High temporal resolution chemical analysis of H72 ice core in east Dronning Maud Land, Antarctica

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Abstract: The H72 ice core collected in east Dronning Maud Land, Antarctica has been analyzed in detail. Concentrations of Na^+ and Cl^- indicate the highest correlation coefficients, so we can say that both ions in the H72 ice core originated from sea salt. The fluctuation pattern of $\delta^{18}O$ below the depth of 45 m proves that the $\delta^{18}O$ distribution is smoothed by water vapor diffusion in the firn layer. An increasing tendency of NO_3^- and $nssSO_4^{2-}$ concentrations in the shallow layer has not been found in the H72 ice core. The H72 ice core is dated as AD 1837 by the periodic concentration fluctuation of MSA at 73.29 m depth. Volcanic signals are detected in 49 layers in the H72 ice core. In the late 19th century many volcanic eruptions were recorded, which explains why many volcanic signals are present in the H72 ice core. It is noted that a year with low temperatures in winter and a low annual minimum $\delta^{18}O$ will have high surface mass balance and more snowfall. Considerable $nssSO_4^{2-}$ has been released into the atmosphere by human activity in the 20th century, but we cannot find traces of a recent increase in deposition of $nssSO_4^{2-}$ at the H72 site.

key words: ice core, chemical detailed analysis, sea salt, water vapor diffusion, volcanic signal

1. Introduction

Japanese Antarctic Research Expeditions (JARE) have been reconstructing the paleo-environment through analysis of ice cores, snow accumulation rate measurement by snow stakes, and observation of the stratigraphic and density profiles of surface snow in east Dronning Maud Land, Antarctica. It is, therefore, now possible to study the surface mass balance and the variation of climate records of temperature and precipitation in this area. Ice cores have been collected in this area over the last decade, in order to evaluate changes in past climate and surface mass balance. These ice cores have been taken and analyzed as part of the International Trans-Antarctic Scientific Expedition (ITASE) program. We report here on the results of detailed analysis of the H72 ice core.

The H72 ice core was collected in September 1998 at the H72 site (69°12′17″S, 41°05′26″ E; 1214 m a.s.l.) in east Dronning Maud Land by JARE-39. Snow does not accumulate every year in the coastal region of east Dronning Maud Land, due to strong

katabatic winds (Watanabe, 1978).   However, the annual surface mass balance at H72 is always positive and the average surface mass balance during the 26 year period April 1972–October 1998 was 0.307 m w.e. yr^{-1} (Nishio *et al.*, 2002).

2.   Analytical methods

The 73.29 m ice core was cut into 50 cm sections on-site immediately after drilling and brought back to Japan in frozen storage.   Then we made assay samples cutting off every 4 through 6 cm in a low-temperature laboratory.   We selected the cutting width to let it be 10 through 20 m*l* on melting, and then the surface of the ice core was scraped off with a ceramic knife washed in extra-pure water in order to remove contamination on the surface of the ice core.   We melted a decontaminated sample in a clean room, after melting putting it in to a teflon bottle washed by extra-pure water.   Then we put the melted sample into a plastic bottle washed by extra-pure water and refrigerated it until just before chemical analysis.   We used the melted sample to do chemical analyses and isotopic analyses, then measured electric conductivity (EC) and pH.   The respective concentrations of the major dissolved components (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, MSA^-, Cl^-, NO_3^-, SO_4^{2-}) were measured by ion chromatography (DIONEX: DX-500 and DX-320).   We determined the isotopic composition of oxygen-18 ($\delta^{18}O$) using a mass spectrometer (Finnigan MAT: delta S) on CO_2 equilibrated with samples.

3.   Results and discussion

3.1.   *Accuracy of sampling procedures and analytical methods*

We divided the H72 ice core into 1470 samples for detailed analysis.   The validity of the chemical analysis results was also assessed for this series of experiments.   We analyzed the major cation (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) and major anion (MSA^-, Cl^-, NO_3^-, SO_4^{2-}) concentrations by ion chromatography.   The total cation equivalent concentration was calculated by adding cations to the H^+ concentration calculated from the pH; the total anion equivalent concentration should be equal to the total cation equivalent concentration.   Therefore, in Fig. 1, we show the relationship between the total cation equivalent concentration and total anion equivalent concentration.   The result of each analysis reflects a ratio of 1 : 1 between the total cation equivalent concentration and total anion equivalent concentration.   Considering the present results, the major ion species were all accounted for in the analysis and the accuracy of the analysis was satisfactory.

3.2.   *Origin of each ion in the H72 ice core*

Table 1 shows the correlation matrix for each ion concentration and EC.   Concentrations of Na^+ and Cl^- indicate the highest correlation coefficient which is 0.982. Both Na^+ concentration and Cl^- concentration indicate the high correlation coefficients to electric conductivity.   There is also a high correlation coefficient of 0.653 between SO_4^{2-} and electric conductivity. We suggest that the high correlation coefficient between Na^+ and Cl^- concentrations at the H72 site, 80 km from the coast, results from the fact that both ions originate from sea salt.   By the same token, Mg^{2+} and SO_4^{2-} are
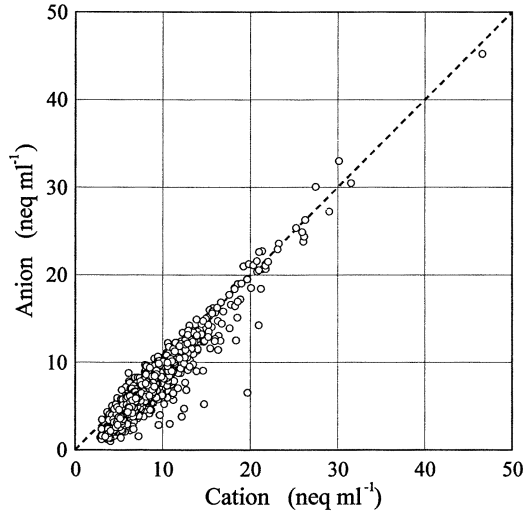
Fig. 1. The relationship between concentrations of total cations and total anions.

Table 1. Correlation matrix of chemical components.

	EC	H^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	MSA^-	Cl^-	NO_3^-
H^+	0.423								
Na^+	0.911	0.043							
K^+	0.270	−0.050	0.330						
Mg^{2+}	0.551	−0.064	0.578	0.183					
Ca^{2+}	0.188	−0.181	0.218	0.227	0.612				
MSA^-	0.325	−0.043	0.397	0.135	0.190	0.126			
Cl^-	0.918	0.067	0.982	0.231	0.576	0.181	0.401		
NO_3^-	−0.024	0.161	−0.185	0.068	−0.062	0.035	−0.152	−0.190	
SO_4^{2-}	0.653	0.153	0.568	0.155	0.425	0.204	0.029	0.568	0.246

most likely derived from sea salt, since the correlation coefficients of Mg^{2+} and SO_4^{2-} concentration with Na^+ concentration are also high. This result accords with a previous report (Suzuki, 1987) that most Mg^{2+} and SO_4^{2-} also originate from sea salt in the snow at a site located near the coast.

Figure 2 shows the relationship between Na^+ concentration and Cl^- concentration in the ice core samples. The broken line in the figure indicates the ratio of concentrations of the two in seawater. Almost all results of analysis of the samples accord with this line, which makes it clear that Na^+ and Cl^- originate from sea salt. The concentration of Na^+ fluctuates from 0.247 neq ml^{-1} to 35.2 neq ml^{-1}. This shows that snow falling at the H72 site varies from purified water snow containing only a small quantity of sea salt to snow containing a relatively high proportion of sea salt according to the weather conditions when the snow has fallen. Some samples indicate either a reduction or enrichment of Cl^- concentration compared with the ratio of concentration in seawater. It is possible that there is an analytical error, but it is also possible that

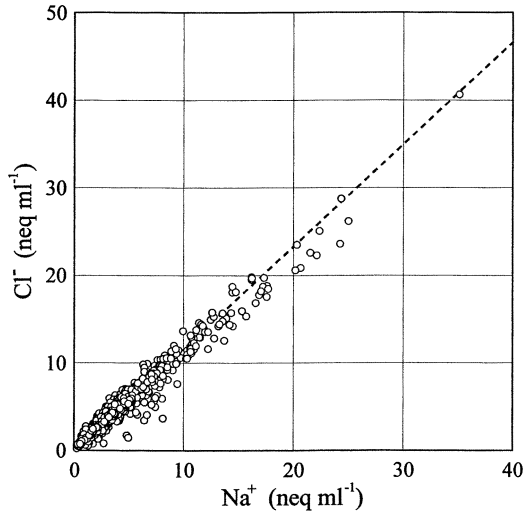Fig. 2.   *The relationship between concentrations of Na⁺ and Cl⁻ in ice core samples.*

there is a chlorine loss in the atmosphere (Eriksson, 1959; McInnes *et al*., 1994; Suzuki *et al*., 1995).

3.3.   *Chemical profiles of the H72 ice core*

Figure 3 shows the results of detailed chemical analysis. Na^+ and Cl^- are not shown in the figure, since both are strongly related to electric conductivity. The average electric conductivity is $0.188\,mS\,m^{-1}$ and standard variation is $0.053\,mS\,m^{-1}$, having less of a fluctuation range. However, occasionally, a layer of high electric conductivity, such as $0.697\,mS\,m^{-1}$ at approximately 15 m depth, can be observed. These correspond to material originating from sea salt of high concentration as already mentioned. It is probable that the H72 site where the layer accumulated was under such weather conditions that snow containing a high concentration of sea salt fell. There is no significant long-term variation, only short-term variation.

The average pH is 5.50, minimum and maximum values are 5.28 and 5.82. According to reports on core analyses in the Northern Hemisphere, there has been a pronounced tendency toward decreasing pH in the shallow layer. This accords with the acidification tendency of precipitation throughout the 20th century (Lee *et al*., 2003; Legrand and Mayewski, 1997; Matoba *et al*., 2002; Suzuki *et al*., 1991). But a decreasing tendency of pH in the shallow layer has not been found in the H72 ice core.

The average $\delta^{18}O$ is $-25.74‰$, the range is between $-20.84‰$ and $-32.27‰$, however, the variation pattern changes on reaching a depth of around 45 m. In other words the fluctuation range of $\delta^{18}O$ is relatively large, and the cyclic change of $\delta^{18}O$ shows a short time variation in the layer shallower than 45 m. On the other hand, the fluctuation range of $\delta^{18}O$ becomes less and the cyclic variation is smooth deeper than 45 m. So it appears that the fluctuation pattern of $\delta^{18}O$ below 45 m proves the smoothing effect of $\delta^{18}O$, resulting from water vapor diffusion in the firn layer (Johnsen,
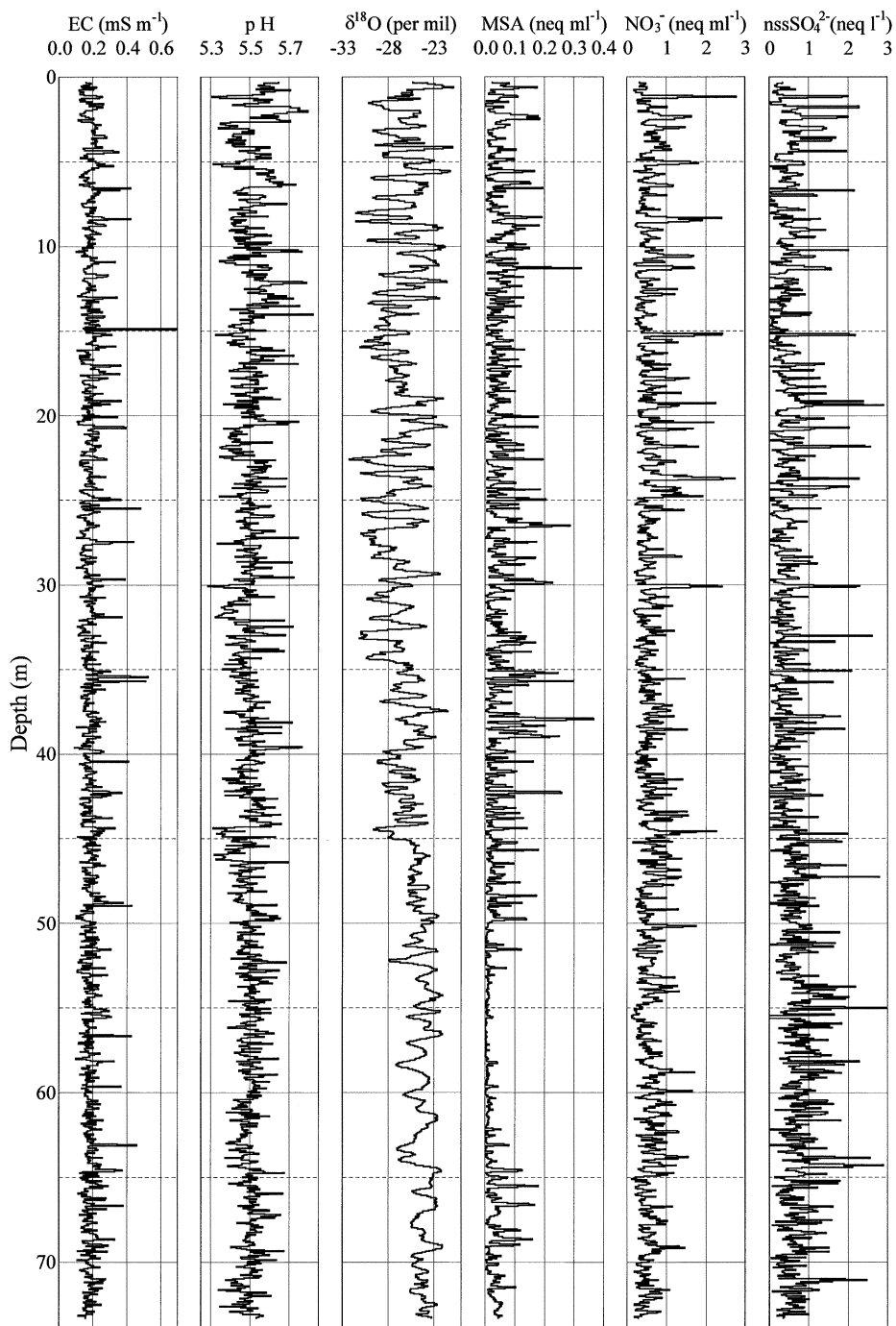
Fig. 3.　Vertical profiles of chemical components of the H72 ice core.

1977). The reason why the smoothing effect is remarkable below 45 m depth is left as a future problem.

The methanesulphonic acid (MSA) concentration shows 0.0423 neq ml^{-1} as its average value, 0.0468 neq ml^{-1} as its standard variation with a large fluctuation range and 0.366 neq ml^{-1} as the maximum value. There are many samples of lower concentration that limit detection as well. There is no clear tendency toward an increase or decrease of MSA deeper down, the concentration is low at depth 50 m to 65 m. So it appears that this low concentration is due to the origin of MSA or particular features of the transport mechanism since the same fluctuation is not observed in other ion concentrations.

The concentration NO_3^- has an average of 0.606 neq ml^{-1}, standard variation of 0.351 neq ml^{-1}, maximum of 2.77 neq ml^{-1} and minimum of 0.120 neq ml^{-1}. This shows that NO_3^- accumulates consistently in all layers. Here there is a graphic representation of $nssSO_4^{2-}$ since SO_4^{2-} has a strong relation with electric conductivity, like Na^+ and Cl^- as already mentioned above. The concentration of $nssSO_4^{2-}$ has an average of 0.583 neq ml^{-1}, standard variation of 0.490 neq ml^{-1}, and maximum of 2.98 neq ml^{-1}. According to core analysis reports on the Northern Hemisphere, there has recently been an increase in concentrations of NO_3^- and $nssSO_4^{2-}$ in the shallow layer in accord with the acidification tendency of precipitation throughout the 20th century. But increases of NO_3^- and $nssSO_4^{2-}$ concentrations in the shallow layer have not been found in the H72 core. It appears that the influence of the release of acidic materials into the atmosphere that increased greatly during the 20th century, as a result of human activity, does not extend to the H72 site. Furthermore, since it is believed that NO_3^- and $nssSO_4^{2-}$ are of anthropogenic origin, in mid-latitude snow in the Northern Hemisphere, and the concentrations of both frequently coincide in one snowfall event. Figure 3 shows that there is no tendency toward synchronization of the concentration fluctuations of NO_3^- and $nssSO_4^{2-}$ at the H72. It appears that the high concentration of $nssSO_4^{2-}$ originates from a volcanic eruption, as described below. MSA concentration is low: from 50 m to 65 m, but, in contrast there is a high concentration of $nssSO_4^{2-}$: from 45 m to 65 m.

3.4. Annual layer determination

The annual layer determination of the H72 ice core will now be examined. MSA is produced by oxidation of dimethyl sulfide (DMS) released by marine phytoplankton; it is an indication of high concentration in summer and low concentration in winter. MSA also reflects seasonal variation in the H72 ice core; counting the number of cycles makes it possible to date the annual layers. The H72 ice core is dated as AD 1837 by the periodic concentration fluctuation of MSA at 73.29 m depth.

Figure 4 shows the annual layer determination according to the periodicity of MSA concentration. We set the beginning of the layer, where concentration is high, as January 1st. Figure 4 shows the fluctuations of MSA, Na^+ and $\delta^{18}O$ from the surface layer until AD 1975. The Na^+ concentration of an ice core at South Pole Station indicates high concentration in winter and low concentration in summer (Patris et al., 2000), but we do not observe a similar tendency from the fluctuation in concentration of Na^+ in Fig. 4. There are some years that show low concentration in summer but a

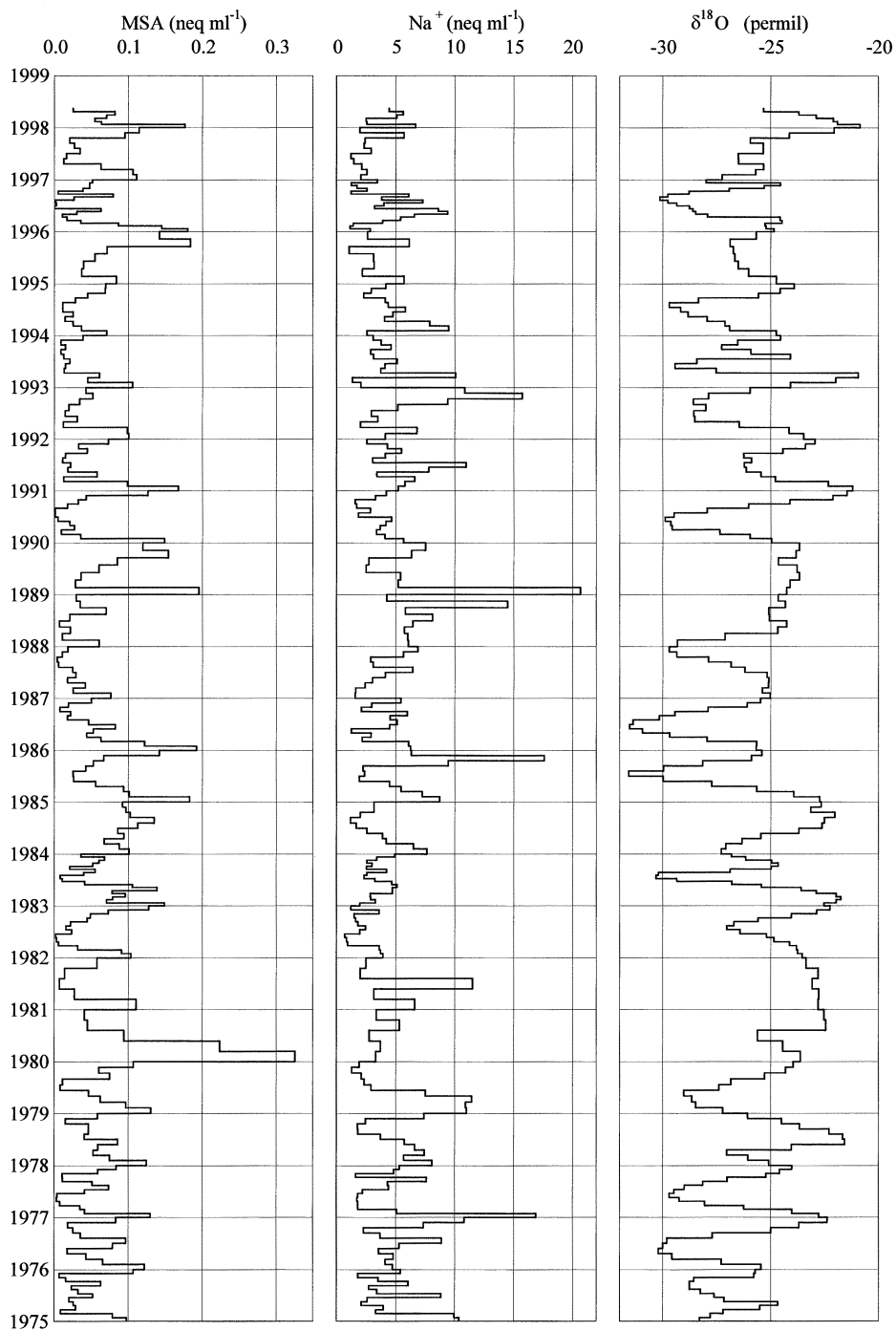MSA (neq ml⁻¹)   Na⁺ (neq ml⁻¹)   δ¹⁸O (permil)

Fig. 4.   Profiles of the concentrations of MSA, Na⁺ and δ¹⁸O value from the surface layer to AD 1975.

number of years show high concentration in summer.   It appears that results collected at the H72 site, close to the coast, reflect the influence of the open sea in summer. $\delta^{18}O$ for precipitation becomes high in summer and low in winter, with a similar seasonal variation in almost all years, as shown in Fig. 4.   Smoothing of the fluctuation of $\delta^{18}O$ appears to relate to water vapor diffusion in the firn layer deeper than 45 m, as earlier mentioned, but it can also be seen that the annual layer determination from MSA concentration is different from the cyclic variation of $\delta^{18}O$ deeper than 45 m.

3.5.   Signals of volcanic eruptions

Volcanic eruptions release a large quantity of sulfur oxides into the atmosphere. This affects concentrations of $nssSO_4^{2-}$ in falling snow after a volcanic eruption.   The $nssSO_4^{2-}$ is also produced by oxidation of DMS in the atmosphere.   The concentrations of $nssSO_4^{2-}$ and MSA in the Antarctic atmosphere are proportional (Davis *et al*., 1998; Mauldin *et al*., 2001).   Volcanic eruptions therefore influence layers with high $nssSO_4^{2-}$ concentration and low levels of MSA concentration (Nishio *et al*., 2002).   In addition, a layer with high concentration of $nssSO_4^{2-}$ influenced by volcanic eruption has a decreased pH value.   To study this, we extract the layer influenced by volcanic eruption from the H72 core.   We judged on MSA level lower than average, together with concentrations of H^+ and $nssSO_4^{2-}$ exceeding the average plus 2σ, as a highly reliable volcanic signal (grade I); while on MSA level lower than average combined with H^+ concentration above average and $nssSO_4^{2-}$ level exceeding the average plus 2σ was considered a clear volcanic signal (grade II).   Figure 5 shows concentrations of H^+, MSA, and $nssSO_4^{2-}$ with year as abscissa.   This gives a record of volcanic eruptions in the Southern Hemisphere with the Volcanic Index in the right column (Simkin and Siebert, 1994; Hayakawa, 1997).   There are five layers with grade I volcanic signals. The influence of volcanic eruptions in the Southern Hemisphere is clear, in accord with dating and the volcanic eruptions of Deception in 1972, Agung in 1963, Michoacan Field in 1943, and Santa Maria in 1902.   There are 49 layers with grade II volcanic signals, 44 excluding the 5 layers measured as grade I.   It is believed that there are records of volcanic eruptions corresponding to each layer except for the 1920s and the signal shows the influence of volcanic eruptions.   In the late 19th century many volcanic eruptions were recorded, commencing with Krakatau in Indonesia in 1883, and a number of volcanic signals in the H72 ice core are dated in the late 19th century. Depths of low concentration of MSA and high concentration of $nssSO_4^{2-}$ as described above accord with this late 19th century period of concentrated volcanic eruption. Thus, it is validated that the annual layer determination can be based on seasonal variations of MSA concentration because of a favorable correlation between volcanic eruption records and the volcanic signal of the H72 ice core.

3.6.   Surface mass balance

We have obtained the surface mass balance for 160 years, from 1838 to 1997, based on the annual layer determination.   Figure 6 shows the surface mass balance.   The average surface mass balance for the 160 years is 0.326 m w.e. yr^{-1}.   The surface mass balance at the H72 site, from 1973 to 1998, by snow-stake observation is 0.307 m w.e. yr^{-1} (Nishio *et al*., 2002), good accordance is observed between the two values.
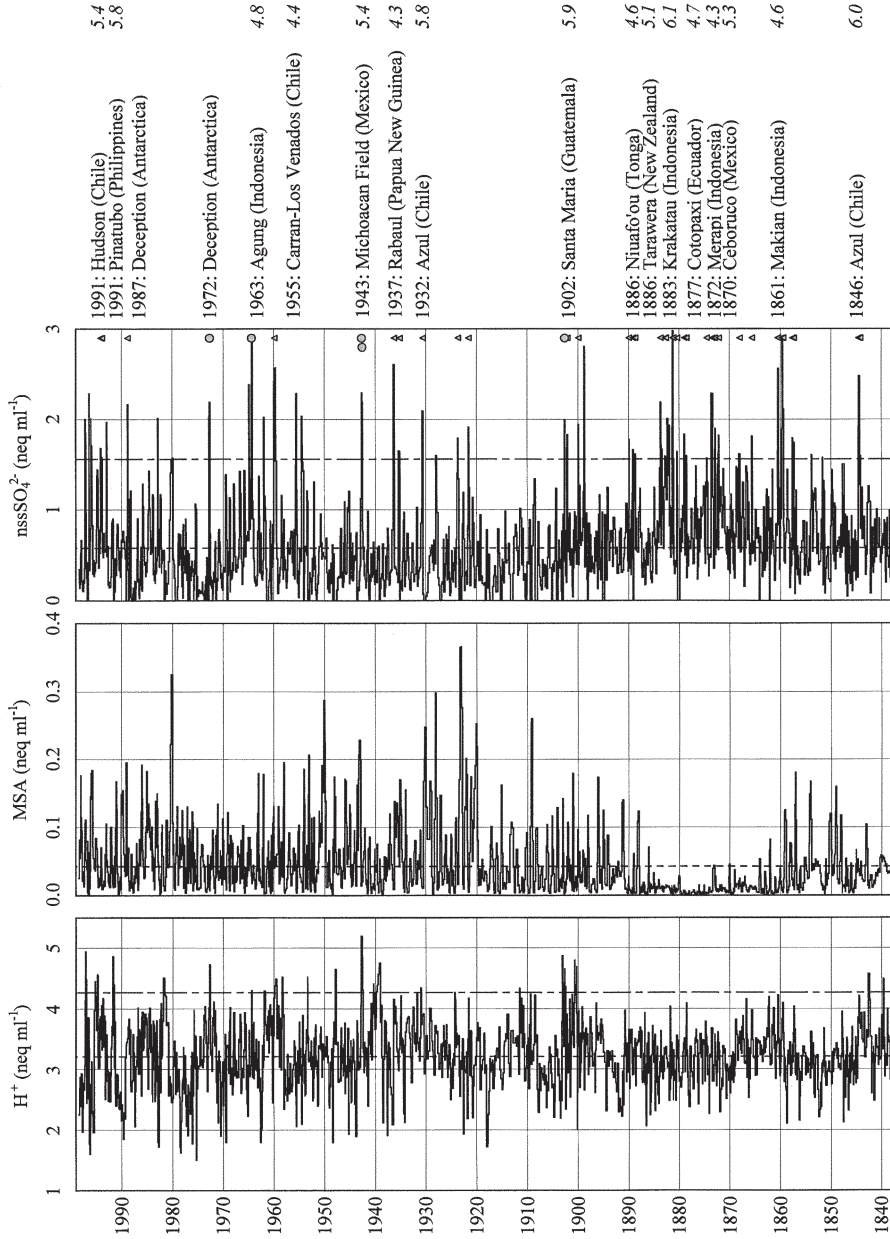
Fig. 5. Profiles of concentrations of H^+, MSA and $nssSO_4^{2-}$ with year as the abscissa. Volcanic indices are denoted in the right column. Circles: highest reliable volcanic signal (grade I). Triangles: clear volcanic signal (grade II).
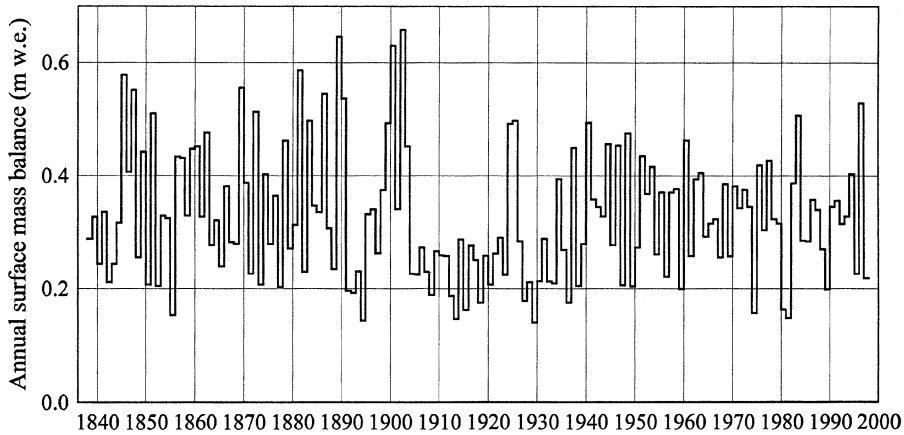
Fig. 6. *Surface mass balance in water equivalent from AD 1838 to 1997.*

The maximum and minimum values of surface mass balance are 0.658 m w.e. yr^{-1} and 0.140 m w.e. yr^{-1} respectively, and the annual fluctuation is relatively large. The 20 years from 1904 to 1923 was a period when the surface mass balance was less than 0.3 m w.e. yr^{-1}, with light amount of snowfall. Figure 5 shows few volcanic signals for this period. On the other hand, there were many years with large surface mass balance before 1903. It appears that there were heavy snowfalls during the late 19th century, since the average surface mass balance was 0.359 m w.e. yr^{-1} from 1838 to 1903; and from 1904 to 1997 the average was 0.303 m w.e. yr^{-1}. We can infer from the number of volcanic signals in the late 19th century that a large quantity of aerosol in the atmosphere produced by volcanic eruptions effectively increased the amount of snowfall by acting as ice nuclei (Robock, 2000).

3.7. Relationship between climatic condition and surface mass balance

Now we examine whether the quantity of snowfall is influenced by some sort of fluctuation of climatic conditions. The value of $\delta^{18}O$ in snow is small when the temperature is low at the time of formation of snow crystals (Suzuki and Endo, 2001), and $\delta^{18}O$ of the H72 ice core is an indicator of the air temperature variation at the time of snowfall. As already mentioned, the fluctuation range of $\delta^{18}O$ becomes less and the cyclic variation is smooth deeper than 45 m, because of the smoothing effect of $\delta^{18}O$ resulting from water vapor diffusion in the firn layer. This depth represents AD 1902. The surface mass balance increased under the influence of volcanic eruptions until AD 1903. So we will examine the relation between $\delta^{18}O$ and the surface mass balance since AD 1904. Figure 7 shows the relationship between the annual minimum $\delta^{18}O$ and the surface mass balance from AD 1904 to 1997. We can see here that years with high temperatures in winter and high values of annual minimum $\delta^{18}O$ have lower values of surface mass balance and less snowfall. Years with low temperatures in winter and low values of annual minimum $\delta^{18}O$ have high values of surface mass balance and more snowfall.

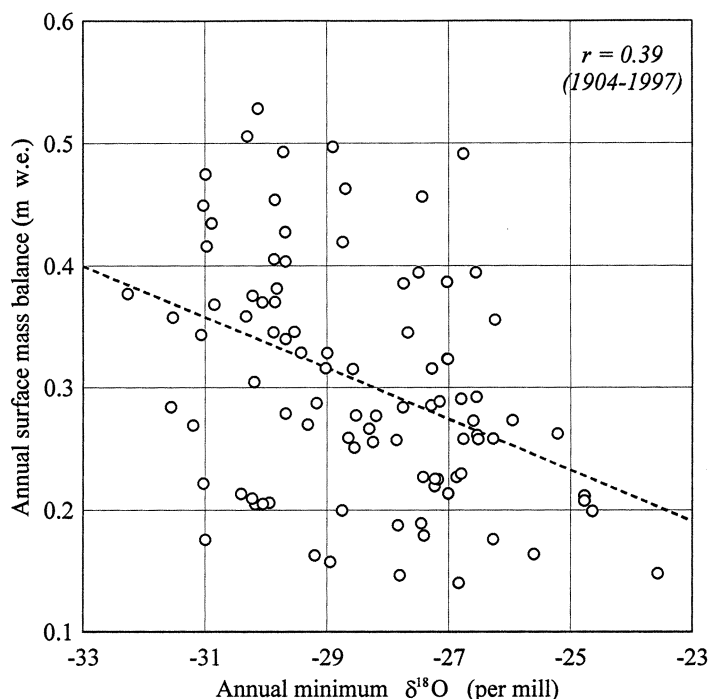Fig. 7. *Relationship between the annual minimum δ¹⁸O and the surface mass balance from AD 1904 to 1997.*

3.8. Deposition rate of ions at H72

We can calculate the average ion concentration for every year based on the annual layer determination. Figure 8 shows ion deposition rates calculated from each average value of ion concentration of Na^+, NO_3^- and $nssSO_4^{2-}$ and the surface mass balance. The surface mass balance was large in the late 19th century and slightly less in the 20th century, though we cannot find any tendency in the deposition rate of Na^+. Even though the variation is large year by year, the average deposition rate of Na^+ for the 160 years from 1838 to 1997 was $1.25\, meq\, m^{-2}yr^{-1}$. Neither can we find any fluctuation of NO_3^- deposition synchronizing with the surface mass balance. As earlier mentioned, we cannot find any recent tendency toward increasing NO_3^- concentration, or NO_3^- deposition. We have already stated that the $nssSO_4^{2-}$ deposition rate became higher in the late 19th century; furthermore, the surface mass balance also became high in the late 19th century. In association with these changes, the deposition of $nssSO_4^{2-}$ became high in the late 19th century. We can see at the H72 site the many volcanic signals caused by volcanic eruptions in the Southern Hemisphere in the late 19th century. We can also see the $nssSO_4^{2-}$, the volcanic product, deposited liberally at the H72 site. The 20 years from 1904 to 1923 was period with less surface mass balance and fewer volcanic signals but also less deposition of $nssSO_4^{2-}$. The $nssSO_4^{2-}$ has been released liberally into the atmosphere by human activity in the 20th century, but we cannot find traces of a recent increase in deposition of $nssSO_4^{2-}$ at the H72 site.
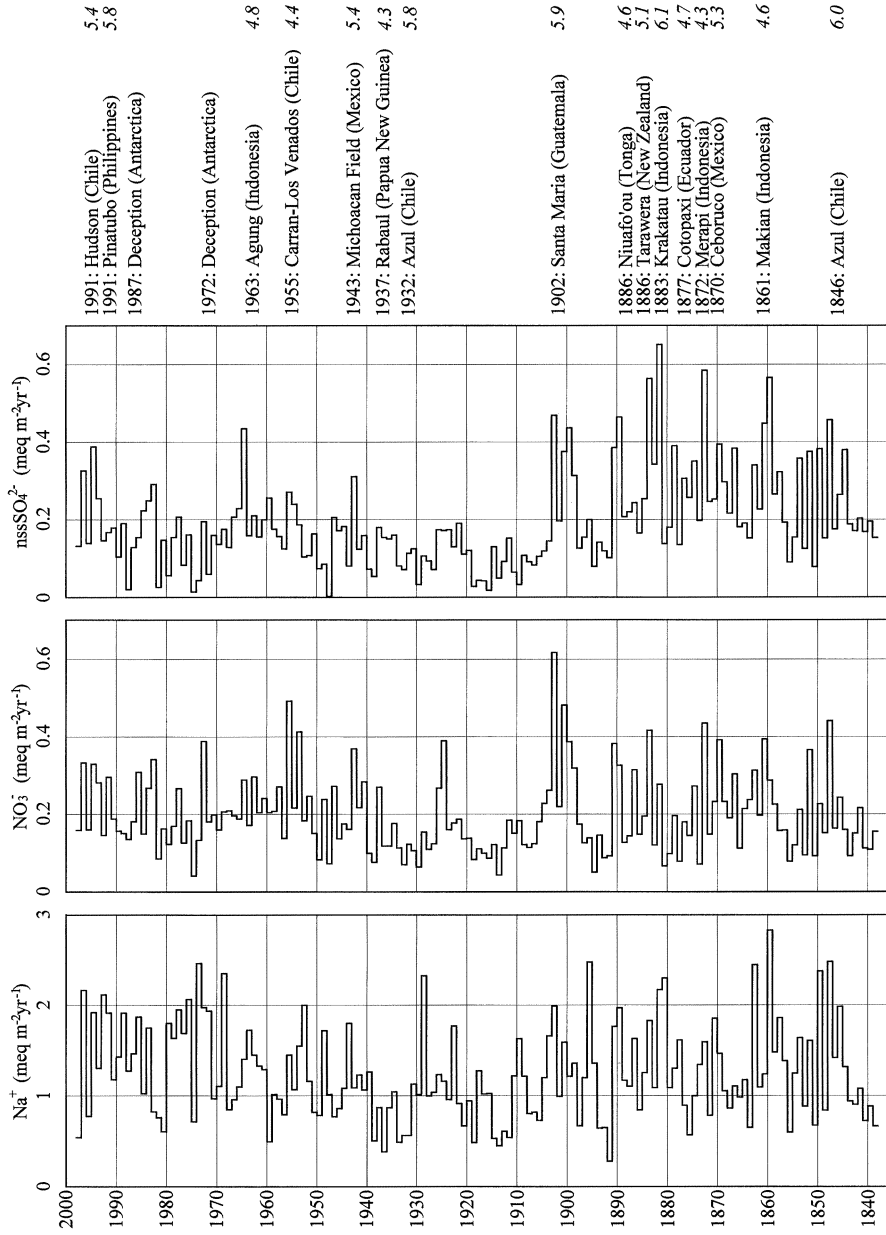
1991: Hudson (Chile) — 5.4
1991: Pinatubo (Philippines) — 5.8
1987: Deception (Antarctica)

1972: Deception (Antarctica)

1963: Agung (Indonesia) — 4.8

1955: Carran-Los Venados (Chile) — 4.4

1943: Michoacan Field (Mexico) — 5.4
1937: Rabaul (Papua New Guinea) — 4.3
1932: Azul (Chile) — 5.8

1902: Santa Maria (Guatemala) — 5.9

1886: Niuafo'ou (Tonga) — 4.6
1886: Tarawera (New Zealand) — 5.1
1883: Krakatau (Indonesia) — 6.1
1877: Cotopaxi (Ecuador) — 4.7
1872: Merapi (Indonesia) — 4.3
1870: Ceboruco (Mexico) — 5.3

1861: Makian (Indonesia) — 4.6

1846: Azul (Chile) — 6.0

Fig. 8. Profiles of deposition rates of Na^+, NO_3^- and $nssSO_4^{2-}$.

4. Conclusions

The H72 ice core collected in September 1998 in east Dronning Maud Land by JARE-39 has been analyzed in detail. The H72 ice core was divided into 1470 samples for detailed analysis. The high correlation coefficient between Na^+ and Cl^- concentrations at the H72 site, 80 km from the coast, appears to result from the fact that both ions originate from sea salt. Concentrations of Na^+ and Cl^- of the H72 ice core fluctuate through a wide range depending on the weather conditions when the snow fell. A decreasing tendency of pH and increasing tendencies of NO_3^- and $nssSO_4^{2-}$ concentrations in the shallow layer have not been found in the H72 ice core. The fluctuation pattern of $\delta^{18}O$ below 45 m proves the smoothing effect of $\delta^{18}O$, caused by water vapor diffusion in the firn layer.

MSA denotes periodic concentration fluctuation reflecting seasonal variation in the H72 ice core; each cycle corresponds to an annual layer. The H72 ice core is dated as AD 1837 at 73.29 m depth by the periodic concentration fluctuation of MSA. The fluctuation of $\delta^{18}O$ appears to be smoothed by water vapor diffusion in the firn layer, deeper than 45 m. It can also be seen that the annual layer determination based on MSA concentration is different from the cyclic variation of $\delta^{18}O$ deeper than 45 m.

Volcanic signals are detected at 49 layers in the H72 ice core. The highest reliable volcanic signals appear five layers corresponding to volcanic eruptions in the Southern Hemisphere. In the late 19th century many volcanic eruptions were recorded, a number of volcanic signals were detected in the H72 ice core.

The surface mass balance of 160 years from 1838 to 1997 is calculated based on the annual layer determination. We can infer from the number of volcanic signals in the late 19th century that a large quantity of atmospheric aerosols caused by volcanic eruptions effectively increased the amount of snowfall by acting as ice nuclei. Years with high temperatures in winter and high annual minimum $\delta^{18}O$ have lower surface mass balance and less snowfall. We can see at the H72 site the many volcanic signals caused by volcanic eruptions in the Southern Hemisphere in the late 19th century. We can also see the $nssSO_4^{2-}$, a volcanic product, deposited liberally at the H72 site.

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