

## A GLACIOCHEMICAL SURVEY OF THE SUMMIT REGION, GREENLAND

by

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### ABSTRACT

Spatial representativeness and an understanding of controls on chemical species distribution are essential requirements of any significant ice core investigation. Snowpit studies provide an essential tool in this process. In preparation for the central Greenland deep drilling effort a series of snowpits was sampled in detail for oxygen isotopes, major anions, major cations, total acidity and radionuclides. The results of this sampling program are used to define: (1) the chemical composition of the snow in the region, (2) the input timing and spatial distribution of major chemical species, (3) the potential dependence of species concentration on accumulation rate, and (4) the signal characteristics identifiable in the region over the last few years.

### INTRODUCTION

Acquisition and interpretation of ice core data are now recognized as unique means of obtaining detailed paleo-environmental records. Deciphering these records depends upon a knowledge of the spatial representativeness of the sample site and an understanding of how signals in ice cores reflect environmental change. This understanding is particularly essential for the interpretation of records of the soluble and insoluble constituents analyzed in ice cores. The

Summit region of central Greenland provides an excellent site for the recovery of the longest ice core record available from the Northern Hemisphere. Therefore, issues concerning sample site representativeness and signal interpretation must be understood for this region.

We report here results obtained from a detailed snowpit survey surrounding the Summit region. The snowpits were sampled for major anions, major cations, total acidity, oxygen isotopes and radionuclides. Results of the measurement of these properties allow us to characterize the timing, source, signature, spatial distribution and accumulation-rate dependence for the chemical signals reaching the Summit region.

### METHODS

A total of seven snowpits (Fig. 1) was sampled during the 1987 field season over an area of 150 km × 150 km. The Summit region study area is within the dry-snow zone (Benson, 1962) and is characterized by relatively gentle relief. A sample interval of 3 cm was maintained for all snowpits to assure sub-seasonal resolution, and snowpits ranged in depth from 2 m (pit 3) to 4 m (pits 2, 4, 5, 6, 7) to 6 m (pit 1). In age they ranged from three years (pit 3) to five years (pits 4 and 5), six years (pit 2), seven years (pit 7), eight years (pit 6), up to ten years (pit 1).

Snowpit sampling was chosen for this study as opposed

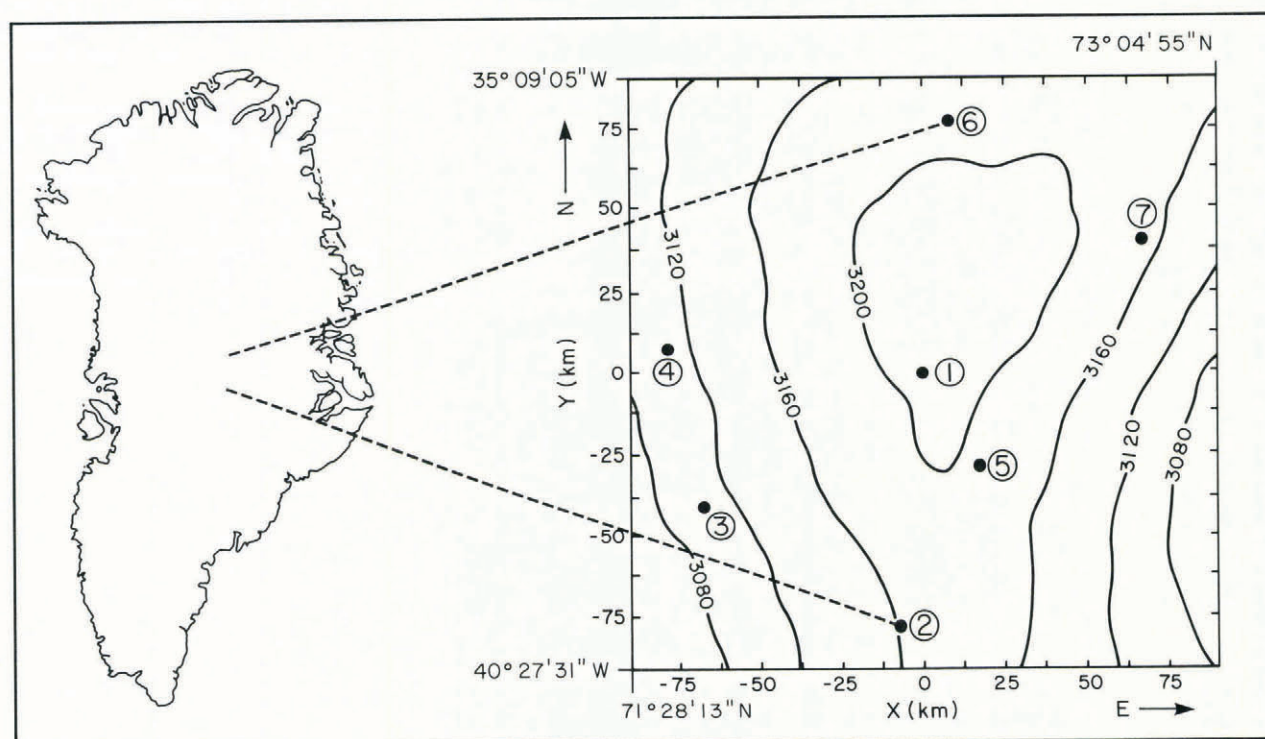


Fig. 1. Snowpit samples sites. Base map modified from Hodge and others (in preparation).



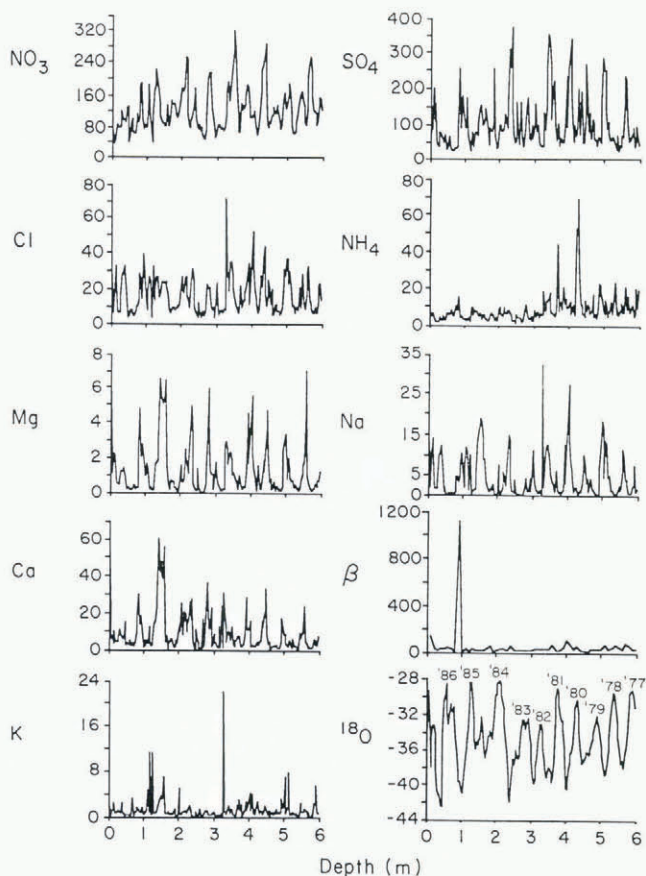


Fig. 2. Data series for snowpit 1. Oxygen isotopes in ‰, anions and cations in ppb ( $\mu\text{g kg}^{-1}$ ) and total beta activity in  $\text{cph kg}^{-1}$  with peak summer dates annotated on the oxygen isotope plot.

to shallow coring in order to assure sufficient sample volume for the broad range of measurements being undertaken, to reduce significantly the possibility of sample contamination and to avoid compaction during sampling. Samples were collected by individuals wearing polyethylene gloves, non-particulating clean suits and masks. Specially-designed sampling tools were used to fill 125-ml polypropylene containers. All tools and sample containers were pre-cleaned in ultrapure water. All samples were maintained frozen in our laboratory at  $-20^\circ\text{C}$  until analysis except for oxygen isotope samples which were melted in the 125 ml collection containers, transferred to 20-ml containers and subsequently refrozen. Samples used for radionuclide analyses were melted, filtered in the field using a strong cation-exchange resin filter and returned to our laboratory (Dibb, 1990, this volume).

Anions and cations were analyzed in our laboratories using a Dionex™ Model 2010 ion chromatograph. Details of the technique are available in Mayewski and others (1986, 1987). Radionuclide analyses were undertaken in our laboratories using a Canberra Model 2404 alpha-beta-gamma counting system. Oxygen isotope analyses were performed in Copenhagen using gas source mass spectrometry.

We performed acidity measurements using a slight modification of the acid titration procedure of Legrand and others (1982).

#### CHEMICAL COMPOSITION

Complete ionic balances were performed on the samples from the deepest of snowpits in the study (pit 1) to characterize the chemical composition of recent snow in the Summit region. An example of the data series for this snowpit appears in Figure 2. In addition, a summary of the data series is presented on a  $\mu$ -equivalent basis in the box plots on Figure 3.

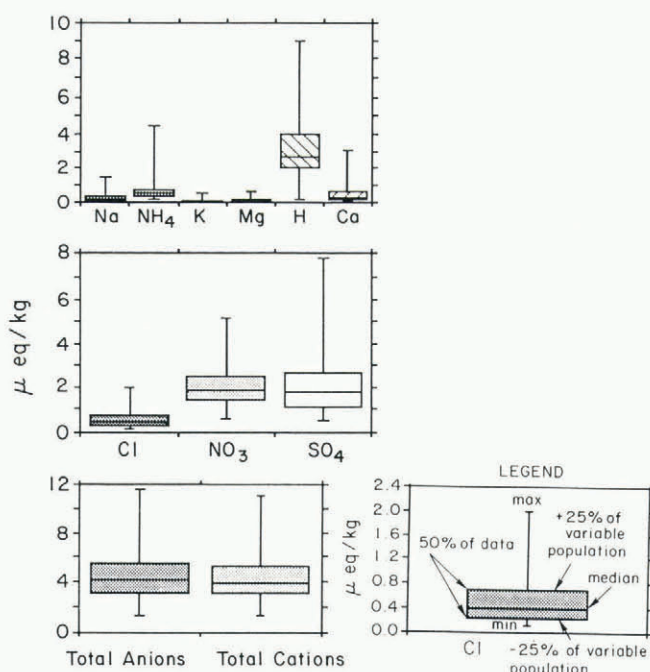


Fig. 3. Box plot summary of snowpit data series.

The hydrogen ion is the predominant cation in most of the samples. However, of the 200 samples from snowpit 1 represented in Figure 3, calcium concentrations are higher than hydrogen ion in 9 samples and ammonium is the dominant cation for 3 samples. As illustrated in Figure 4, calcium inputs probably in the form of calcium carbonate serve as a very effective neutralizing agent for the hydrogen ion. The general order of dominance in anions is nitrate slightly more than sulfate followed by chloride. The balance between cations and anions is excellent with the three anions (chloride, nitrate and sulfate) balancing on average 97% of the total cations present. The remainder of the cations may be associated with anions such as acetate or formate which were not determined for this study.

A detailed summary of the sources of the anions and cations in Greenland snow is available in Mayewski and others (in press). Only significant additions to this summary are presented here. In particular, the role of sea salt as a source of sulfate, chloride, potassium, calcium and magnesium can be defined (Fig. 5). The sea-salt component of these species was determined by ratioing to sodium. Since a portion of the sodium is crustally derived, this yields a minimum value for the non-sea-salt component. Sea salt plays a major role as a source only for chloride. Sources for excess components of each species are discussed below.

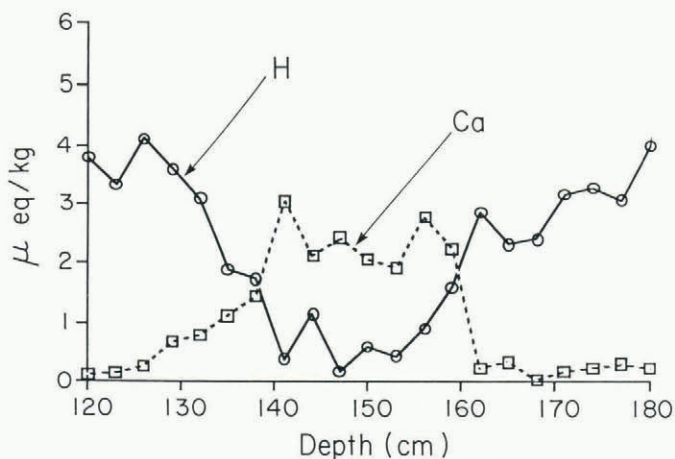


Fig. 4. Calcium versus hydrogen for a portion of snowpit 1.



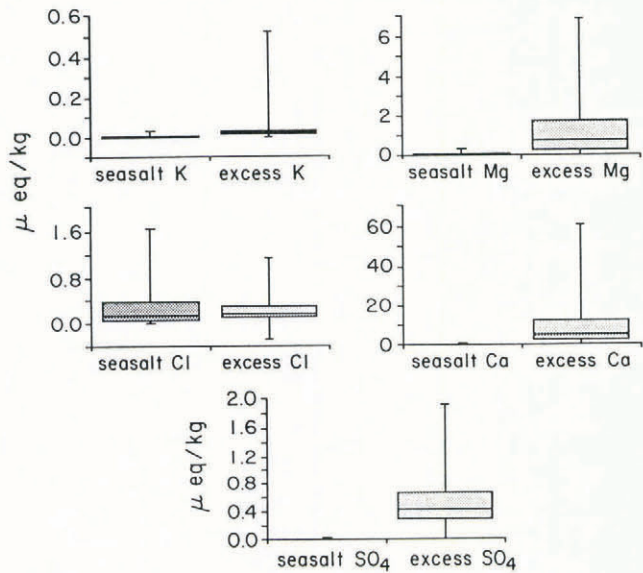


Fig. 5. Box plot summary of sea-salt versus non sea-salt (excess) sources for snowpit 1 data series. For box plot legend see Figure 3.

Excess chloride may be derived from a combination of the gaseous HCl which is released upon reaction of  $H_2SO_4$  with sea-salt aerosols (Herron, 1982) and/or gaseous HCl emitted during volcanic eruptions. The excess sulfate could be due to: the oxidation of DMS produced by phytoplankton and emitted from the oceans; natural stratospheric sulfate aerosols; oxidation of sulfur dioxide by hydroxyl radical, hydrogen peroxide and other oxidants; volcanic emissions and oxidation of sulfur dioxide from anthropogenic sources. Since the concentrations of sulfate in the Summit region are very similar to those in southern Greenland where anthropogenic sources have been demonstrated to be a major source of sulfate (Nefel and others, 1985; Mayewski and others, 1986) by analogy this is probably a major source for Summit region sulfate. Sources for excess potassium include crustally derived aerosols, biomass burning and possibly anthropogenic activity. A likely source for both excess calcium and excess magnesium is crustally-derived aerosols. Crustally-derived material appears to be a major contributor to the study region.

INPUT TIMING

Seasonal chronologies for the snowpits were defined by overlapping oxygen isotope and chemical species data series. The total beta activity peak corresponding to inputs from the Chernobyl nuclear accident (Fig. 2) served as an absolute time stratigraphic marker and as a check on the oxygen isotope chronology.

Chemical species peak concentrations have the following pattern: mid-winter to spring-maximum peaks in total chloride, sea-salt chloride, sodium, sea-salt potassium, calcium, magnesium, total sulfate, sea-salt sulfate and excess sulfate; spring to summer-maximum peaks in excess chloride and nitrate; and summer-maximum peak in ammonium. Since maxima for total and excess potassium occur during both mid-winter and summer with no apparent regularity, a unique input timing could not be determined.

The input timing presented in this study is similar to that identified by Langway and others (1975) for sodium, magnesium and calcium in southern and central Greenland; by Busenberg and Langway (1979) for ammonium, sulfate, chloride, calcium and sodium in southern Greenland, and by Mayewski and others (1986) for excess sulfate, nitrate, chloride and sodium in southern Greenland. Therefore, we infer from this preliminary comparison that input timing for chemical species is probably uniform over the entire inland portion of the Greenland ice sheet. Results of our 1988 sampling program in northwestern Greenland are forthcoming and should provide a more definitive view of the homogeneity of species input timing for the entire ice sheet.

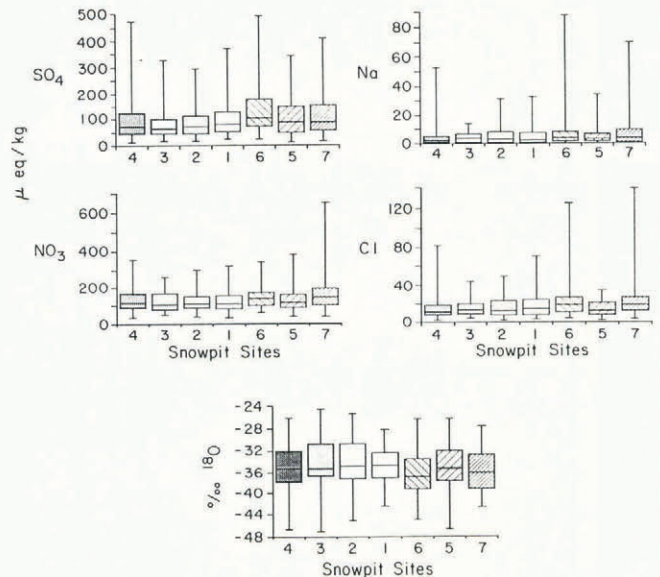


Fig. 6. Box plot summary for all snowpits (see Figure 1 for snowpit locations). For box plot legend see Figure 3.

Little is known about the input timing of chemical species in aerosols for the Greenland ice sheet. Davidson and others (1989) note that the timing of peak concentrations in sulfate and chloride in aerosols coincides with those in snow. The same study suggests that the peak in aerosol nitrate in winter is not reflected in the snow due to the influence of riming which produces a peak concentration for nitrate in summer. However, since Davidson and others (1989) compare chemical species concentrations from snowpits on the ice sheet with aerosol concentrations surrounding the ice sheet the results may not be a true reflection of the air/snow relationship. Assuredly, simultaneous aerosol and snow studies aimed at processes and mechanisms of atmospheric removal and deposition on ice sheets need to be undertaken.

SPATIAL DISTRIBUTION

Box plots (Fig. 6, see Fig. 3 for legend) for oxygen isotopes, nitrate, sulfate, chloride and sodium integrated over each snowpit provide a spatial perspective of the distribution of these important properties. For purposes of display on the box plots the snowpits are arranged roughly in west to east order (left to right on each box plot) although the actual pattern (Fig. 1) includes snowpits to the north (6) and south (2).

Median values for oxygen isotopes are relatively constant for all snowpits except the northernmost (6). This snowpit has the lowest median value, e.g. coldest temperatures. The lowest range in variable population, e.g. smallest range in seasonal signal, is found at the ice divide snowpit (1).

Box plots for nitrate have similar median values for all snowpits except 6 and 7 which have slightly higher values. In addition, the range from maximum to minimum shows a general trend. If the range and median trends are interpreted as source direction with highest concentration located closest to source, the Summit region is in general influenced more by sources of nitrate directed from the north and east.

The sulfate box plots reveal a median pattern similar to that of nitrate, no definable trend in maximum to minimum range and a high variability in the range  $\pm 25\%$  about the median for snowpits 5-7. Sulfate sources from the north and east appear to be slightly more important as contributors to the Summit region.

Median values of chloride and sodium are fairly consistent for snowpits 1-4 and 5 and highest for snowpits 6 and 7. Trends in the range maximum to minimum follow roughly northeast to southwest.

An automatic weather station is currently operational in the Summit region (personal communication from C. Stearns)



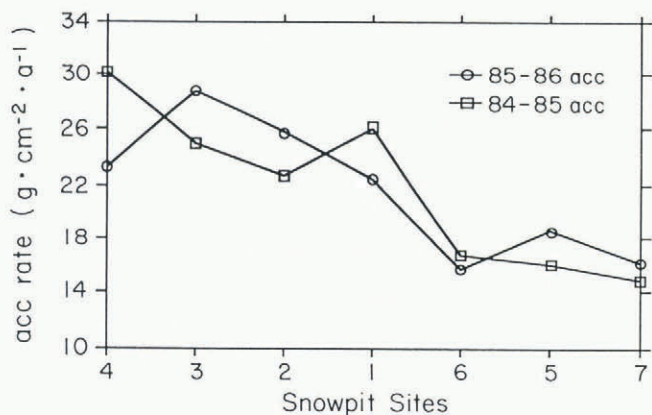


Fig. 7. Accumulation rate as a function of snowpit site. See Figure 1 for snowpit location.

and year-round meteorological records should be available for comparison with the snowpit-derived interpretations in the coming months.

CHEMICAL SPECIES DEPENDENCE ON ACCUMULATION RATE

Accumulation rate, as determined using the oxygen isotope record, increases generally from northeast to southwest through the study area (Fig. 7). This trend bears some similarity to the spatial trends in concentration of nitrate, sulfate, chloride and sodium revealed from the box plots (Fig. 6). The similarity in accumulation rate and chemical species trends force some consideration of dependency. Herron (1982) has ascribed some of the spatial variations in sulfate and nitrate in snow to differences in accumulation rate. Since the sources of these two species are linked to gas-to-particle conversion processes, a constant production rate would result in an inverse relationship with respect to accumulation rate, which, as it turns out, is apparent primarily for the lower range of accumulation rates (Herron, 1982). Legrand and Delmas (1986) working in Antarctica have suggested that this dependency is not straightforward for nitrate. Clearly, studies that separate dry versus wet deposition influences and input patterns will be useful in solving this problem.

Nitrate and sulfate concentration versus accumulation rate are plotted in Figure 8 to display the test for dependency. The data points represent a mixture of all snowpits for the accumulation years 1984-85 and 1985-86 in order to test dependency over the study area and for the accumulation years 1980-86 for snowpit 1 to test at a fixed point. A weighted least-square fit appears on each plot. Although not straightforward there is a fairly marked difference in sulfate and nitrate concentrations associated with accumulation rates less than 18-22 g · cm<sup>-2</sup> · a<sup>-1</sup> and concentrations associated with higher accumulation rates for which concentration appears to be less dependent on accumulation rate. However, the difference in accumulation rate cannot be uniquely separated from geographic location, since the snowpits with lower accumulation rates are all in the same area (snowpits 5, 6 and 7), hence the variability in concentration could be source-dependent and/or transport-dependent. Snowpit sampling planned for other low accumulation-rate sites in the Summit region should help to resolve this issue.

If there is an accumulation-rate effect there are two potentially important cautions that relate to the overall interpretation of chemical records from this region. First, if this effect exists it is sufficient to account for the differences in median values in the box plots used to assess spatial trend (Fig. 6). Therefore, the Summit region could be perceived as receiving a uniform "covering" of nitrate and sulfate on an annual basis. Secondly, to determine whether or not geographical trends or patterns in nitrate and sulfate concentrations are real, as opposed to accumulation-rate-dependent, requires a signal-to-seasonal-

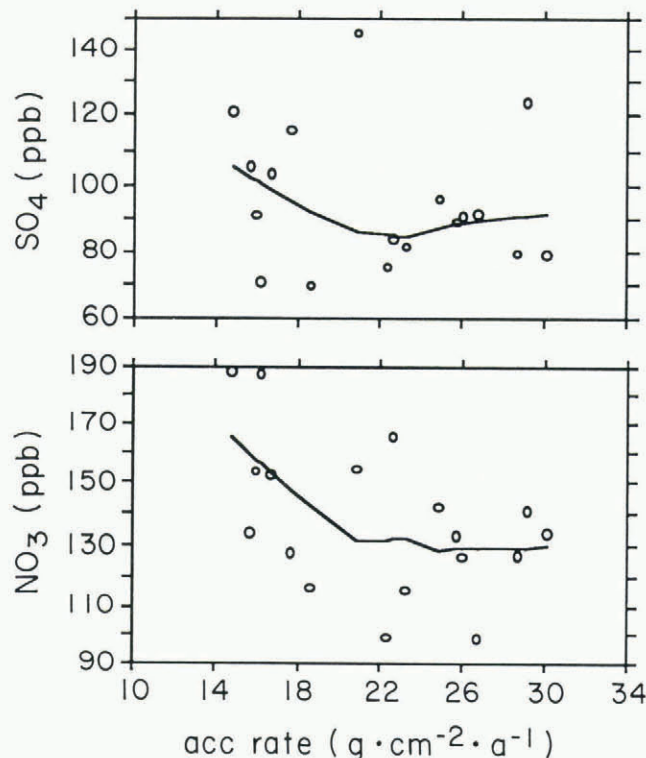


Fig. 8. Accumulation rate versus concentration of sulfate and nitrate.

maximum ratio of at least 2:1, since the potential effect produced by dropping below an accumulation rate of 18-22 g · cm<sup>-2</sup> · a<sup>-1</sup> could be of the order of a 50-100% increase in species concentration (Fig. 8).

UNIQUE EVENTS AND YEAR-TO-YEAR TRENDS

The presence of unique events in the chemical record was determined by detailed comparison within and between snowpits. Unique events are defined by anomalous features containing a minimum of two data points to avoid spurious outliers and by the 2:1 signal-to-seasonal-maximum ratio proposed above. Due to the length limitations on this paper the complete data sets used to define these events cannot be included. A summary of the results follows.

Perhaps the single most prominent event is the peak in total beta activity marking the Chernobyl nuclear reactor accident. This event (Fig. 2) serves as a distinct stratigraphic marker for the period spring 1986 throughout the Summit snowpit survey region and the Greenland ice sheet in general (Dibb, 1990, this volume).

Events that could be categorized as relative highs or lows and/or by anomalous timing of peaks for the period May 1987 through 1982 were picked out of the data series. There is a general tendency toward clustering of events by location and season. Summarized chronologically it appears that: 1987 had a relatively cold spring (low oxygen isotope values) accompanied by relatively high concentrations of nitrate and chloride for sites north and east of the ice divide; 1986 had no discernible trends in the data series; 1985 had a relatively cold winter-to-spring for the southeastern portion of the study site and relatively high concentrations of nitrate during the summer and of sodium during winter/spring for most of the study area; 1984 had a relatively warm winter for the divide region, high summer nitrate east of the divide and an anomalous fall peak in sulfate that affected the southern portion of the study site; 1983 had a relatively cold summer throughout all of the study region and a relative high in winter sulfate directed from the northwest; and 1982 had a relatively cold summer throughout the study region, anomalous spring/summer chloride peaks and/or relatively high concentrations of winter chloride throughout much of the study area. Only a preliminary interpretation of the preceding will be presented



here. Once a full year of meteorological data is available from the Summit region, more definitive interpretations will be possible.

The most dramatic trend in oxygen isotopes is the relatively low summer values (cold temperatures) throughout the study region for the summers of 1982 and 1983. During this time period the effects of both El Chichon and the El Niño/Southern Oscillation could have influenced temperatures in the study area.

Since anthropogenic sources of nitrate and sulfate comprise at least half of the total concentration of these species in Greenland snow (Mayewski and others, 1987) it is likely that prominent "anthropogenic influences" had an effect on this region in spring 1987, fall 1984 and winter 1983.

Davidson and others (1989) suggest that winter peaks in chloride represent transport of long range marine aerosols from North Atlantic storms while summer peaks reflect transport of sea-spray from coastal Greenland. The chloride peaks in spring 1987 and spring/summer 1982 and winter 1982 represent periods of increased marine influence from these sources. Since the winter/spring 1985 high in sodium was not accompanied by a chloride high, this may have been a crustal dust event.

## SUMMARY

The study presented in this paper provides a basis to understand the character and distribution of the primary chemical species deposited in snow in the Summit region. Ionic balance determinations reveal that this study identified all of the major chemical species entering the region. Ranked by median, on a  $\mu$ -equivalent basis, the major anions are nitrate, sulfate and chloride, and the major cations are the hydrogen ion, ammonium, calcium, sodium, magnesium and potassium. Major sources of chemical species to the area are anthropogenic activity and marine- and crustally-derived aerosols. Input timing for the maximum concentration of most of the chemical species studied appears to be highly consistent on an annual basis. The only major exception was excess potassium, for which no regular input timing could be defined. Interplay of crustal and anthropogenic sources for excess potassium may explain this situation. Comparison with input timing defined from other studies on the Greenland ice sheet suggests that the entire inland portion of this ice sheet may receive inputs synchronously.

Nitrate, sulfate, chloride and sodium all have an apparent concentration gradient, high to low, oriented approximately northeast to southwest. However, there is also an inverse gradient in accumulation rate in the region. A test of chemical species concentration dependency on accumulation rate, although not definitive, could be sufficient to explain the species gradient. This dependency may be significant only for chemical concentrations accompanied by accumulation rates less than  $18\text{--}22\text{ g}\cdot\text{cm}^{-1}\cdot\text{a}^{-1}$ . Below this value concentrations rise as accumulation rate decreases. A conservative view of the problem requires that all chemical species interpretations conducted for this region include companion accumulation-rate measurements. Only chemical concentrations on the order of twice the annual maximum should be considered as accumulation-independent signals. Several recognizable chemical events emerge from the snowpit record for the period 1982–87. The fact that these events are definable by more than one snowpit, and that these events cluster by season and location, suggests that the Summit region will

provide a sensitive record of changes in the source and/or transport path of chemical species.

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