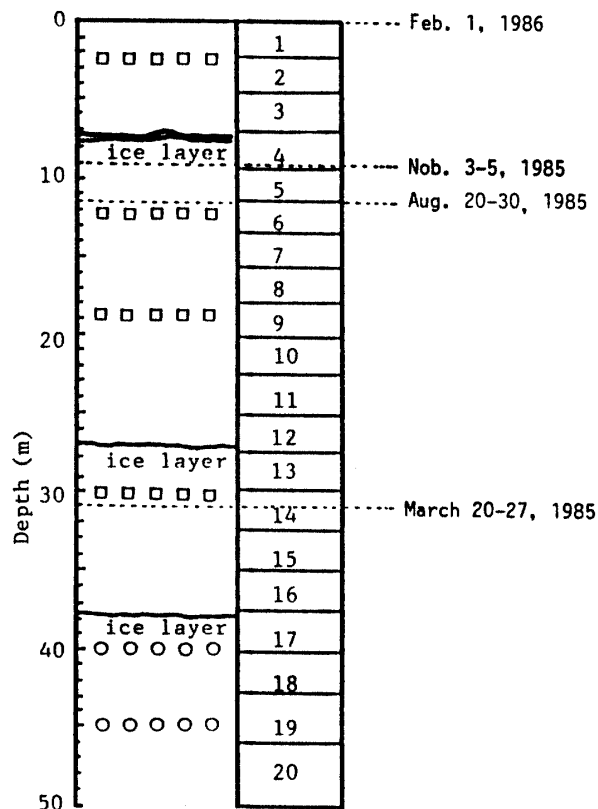


Fig. 2. Overview of vertical section of deposited snow from the site S25 and the mode of subsampling.

to get "the particulate fraction". Next, a part of the filtrate was processed through reverse-phase column of ODS for separation of organic heavy metal compounds. They are eluted with methanol, digested by heating with small amounts of  $\text{HNO}_3$  and  $\text{HClO}_4$ , and analyzed to get "the organic (I) fraction". Relatively large and nonpolar organic molecules are separated by this process. Another part of the filtrate is digested by heating with small amounts of  $\text{HNO}_3$  and  $\text{HClO}_4$  and analyzed for "the total dissolved amount". "The free inorganic fraction" is measured by analyzing the filtrate directly. "The organic (II) fraction" is obtained by subtracting "the organic (I) fraction" and "the free inorganic fraction" from "the total dissolved amount". "The organic (II) fraction" contains relatively small and polar organic molecules which pass through the column.

#### 4. Results and Discussion

##### 4.1. Major constituents

The distribution of major species in the firn block sample are illustrated in Fig. 3. Within the snow layer deeper than 37.5 cm of the sample block (subsample no. 17–20), concentrations of Na and Cl show constant and low level,  $\text{Cl}/\text{Na}$  ratio is close to that in sea salt as illustrated in Fig. 4, and  $\text{SO}_4/\text{Na}$  ratio is high as shown in Fig. 5. These results are in good harmony with reported low supply of sea salt aerosols and high input of excess  $\text{SO}_4$  which are characteristic of the Antarctic summer atmosphere (KOIDE *et al.*, 1981; ITO, 1983). This layer seems to be formed in the late summer after January 14–18 of 1985 and it is not inconsistent with the observation by the use of

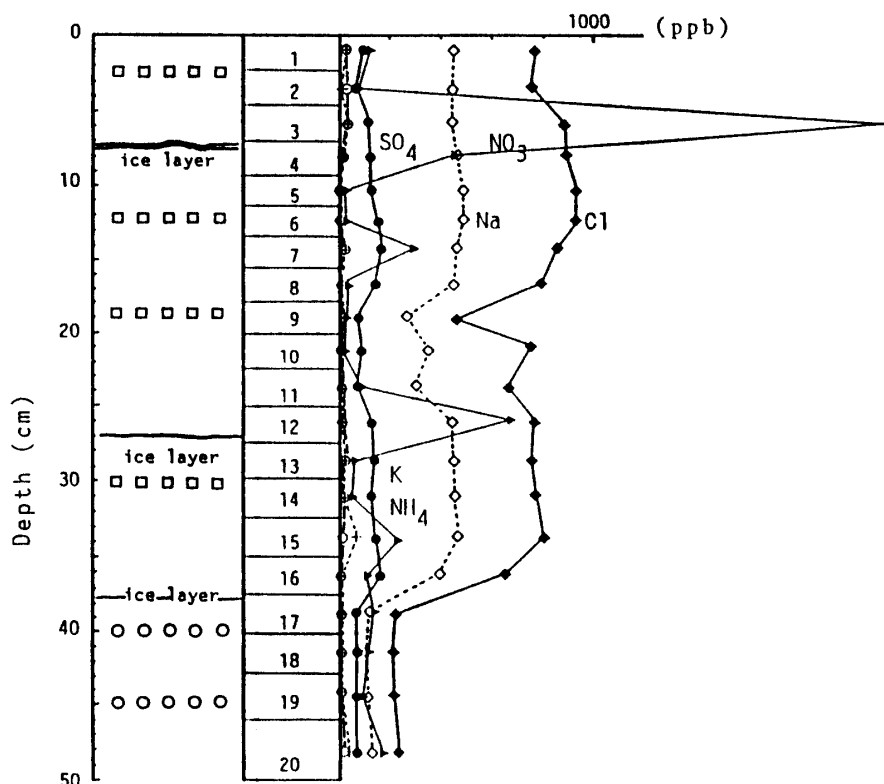


Fig. 3. Distribution of  $\text{Cl}$ ,  $\text{SO}_4$ ,  $\text{NO}_3$ ,  $\text{Na}$ ,  $\text{K}$ , and  $\text{NH}_4$  in the deposited snow from the site S25.

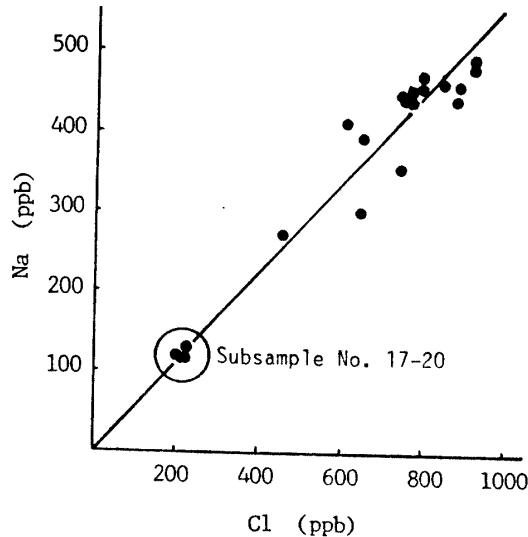


Fig. 4. Linear relationship between Na and Cl in deposited snow from the site S25. The straight line shows the Cl/Na ratio in sea salt.

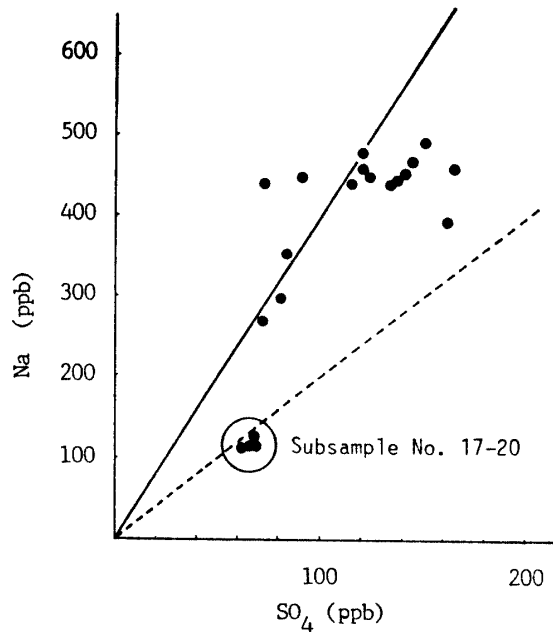


Fig. 5. Linear relationship between  $SO_4$  and Na in deposited snow from the site S25. The straight line shows the  $SO_4/Na$  ratio in sea salt and the broken line that with twice the ratio.

snow stick (Table 1).

Next, follow the spring, winter, and autumn layers which accumulate to the depth of 9 cm from the surface before November 3–5 (subsample no. 4–16). In these layers, concentrations of Na and Cl shift to high levels and both Cl/Na and  $SO_4/Na$  ratios keep nearly constant value close to those in sea salt (Figs. 4 and 5). The enhanced supply of sea salt aerosols by storm activity in these seasons and reduced input of excess  $SO_4$  aerosols in the dark period are consistent with the above observation.

According to the observation by the use of snow stick, the remaining uppermost part of the sample (subsample no. 1–4) was formed in the early summer before February 1 of 1986 (Table 1). The high levels of Na and Cl concentrations and low excess  $SO_4$  in this part are comparable to those found in the seasons of spring, winter, and autumn and in sharp contrast with those in the other summer layer at the lowest part of the sample. This may be due to that the upper summer layer was formed in early summer, after November 3–5 of 1985 and before February 1 of 1986, and the weather condition prevailing while the sample was accumulated was rather similar to that in autumn. This will be confirmed by study of snow layer accumulated after November of 1986.

MURAYAMA (1987) continued sampling of the drifting snow at the northern sea side of Syowa Station during the same time period as our sample covers and observed the variation with time of the concentration levels of Na, K, Ca, Mg, Cl, and  $SO_4$  in it. The enrichment factors of these elements in respect to sea water ranged from 0.8 to 1.1 and indicated their sea salt origin. Their concentration levels were distinctively high in the period from April 4 to July 12 of 1986, whereas they dropped down to the

lower levels in the remaining period. However, his observation also includes occasional high values even in the summer season (for example, high values on December 13 of 1985 and February 26 of 1986), and support the above discussion upon high sea salt content in the upper 9 cm layer of the present sample.

NO<sub>3</sub> is reported to have a peak in the summer (HERRON, 1982) and, in the present study, also showed variable concentration with a sharp peak in the early summer. K and NH<sub>4</sub> show minor variations.

#### 4.2. Heavy metal elements

The average total concentration of Al, Fe, Zn, and Cu are given in Table 2 with their range of variation. Though these values are apparently high as compared with those measured on snow and ice from inland areas, they are close to the measurements of surface snow by NISHIKAWA *et al.* (1985) at Tottuki Cape and the site S16 (Fig. 1).

The average percentage contributions of "the particulate fraction", "the organic (I) fraction", "the organic (II) fraction", and "the soluble inorganic fraction" are given in Table 3. As seen from the table, the contribution of organic form to total heavy metal content is very significant. Though the determinations of "the soluble inorganic fraction" of Al and Fe were unsuccessful, contribution of the fraction is expected to be not high according to their chemical behaviors and, therefore, that of "the organic (II) fraction" of Al is suggested to be appreciable. The only element with high contribution of "the soluble inorganic fraction" is Zn and, for the other three elements, more than 50% of them are in organic form.

The nature of these organic heavy metal compounds is not clear but the possibility that these compounds in the Antarctic snow are originally formed through biological activities is high. The formation of them has not likely taken place at snow surface or subsurface layer because considerable amounts of these organic heavy metal compounds have been found in atmospheric aerosols collected at Antarctic snow field and they could be the direct source of those in Antarctic snow. The same

Table 2. Total concentration and its range of variation of Al, Fe, Zn, and Cu in deposited snow at the site S25.

	Average concentration (ppt)	Range of variation (ppt)
Al	323	47-755
Fe	251	0-630
Zn	435	190-738
Cu	118	31-300

Table 3. Contribution of various forms of Al, Fe, Zn, and Cu to the total concentration.

	Total (ppt)	Particulate (%)	Organic (I) (%)	Organic (II) (%)	Inorganic (%)
Al	323	0.2	38.6		61.2
Fe	251	14.5	61.0		24.5
Zn	435	2.7	7.6	6.3	83.4
Cu	118	12.4	10.7	51.7	25.2

Table 4. Comparison of average concentration of major species and Zn and Cu species between in winter-type\* and in summer-type\* of relative abundance.

Chemical species	Winter-type*	Summer-type*
Cl	766	219
NO <sub>3</sub>	258	125
SO <sub>4</sub>	119	63.8
excess SO <sub>4</sub>	12.5	34.4
Na	425	117
NH <sub>4</sub>	15.4	7.0
Zn <sub>free</sub>	354	328
Zn <sub>org</sub>	29.7	172
Zn <sub>total</sub>	384	500
Cu <sub>free</sub>	30.8	26.5
Cu <sub>org</sub>	64.9	110
Cu <sub>total</sub>	95.7	137

\* See text.

organic heavy metal compounds also have been detected in the atmospheric aerosols collected on board in the North and the South Pacific Oceans and also in the campus of Nagoya University and global distributions of them are suggested. The study on the organic heavy metal compounds in atmospheric aerosols is in progress and will be discussed in another article.

According to the above discussion on seasonal variation of Na, Cl, and SO<sub>4</sub>, there are two patterns of relative abundance of these species. One is the pattern found in the lower 12.5 cm of the sample block, which corresponds to the late summer of 1985, where concentration levels of Na, Cl, and SO<sub>4</sub> are low but SO<sub>4</sub>/Na ratio is high. The other one is that found in the upper 37.5 cm, which corresponds to autumn, winter, spring, and early summer, where concentration levels of these species are high and the SO<sub>4</sub>/Na ratio is close to that in sea salt. Here, for convenience, the former pattern will be referred to as "summer-type" and the latter "winter-type". The average concentrations of major species as well as those of Zn and Cu species in both types are compared in Table 4, where Zn<sub>free</sub> and Cu<sub>free</sub> refer to the concentration of "the free inorganic fraction" and Zn<sub>org</sub> and Cu<sub>org</sub> refer to the summed concentration of "the organic (I) fraction" and "the organic (II) fraction". The values of Zn<sub>free</sub> and Cu<sub>free</sub> are almost comparable among two types whereas the values of Zn<sub>org</sub> and Cu<sub>org</sub> are low in the winter-type and high in the summer-type. This suggests that origin or path of the metal organic compounds of Zn and Cu is related to the Antarctic summer atmosphere in some unknown way or that they reflect the seasonal variation of aerosol composition in the air over the sea area surrounding the Antarctica or over the global ocean.

## 5. Concluding Remarks

1) The distributions were observed for Cl, SO<sub>4</sub>, NO<sub>3</sub>, NH<sub>4</sub>, Na, K, Al, Fe, Zn, and Cu in the firn block, with 50 cm depth from the surface and taken at the site S25 on Antarctic ice sheet near Syowa Station.

2) The distributions of main constituents of sea salt origin showed a characteristic pattern with a high level in the upper 37.5 cm of sample block, which accumulated within the period from the autumn to the early summer, and a low level in the lower 12.5 cm, which accumulated within the late summer.

3) The average concentrations of Al, Fe, Zn, and Cu were 47–755 ppt with an average of 323 ppt, 0–630 ppt with a 251 ppt average, 190–738 ppt with a 435 ppt average, and 31–300 ppt with a 118 ppt average, respectively, and they are in harmony with reported values.

4) The metal organic compounds of Al, Fe, Zn, and Cu were determined in Antarctic snow for the first time. The contribution to the total amounted to over 50% for Al, Fe, and Cu whereas soluble inorganic fraction dominated for Zn.

5) The organic Cu and Zn compounds are expected to be introduced to the snow accompanying with aerosol particles. The results that their concentrations are high in the late summer and low in the other seasons suggests that their origin has some connection with the Antarctic summer atmosphere or that they reflect the global biological activity.

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#### References

- HERRON, M. M. (1982): Impurity sources of F, Cl, NO<sub>3</sub>, and SO<sub>4</sub> in Greenland and Antarctic precipitation. *J. Geophys. Res.*, **87**, 3052–3060.
- ITO, T. (1983): Study on properties and origin of aerosol particles in the Antarctic atmosphere. *Pap. Meteorol. Geophys.*, **34**, 151–219.
- KANAMORI, S., KANAMORI, N., OSADA, K., ISA, E., NISHIKAWA, M., WATANABE, O. and NISHIO, F. (1987): Preliminary report on the contamination control for chemical analyses of Antarctic ice. *Proc. NIPR Symp. Polar Meteorol. Glaciol.*, **1**, 132–139.
- KAWAGUCHI, S. and KANZAWA, H. (1988): *Nankyoku no Kagaku*, 3. Kishō (Science in Antarctica, 3. Meteorology). Tokyo, Kokon Shoin, 334 p.
- KOIDE, T., ITO, T., YANO, N. M. and KOBAYASHI, T. (1981): Chemical composition of large and giant aerosols at Syowa Station, Antarctica. *Mem. Natl Inst. Polar Res., Spec. Issue*, **19**, 150–159.
- KOYAMA, M. (1986): Radioactivation analysis of Antarctic ice and snow samples for minor elements and its problems. *Studies on Establishment of Method for Antarctic Ice Core Analyses*, ed. by S. MAE. Tokyo, Ministry of Education, Science and Culture, Japan.



- MURAYAMA, T. (1987): Chemical composition of salts contained in the snow—Syowa Station, 1985. Proceeding of Annual Meeting, Geochemical Society of Japan, 1987 Tokyo, 71.
- NISHIKAWA, M., AMBE, Y. and CHUBATI, S. (1985): The minor element concentration in sedimented snow collected around Syowa Station. Proceeding of Annual Meeting, Geochemical Society of Japan, 1985, p. 196.

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