

# Isotopic and ionic changes in a snow cover at different altitudes: observations at Austre Okstindbreen in 1991

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**ABSTRACT.** Ionic and isotopic analyses of snow samples collected at four sites at the Norwegian glacier Austre Okstindbreen during two field seasons in 1991 showed that, before melting started, the snowpack was vertically inhomogeneous. Patterns of variation with depth of both ions and oxygen isotopes were maintained throughout the pre-melt period. Horizontal variations of ionic concentration were smaller than vertical ones. The stratigraphic pattern of ionic concentrations in the pack at lower altitudes reflected the influence of melting-refreezing processes, as well as original variations in the falling snow. The mean ionic content of the first set of samples collected at the lowest site was much lower than that at the others, indicating that ions had already been removed by meltwater. Much liquid water was present in the snowpack when drainage started, and ions were removed quickly with the first meltwater. During the melting phase, comparative rates of loss of ions resulting from differential movement through the pack were  $\text{SO}_4^{2-} > \text{Na}^+ > \text{Cl}^-$ . At 1475 m, only 13% of the winter accumulation melted between 6 June and 9 July, but at least 88% of the  $\text{Na}^+$ , 89% of the  $\text{Cl}^-$  and about 100% of the  $\text{SO}_4^{2-}$  was lost. Initially, there was no altitudinal trend in the mean  $\delta^{18}\text{O}$  values of the snowpack. Warming of the pack was accompanied by a tendency towards isotopic homogenisation. At the three sites at which snow remained in July, considerable  $^{18}\text{O}$  enrichment had occurred since the middle of June.

## INTRODUCTION

Seasonal snow cover can be significant in the chemical dynamics of ecosystems in many temperate, alpine and subarctic regions, but less is known about the chemical composition and dynamics of seasonal snowpacks than about physical processes (Davies and others, 1991). The contribution of melting snow to river discharge varies seasonally, with consequent effects on water quality. Early in the summer, melting snow makes a substantial contribution to the discharge of the river which issues from the Norwegian glacier Austre Okstindbreen, and the water is relatively depleted of the heavy isotope of oxygen,  $^{18}\text{O}$  (Theakstone, 1988). Later, as the  $^{18}\text{O}$  content increases, the chemical composition of the river water is characterised by systematic patterns of variation, upon which are superimposed some apparently random deviations (Theakstone and Knudsen, 1989). Concentrations of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the glacier river vary from year to year, as well as within a particular summer, although they generally decrease through the summer (Knudsen, 1990).

The concentrations of ionic species in the accumulated

snow at Austre Okstindbreen reflect the prevailing climatic conditions, as does the isotopic composition of the snow (He and Theakstone, this volume). However, ionic concentrations in the snow change with time; even when the temperature is below  $0^\circ\text{C}$ , chemical dynamics in the pack are not totally suppressed. In order to obtain data relating to the chemical evolution of the snowpack in both the pre-melt and melting stages, the snow cover at Austre Okstindbreen was sampled between late April and mid-July 1991 at sites along the glacier's centre line, ranging from 1475 m to 810 m a.s.l. The start of the melt season was later than usual: a sharp rise of air temperature on 2 June was followed by a period of warmer conditions and the onset of melting. Personnel were not available to maintain the programme between the end of the late winter field season, in mid-June, and a summer field season (July–August). At each of the study sites, snow temperature and density were measured whenever samples were collected, and the liquid water content of the pack was determined by a dielectric technique. Anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) were determined by high-pressure liquid chromatography, cations ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ) by atomic absorption spectrophotometry.

metry at the Aarhus University Geological Institute. Oxygen isotope analyses were undertaken at the Copenhagen University Geophysical Isotope Laboratory.

### SAMPLE COLLECTION

Austre Okstindbreen heads at about 1510 m and terminates at 730 m (He Yuanqing and Theakstone, this volume, figure 1). The local topography influences accumulation patterns at the glacier. In late April and early May 1991 pits were excavated in the snow cover. At 1475 m the dirty 1990 summer surface was at a depth of 5.0 m; the pit was extended slightly into the underlying firn. At 1240 m, 1000 m and 810 m, glacier ice was covered by snow to depths of 3.0 m, 2.95 m and 2.7 m, respectively. Samples collected at 1475 m (three sets) and 1240 m (five sets) represented pre-melt conditions (Fig. 1).

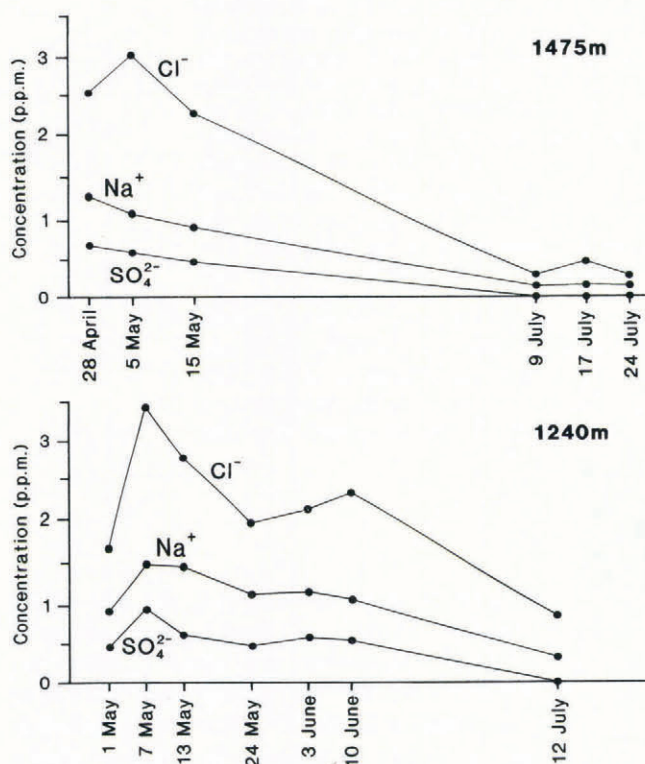


Fig. 1. Mean ionic concentrations in the snowpack at the two highest sites at Austre Okstindbreen were higher during the pre-melt phase than during the later melting phase.

During the late winter field season, which ended in mid-June, some heavy snowfalls occurred: at 1240 m the thickness of the pack increased by about 0.7 m between 7 May and 1 June. Additional samples were collected during a summer field season (6 July–1 August). In early July no snow remained at 810 m, only 0.4 m at 1000 m, and 1.2 m at 1240 m. At 1475 m the pack still was some 4 m deep.

Samples, each 0.24 m long, were collected from pit walls which were not exposed to direct solar radiation.

On each visit, snow which had fallen, or drifted into, the pits was removed, and the pits then were extended laterally by 0.5–1.0 m before another set of samples was collected from the surface downwards. At some sites it was not easy to establish a sampling datum at the base of the snowpack, because the underlying glacier ice surface was not horizontal. New snow fell between sampling dates, and samples taken at different times at a particular site therefore were not invariably from the same part of the pack: a snow layer contained within a single sample on one occasion might have been split between two adjacent samples on another.

During sampling, protective clothing was worn to avoid contamination. Samples were allowed to melt in sealed polythene bags before being transferred to pre-cleaned polyethylene flasks and vials. Until they were analysed, they were kept at a temperature close to 0°C. Because of the low particulate content of the snow, filtration was not carried out; analyses of snow samples from other remote, high-altitude sites have been conducted in a similar manner (Puxbaum and others, 1991).

### SNOW TEMPERATURES AND LIQUID WATER CONTENT

When samples were first collected at 810 m (27 April) the snowpack was already almost isothermal at 0°C. At 1000 m on 2 May, sub-zero temperatures were present in the uppermost 0.75 m, but the rest of the pack was close to 0°C. At the higher sites, temperatures were lower, with means of -2.6°C and -6.7°C at 1240 m and 1475 m, respectively. Near-isothermal conditions were not attained at 1240 m until 10 June. At 1475 m, melting-point temperatures were not recorded at depth before the end of the late winter field season (13 June). Pre-melt conditions prevailed when five sets of samples were collected at 1240 m and three sets at 1475 m.

At the 1000 m pit, the snow surface gradient was about 10°. Immediately up-glacier, it was steeper. Horizontal movement of water would become slower where the gradient decreased, at and down-glacier of the site. During the first stage of melting, impermeable ice layers probably facilitated horizontal movement of water whilst hindering vertical movement. After the onset of melting, the number of ice layers in the pack increased. A few days later, however, the snow took on a more homogeneous appearance. Before 1 June, a liquid water content in excess of 2% was detected only in the highest part of the pack. Between 1 and 7 June, the liquid water content rose from 0.50% to 5.75%, equivalent to an increase of 0.17 m water, and the mean density increased from 0.52 Mg m<sup>-3</sup> to 0.57 Mg m<sup>-3</sup>, although the snow depth was the same (3.32 m) on both dates (Fig. 2). Between 7 and 12 June, the mean liquid water content did not change significantly, but the snow thickness decreased by 0.32 m (equivalent to 0.18 m water) of which 0.21 m (0.12 m w.e.) was the result of melting and 0.11 m (0.06 m w.e.) of compaction. Variations of liquid water content at different depths indicated that vertical movement of water was not constant, but occurred in a pulsating manner.

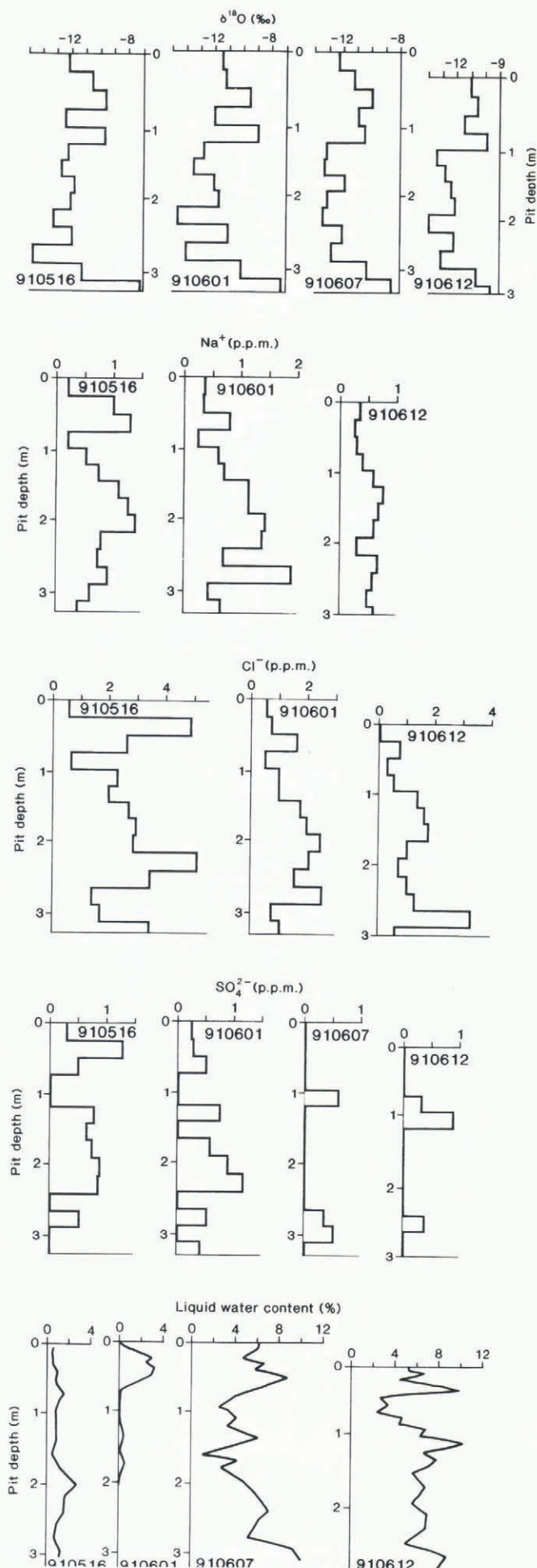


Fig. 2. Variations of snowpack thickness, chemistry and liquid water content at 1000 m, Austre Okstindbreen, 1991.

## RESULTS OF IONIC ANALYSES: THE PRE-MELT PHASE

Ionic concentrations in snow which fell during the late winter field season were lower than those in the snow which had accumulated previously. Their spatial variations confirmed that a particular precipitation event does not provide equal concentrations of ions to all parts of the catchment.

Samples obtained at the two highest sites (1475 m and 1240 m) represented pre-melt conditions. The snowpack was vertically inhomogeneous, with marked differences of ionic concentrations between adjacent samples. The stratigraphic variations reflected the differing chemistry of snow which had accumulated in successive episodes. Snow drifting had caused some variations of ionic concentration, but horizontal differences were smaller than vertical ones: at 1240 m, the vertical pattern in the c. 3 m deep pack barely changed as the pit was extended laterally by 2.1 m during the period of sampling (Fig. 3). The stratigraphic variations of ionic composition of the snowpack were retained through the pre-melt phase at both 1475 m and 1240 m.

The highest measured concentrations of  $\text{Na}^+$  and  $\text{Cl}^-$ , and the second highest of  $\text{SO}_4^{2-}$ , were in the sample collected at the 1475 m pit on 28 April at a depth of 0.72–0.96 m (c. 4.2 m above the firn). Concentrations still were high at this part of the pack on 5 May and 15 May, but the maximum was barely recognisable when the last set of winter season samples was collected, on 6 June. Its apparent disappearance may have resulted from it having been split between two samples. Particularly high concentrations of  $\text{Na}^+$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  were registered at a level coincident with 58% of the winter accumulation at the two highest sampling sites (about 2.5 m above the firn surface at 1475 m, and 1.7 m above the glacier ice at 1240 m).

## RESULTS OF IONIC ANALYSES: THE MELTING PHASE

At 1000 m, surface melting and meltwater percolation occurred during the period of sample collection. The correlation coefficients for the concentrations of  $\text{Na}^+$  and  $\text{Cl}^-$  and for  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  from 1000 m were lower than those for samples collected during the pre-melt phase at 1240 m (Table 1). This indicates that some of the original ionic variations in precipitation at 1000 m changed as a result of melting/refreezing processes. The correlation coefficients for the 68 samples collected during the early visits to the 1000 m site, between 2 May and 1 June, were markedly higher than those for the 27 samples collected on 7 and 12 June, after the onset of melting. This reflected differential movement of ions in the melting pack. An increase of mean ionic concentrations at 1000 m during the first half of June resulted from sub-horizontal movement of water through the snowpack. The proportion of samples at this site in which  $\text{SO}_4^{2-}$  was below the detection limit (0.25 ppm) increased from 31% before 2 June to 78% after that date, indicating rapid elution and/or transport. The relationship between  $\text{Na}^+$  and  $\text{Cl}^-$  also changed, the correlation coefficient falling from 0.55 to

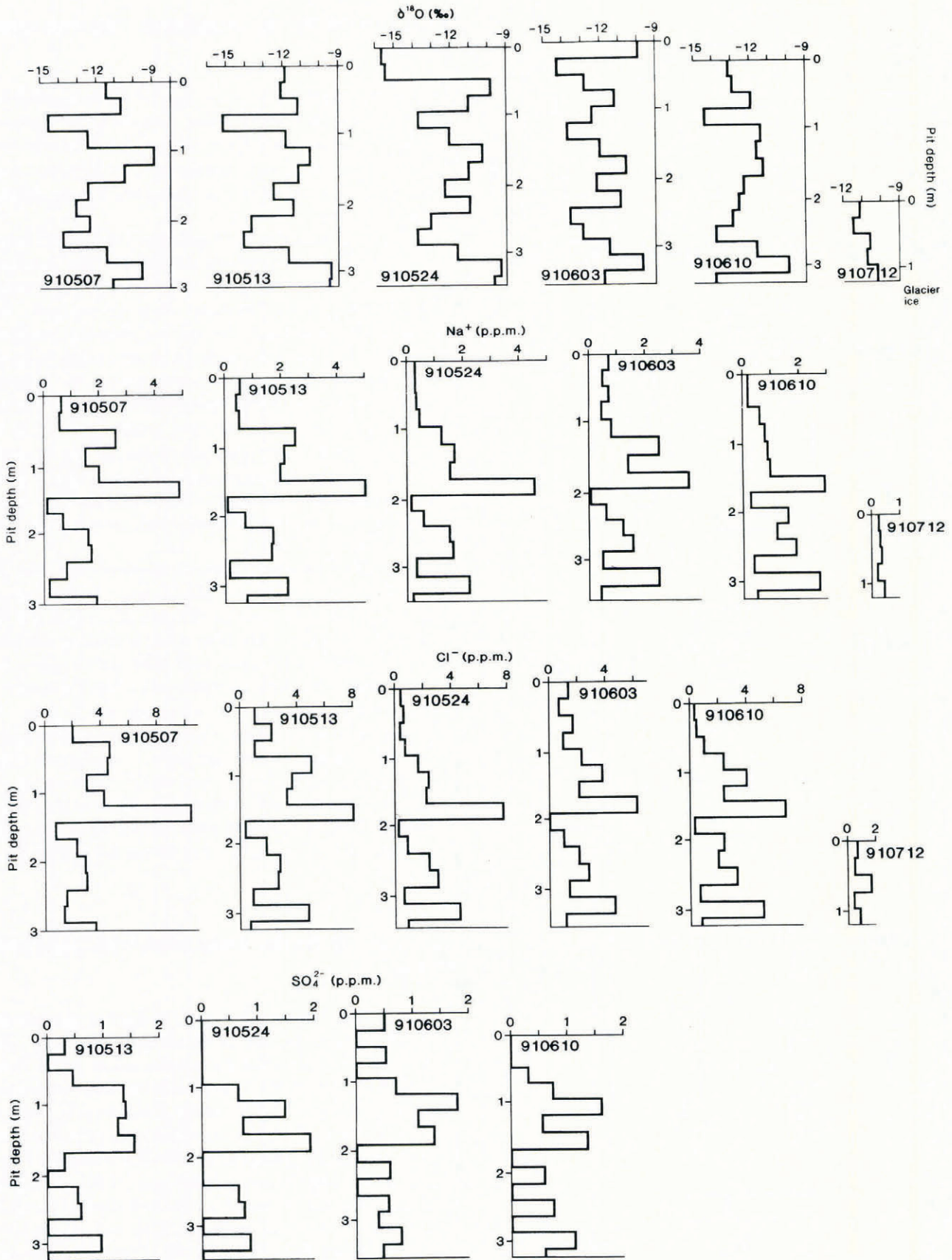


Fig. 3. Variations of snowpack thickness and chemistry at 1240 m, Austre Okstindbreen, 1991. ( $SO_4^{2-}$  was not detectable in the samples collected from the pack on 12 July.)

0.44. This indicated that  $Na^+$  was removed slightly more quickly than  $Cl^-$ . Comparative rates of loss were  $SO_4^{2-} > Na^+ > Cl^-$ .

At 810 m the mean ionic content of the first set of

samples, collected on 27 April, was much lower than that at the higher sites, indicating that ions already had been removed by meltwater. On each subsequent sampling, the mean concentrations of  $Na^+$ ,  $Cl^-$  and  $SO_4^{2-}$  varied

Table 1. Correlation coefficients for concentrations of three ions in the snowpack at four sites, Austre Okstindbreen, 1991. Separate coefficients for the pre-melt and melting phases at 1000 m are shown (*N*, number of samples)

	$Na^+ : Cl^-$	$Na^+ : SO_4^{2-}$	$Cl^- : SO_4^{2-}$	<i>N</i>	Sampling period
1475 m	0.86	0.73	0.75	86	28 April–6 June
1240 m	0.95	0.75	0.80	70	1 May–3 June
1000 m	0.55	0.78	0.62	68	2 May–1 June
1000 m	0.44	0.40	0.14	27	7 June–12 June
810 m	0.75	0.51	0.62	81	27 April–11 June

markedly; the variations were not synchronous. The correlation between  $Na^+$  and  $Cl^-$  in all the samples from this site was much poorer than that for the samples collected during the pre-melt phase at 1240 m (Table 1). On 3 May particularly high concentrations of all three ions coincided with an increase of the liquid water content of the pack at a depth of 0.96–1.20 m. Concentrations also were high in the lowest 0.02 m of the pack, where a water content of 5% showed that meltwater was running within the snow immediately above the glacier surface.

Only 0.36 m w.e. (13% of the winter accumulation) melted at the 1475 m site between 6 June and 9 July, but the loss of ions totalled 88% ( $Na^+$ ), 89% ( $Cl^-$ ) and c. 100% ( $SO_4^{2-}$ ). Since precipitation must have supplied some ions to the pack during the melting phase, losses of  $Na^+$  and  $Cl^-$  must have been still higher. None of the 40 samples collected at 1475 m in July had an  $SO_4^{2-}$  concentration above the detection limit.

## RESULTS OF ISOTOPIC ANALYSES

Stratigraphic variations of the isotope content of the snowpack in late winter reflect the isotopic composition of discrete snowfalls, and the amount of snow which has accumulated at different rates at different times.  $\delta^{18}O$

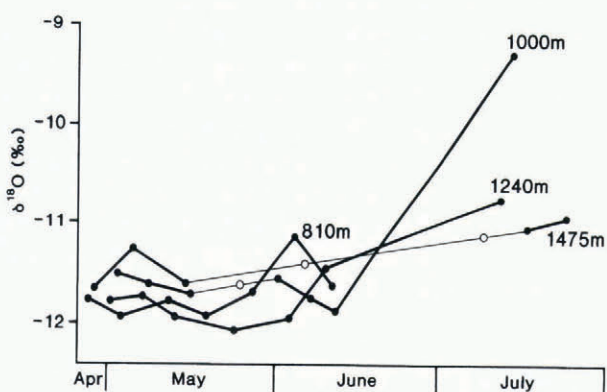


Fig. 4. Mean  $\delta^{18}O$  values in the snowpack at Austre Okstindbreen in late winter 1991 did not vary systematically with altitude. Values increased during the melting phase, as a result of the relative enrichment in the heavy isotope. (Open symbols indicate that a sample was lost, and that the mean was determined for the remaining samples.)

values in falling snow depend in part on temperature. However, the influence of topography on snow accumulation rates, and on the depth of the pack, may modify altitude-related patterns (He Yuanqing and Theakstone, this volume). There was no altitudinal trend in the mean  $\delta^{18}O$  values of the snowpack when samples were first collected in late winter (Fig. 4). Vertical inhomogeneity was characteristic at each site, and the distinct stratigraphic variations remained evident for several weeks.

On 27 April the mean  $\delta^{18}O$  value of the accumulated snow at 1475 m was  $-11.87\%$ . The underlying firn was richer in  $^{18}O$  than was most of the snow. The composition of new snow which had accumulated during the late winter period varied: that which fell between 5 and 15 May was strongly depleted of  $^{18}O$ , but that which accumulated later was  $^{18}O$ -rich when sampled on 6 June. Warming of the pack was accompanied by a tendency towards isotopic homogenisation. In July  $\delta^{18}O$  values were less variable than in late winter; the mean for the 3.4 m of snow remaining on 17 July was  $-11.03\%$ .

At 1240 m, the isotopic profile reflected the presence of two ice layers, 2.2 m and 1.2 m above the glacier surface. Their  $\delta^{18}O$  values differed; on 13 May, that of the higher layer was  $-11.29\%$ , whilst that of the lower one was  $-9.26\%$ . New snow sampled on 24 May was  $^{18}O$ -depleted ( $\delta^{18}O$  value:  $-15.66\%$ ), but on 1 June the  $\delta^{18}O$  value of the top sample was  $-9.92\%$ . As little snow fell during the intervening period, the change is likely to have resulted principally from evaporation. Between 1 and 10 June, the snowpack became 0.3 m thinner, more ice layers became visible, and the central part of the pack became more homogeneous (Fig. 3). On 12 July, the mean  $\delta^{18}O$  value of the 1.2 m of snow which remained ( $-10.76\%$ ) indicated that considerable  $^{18}O$ -enrichment had occurred as surface melting occurred during the preceding 32 days.

At 1000 m, a  $\delta^{18}O$  maximum at about 2 m above the glacier ice was a prominent feature of the isotope profile for much of May (Fig. 2). The lowest part of the pack was relatively rich in  $^{18}O$ . When the first set of samples was collected, isotopic variations in the top metre were relatively small. Between 2 and 8 May an increase in the number of visible ice layers was accompanied by changes of  $\delta^{18}O$  values. Although the snow-cover thickness decreased by 0.32 m between 7 and 12 June, the influence of the ice layer responsible for the  $\delta^{18}O$  maximum remained; below it, the  $^{18}O$  content of the pack tended to increase towards the bottom. On 14 July the thin snow cover was  $^{18}O$ -rich.

## DISCUSSION

The liquid water content of the pack throws light on processes occurring during melting. At 1000 m, before melting became widespread, water was draining slowly in certain strata within the pack, where high ionic concentrations coincided with a high liquid water content. In parts of the pack beneath a sloping snow surface there was more than 10% liquid water, apparently because water arriving from higher-lying areas was unable to drain freely to lower areas. As the first meltwater was released, variations of the amount of free water within the pack resulted from restriction imposed on vertical drainage by ice layers, some of which had formed at non-horizontal discontinuities within the pack. Many smaller ice layers disappeared as melting proceeded, but others became thicker. As the ice layers changed, the liquid water content of the snow and firn varied in a manner which suggested that drainage occurred in "waves".

Before melting started, large vertical variations of ionic concentrations were present in the snow cover: at particular levels, concentrations were high. Such variations in the accumulated snow result principally from varying concentrations in falling snow. There was no marked dependence of concentrations on altitude and, with the exception of snow which fell on 4 May, altitudinal gradients and high ionic concentrations were not evident in late winter snowfalls.

Compared with vertical variations of ionic concentrations, horizontal variations at each site were relatively small. Stratigraphic differences persisted during lateral extension of pits over distances equivalent to, or greater than, the depth of the snowpack. During the pre-melt phase at 1475 m and 1240 m, the coefficients of variation of individual ion concentrations were moderate. When melting occurred, metamorphism and melting/refreezing processes caused ions to become concentrated at particular horizons. At 1475 m, warming of the deep (c. 5 m) cold (c.  $-7^{\circ}\text{C}$ ) snowpack to the melting point, largely by heat transfer from the upper surface, resulted in downward migration of ions at the melting front. Ions were particularly abundant where the temperature gradient within the pack was steep, and downward percolation of water was slow. As the temperature of a snowpack rises to the melting point, it is likely that ions with high mobility, displaced from the upper part, become concentrated in the snow immediately above the level to which melting has penetrated.

High correlations between  $\text{Na}^+$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  in a vertical profile reflect their common origin. At Austre Okstindbreen the correlation between  $\text{Na}^+$  and  $\text{Cl}^-$  was stronger than those between  $\text{SO}_4^{2-}$  and the other ions, because about 50% of the  $\text{SO}_4^{2-}$  transported to the surface of the glacier during the 1990–91 winter had a non-marine origin. At 810 m where some ions probably were removed during winter periods of melting, and thawing/refreezing processes began to operate before they did at greater altitude, ionic concentrations were lower than at the higher sites.

Pre-melt stratigraphic variations of isotopic composition of the snowpack reflect the discrete nature of snow accumulation events. When melting starts, percolation of

meltwater into the pack results at first in only slight changes of  $\delta^{18}\text{O}$  values; major stratigraphic differences are retained for some time after temperatures rise to the melting point. Eventually, however, reactions between phases lead to a more homogeneous state (Stichler, 1987). The rate of change of the original vertical variations of the  $^{18}\text{O}/^{16}\text{O}$  ratio at a site depends on the thermal conditions, and on the formation, growth and decay of ice layers within the pack. The changes are much greater during the melt season than during the pre-melt phase.

## CONCLUSIONS

Large amounts of liquid water are present in the snowpack when drainage starts, and ions are removed quickly with the first meltwater. The order of elution,  $\text{SO}_4^{2-} > \text{Na}^+ > \text{Cl}^-$ , agrees with previous investigations elsewhere (Tranter, 1991). At 1475 m, in 1991, more than 85% of the ions had been removed after only 13% of the meltwater had left the pack, indicating that ions are exposed to removal with the first meltwater as a consequence of metamorphism which accompanies thawing and refreezing episodes during slow warming. Ions draining from the inhomogeneous snow pack at 1475 m were removed more quickly than predicted by a model of a homogeneous pack (Bales, 1991).

Melting of the snowpack is accompanied by  $^{18}\text{O}$ -enrichment and a trend towards a more homogeneous isotopic composition. As isothermal conditions develop and ice layers have a more pronounced effect on meltwater percolation, the composition of the ice layers changes. Combined studies of ions, isotopes and liquid water content provide more information about the evolution of the snowpack during the pre-melt and early melting phases than does a single-parameter investigation.

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