

Temporal changes in chemical stratigraphy of snow cover

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ABSTRACT. Chemical stratigraphy in association with the texture of snow cover was studied during the period from the severe winter to the early snowmelt season. The vertical concentration profiles of NO_3^- , SO_4^{2-} , Cl^- and Na^+ were generally preserved until the initial stage of the snowmelt season, while there were appreciable variations in ionic concentrations. At the initial stage of the snowmelt season, redistribution of chemical constituents in the snow cover occurred in a complicated way, dependent on both the structure of internal layers and the chemical species. Major peaks, however, still remained in the profiles.

INTRODUCTION

Snow undergoes a transformation after its deposition on to the ground or on to a snow cover. Water-related phenomena, such as melting, refreezing and rainfall, accelerate the metamorphism drastically (Wakahama, 1968, 1975). In the course of the metamorphism, chemical stratigraphy of a snow cover is expected to change due to the redistribution of both H_2O and chemical constituents. To reconstruct the past climate and environment from chemical analyses of ice cores, it is important to evaluate the effects of these changes after the snow deposition.

It has been recognized that the first fraction of meltwater from a melting snow cover shows ionic concentrations much higher than those contained in the snowpack itself (e.g. Johannesen and others, 1977; Johannesen and Henriksen, 1978; Suzuki, 1982). This indicates a decrease of ionic concentrations in the snow cover. Suzuki (1982) found that concentrations of chemical constituents in the whole snow cover decreased during the snowmelt season when the entire snow cover was soaked with meltwater. He also suggested that only the surface snow layer shows a decrease in concentration of chemical constituents during temporary snowmelts and the initial stage of snowmelt.

Although similar works in the field and the laboratory have been published previously (Jones, 1985; Jones and Sochanska, 1985; Tsiouris and others, 1985; Brimblecombe and others, 1985; Bales and others, 1989, 1990), temporal changes of vertical concentration profiles of individual ions during the early snowmelt season have not been clarified in detail. The previous studies focused on the processes during heavy melting, and little is known

about how well the detailed chemical stratigraphy is preserved in a snow cover before the beginning of severe melting. This degree of preservation is of special significance in ice core analyses. Chemical changes in snow at the very beginning of the snowmelt are also important to chemical release from seasonal snow covers. Sigg and Nefstel (1987) showed that the concentration profiles of ions did not change in the snow cover at Weissfluhjoch, Switzerland, but the snow temperature was below 0°C throughout their observation period, except for a few days when thin melt layers were formed at and near the surface. In order to understand the post-depositional changes of snow chemistry associated with melt process or rain, we traced the detailed concentration profiles of chemical constituents in seasonal snow cover until the beginning of the snowmelt season.

METHODOLOGY

Snow pit observations

We conducted snow pit studies and collected snow pit samples seven times between 29 January and 22 March 1992 at intervals of 5–14 days. The observation site was located at Sasagamine, Niigata, Japan ($36^\circ 52' \text{N}$, $138^\circ 03' \text{E}$, 1300 m a.s.l.), which is 7 km away from the nearest ski area and is considered to be free from direct local contamination. A pit, 1 m wide \times 2 m long, was dug through the snow cover to the ground. For each sampling, a new pit was dug 0.5–2 m away from the previous pit. Pieces of white tissue paper were buried at the snow surface in order to recognize the layer during the next observation. Vertical profiles of snow temperature

and snow density along with the visible stratigraphy were recorded each time. Besides the snow pit studies, the depth and water equivalent of the snow cover, air temperature, precipitation, and solar radiation were continuously measured at the observation site with automated equipment.

Sampling and analytical procedures

Snow samples were collected from the pit wall into pre-cleaned polypropylene wide-mouth bottles, using either a pre-cleaned polypropylene scoop or a pre-cleaned teflon scoop. On 9 March and 22 March, a pre-cleaned stainless steel knife was also used to collect thin hard layers. The scoops and the knife were rinsed with the snow at the sampling depth prior to each sampling. The sampling was basically carried out continuously throughout the snow pack, although there were some exceptions. We collected 20–40 samples from each snow pit. The vertical length of each sample was 0.5–15 cm.

Snow samples collected at the observation site were brought back to the laboratory and analyzed for Cl^- , NO_3^- , SO_4^{2-} and Na^+ . Concentrations of the first three ions were measured with a Dionex Dx-100 ion chromatograph and concentrations of Na^+ were measured with a Seiko SAS 7500 atomic absorption spectrophotometer with a flame atomizer.

RESULTS

Visible stratigraphy of the snow cover and the meteorological conditions

Records of visible stratigraphy of the snow cover are shown in Figure 1. The structure of the snow cover reflects the main snowfall and melt events. To interpret the time-series of snow-cover stratigraphy in association with these meteorological events, we plotted the air temperatures and snow-cover depth in Figure 2. Possible rainfall events, indicated by arrows, were derived from the combined records of quarter-hour averaged precipitation, air temperature and snow-cover depth: we assumed rainfall events when there was precipitation at a temperature above 0°C with no increase in snow-cover depth.

As seen from Figure 2a, our field study started in the severe winter when daily average air temperature was below 0°C. The average temperature did not exceed 0°C before 27 February. Since a snowfall event at Sasagamine was generally associated with a temperature drop (Fig. 2), the major portion of the snow cover originated from dry snowfall. The temperature in the snow pack was below 0°C at the observations from 29 January through 17 February, with the exception of one wet-snow layer: the new snow layer at the surface of the snow cover on 29

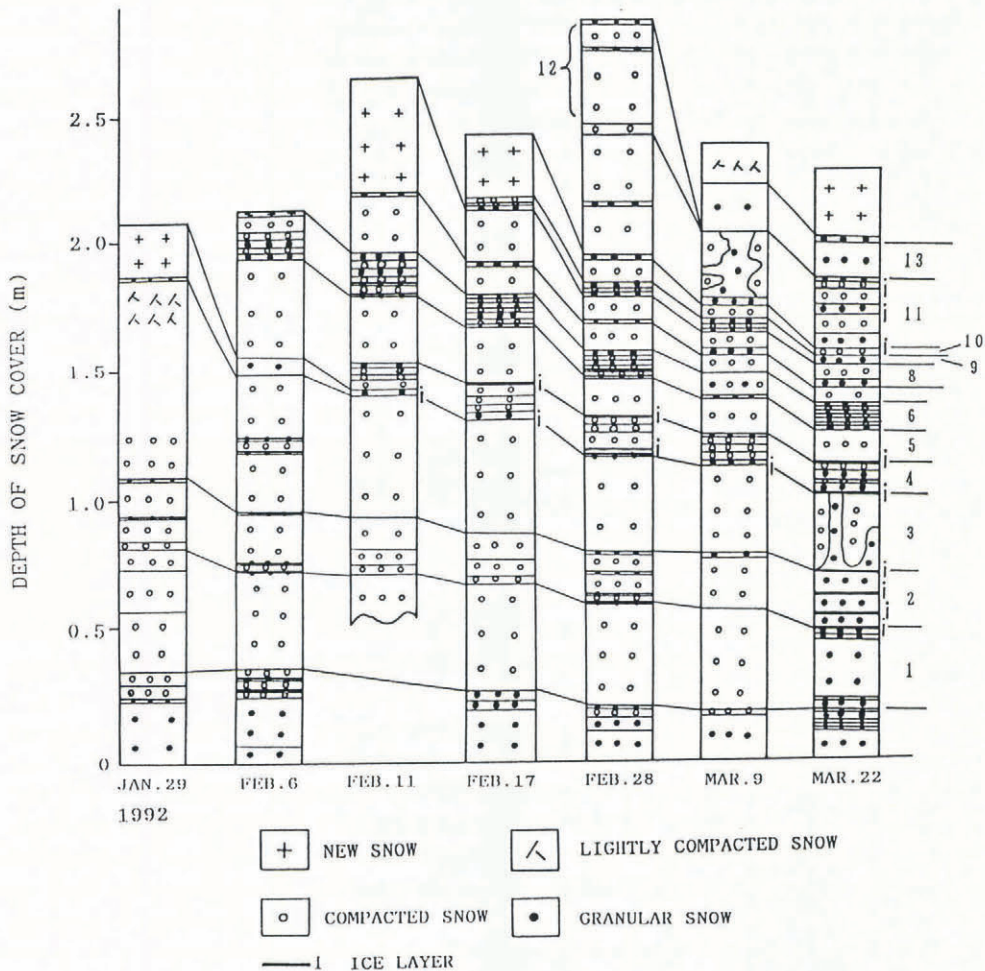


Fig. 1. Visible stratigraphy of the snow cover with layers 1–13 numbered on right.

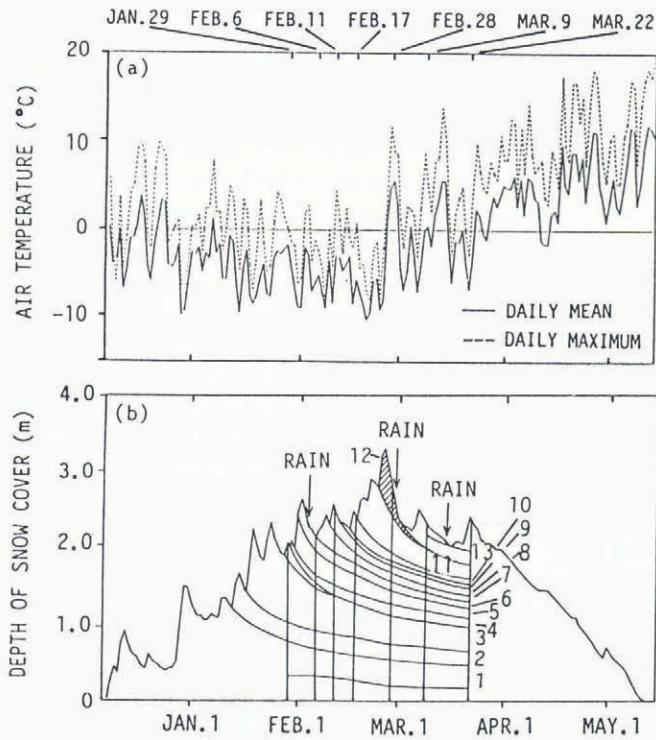


Fig. 2. Meteorological data obtained with an automated weather station. (a), daily mean air temperature and daily maximum air temperature; (b), depth of the snow cover and individual layers. (The dates on which pit observations were made are ticked on the horizontal axis.)

January (Fig. 1) consisted of wet snow accumulated on that particular day. The layer remained wet at least until the next observation time on 6 February. The wet layer seems to have been insulated by new dry snow deposited just after the wet snow. These successive wet and dry snow layers apparently turned into a dry layer (layer 4), which consisted at later stages of alternating thin layers of compacted snow and granular snow. On 11 February an ice layer whose thickness varied spatially was found at the bottom of layer 4.

During the severe winter period, the snow cover was mainly composed of new snow, lightly compacted snow and compacted snow, in which thin granular-snow layers and ice layers were sandwiched (Fig. 1). Layers with complex structures (e.g. layers 4, 6, 8 and 9) were generally created by the effects of liquid water in the form of wet snow, rain or surface melt. Layer 4 was associated with wet snowfall as stated above and layer 6 with rain. Both layers 8 and 9 were subjected to melting, since they were at the surface of the snow cover when the daily maximum temperature rose above 0°C. However, the liquid water seems to have affected the surface layers only. No noticeable loss of the total water equivalent of the snow cover was observed by the end of February (Fig. 3a) and no trend in the water equivalent of individual layers was found for layers 1–10.

On 27 February the daily mean air temperature started to rise above 0°C. At the observation in the following afternoon (1630 h), however, the snow temperature was lower than 0°C in the snow layers below the upper 5 cm. No evidence of melting was found in the visible stratigraphy of the snow cover underneath surface

layer 12. On 9 March the entire snow cover was 0°C in temperature. The rainfall at high air temperatures on 29 February and 1 March probably raised the snow-cover temperature. The first recognizable melt since the severe winter occurred during these two days (Fig. 3a). The snowmelt season in 1992 started around 29 February. Layer 12 completely melted by 9 March. In addition to the changes in the surface layer, a water channel consisting of granular snow was formed in the compacted-snow layer 11 (Fig. 1). In contrast, structures of compacted snow layers below layer 11 did not appear to have changed considerably. While layer 12 disappeared and the water equivalent of layer 11 decreased by 3.5 cm in this period (Fig. 3b), the sum of the water equivalents of layers underneath layer 11 did not increase. This indicates that most of the meltwater produced from layers 11 and 12 ran off through water channels as seen in layer 11.

By 22 March, many of the compacted-snow layers turned into granular-snow layers. Moreover, the number and the thickness of ice layers had increased. A water channel was found in layer 3. Although the daily maximum air temperature frequently fell below 0°C after 9 March, the temperature of all the snow except that in the surface 40 cm was 0°C on 22 March. Since water equivalent of each layer below 13 remained approximately constant between 9 and 22 March (Fig. 3),

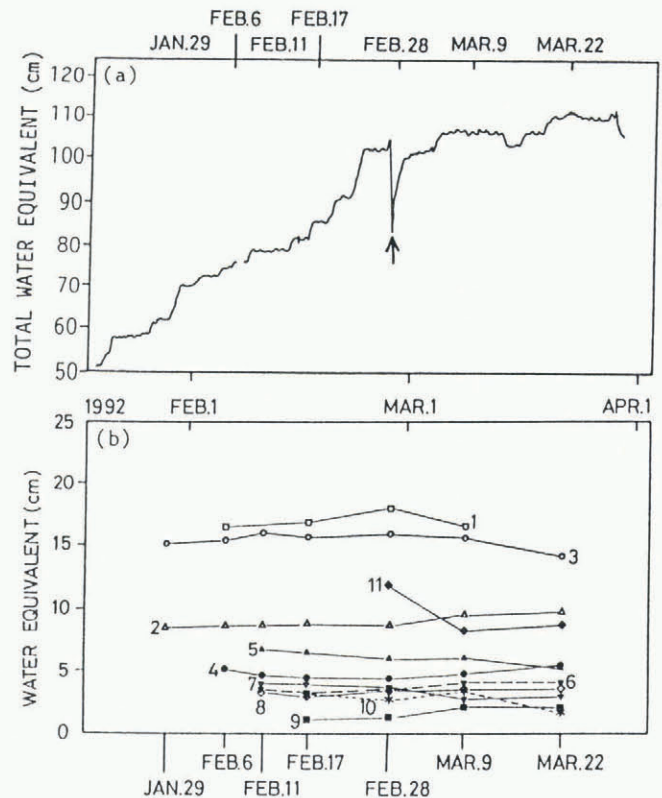


Fig. 3. a, temporal change in total water equivalent of the snow cover measured with an automated snow-weight meter. Arrowed dip in the curve is exaggerated due to an erroneous measurement resulted from a sudden melting by rainfall. Decrease in the water equivalent during this period was estimated to be 5–10 cm. b, temporal change in water equivalent of each layer. (Figures beside the curves indicate internal layers defined in Fig. 1.)

impermeable layers between different strata seem to have prevented the downward movement of meltwater across the inter-layer boundaries during this period. A simple calculation using the meteorological data (Kojima and others, 1983) showed that runoff water released from the snowpack between 28 February and 22 March was about 15% of the total pack weight. During this initial stage of snowmelt, runoff was not continuous. This early phase of snowmelt was followed by the heavy snowmelt season, which started around the end of March, and the snow cover melted away by 13 May.

Chemical stratigraphy of the snow cover

Figure 4 shows detailed concentration profiles of Cl^- , NO_3^- and SO_4^{2-} in each pit. As concentrations of Na^+

were strongly correlated with those of Cl^- (correlation coefficient = 0.97), we do not present concentration profiles of Na^+ in Figure 4. The major peaks in chemical concentration profiles were recognizable until the early stage of the snowmelt season.

We plotted for each layer the temporal variation of the mean concentration levels of Cl^- , NO_3^- and SO_4^{2-} (Fig. 5), which were calculated from the concentration, density and layer-thickness data. As seen from Figure 5, the average concentrations varied appreciably even in the severe winter. Up until 28 February, concentration levels in the layers affected by melts (i.e. layers 4, 6 and 8) generally showed more scatter than those in other layers. (Only two severe-winter data points for layer 9, which was also affected by melting, are not sufficient to discuss the scatter of the data in this period.) When granular

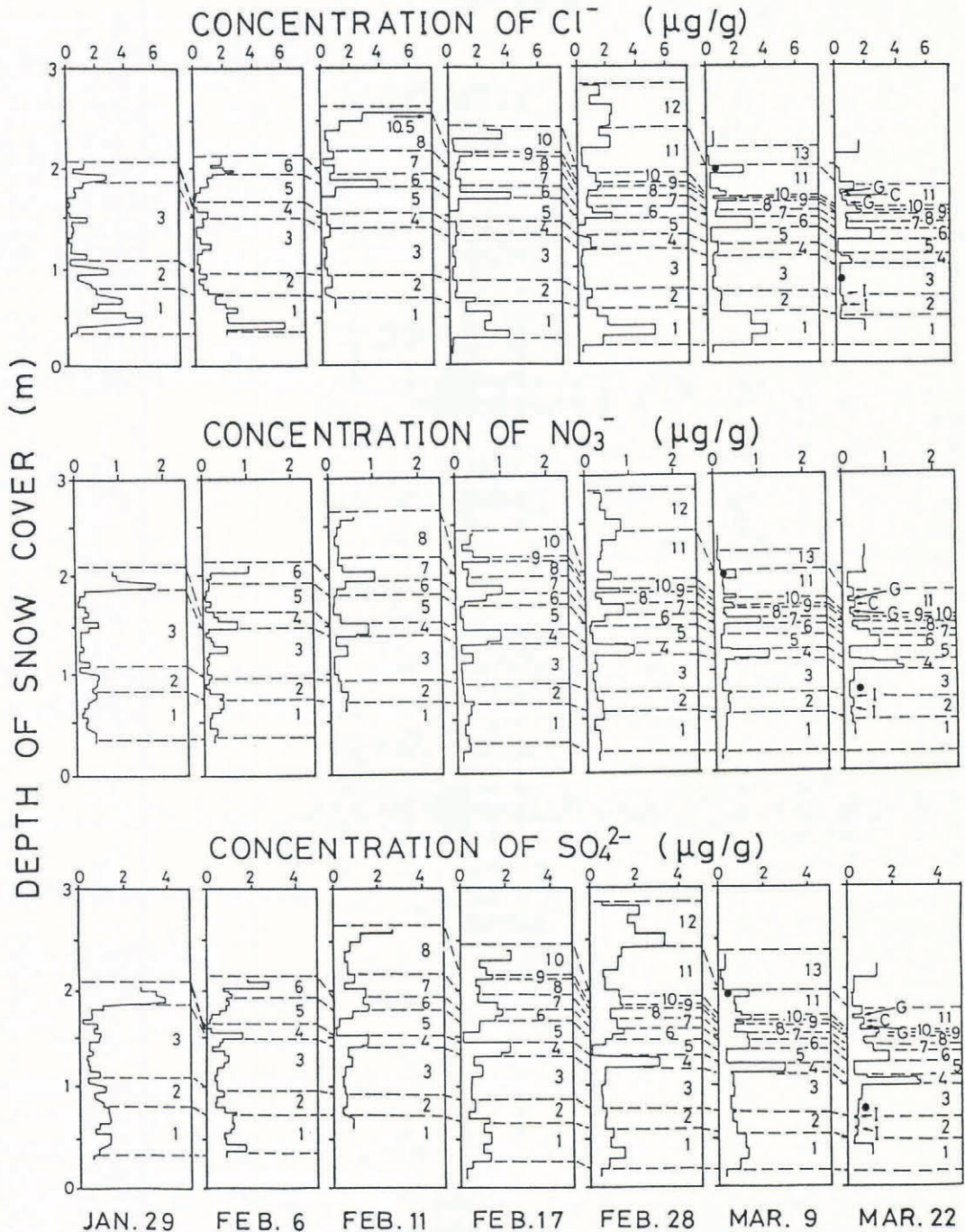


Fig. 4. Detailed concentration profiles of anions in each pit. G, granular snow layer; C, compacted snow layer; I, ice layer; ●, concentration level of a duplicate sample from the water channel.

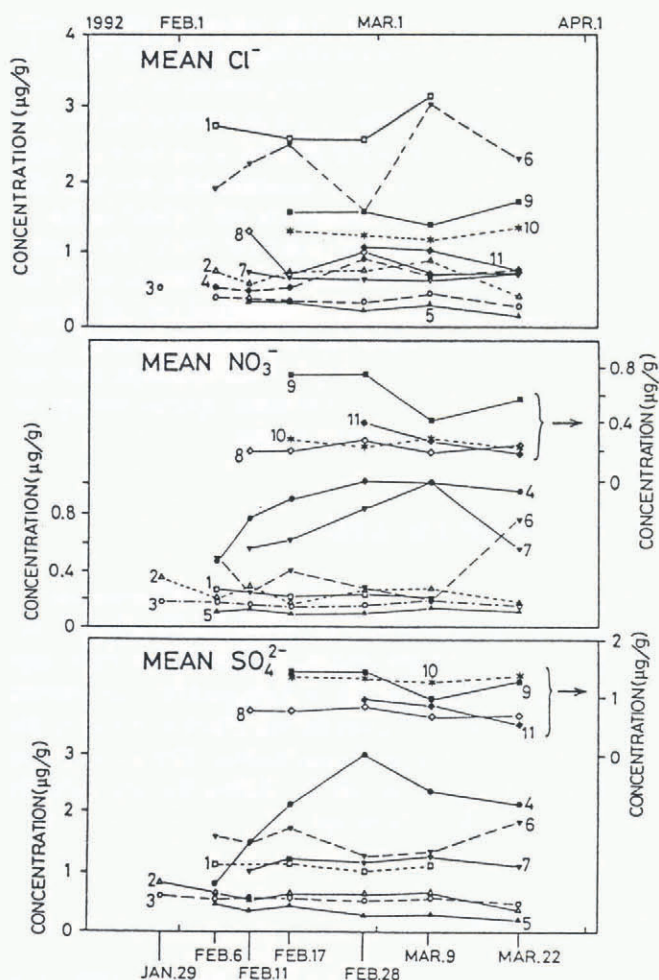


Fig. 5. Mean concentrations of anions in each layer. (Figures beside the curves indicate internal layers defined in Fig. 1.)

snow is formed by repeated melting and refreezing, concentrations of chemical constituent change both in snow particles and meltwater through a segregation process (Suzuki, 1982). Since the melting and refreezing process were not uniform in a layer, concentrations of chemical constituents in the layer with melt effects exhibited more lateral variations than those in a layer without melt effects. This lateral variation seems to have caused the apparent temporal fluctuations, since we took snow samples from different, but nearby, pits.

When the water equivalent of layer 11 decreased by 30% between 28 February and 9 March, mean concentrations in the layer of NO_3^- and SO_4^{2-} , calculated with the concentration levels in samples from outside the water channel, decreased by 30% and 10%, respectively, and those of Cl^- and Na^+ did not change appreciably. During the same period, mean concentrations of NO_3^- and SO_4^{2-} in layer 9 decreased by 55% and 70%, respectively, while those of Cl^- and Na^+ showed much less variation (Fig. 5). These results seem to indicate that NO_3^- and SO_4^{2-} were released earlier than Cl^- and Na^+ , although this trend was not seen in layer 11 between 9 and 22 March: during this period mean concentrations of NO_3^- , SO_4^{2-} , Cl^- and Na^+ in layer 11 decreased almost uniformly by 60–70%. The above results also indicate that the elution of NO_3^- took place earlier than that of SO_4^{2-} , since the rate of NO_3^- decrease

was greater. This is in contrast with previous works (Davies and others, 1982; Brimblecombe and others, 1985, 1987). More study, however, is necessary to come to a firm conclusion, because fluctuations in our data are rather large.

Mean concentrations of NO_3^- and SO_4^{2-} decreased in layers 7 and 11 and those in layers 6 and 9 increased between 9 and 22 March, while concentrations in layers 5, 8 and 10 did not change as much. It is interesting to note that the decrease in NO_3^- and SO_4^{2-} load in layer 7 is too small to create the increase in those ions in layer 6. The deficiency can be explained in terms of the input from the upper layer 11, since the increase in NO_3^- and SO_4^{2-} load in layer 9 is much smaller than the decrease in layer 11.

Concentration levels of Cl^- , NO_3^- , SO_4^{2-} and Na^+ were much lower in a duplicate sample from the water channel in layer 11 than levels in samples from outside the channel (Fig. 4). This indicates that elution of ionic load in layer 11 occurred predominantly from the channel.

The detailed concentration profiles in Figure 4 show the complicated behavior of chemical constituents in the early phase of snowmelt. In layer 11 on 22 March, NO_3^- and SO_4^{2-} in sub-layers of granular snow showed lower concentrations than those in sub-layers of compacted snow. Although concentration levels of Cl^- , NO_3^- , SO_4^{2-} and Na^+ in a duplicate sample from the water channel in layer 11 on 9 March were lower than those in compacted snow at the same depth, as described above, concentration levels of all the ions in a duplicate sample from the water channel in layer 3 on 22 March were slightly higher than those in the compacted-snow layer at the same depth (Fig. 4). On the other hand, concentration levels of Cl^- , NO_3^- , SO_4^{2-} and Na^+ in thin sub-layers of ice (e.g. ice layers in layer 2 on 22 March) were similar to those in the adjacent sub-layers of granular snow (Fig. 4).

DISCUSSION

When snow melts, concentrations of chemical constituents decrease in snow and increase in meltwater as a result of the segregation process (Suzuki, 1982). Suzuki (1982) found that when the meltwater produced at the surface layer was refrozen at a lower layer in the early phase of the snowmelt season, the concentrations of chemical constituents did not increase in the lower layer, while the water equivalent of the layer increased. According to Suzuki, the chemical constituents flowed further downwards and ran off out of the snow cover because they are difficult to refreeze. However, at the very beginning of the melt season, we observed increases in the concentrations of chemical constituents in some internal layers of the snow cover. It is suggested that chemical constituents as well as water were blocked by impermeable layers and were refrozen at the layers. At the very beginning of the snowmelt season, many layers would work as impermeable layers, even for meltwater with high ion concentrations. Since the distribution of these impermeable layers is not uniform, and since the layers may become permeable under different melting conditions, behavior of chemical constituents is complicated in the initial phase of the snowmelt season.

In ice cores from near Dye 3, south Greenland (Langway and others, 1985), ice layers with extremely high NO_3^- concentration levels were found (Finkel and others, 1986; Clausen and Langway, 1989). Ice layers associated with extremely high concentrations of both NO_3^- and SO_4^{2-} were also found in a different core from near Dye 3 (personal communication from Langway and Goto-Azuma). Sigg and Neftel (1987) found increased concentrations of ions in ice layers in a snow cover. However, ice layers were not always associated with high concentrations of chemical constituents. These facts could be explained by the following process: The meltwater created at the ice sheet surface, which is rich in chemical constituents, flows down through the layers underneath. When the water refreezes at an impermeable layer, chemical constituents remaining in highly concentrated brine are allowed to flow further downwards. The ice layer formed at this stage is not rich in chemical constituents. The water with more concentrated chemical constituents finally refreezes in a lower layer where the temperature is much lower. Consequently, melt layers with highly concentrated chemical constituents are created just above the impermeable layer. Wet snow deposition, as observed on 29 January in our study, could also produce a melt layer with high concentrations of NO_3^- and SO_4^{2-} , since wet snow could more effectively scavenge NO_3^- and SO_4^{2-} in the atmosphere than could dry snow.

The present study indicates that the concentration changes in a layered snowpack differ from species to species. This would explain the fact that ice layers in ice cores are usually not associated with high Cl^- concentration levels (personal communication from Langway and Goto-Azuma), although NO_3^- and SO_4^{2-} concentrations are often high in ice layers. In the ice core from the Dye 3 area mentioned above, ice layers are more frequently associated with NO_3^- peaks than with SO_4^{2-} peaks. This may be the result of preferential release of NO_3^- to SO_4^{2-} as suggested by the present work. The concentration changes in a layered snow cover also differ from layer to layer. Since the initial distribution of ionic concentrations in a snowpack plays an important role in the elution sequence of ions in runoff water (Bales and others, 1989), one must bear in mind that complicated redistribution of ionic concentrations, which is dependent on the texture of each internal layer in the pack, occurs at the very beginning of the snowmelt.

In spite of the complex behavior of chemical constituents during melting of the snow cover, major peaks in concentration profiles of individual chemical constituents were generally recognizable until the initial stage of the snowmelt season. Even after the temperature of the whole snow cover reached 0°C , major peaks in the concentration profiles were still apparent.

CONCLUSIONS

The overall chemical profile of the snow cover was generally preserved throughout the severe winter and the early snowmelt season, while there was appreciable variability in ionic concentrations with time. In the severe winter, only the surface layer was affected by

melting, which introduced both complex texture and spatial variation in chemical stratigraphy in the layer. At the initial stage of the snowmelt season, some internal layers showed an increase in the concentration level of particular ions, while others showed a decrease or little change. Intricate behavior of impermeable layers in the snow cover seemed to complicate the redistribution of chemical constituents, in contrast with the heavy snowmelt season in which the concentrations of all chemical constituents simply decreased in all layers. Furthermore, some layers were enriched in NO_3^- and SO_4^{2-} but not in Cl^- and Na^+ . This indicates that the concentrations of different chemical species change in different ways in a layered snowpack.

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