Bulletin of Glaciological Research 17 (2000) *11–16*

Article

Post-depositional loss of nitrate in surface snow layers of the Antarctic Ice Sheet

Kazuki NAKAMURA[1]*, Masayoshi NAKAWO[1], Yutaka AGETA[1], Kumiko GOTO-AZUMA[2] and Kokichi KAMIYAMA[3]**

1 Institute for Hydrospheric-Atmospheric Sciences, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8601 Japan

2 Nagaoka Institute of Snow and Ice Studies, National Research Institute for Earth Science and Disaster Prevention, Science and Technology Agency, 187-16, Maeyama, Suyoshi-cho, Nagaoka 940-0821 Japan

3 National Institute of Polar Research, 1-9-10 Kaga, Itabashi-ku, Tokyo 173-8515 Japan

(Received October 25, 1999 ; Revised manuscript received December 27, 1999)

Abstract

Post-depositional loss of nitrate from surface snow layers has been examined with samples from Dome Fuji area in eastern Antarctica. Nitrate concentration decreased with depth very rapidly within the surface snow layers between 0 to 1m in depth. Average snow particle size, on the other hand, increased gradually with depth, although the size distribution pattern did not change. The sharp decrease of nitrate concentration was explained in terms of grain growth of snow particles, assuming that nitrate distributed homogeneously within original snow particles is emitted from sublimated part of snow crystals in association with the grain growth. The temporal decrease of nitrate concentration was thus evaluated quantitatively, and the calculation result agreed with the observed vertical profile of nitrate concentration.

1. Introduction

Rapid decrease of nitrate concentration with depth has been found in surface snow layers at various sites in Antarctica. Mayewski and Legrand (1990) suggested that the profile of nitrate concentration at Vostok and Dome C must be treated with caution because of the possibility of post-depositional alteration but might link mainly to changes of nitrate concentration in the atmosphere. However, several researchers have suggested that the decrease of nitrate concentration with depth is not caused by the recent increase of nitrate in the atmosphere, but by the post-depositional change within the surface snow layers in Antarctica.

Neubauer and Heumann (1988) and Mulvaney *et al.* (1993) reported that the concentration of nitrate in fresh surface snow is higher than in old surface snow and aged firn core of ice shelves in Antarctica. They concluded that the decrease of the nitrate concentration in the surface snow layers would be due to the post-depositional loss of HNO_3 from the snow to the atmosphere. Neubauer and Heumann (1988) suggested that evaporation or photolysis causes nitrate loss. Mulvaney and Wolff (1994) reported that post-depositional loss of NO_3^- is important at low-accumulation sites (*e.g.* Vostok and Dome C) by the reliable data across Antarctica. De Angelis and Legrand (1995) suggested that HNO_3 loss or at least remobilization could have occurred in surface firn layers at South Pole, although to a much lesser extent than Dome C or Vostok. Dibb and Whitlow (1996) concluded also that post-depositional loss of NO_3^- is occurring in upper 0.5-1.0 m firn layers at South Pole, by comparing the depth profile of NO_3^- concentration in 1994 pits with the profile in 1988 pit. Bales (1995) and Wolff (1995)

* Present address: Hokkaido Regional Head Office, Japan Weather Association, Kita-4 Nishi-23, Tyuo-ku, Sapporo 064-8555 Japan

** Present address: National Institute of Polar Research, 1-9-10 Kaga, Itabashi-ku, Tokyo 173-8515 Japan

discussed about the cause of the HNO_3 loss in detail. Legrand *et al.* (1996) reviewed ice core data and discussed about air-snow relationships of HNO_3.

The quantitative assessment of the post-depositional loss, however, has not been made so far, and the present paper discusses the process quantitatively based on the grain coarsening of snow particles within surface snow layers.

2. Sampling and analysis

Samples for the present analysis were taken from Dome Fuji area, inland in eastern Antarctica, where a deep ice core was retrieved (Dome-F Deep Coring Group, 1998; Dome-F Ice Core Research Group, 1998). Mean annual net accumulation is 3.2 cm of water equivalent at Dome Camp (77°00′01″S, 35°00′00″E; 3761 m a.s.l.) (Kamiyama *et al.*, 1989; Ageta *et al.*, 1989), which is located 120 km west-northwest of Dome Fuji Station (77°19′01″S, 39°42′12″E; 3810 m a.s.l.), and between 2.5 and 3.0 cm of water equivalent at Dome Fuji Station (Watanabe *et al.*, 1997b). Annual mean 10 m snow temperature is -57.3°C (Kameda *et al.*, 1997) and annual average wind speed is about 5.4 m/s at Dome Fuji Station (Fujii and Kawada, 1999). The snow layer structures are rather simple without sastrugi in the Dome Fuji area (Watanabe *et al.*, 1997a).

The surface sample (0-1.5 m in depth) used for our study was taken in 1992 by the 33rd Japanese Antarctic Research Expedition (JARE). The sampling point was Site DS40 (77°44′08″S, 39°07′78″E; 3770 m a.s.l.), which is located about 50 km south-southwest of Dome Fuji Station. Another shallow sample (8-10 m in depth), which was taken at Dome Camp in 1985 by the 26th JARE, was also used, in order to compare the surface sample with the shallow one. It is considered that the sample transport/storage would not have affected the sequent results of analysis because these samples were kept clean and in good condition with a prudent attention during transport and storage.

These samples were subjected to chemical analysis in association with measurements of density, $\delta^{18}O$ and snow crystal size. The visible stratigraphy was recorded at the sampling sites. Chemical composition, snow crystal size and $\delta^{18}O$ were measured at 1 cm intervals of depth in order to observe details of post-depositional changes, because average annual snow accumulation is low, about 8.8 cm of snow at Dome Fuji Station (Kameda *et al.*, 1997).

Concentrations of Cl^-, NO_3^- and SO_4^{2-} were measured with an ion chromatograph (Dionex DX-100), and $\delta^{18}O$ with a mass spectrometer (Varian MAT 250). The diameter of snow crystals was measured with a digitizer connected with a personal computer by digitizing the snow crystal size from photographs of loosened snow crystals for each sample. Density was measured by measuring the mass in a certain volume with a snow sampler for each snow layer.

3. Results and discussion

Figure 1 shows the vertical profiles of the measured parameters for both the surface sample (0-1.5 m in depth) and the shallow sample (8-10 m in depth). Nitrate concentration decreases rapidly from the surface to about 1 m in depth, and keeps the low level at lower depths (8-10 m in depth). The characteristic of the profile is different from those of chloride and sulfate, which keep a certain level with changes like seasonal variations. Average diameter of snow crystals, on the other hand, increases almost linearly from the surface to about 1 m in depth. Density also increases gradually with depth. The value of $\delta^{18}O$ shows changes with a large amplitude from surface to 1 m in depth. A development of depth hoar crystals can be seen in the stratigraphy, suggesting a temperature gradient within surface snow layers: snow crystals would grow by sublimation/condensation through the movement of water vapor in pore spaces from the surface to about 1 m in depth mainly.

Raymond and Tusima (1979) examined in detail the evolution of particle size distribution of water-saturated snow. They showed that the average diameter of snow crystals increases almost linearly with time, while the number of relatively small particle decreases and that of big particle increases. They proposed the following equation to represent the cumulative frequency curve for the size distribution of snow crystals during the grain coarsening of wet snow.

$$\Psi^*\left(\frac{\nu}{\nu_m}\right)=\left(1-\frac{a\nu}{b\nu_m}\right)^{\frac{1}{a}} \quad \dots (1)$$

where, Ψ^* is cumulative frequency, ν is particle volume, ν_m is median volume and a and b are constants. In the experiment of water-saturated snow by Raymond and Tusima (1979), it was found that $a=0.23$ and $b=1.55$. Equation (1) indicates that snow particle size distribution pattern does not change with time if

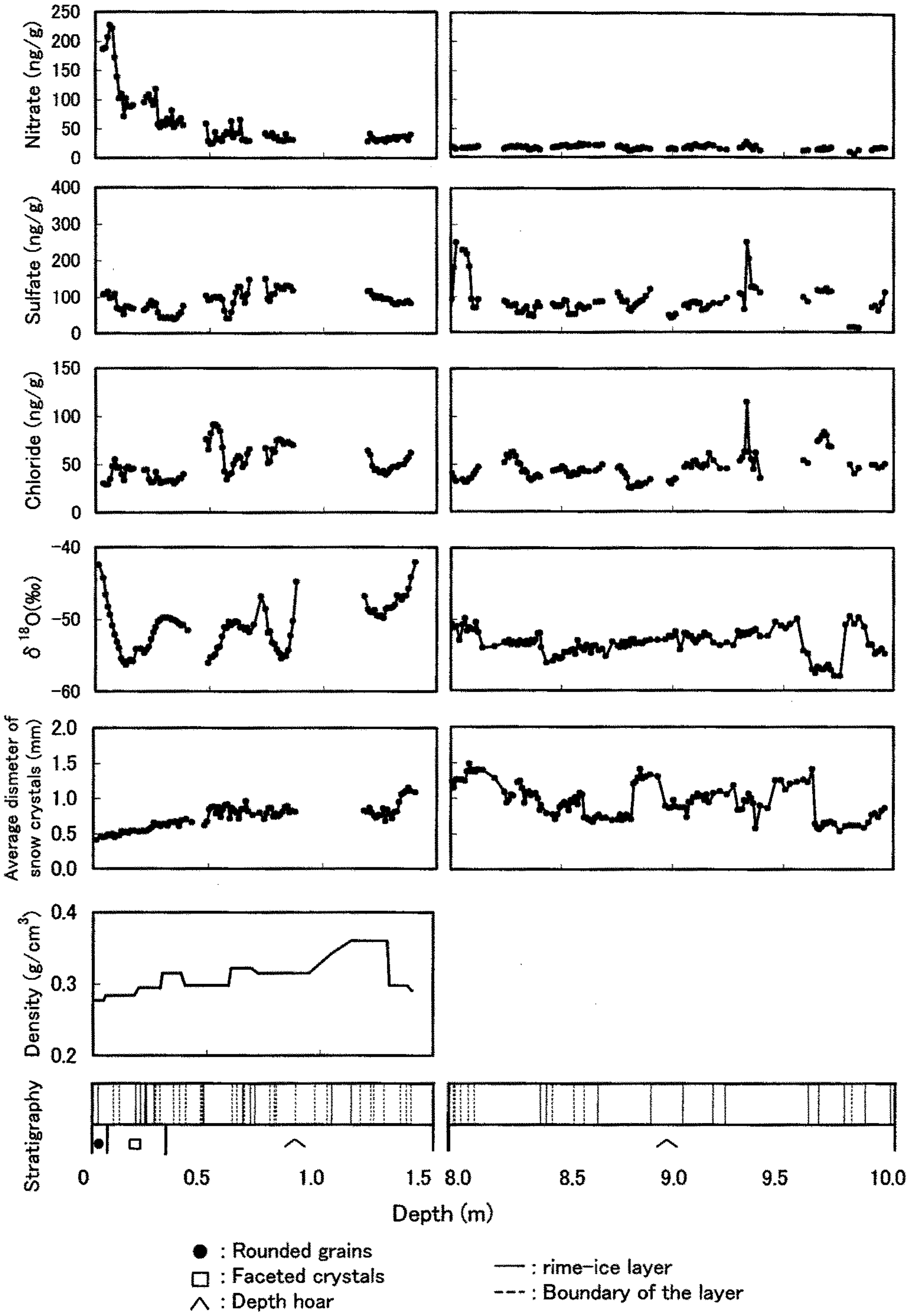

Fig. 1 Profiles of the surface sample (0–1.5 m depth) and those of the shallow sample (8–10 m depth) at Dome Fuji. Missing data indicates samples of poor quality.

volume ν is normalized with median volume ν_m, which is a linear function of time.

On the basis of this statistical fact alone, Raymond and Tusima (1979) developed many useful equations for snow particles. Furthermore, Nakawo *et al.* (1993) showed the melting/freezing fraction for the initial volume of wet snow, by using equations of Raymond and Tusima (1979). If constants (a and b) from the measurement results for Dome Fuji are adjusted to fit Equation (1), their equations for wet snow can be applied to those for dry snow in the surface layer at Dome Fuji, because their equations depend on the statistical result from Equation (1) alone.

Particle size distribution for our surface sample from Dome Fuji are shown in Fig. 2, where the cumulative frequency Ψ^* is plotted as a function of ν/ν_m. It shows that the distribution for any depth is expressed with a functional form of ν/ν_m. A least square fit of Equation (1) resulted in a=0.135 and b=1.55 as shown with a solid line in Fig. 2. This result indicates that snow particle size distribution pattern, at Dome Fuji, is not dependent on time (depth) as was found with wet snow.

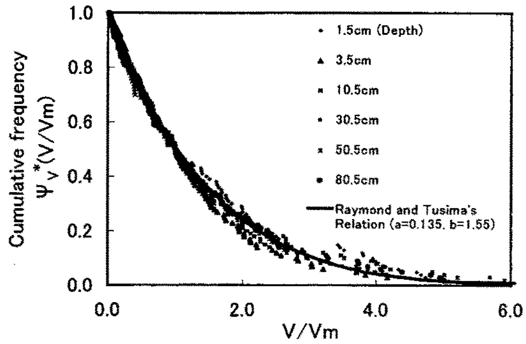

Fig. 2 An example of cumulative distribution of particle volumes of dry snow plotted as a function of V/Vm at Dome Fuji.

The frequency curve ϕ^*, differential form of Ψ^*, is given by the following equation as suggested by Raymond and Tusima (1979).

$$\phi^*\left(\frac{\nu}{\nu_m}\right)=\frac{1}{b\nu_m}\left(1-\frac{a\nu}{b\nu_m}\right)^{\frac{1-a}{a}} \quad \text{... (2)}$$

Raymond and Tusima (1979) also derived the freezing rate S (v, t) for a particle with the volume v.

$$S(\nu, t)=\frac{d\nu_m}{dt}\left\{(1+a)\frac{\nu}{\nu_m}-b\right\} \quad \text{... (3)}$$

where, t is time.

Nakawo *et al.* (1993) showed further that the rate of increase in freezing fraction for the total of snow particles can be given by

$$\frac{df}{dt}=\frac{1}{V}\int_{b\nu_m/(1+a)}^{b\nu_m/a} N(t)\cdot\phi^*\left(\frac{\nu}{\nu_m}\right)\cdot S(\nu, t)d\nu \quad \text{... (4)}$$

where, V is the total ice volume for a give system, N is the number of snow particles in the system, and f is the freezing fraction. In our study, f is the sublimation/condensation fraction, which can be estimated with Equation (4), since ϕ^* and $S(\nu, t)$ are given by Equations (2) and (3) respectively, and $N(t)$ is given by $(1+a)V/(bV_m)$ (Raymond and Tusima, 1979). The grain coarsening takes place only for particles larger than the average grain volume given by $b\nu_m/(1+a)$ (Raymond and Tusima, 1979) and smaller than the biggest grain volume, $b\nu_m/a$. The integration, therefore, is to be made from $b\nu_m/(1+a)$ to $b\nu_m/a$. The integration resulted in

$$f=\beta\ln\left(1+\frac{\gamma}{\nu_0}t\right) \quad \text{... (5)}$$

where, $\beta=(1/(1+a))^{1/a}$, $\gamma=d\nu_m/dt$, and ν_0 is the initial median volume (Nakawo *et al.*, 1993).

Figure 3 shows the median volume for samples of the surface snow layer at Dome Fuji against time (age), which was estimated with the average annual net accumulation of 3.2 cm in water equivalent obtained at Dome Camp near Dome Fuji Station (Kamiyama *et al.*, 1989; Ageta *et al.*, 1989). Roughly 85cm deep snow corresponds to the time of 8 years. The figure indicates that average grain volume increases almost linearly, as the regression line shows in the figure: $d\nu_m/dt$ can be assumed constant. The value of f was thus calculated by Equation (5) with these data.

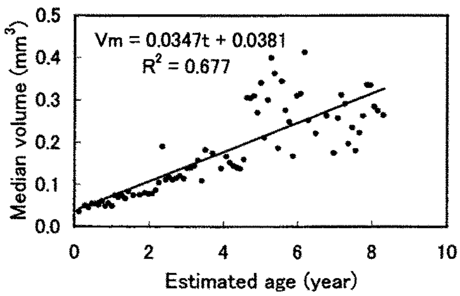

Fig. 3 Median volume versus age for samples of the surface snow layer at Dome Fuji.

Figure 4 shows sublimation/condensation fraction as a function of age at Dome Fuji. It indicates that about 80% of the solid ice consisting of snow particles sublimates to become water vapor and then condenses in the first 7 years after deposition at the surface. The amount of water vapor moved via sublimation/condensation was thus estimated with data of the distribution of snow crystal size.

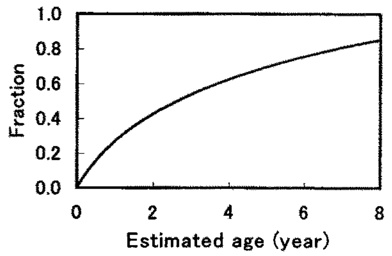

Fig. 4 Sublimation/condensation fraction for the initial volume of the snow on the surface plotted as a function of age at Dome Fuji.

It was assumed here for simplicity that nitrate exists homogeneously in original snow crystals deposited at the surface and that all nitrate included in sublimation/condensation fraction is re-emitted, for some reason, into the atmosphere. The nitrate concentration remained in snow particles is then expressed by the following equation, since condensed portion was assumed nitrate free, *i.e.* only water vapor condenses.

$$C = C_0 \times (1 - f) \quad \text{... (6)}$$

where, C is nitrate concentration, C_0 is initial nitrate concentration at the snow surface and f is sublimation/condensation fraction. Substituting the measured value of the shallowest sample for C_0, C was calculated for time, t, with Equations (5) and (6).

Figure 5 shows the calculated nitrate profile compared with the measured concentration profile found at Dome Fuji. The actual nitrate loss and the calculated one agree fairly well, although the actual one is a little steeper than the calculated one. This may be due to the inhomogeneous distribution of nitrate in the snow particle, because it is thought that the soluble gas such as HNO_3 absorbs to the outer parts of the snowflakes in the atmosphere, mainly. Therefore the post-depositional loss of nitrate can be explained with the process of grain growth in the surface snow layers. The process of nitrate loss in the surface snow layers is schematically shown in Fig. 6.

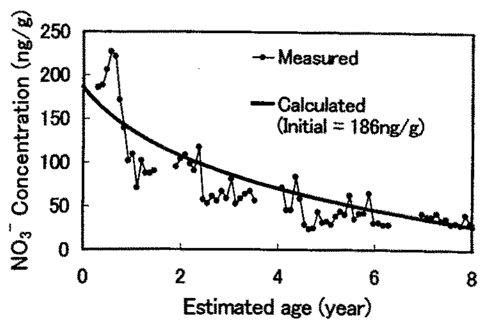

Fig. 5 Measured and calculated nitrate profiles at Dome Fuji.

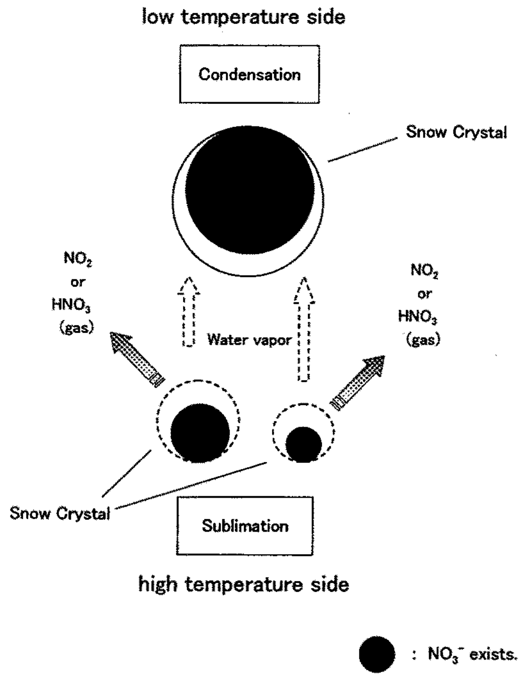

Fig. 6 Nitrate loss during the growth of snow crystals by sublimation/condensation at Dome Fuji.

A circle in Fig. 6 shows an individual snow particle, and the shaded part indicates the presence of nitrate, whereas the non-shaded part indicates the absence of nitrate. When new snow particles have fallen on the snow surface, nitrate is distributed throughout the particles. The snow layer, however, is subjected to a temperature gradient over time. With the temperature gradient, the snow particles tend to sublimate, in particular at rather small particles. The water vapor would then condense at colder sites, especially to rather large particles. As a result, small particles would decrease in number, and accordingly the average particle size would increase with time (with depth). Nitrate included in the sublimated part would be re-emitted as gas (*e.g.* NO_2 or HNO_3), by some reason (*e.g.* photolysis, volatilization, or reaction with other substances, on the surface of sublimated snow crystals), to the atmosphere.

4. Conclusion

From the analysis of snow samples, the nitrate concentration was found to have decreased rapidly with depth in the surface layers of the ice sheet at Dome Fuji, Antarctica. The decrease was explained quantitatively in terms of grain growth of snow particles: nitrate contained in the sublimated part of snow crystals, with the process of sublimation/condensation, is emitted from the surface of snow crystals to the atmosphere as gas during the snow metamorphism.

Acknowledgments

We wish to thank the members of the 26th and 33rd Japanese Antarctic Research Expedition for supporting the sample collection. We also wish to thank the staffs of Institute for Hydrospheric-Atmospheric Sciences, Nagaoka Institute of Snow and Ice Studies and National Institute of Polar Research for helping the measurement and the analysis of the samples. Suggestions by Dr. R. M. Koerner greatly helped to improve this manuscript. We wish to thank him very much.

References

Ageta Y., Kamiyama K., Okuhira F. and Y. Fujii (1989) : Geomorphological and glaciological aspects around the highest dome in Queen Maud Land, East Antarctica, Proc. NIPR Symp. Polar Meteorol. Glaciol., **2**, 88-96.

Bales R. C. (1995) : Nitric acid in firn: discussion, in Ice core studies of global biogeochemical cycles, edited by R. J. Delmas, NATO ASI Series Vol. **I 30**, Springer-Verlag, Berlin Heidelberg, 241-245.

De Angelis M. and Legrand M. (1995) : Preliminary investigations of post depositional effects on HCl, HNO_3, and organic acids in polar firn layers, in Ice core studies of global biogeochemical cycles, edited by R. J. Delmas, NATO ASI Series Vol. **I 30**, Springer-Verlag, Berlin Heidelberg, 361-381.

Dibb J. E. and Whitlow S. I. (1996) : Recent climate anomalies and their impact on snow chemistry at South Pole, 1987-1994, Geophys. Res. Lett., **23**, 1115-1118.

Dome-F Deep Coring Group (1998) : Deep ice-core drilling at Dome Fuji and glaciological studies in east Dronning Maud Land, Antarctica, Ann. Glaciol., **27**, 333-337.

Dome-F Ice Core Research Group (1998) : Preliminary investigation of palaeoclimate signals recorded in the ice core from Dome Fuji station, east Dronning Maud Land, Antarctica, Ann. Glaciol., **27**, 338-342.

Fujii Y. and Kawada K. (1999) : Activities of the wintering party of the 37th Japanese Antarctic Research Expedition in 1996-1997 (in Japanese), Nankyoku Shiyo (Antarct. Rec.), **43**, 255-290.

Kameda T., Takahashi S., Enomoto H., Azuma N., Shiraiwa T., Kodama Y., Furukawa T., Watanabe O., Weidner G. A. and Stearns C. R. (1997) : Meteorological observations along a traverse route from coast to Dome Fuji station, Antarctica, recorded by automatic weather stations in 1995, Proc. NIPR Symp. Polar Meteorol. Glaciol., **11**, 35-50.

Kamiyama K., Ageta Y. and Fujii Y. (1989) : Atmospheric and depositional environments traced from unique chemical compositions of the snow over an inland high plateau, Antarctica, J. Geophys. Res., **94**, 18515-18519.

Legrand M., Leopold A. and Domine F. (1996) : Acidic gases (HCl, HF, HNO_3, HCOOH, and CH3COOH): A review of ice core data and some preliminary discussions on their air-snow relationships, in Chemical exchange between the atmosphere and polar snow, edited by E. W. Wolff and R. C. Bales, NATO ASI Series Vol. **I 43**, Springer-Verlag, Berlin Heidelberg, 19-43.

Mayewski P. A. and Legrand M. R. (1990) : Recent increase in nitrate concentration of Antarctic snow, Nature, **346**, 258-260.

Mulvaney R., Coulson G. F. J. and Corr H. F. J. (1993) : The fractionation of sea salt and acids during transport across an Antarctic ice shelf, Tellus, **45B**, 179-187.

Mulvaney R. and Wolff E. W. (1994) : Spatial variability of the major chemistry of the Antarctic ice sheet, Ann. Glaciol., **20**, 440-447.

Nakawo M., Chiba S., Satake H. and Kinouchi S. (1993) : Isotopic fractionation during grain coarsening of wet snow, Ann. Glaciol., **18**, 129-134.

Neubauer J. and Heumann K. G. (1988) : Nitrate trace determinations in snow and firn core samples of ice shelves at the Weddell Sea, Antarctica, Atmos. Environ., **22**, 537-545.

Raymond C. F. and Tusima K. (1979) : Grain coarsening of water-saturated snow, J. Glaciol., **22**, 83-105.

Watanabe O., Shimada W., Narita H., Miyamoto A., Tayuki K., Hondoh T., Kawamura T., Fujita S., Shoji H., Enomoto H., Kameda T., Kawada K. and Yokoyama K. (1997a) : Preliminary discussion of physical properties of the Dome Fuji shallow ice core in 1993, Antarctica, Proc. NIPR Symp. Polar Meteorol. Glaciol., **11**, 1-8.

Watanabe O., Y. Fujii, H. Motoyama, T. Furukawa, H. Shoji, H. Enomoto, T. Kameda, H. Narita, R. Naruse, T. Hondo, S. Fujita, S. Nae, N. Azuma, S. Kobayashi, M. Nakawo, and Y. Ageta (1997b) : A preliminary study of ice core chronology at Dome Fuji station, Antarctica, Proc. NIPR Symp. Polar Meteorol. Glaciol., **11**, 9-13.

Wolff E. W. (1995) : Nitrate in polar ice, in Ice core studies of global biogeochemical cycles, edited by R. J. Delmas, NATO ASI Series Vol. **I 30**, Springer-Verlag, Berlin Heidelberg, 195-223.