

ATMOSPHERIC CONDITIONS REFLECTED IN CHEMICAL
COMPONENTS IN SNOW OVER EAST QUEEN
MAUD LAND, ANTARCTICA

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Abstract: The precise vertical distribution of H₂O₂ in the surface snow layer at three different sites in the inland region of Antarctica was measured. The seasonal variation, traced from the vertical distribution of snow cover, reflects photochemical processes in the atmosphere and coincides with that of δ¹⁸O. The values of pH and the concentration of micro-particles are also discussed in consideration of photochemical and migration processes in the atmosphere. Almost all substances occurring in snow have unique origins; some of them reflect physical and chemical processes in the atmosphere.

1. Introduction

Snow particles are formed under certain atmospheric conditions and deposit onto the ice sheet surface. These snow particles retain information on local atmospheric conditions in their chemical and physical characteristics. The snow on the ice sheet is apparently divided into 3 types: falling snow from the atmosphere; snow transported over the ice sheet which settles on the snow surface and is blown again by the wind; and snow deposited on the ice sheet to form a layer in stratification. The snow characteristics possibly depend upon snow type; they are affected by the atmospheric condition at first, and undergo metamorphosis depending upon the glaciological conditions in the ice sheet. Here we try to clarify the characteristics of the deposited snow.

We have estimated the atmospheric environmental condition which affect the snow characteristics over East Queen Maud Land, Antarctica. The surface snow deposited during a certain duration has been sampled for investigation of the present atmospheric and glaciological environmental condition over the ice sheet. The snow columns were cut from walls of 2 m deep snow pits at observation sites in order to obtain information on the past environments. Both the seasonal and local atmospheric environments are reflected in the chemical characteristics of snow.

Hydrogen peroxide (H₂O₂) is produced through photochemical processes in the atmosphere, increasing in summer/daytime and decreasing in winter/night, in

the precipitation and the water vapor as shown by KAMIYAMA and NAKAYAMA (1992). H_2O_2 , after being absorbed into snow, is accumulated in the ice sheet and snow has been confirmed in the ice core at Siple Station, West Antarctica (SIGG and NEFTEL, 1988). In addition to the H_2O_2 content, the oxygen isotope ratio ($\delta^{18}\text{O}$) in snow precipitation shows a seasonal distribution that increases in summer and decreases in winter, which reflects the atmospheric temperature.

It was reported by KAMIYAMA *et al.* (1987, 1989) that high concentrations of HCl and HNO_3 , low level of pH and higher level of artificial radio nuclides in snow were observed in snow on the inland high plateau, East Queen Maud Land, suggesting direct inflow of substances into the area through the upper atmosphere and stratosphere over the ice sheet. Taking into consideration the unique characteristics of the atmospheric environment over the inland high plateau, we will discuss the formation processes of vertical profiles of H_2O_2 and $\delta^{18}\text{O}$ in the surface snow layer in three different regions: coast, katabatic slope and inland plateau. Such investigations will make clear the relationship between the atmospheric environments and the glaciological characteristics over the ice sheet.

2. Sampling and Analytical Procedures

We have determined detailed vertical profiles of H_2O_2 in snow layers in the three different regions in East Queen Maud Land shown in Fig. 1 and described in Table 1. The uppermost surface snow cover samples at station γ -8 were obtained in 1986. The vertical distribution of H_2O_2 has been reported by KAMIYAMA and NAKAYAMA (1992). The $\delta^{18}\text{O}$ was determined from the residues of the same samples. Snow samples from the walls of snow pits at stations H270 and B were obtained in 1988 and brought back to the laboratory frozen. Precise stratigraphic observation of the walls, sampling for $\delta^{18}\text{O}$ determination and chemical analyses were carried out *in situ* by WATANABE (1992). For the determination of H_2O_2 , small segments of samples, taken continuously from the snow column in the laboratory, were prepared after removing the exterior part to remove contaminants. The samples were kept frozen and melted just before the analytical procedures. The pH values and micro-particle concentrations were determined for the residues of the samples from stations H270 and B.

Table 1. Sampling site of the hydrogen peroxide determination.

Station	H270	B	γ -8
Location	69°54.5'S 42°48.7'E	72°5.9'S 44°58.5'E	76°0.2'S 31°23.3'E
Elevation (a. s. l.)	1780 m	2771 m	3648 m
Distance from sea (approximately)	200 km	400 km	700 km

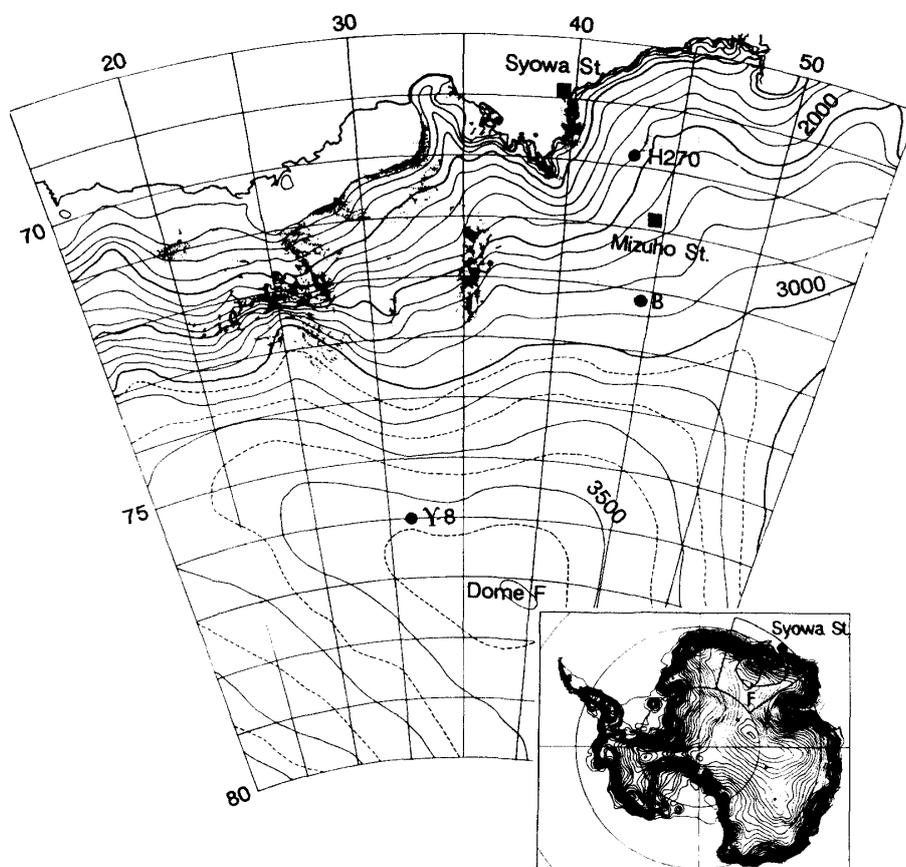


Fig. 1. The location of observation station in East Queen Maud Land, Antarctica.

3. Results and Discussion

3.1. Distribution of H_2O_2 in snow

The vertical profiles of H_2O_2 in the surface snow cover are shown in Fig. 2. It is clearly seen that the concentrations of H_2O_2 show periodic change at every station. The periodic distribution is caused by seasonal variation in the concentration of H_2O_2 in the snow deposit, since the activity of the photochemical process in the atmosphere increases in summer and decreases in winter. Higher concentrations in the vertical profiles seem to occur in the higher inland region ($\gamma-8 > B > H270$). However, the fluctuation level at $\gamma-8$ remains inconclusive due to inadequate data.

There are two possible reason for the higher level of H_2O_2 in inland precipitation.

1) H_2O_2 is considered to be an important oxidizing agent in atmospheric liquid water. The substances consuming H_2O_2 in the atmosphere, such as SO_2 , must be carried into the inland region from outside. During the migration process, almost all of the substances are converted to oxidized forms, such as SO_4 . In consequence, H_2O_2 in the atmosphere appears in the deposited snow with little consumption.

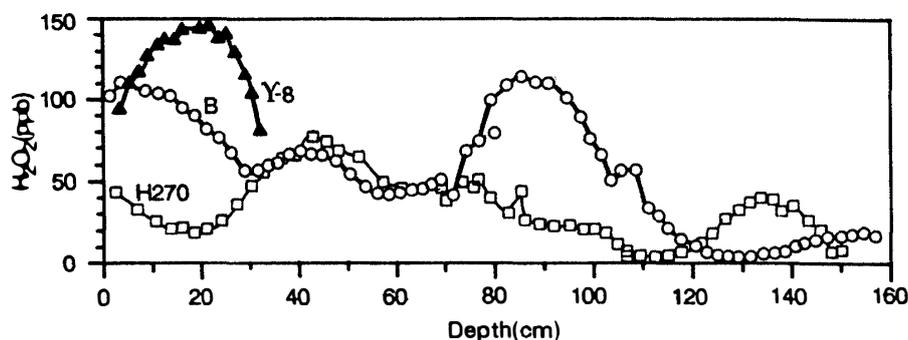


Fig. 2. The vertical profiles of H_2O_2 in snow at stations H270, B and γ -8.

2) In the stratosphere, various substances are produced through chemical and photochemical processes, in which only H_2O_2 , HCl and HNO_3 are physically able to reach the ground through precipitation (BRASSEUR and VERSTRAETE, 1989). The extremely low temperature in the stratosphere over the inland region enhances the possibility combined with the distinctive polar atmospheric circulation. Actually high concentrations of H_2O_2 , HCl and HNO_3 are observed at high altitude in the atmosphere (MAY and WEBSTER, 1989). The vertical downward migration process of substances from the upper atmosphere to the surface (KAMIYAMA *et al.*, 1989) also suggests to us the appearance of a high H_2O_2 level in snow precipitation in the inland region. The inland region of Antarctica appears to be unique on the earth.

3.2. Relationship between H_2O_2 and other components in snow

3.2.1. Oxygen isotope ratio

$\delta^{18}O$ in snow precipitation plays an important role in estimating the atmospheric temperature, increase of $\delta^{18}O$ in summer and decrease in winter. Clear seasonal variations were observed in vertical profiles of both H_2O_2 and $\delta^{18}O$ in the ice core in Greenland, where H_2O_2 maxima coincided more or less with $\delta^{18}O$ maxima (SIGG and NEFTEL, 1988). The vertical distributions of $\delta^{18}O$ are shown in Fig. 3 together with the distributions of H_2O_2 in similar depth ranges. The mean value of $\delta^{18}O$ at each station, reflecting the local climatic tendency, corresponds to the altitude, as shown in Table 1. At station γ -8, $\delta^{18}O$ and H_2O_2 were determined with the same samples. At stations H270 and B, we tried to clarify the relationship between fluctuations of H_2O_2 and $\delta^{18}O$. H_2O_2 and $\delta^{18}O$ were determined with two series of samples obtained by the different methods in the same snow pit. The series for $\delta^{18}O$ were obtained *in situ*, and the series for H_2O_2 were obtained in the laboratory from vertical snow columns of 70 cm length cut from the pit wall. The vertical profiles of H_2O_2 and $\delta^{18}O$ show time dependent fluctuation, and values at the same depth do not always coincide with the same sequence of deposition. The deposition does not always occur horizontally, as was observed in the stratigraphic diagram (WATANABE, 1992). Accumulation and erosion processes on the snow surface are recorded in the deposition structure and snow texture, which is useful to identify the annual and seasonal

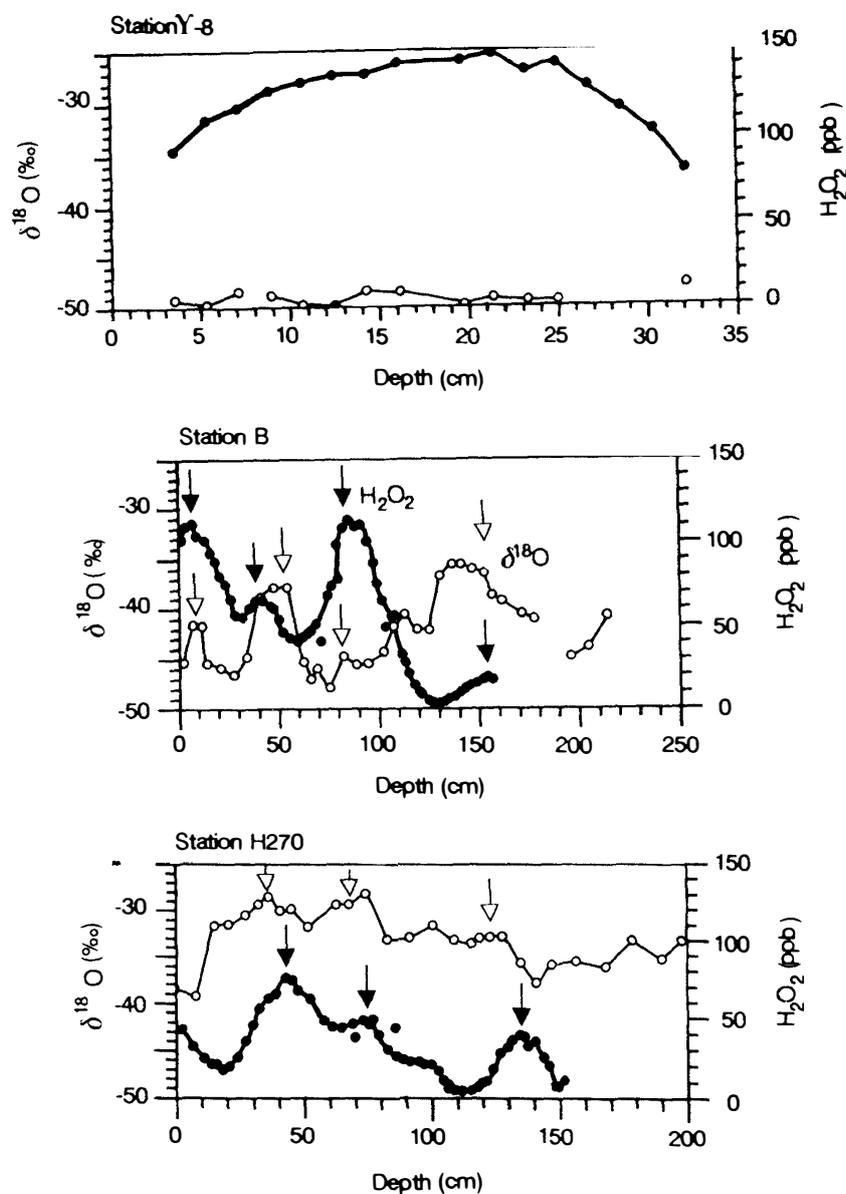


Fig. 3. The vertical profile of $\delta^{18}\text{O}$ and H_2O_2 in snow cover at stations H270, B and γ -8. Black and open arrows indicate summer layers on H_2O_2 and $\delta^{18}\text{O}$ profiles respectively.

snow layers. The thick ice crusts and hard snow layers are presumed as deposition structure formed in summer. The depths of these layers are shown in Fig. 3 by arrows. Maxima of both H_2O_2 and $\delta^{18}\text{O}$ appear in thick ice crusts and hard snow layers. The maximum values differ from each other, implying complicated atmospheric environments. The maximum values of H_2O_2 in summer depend on atmospheric circumstances, as H_2O_2 is created by photochemical processes and consumed by chemical reactions. The consumption rate of H_2O_2 depends on chemical reaction in the atmosphere, while the production rate of H_2O_2 in the atmosphere increases in summer. For example, SO_2 , distributed by volcanic eruptions, decreases the atmospheric H_2O_2 level by being oxidized into SO_4 . In

several volcanic events, such atmospheric chemical processes have been recognized from the vertical profiles of H_2O_2 and SO_4 in ice core (LAJ *et al.*, 1990). Further investigations will successfully make clear the past atmospheric environments from records of snow layers. For precise discussion, we might take into consideration the possible occurrence of secondary metamorphic processes after snow deposition.

3.2.2. Acidity and micro-particles

After the determination of H_2O_2 profiles at stations H270 and B, the sample residues were used for measurement of acidity (pH) and concentration of micro-particles. The vertical distributions of pH are shown in Fig. 4 with the vertical profiles of H_2O_2 . The distribution of pH in surface snow cover over East Queen Maud Land was investigated by KAMIYAMA *et al.* (1987), where the pH level of snow in the inland region was reported to be distributed between 4.8 and 6.0, generally decreasing with distance from the coast; an extremely low level was detected around the highest dome area. Lower values of pH were observed at point B than at point H270, which is supported by the results given above. In the vertical profiles of pH and H_2O_2 , it seems that the decrease in pH value corresponds to the increase in H_2O_2 concentration, as shown in Fig. 4. There possibly exists a relationship between the values of pH and H_2O_2 . One reason is that the intrusion of substances occurring in the stratosphere, as described before, will give the snow low pH and high H_2O_2 concentration. The other is that oxidation in the atmosphere, such as the transformation of SO_2 into SO_4 , becomes active in summer with the increase of H_2O_2 concentration.

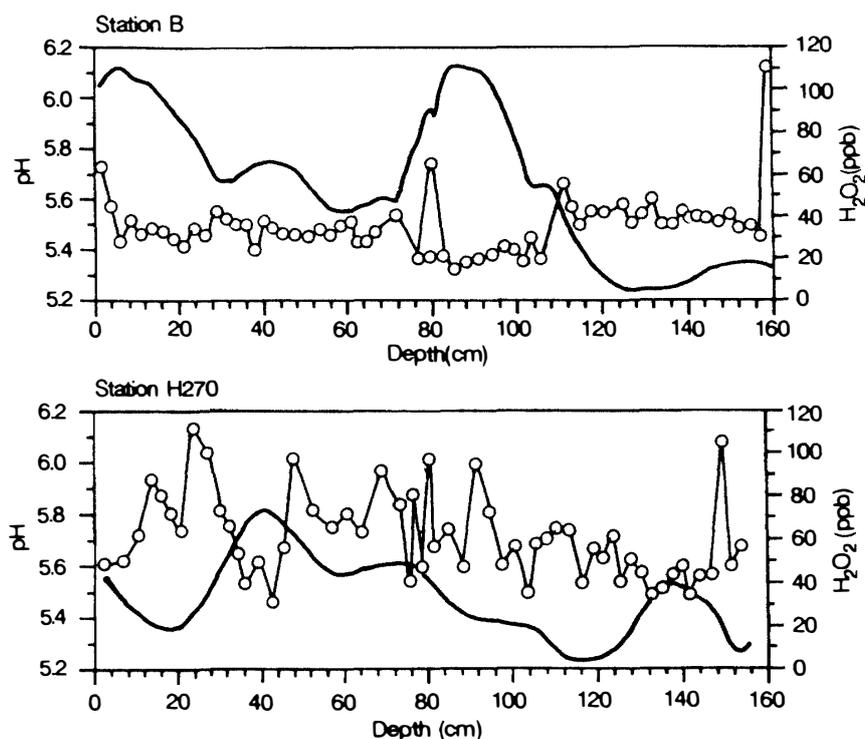


Fig. 4. The vertical profile of pH (open circle) and H_2O_2 (solid line) in snow cover at stations B and H270.

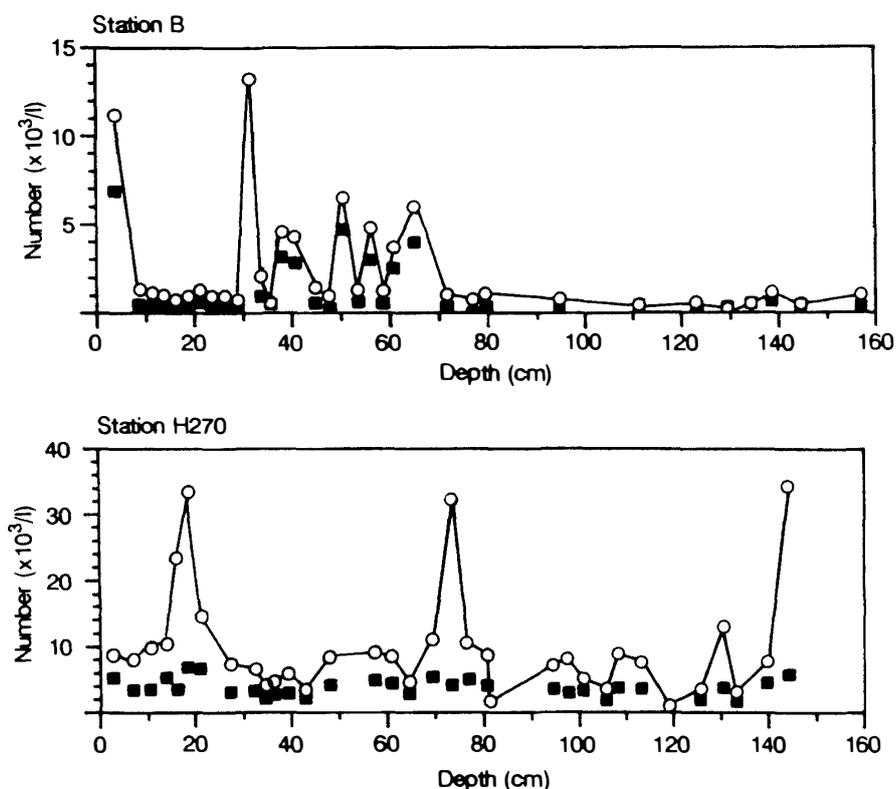


Fig. 5. The vertical profile of micro-particle concentration at stations B and H270; open symbols indicate total number concentration and black squares indicate large particle number.

Vertical profiles of micro-particle concentration are shown in Fig. 5. The concentration of micro-particles was higher at station H270 than at station B. Station B is farther from the coastal bare rock area than station H270. The location, depending on distance from the micro-particle source area, is possibly responsible for the average concentration. Through the migration process in the atmosphere over the ice sheet, the particles are considered to be eliminated from the atmosphere with distance from the coast.

3.2.3. Oxidation products of sulfide species

WATANABE (1992) reported the vertical distributions of chemical components (Na, K, NH₄, Cl, NO₃, SO₄ and MSA) in the same samples used for $\delta^{18}\text{O}$ measurements. The profiles of sulfate (SO₄) at stations B and H270 are shown in Fig. 6 with the ratio of sulfate of non-sea salt origin to total sulfate (nssSO₄/SO₄). Here, nssSO₄ is defined as the excess amount of SO₄ from the contribution of the sea salts. It is assumed that all Na is of marine origin.

The ratio (nssSO₄/SO₄) is higher at station B than at station H270, though the concentration of SO₄ is similar at both stations. Almost all SO₄ content at station B consists of nssSO₄. The black and open triangles show snow layers with high and low $\delta^{18}\text{O}$ values (summer and winter layers), respectively. The ratios (nssSO₄/SO₄) decreased in winter and increased in summer. The nssSO₄ contributed to the SO₄ fraction in summer. We discuss the summer anomalies in more

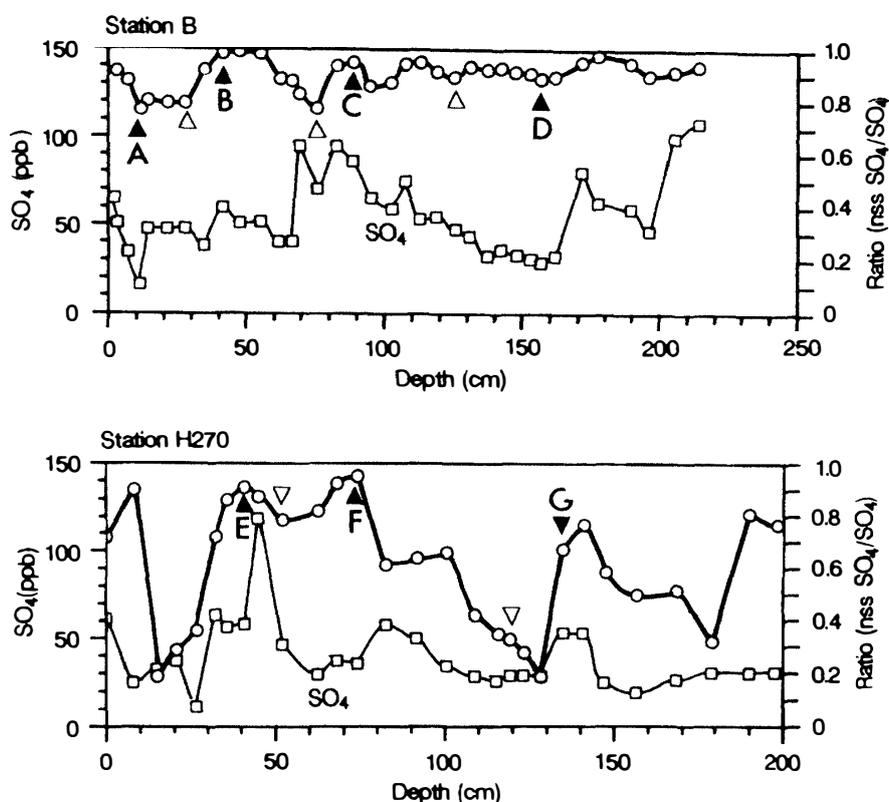


Fig. 6. The vertical profiles of SO_4 and the ratio ($\text{nssSO}_4/\text{SO}_4$) at stations B and H270. Triangle symbols indicate the season of layer formation; black (summer) and open (winter).

detail. The relatively higher values of H_2O_2 maxima, observed near layers A, C and E, were followed by high SO_4 content. Conversely, relatively low levels of SO_4 were observed with comparatively low H_2O_2 content near the summer layers B, D, F and G. SO_4 content in snow possibly depends on the H_2O_2 concentration. There seems to exist a positive correlation between H_2O_2 and SO_4 in snow. SO_4 in summer derives from nssSO_4 , because nssSO_4 occupies the greater part of SO_4 in summer at both stations. It is suggested that high H_2O_2 and SO_4 levels occur with the atmospheric circulations over each station and the intensity depends on local atmospheric conditions. These regional and seasonal characteristics of atmospheric environments can explain the difference in the snow chemical composition from the results obtained by LAJ *et al.* (1990).

In order to discuss the atmospheric environments based on various type of information recorded in snow, we must evaluate the local and seasonal fluctuations.

The vertical distributions of methane-sulphonic acid (MSA) in the surface snow at stations B and H270 are shown in Fig. 7 with the ratio of $\text{MSA}/\text{nssSO}_4$. Higher concentration of MSA in snow was observed at station H270 than station B, possibly depending on distance from the coast. The ratio ($\text{MSA}/\text{nssSO}_4$) was also higher at station H270 than station B. MSA and SO_4 are possible oxidation products of dimethyl-sulfide (DMS) in the marine atmosphere, and SO_2 is

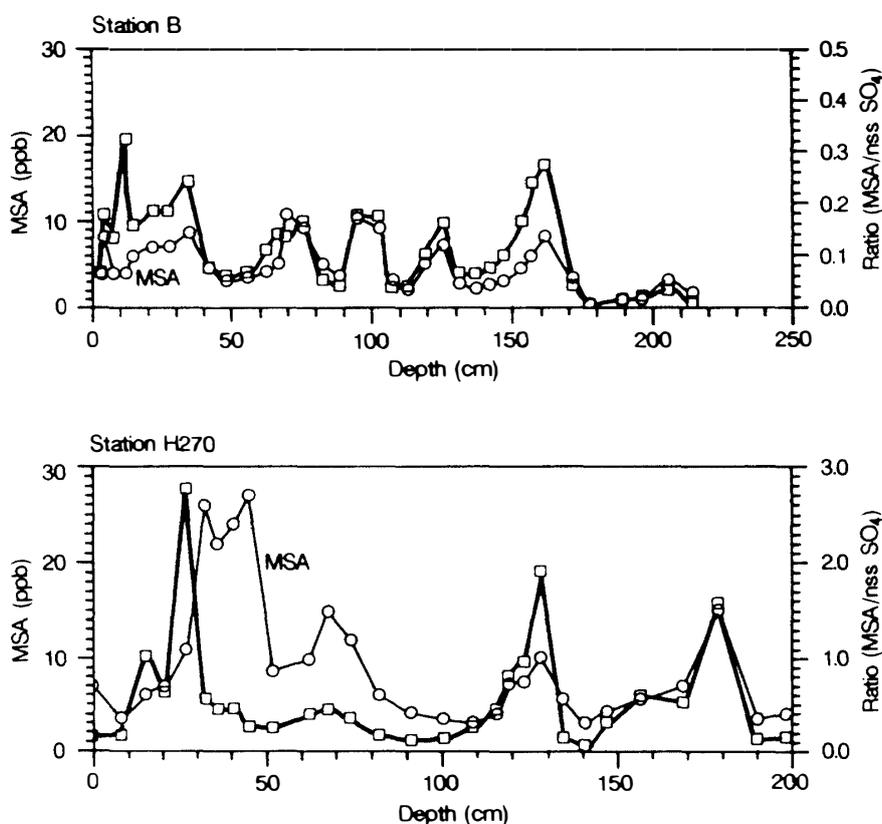


Fig. 7. The vertical profile of MSA (circle) and the ratio of $MSA/nssSO_4$ (square) at stations B and H270.

additionally oxidized to SO_4 (ANDREAE, 1990). MSA and SO_4 are present in the atmosphere, predominantly in the form of aerosol particles, because of their low volatility. MSA is efficiently scavenged by cloud droplets and precipitation because of high solubility (CLEGG and BRIMBLECOMBE, 1985). MSA is considered to be a more direct indicator of marine materials. $MSA/nssSO_4$ also indicates the portion of marine origin. In discussing the origin of substances in the precipitation, the ratio is better than the concentration, because the fluctuation in the precipitation rate has more direct effect on the concentration than on the ratio. MSA and $nssSO_4$ in aerosol, reported by PROSPERO *et al.* (1991), increase in summer and decrease in winter with fluctuation in the ratio from 0.1 to 0.4. A similar value of the ratio was observed in snow at Law Dome, located relatively close to the coast (IVEY *et al.*, 1986). Relatively low values from 0.02 to 0.20 were observed in the Vostok ice core (LEGRAND *et al.*, 1991). Summer minima in both MSA and $MSA/nssSO_4$ were clearly observed at station B, while the range in the ratio was similar to that reported previously. A decrease in the influence of marine origin in summer was clearly shown at station B. $MSA/nssSO_4$ at station H270 was higher than has ever been reported, and summer maxima in both MSA and $MSA/nssSO_4$ were observed. The results suggest a complicated pathway of MSA transportation through atmospheric environments.

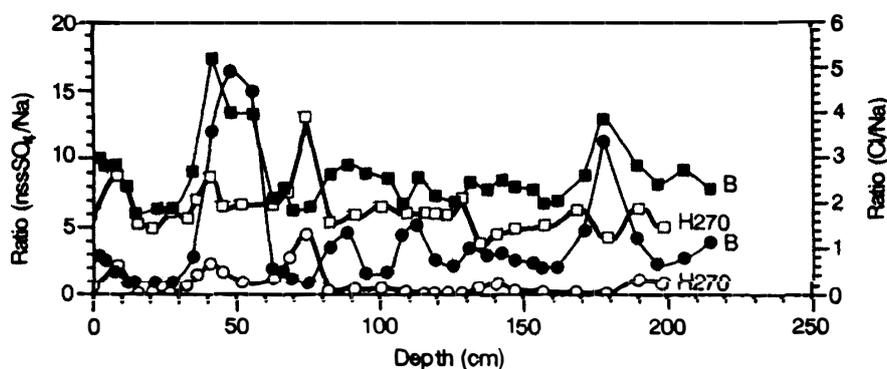


Fig. 8. The vertical profiles of the ratio of $nssSO_4/Na$ (circle) and Cl/Na (square) at stations B and H270.

Finally, we discuss $nssSO_4$ and chloride (Cl). It is generally considered that sodium (Na) in snow is of sea salt origin. The geographical location will affect the ratios of $nssSO_4$ and Cl to Na ($nssSO_4/Na$ and Cl/Na) through the effect of the atmospheric environment over the ice sheet, as shown in Fig. 8. The addition of Cl into snow in the inland region depends on its volatility in the atmosphere (LEGRAND and DELMAS, 1988) and/or on photochemical production at high altitude (BRASSEUR and VERSTRAETE, 1989). Both $nssSO_4/Na$ and Cl/Na were higher at station B than station H270. And both ratios showed similar fluctuations, increasing in summer and decreasing in winter, at both stations. These substances, such as $nssSO_4$ and Cl, have relatively longer residence time in the atmosphere and increase in the ratio in the inland region and in summer. In summer the atmospheric environment over the coastal region becomes more like that over the inland region.

4. Concluding Remarks

The vertical distribution of H_2O_2 in snow layer was obtained in three different regions of the Antarctic ice sheet. The seasonal variation of H_2O_2 coincides with that of $\delta^{18}O$. Increase in H_2O_2 with decrease in pH was observed in the higher inland region. Conversely, the concentration of micro-particles was higher in the coastal region and was unrelated to H_2O_2 . The precise records in the vertical profiles of H_2O_2 , $\delta^{18}O$, pH and micro-particles provide valuable information about chemical reactions and migration of chemical substances in the atmosphere. We also discussed the seasonal and local distributions of SO_4 , MSA and Cl in snow and tried to estimate the atmospheric environments from the records of chemical compositions of the snow cover.

Direct information about the upper atmosphere, such as the stratosphere, is obtained from snow deposits.

References

- ANDREAE, M. O. (1990): Ocean-atmosphere interactions in the global biogeochemical sulfur cycle. *Mar. Chem.*, **30**, 1–29.
- BRASSEUR, G. and VERSTRAETE, M. M. (1989): Atmospheric chemistry-climate interactions. *Climate and Geo-Sciences*, ed. by A. BERGER *et al.* Dordrecht, Kluwer Academic, 279–302.
- CLEGG, S. L. and BRIMBLECOMBE, P. (1985): The solubility of methanesulphonic acid and its implications for atmospheric chemistry. *Environ. Technol. Lett.*, **6**, 269–278.
- IVEY, J. P., DAVIES, D. M., MORGAN, V. and AYERS, G. P. (1986): Methanesulphonate in Antarctic ice. *Tellus*, **38**, 375–379.
- KAMIYAMA, K. and NAKAYAMA, E. (1992): Determination of hydrogen peroxide in snow: Preliminary results for snow samples in the inland region, Antarctica. *Proc. NIPR Symp. Polar Meteorol. Glaciol.*, **5**, 113–119.
- KAMIYAMA, K., AGETA, Y., OKUHIRA, F., FUJII, Y. and WATANABE, O. (1987): Glaciological and chemical characteristics of snow in the inland plateau, East Queen Maud Land, Antarctica. *Nankyoku Shiryo (Antarct. Rec.)*, **31**, 163–170.
- 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.
- LAJ, P., DRUMMEY, S. M., SPENCER, M. J., PALAIS, J. M. and SIGURDSSON, H. (1990): Depletion of H₂O₂ in a Greenland ice core: Implications for oxidation of volcanic SO₂. *Nature*, **346**, 45–48.
- LEGRAND, M. and DELMAS, R. (1988): Formation of HCl in the Antarctic atmosphere. *J. Geophys. Res.*, **93**, 7153–7168.
- LEGRAND, M., FENIET-SAIGNE, C., SALTZMAN, E. S., GERMAIN, C., BARKOV, N. I. and PETROV, V. N. (1991): Ice-core record of oceanic emissions of dimethylsulphide during the last climate cycle. *Nature*, **350**, 144–146.
- MAY, R. D. and WEBSTER, C. R. (1989): *In situ* stratospheric measurements of HNO₃ and HCl near 30 km using the balloon-borne laser *in situ* sensor tunable diode laser spectrometer. *J. Geophys. Res.*, **94**, 16343–16350.
- PROSPERO, J. M., SAVOIE, D. L., SALTZMAN, E. S. and LARSEN, R. (1991): Impact of oceanic sources of biogenic sulphate aerosol concentrations at Mawson, Antarctica. *Nature*, **350**, 221–223.
- SIGG, A. and NEFTEL, A. (1988): Seasonal variations in hydrogen peroxide in polar ice cores. *Ann. Glaciol.*, **10**, 157–162.
- WATANABE, O. (1992): How are climatic and environmental signals preserved in an ice sheet? *J. Geogr.*, **100**, 988–1006.

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