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## Preservation of glaciochemical time-series in snow and ice from the Penny Ice Cap, Baffin Island

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**Abstract.** A detailed investigation of major ion concentrations of snow and ice in the summit region of Penny Ice Cap (PIC) was performed to determine the effects of summer melt on the glaciochemical time-series. While ion migration due to meltwater percolation makes it difficult to confidently count annual layers in the glaciochemical profiles, time-series of these parameters do show good structure and a strong one year spectral component, suggesting that annual to biannual signals are preserved in PIC glaciochemical records.

### Introduction

Ideally, ice cores are recovered from sites which experience very little if any melt. However, these types of sites are limited to the summit regions of the Greenland and Antarctic ice sheets, and some select high elevation glaciers. Fortunately, valuable ice core records are also available from glaciers around the globe that experience occasional to moderate melt, such as sites in the Arctic (e.g., Koerner and Fisher, 1990; Koerner, 1997), the Andes (e.g., Thompson et al., 1984), and central Asia (e.g., Wake et al., 1993).

We report here on a continuous record of major ion and oxygen isotope variability from four 2 m snowpits and the upper 100 years of the 334 m ice core collected from the summit region of the Penny Ice Cap (PIC) (67°N, 65°W; 1900 m a.s.l.), southern Baffin Island. The density corrected melt percent of bubble free ice that forms in summer by meltwater averages 50% for the upper 100 years of the PIC ice core. This site therefore provides an opportunity to investigate the preservation of the major ion record in a snowpack which experiences seasonal melting events.

### Methods

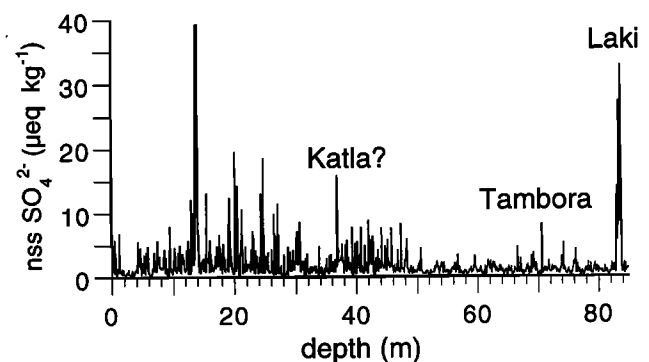
During the spring of 1995 we recovered a 334 m ice core and collected samples from four 2 m snowpits in the summit region of the PIC. Three snowpits were located within 1 km of the deep drill site, and the fourth was located adjacent to an automatic weather station (AWS), 6 km to the north. The upper 40 m of the deep core and the snowpits were sampled continuously using a 5 cm sample interval.

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Once collected, the snow/ice samples remained frozen until just prior to analysis with a Dionex Model 4000i ion chromatograph to determine concentrations of  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  (Buck et al., 1992). Ion balance calculations yield a cation deficiency, which is assumed to represent the hydrogen ion and is consistent with ion balance calculations at other Arctic sites (Mayewski et al., 1990). Standard sea-salt ratios were used to partition  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$  into sea salt (ss) and non-sea salt (nss) components.

An average annual snow accumulation rate of 0.38 m ice eq. was determined for the last 32 years through the identification of the 1963 peak in the beta activity profile measured on a dedicated 20 m firn core. This value compares favorably to the 0.48 m ice eq. determined by Holdsworth (1984) for the period 1949-1979. Below 15 m, the largest spike in the nss  $\text{SO}_4^{2-}$  record occurs at 83 m (Fig. 1) and has been identified as representing the Laki eruption in 1783-1784. This corresponds to a mean annual accumulation rate of 0.36 m ice eq. which is very close to the value measured for the last 32 years, suggesting that little if any thinning of annual layers has occurred at this depth. A depth-age scale was developed for the upper 85 m of the ice core using a linear fit to the depth-age relationships provided by the beta activity and Laki reference horizons.

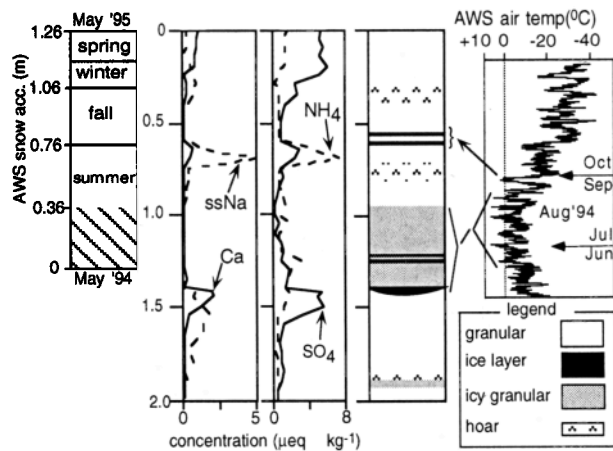


**Figure 1.** Non sea-salt sulfate concentrations in the upper 85 m of the Penny ice core. Peaks relating to the Laki (AD 1783-84), Tambora (AD 1815) and Katla (1914) eruptions are identified. The obvious change in the variability and peak values at 48 m depth (ca. 1880) represents the onset of anthropogenic sulfate deposition to the Penny ice cap.

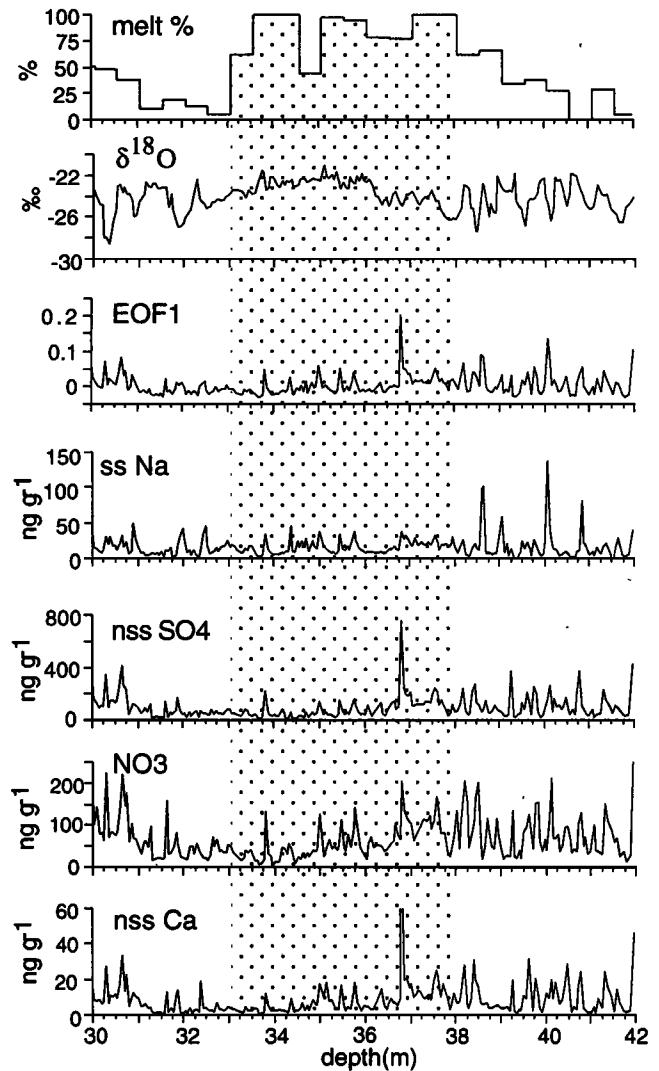
## Results

AWS temperature data were used to correlate ice layers in pit 4 to time periods when temperatures were above zero on the summit of the PIC (Fig. 2). Two thin ice layers between 0.55–0.60 m represent the short period of above freezing temperatures in late September 1994. At 0.95 m, a sharp contact marks the beginning of a 0.50 m layer composed of dense icy granular snow with several ice layers. This entire layer represents summer and underlying spring snow layers into which meltwater has percolated and refrozen. The chemical peaks around 1.50 m occur over a 0.15 m section of firn below the 20 to 50 mm ice layer and represent accumulation during the preceding season, late winter/early spring 1994. Figure 1 also illustrates enhancements of  $\text{ssNa}^+$ ,  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  at 0.70 m, corresponding to the late summer/early autumn of 1994. While the actual depths vary slightly, the major physical and chemical stratigraphy in pits 1, 2 and 3 (not shown) are similar to those of pit 4.

The seasonal chronology of the snowpit chemistry was also defined by comparing chemical depth profiles to monthly AWS depth sounder data. We converted the daily AWS depth sounder data to seasonal cumulative values; fall (Sept.-Nov.), winter (Dec.-Feb.), spring (March-May) and summer (June-Aug.) (Fig. 2). We have assumed that the influence of post-depositional affects, such as scouring and drift are averaged out when seasonal snowfall values are calculated from the AWS data. The density of snow in the upper 0.90 m of the snowpit ( $0.35 \text{ g cm}^{-3}$ ) is similar to the average fresh snowfall density as measured in the top layer of each snowpit and therefore does not need to be density corrected. However, the thick icy granular and ice layer section from 0.90–1.40 m has an average density of  $0.49 \text{ g cm}^{-3}$ . The 0.50 m of snow accumulation measured by the AWS in the summer of 1994 has therefore been density corrected to 0.36 m (this snow is identified by cross hatches on the snow accumulation profile of Fig. 2). Based on the seasonal interpretation from the AWS data and the physical stratigraphy of the snowpack, we have assigned the first chemical enhancement (0.70 m) in pit 4 to fall 1994 and the second enhancement (1.50 m) to spring 1995. The profiles of the other 3 pits (not shown) also display this



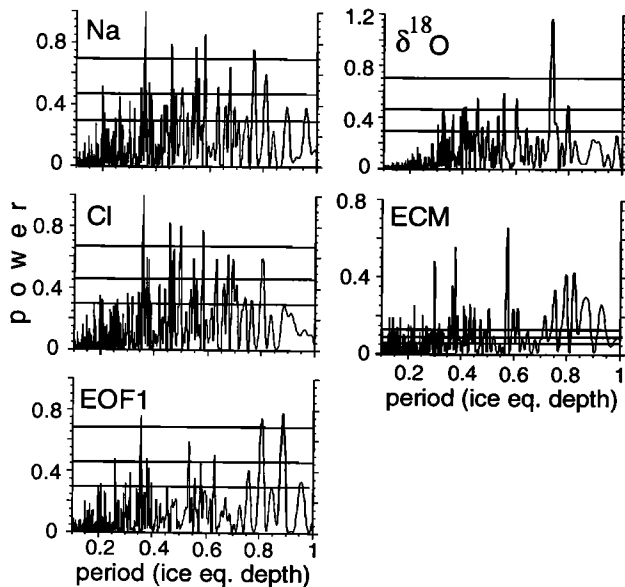
**Figure 2.** Major ion profiles and visible stratigraphy from snowpit 4 compared with automatic weather station (AWS) seasonal snow accumulation and temperature data. The cross hatching on the AWS snow accumulation profile identifies snow that has been density corrected (see text).



**Figure 3.** Physical and chemical characteristics of the Penny ice core from 30 to 42 m. The stippled pattern outlines the section of core that shows the highest average melt percent for at least the last 1000 years.

seasonal doublet of maximum chemical deposition in the fall and spring months.

The major ion and oxygen isotope profiles for the upper 85 m of the ice core show substantial structure (e.g.  $\text{nss SO}_4^{2-}$  shown in Fig. 1). Preliminary counting of peaks down to the beta activity and Laki reference horizons suggests that the peaks represent annual signals. The sub-annual structure observed in the 2 m snowpits appears to have been modified in the ice core record, even though the seasonal doublet is preserved during some years as a "shoulder" (i.e. the baseline remains elevated between peaks; Fig. 3). In order to test to see if the peaks represent annual signals, we performed a Fourier spectral analysis (Meeker et al., 1995) on the upper 40 m (100 years) of the major ion, ECM, and oxygen isotope data series (Fig. 4). The  $\text{Na}^+$  and  $\text{Cl}^-$  records show the strongest high frequency spectral component at 0.36 m ice eq. which is almost identical to our average measured annual accumulation over the past 32 years. The higher resolution (1 cm) ECM record shows strong spectral power on an annual basis (0.38 m ice eq.), as well as signals that may represent seasonal signals (0.30 m and 0.57 m ice eq.). Surprisingly, the oxygen isotope



**Figure 4.** Results from a Fourier analysis of the major ion, first empirical orthogonal function (EOF1), and ECM records from the upper 40 m of the Penny ice core plotted versus ice equivalent depth. The horizontal lines on each graph represent (from top to bottom) the 99.9%, 99% and 95% confidence limits.

series shows a strong signal at 0.73 m w.e., suggesting the preservation of a bi-annual signal. We also performed empirical orthogonal function (EOF) analysis (Meeker et al., 1995) on seven of the eight major ion series ( $\text{NH}_4^+$  was not included in the analysis as it shows substantially different behavior on annual time scales) in order to quantify their common behavior. The first empirical orthogonal function (EOF1) explains 63% of the total variance of seven major ion series; spectral analysis of EOF1 also reveals a strong annual signal (0.36 m ice eq). All of the peaks in the spectral analysis mentioned above are significant at the 99.9% confidence level.

We also investigated a 5 m section in the ice core (33–38 m) that is characterized by melt percent ranging from 65% to 100% based on one meter averages (Fig. 3), and represents the highest percent melt for at least the past 1000 years. This section correlates to the warming of the early 1920's (e.g., Hansen and Lebedeff, 1987). Contrary to what might be expected in a section of core that has experienced high melt, quasi-annual peaks can still be identified in the major ion series. However, the baseline values between 32 m and 36.8 m in the  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  profiles appear to be reduced and the concentration of peaks tends to be lower. Conversely, from 36.8 to 37.8 m, the  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{Ca}^{2+}$  profiles show elevated baselines, suggesting an accumulation of these ions due to meltwater percolation. Annual signals in the oxygen isotope profile are also more difficult to identify in the section from 32 to 38 m as the time-series lacks the seasonal variability observed elsewhere.

Several studies on glaciers and seasonal snowpacks suggest that some ions are eluted from the snowpack more rapidly than others;  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{Mg}^{2+}$  appear to be the most mobile ions while  $\text{Cl}^-$  and  $\text{Na}^+$  are retained longer in the snowpack (e.g., Davies et al., 1982; Koerner, 1997). In order to examine this further, ratios of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{Mg}^{2+}$  to  $\text{Na}^+$

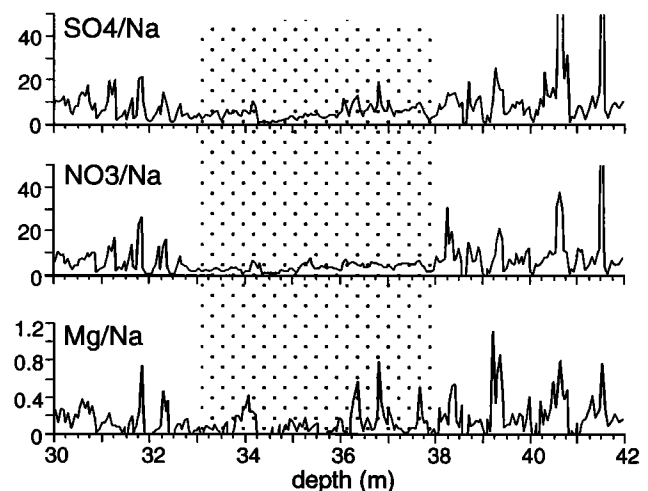
were plotted over the section from 30 to 42 m (Fig. 5). The plots suggest that preferential elution of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  has occurred to at least some extent over the sections from 33 to 38 m while  $\text{Mg}^{2+}$  does not appear to have been affected as much.

Another striking characteristic of this high melt section is the large nss  $\text{SO}_4^{2-}$  peak at 36.8 m (Fig. 3). While this nss  $\text{SO}_4^{2-}$  peak is accompanied by peaks in dust related species it is unlikely that this nss  $\text{SO}_4^{2-}$  peak is solely the result of preferential elution as the nss  $\text{SO}_4^{2-}/\text{ssNa}^+$  and nss  $\text{SO}_4^{2-}/\text{NO}_3^-$  ratios increase three fold for this peak and there is no increase in  $\text{Cl}^-$  and  $\text{NH}_4^+$  concentrations. Furthermore, this nss  $\text{SO}_4^{2-}$  peak is unprecedented in the top 85 m except for the 1783 (83.5 m) Laki eruption and an increase in baseline during the onset of industrialization circa 1880 (Fig. 1). Our depth-age scale dates this peak at ca. 1914. Initial analysis of individual particles in the section of core containing the elevated  $\text{SO}_4^{2-}$  indicates the possible presence of basaltic glass (M. Jercinovic, pers. comm). The source of this glass is likely the Icelandic eruption of Katla in 1918, although one of the several very small Icelandic eruptions in 1913 cannot be ruled out.

## Discussion

Seasonal signals in the PIC major ion series can be related to the migration of the Arctic front during the fall and spring months and to the frequent occurrence of low pressure systems to the south of the PIC during these time periods (e.g., Barry, 1967). Consequently storm activity is more common during the fall and spring months and is likely responsible for the seasonal doublet observed in both our PIC chemistry data and that of Holdsworth (1984).

A primary consequence of meltwater percolation is the migration of insoluble and soluble impurities in the snowpack. Mayewski and Lyons (1981) and Davies et al. (1982) show that the baseline concentration of a chemical record that has undergone significant ion migration (from percolating meltwater) will lack noticeable variation. At other sites, seasonal variations in major ions are preserved in snowpacks that experience melting and subsequent



**Figure 5.** Ratio of sulfate, nitrate, and magnesium to sodium in the Penny ice core from 30 to 42 m. The stippled pattern is the same as for Fig. 4.

percolation of meltwater (e.g., Thompson et al., 1984; Wake 1989; Goto-Azuma et al., 1995).

While the glaciochemical records from the PIC over the last 100 years do not show the regular seasonal variations seen in records from, for example, the summit region of the Greenland Ice Sheet (e.g., Whitlow et al., 1992), neither do they show a record that is completely washed out. As Figure 1 and 3 illustrate, there are quasi-annual signals in all of the data series. The results of the spectral analysis indicate that annual signals are indeed preserved in the  $\text{Na}^+$ ,  $\text{Cl}^-$ , ECM and first EOF data series. One might argue that the annual signals are solely the result of the concentration of ions due to ion migration with percolating meltwater and concentration in ice layers. However two aspects of the data argue against this. First, a detailed analysis of the position of peaks in all eight major ion series with respect to ice layers reveals that peaks occur about equally in melt versus non-melt layers. In addition, the major ion peaks in the snowpit do not occur in conjunction with ice layers or the icy granular layer (Fig. 2). Second, the first EOF explains 63% of the variability in the record; we would expect this value to be substantially higher if the temporal variation in the major ion series were due only to the percolation and refreezing of meltwater.

Even in the 5 m section of the core that has experienced 65% to 100% melt, where we see evidence of reduced seasonal variations in the oxygen isotope record and preferential elution of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ , quasi-annual signals remain. Furthermore, the identification of a volcanic signal at 36.8m provides further evidence that despite substantial summer melting, a volcanic reference horizon has been preserved.

How can these annual signals be preserved in an ice core that has experienced significant melt? In a detailed study of water movement and ice-layer formation in a snowpack on a small ice cap in west-central Greenland, Pfeffer and Humphrey (1996) show how meltwater percolates downward and initially spreads out laterally along stratigraphic and hydraulic boundaries created by a change from fine to coarse grained snow. Initially, vertical percolation stops and refreezes, allowing lateral flow to continue. At this point, the process of hydraulic break-through of the horizontal layer and pore close-off compete at the barrier. If water at the barrier freezes sufficiently quickly to form an ice layer, further meltwater will accumulate on the now impermeable layer. AWS data on the PIC indicate that above melting temperatures during the summer days are consistently followed within a few days or nights by below freezing temperatures. Ice layers created during this cycle of melting and refreezing have the potential to preserve annual signals in the PIC record by providing physical barriers to further ion migration.

## Conclusions

We have investigated the influence of meltwater percolation on the glaciochemical records preserved on the Penny Ice Cap (PIC) over the past 100 years. Despite an average of 50% melt over this time period, there exist quasi-annual peaks in the major ion, oxygen isotope and ECM time-series. While it is difficult to confidently identify annual layers in any individual record, the annual nature of the glaciochemistry signals is verified by the presence of a strong one year spectral

components in the PIC  $\text{Na}^+$ ,  $\text{Cl}^-$ , EOF1 and ECM records. Further, while a 5m section of ice core that experienced high melt (65-100%) shows the influence of meltwater percolation, the section still contains quasi-annual peaks as well as a preserved volcanic signal. Our analysis of the Penny ice core suggests that despite the influence of meltwater percolation, the glaciochemical record can still be interpreted on annual to biannual time scales with moderate confidence, and on sub-decadal scales with high confidence.

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