TRACE-ACID ION CONTENT OF SHALLOW SNOW AND ICE CORES
FROM MOUNTAIN SITES IN WESTERN CANADA

by

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ABSTRACT

An historical record of the deposition of common acids is contained in snow and ice cores taken from suitable sites in the accumulation zone of certain glaciers. Spatial and time-series data sets for trace-mineral acids have been obtained from snow-pit samples and ice cores from a number of mountain sites in Alberta, British Columbia, and the Northwest and Yukon Territories. In Alberta, it is possible to use temperate firn sites above 3460 m, although elution occurs during certain summers as indicated by isotopic and ionic data. This would also apply to sites of a similar latitude (52° ± 2° N) in British Columbia. In the Yukon Territory (360.5° N) reliable time series for the acid anions may be obtained from sites at altitudes above 3000 m. Elution provides a natural control for demonstrating that field sampling and subsequent analytical procedures do not introduce significant contamination. The Yukon data are compared with the net annual accumulation rate and with altitude. Recent data from the 5340 m Mt Logan site do not indicate any significant increase in natural background levels of snow acidity. Lightning, which is responsible for numerous forest fires in all provinces, is a possible natural source of nitric acid. Spring-summer peaks in nitrate concentration usually occur. In addition, forest-fire smoke may be a significant contributor to the mountain snow-pack chemistry in some years and must be considered when interpreting the Mt Logan core data. One Yukon profile seems to contain the signature from the 1986 Augustine volcanic eruption.

INTRODUCTION

Recent concern about the extent of acid precipitation in industrialized regions of the Northern Hemisphere has initiated base-line studies, in remote glaciated regions, of pH and anions commonly thought to be associated with acidity. In southern Greenland (Neftel and others 1985, Mayewski and others 1986) and the north-eastern Canadian Arctic (Koerner and Fisher 1982), the chemical analysis of ice cores provides some evidence for an increase in the acidity of precipitation during this century. However, at Crete (in central Greenland) no direct evidence was found for a significant increase in acidity during this century (Hamber 1977). This is also the case for a mid-troposphere site in the Yukon Territory (Holdsworth and Peake 1985). Furthermore, in the continental U.S.A. over the period 1978-83, there was no clear pattern of changes in acidity associated with SO$_2^-$ and NO$_3^-$. In some places there were even significant decreases in [SO$_4^{2-}$] and [NO$_3^-$] (Anonymous 1986). Therefore it is necessary to have a wide geographic distribution of sampling sites which provide information on the vertical distribution of acid anions in snow and ice cores. This might enable the identification of the sources of some of the acidic components.

In an attempt to meet these requirements, mountain sites in Alberta, British Columbia, and the Northwest and Yukon Territories that had previously yielded cores for climate-change studies were used in the present study. The process of elution (Brimblecombe and others 1985), prevalent at many of the sites, effectively limits the applicability of some of the data, but there is a side benefit: the very low ionic concentrations in the melt-water from the temperate or near-temperate sites provide a natural control for demonstrating that field sampling and subsequent analytical procedures cannot be introducing significant contamination. In extreme cases, the levels of [NO$_3^-$] and [SO$_4^{2-}$] are both below detection limits (1-2 ng g$^{-1}$). At sites where elution precludes obtaining useful information previous to the last summer, pit samples collected in the spring before the onset of the melt season provide at least 9 months of data.

Observations of thunderstorm activity, forest-fire smoke, and volcanic activity in relation to the various sites occupied in the summer of 1986 have enabled some interpretations, which otherwise might not have been possible, to be placed on the data. In principle, these observations should be extremely useful in interpreting the time series of nearly 300 years for the Mt Logan core.

Interpretation of the data is limited by the fact that a complete ion balance was not carried out on the samples. However, for the Yukon sites we assume that the results of Delmas and others (1985) are applicable: namely that the strong mineral acids are essentially unneutralized. This is also supported qualitatively by the pH data presented here and, even if some significant (local) neutralization of the acids has taken place, the measured sulfate and nitrate concentrations still indicate the original levels of the corresponding acids and are thus an indicator of the original acid levels in the atmosphere above the site.

This study and the interpretations of the data provided herein contribute to two Canadian projects: LRTAP (Long Range Transport of Airborne Pollutants), which is a project sponsored by the Federal Government, and ADRP (Acid Deposition Research Project), which is administered by Alberta Environment.

METHODOLOGY

Pit and ice-core samples were collected between 1980
and 1986 at sites in Alberta, British Columbia, and the Yukon and Northwest Territories at the locations listed in Table I and shown in Figure I. These samples were analyzed for oxygen isotopes, pH, conductivity, nitrate, sulfate, and chloride by methods which have been described previously (Holdsworth and Peake 1985).

RESULTS AND DISCUSSION

The Yukon sites

Results for the Mt Logan and the Eclipse sites before 1983 have been reported elsewhere (Holdsworth and Peake 1985). In 1984 chemical analysis of pit and ice-core samples from the upper Seward Glacier confirmed that excessive elution had rendered that core unsuitable for long-term atmospheric chemistry studies. However, it did provide confirmation of the assumption that no significant contamination of the samples is occurring. The oxygen-isotope profile, although highly diffused and essentially homogenized by 11 m depth is reached, showed the net annual accumulation rate to be 2.45 m water equivalent (w.e.) for 1983-84, and 1.6 m w.e. for 1982-83. The mean, 2.07 m, compares favourably with a value of 2.12 m w.e. given by Marcus and Ragle (1970) for the 1964-65 balance year for a central Seward Glacier site.

Figure 2 shows analytical data for the Seward Glacier site plotted to a depth of 8 m. Nitrate appears to be preferentially eluted with respect to sulfate. At the time of sampling, a new snowfall enabled the collection of an uneluted sample which contained the expected levels of both $\text{NO}_3^-$ and $\text{SO}_4^{2-}$.

In September 1985 the divide of Kaskawulsh Glacier was occupied to determine when elution had effectively homogenized the $\delta^{18}O$ signal and removed the anions. Three balance years of net accumulation could be recognized (Fig. 3), providing a mean accumulation rate of about 1 m w.e. per year—a rate comparable with the earlier data of Marcus and Ragle (1970). Only nitrate data is available (obtained by a colorimetric method using a Technicon TM auto-analyzer). These show less nitrate elution than on Seward Glacier, but on their own the data are of limited use. Specific electrolytic conductivities of the melt water indicate low levels of the other ionic species.

In 1986 a series of pit samples was obtained during an ascent of Mt Logan, and later at the Eclipse site (Fig. 1). The results from the analyses of these samples will be presented and discussed in chronological order.

TABLE 1. SAMPLING SITES

<table>
<thead>
<tr>
<th>Location</th>
<th>Altitude</th>
<th>Year</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Yukon Territory</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1) Mt Logan (NW Col)</td>
<td>60°37.5N, 140°30’W</td>
<td>5340 m (1980, 81, 86)</td>
<td>P, C</td>
</tr>
<tr>
<td>2) Mt Logan (AINA Pk)</td>
<td>60°37’N, 140°32’W</td>
<td>5630 m (1986)</td>
<td>P</td>
</tr>
<tr>
<td>3) King Col</td>
<td>60°36’N, 140°36’W</td>
<td>4200 m (1986)</td>
<td>P</td>
</tr>
<tr>
<td>4) King Trench</td>
<td>60°36’N, 140°40’W</td>
<td>3360 m (1986)</td>
<td>P</td>
</tr>
<tr>
<td>5) Quintino Sella Glacier</td>
<td>60°36’N, 140°45’W</td>
<td>2850 m (1986)</td>
<td>P</td>
</tr>
<tr>
<td>6) Eclipse</td>
<td>60°50’N, 139°50’W</td>
<td>3017 m (1982, 83, 86)</td>
<td>P, C</td>
</tr>
<tr>
<td>7) Kaskawulsh Glacier</td>
<td>60°46’N, 139°40’W</td>
<td>2600 m (1985)</td>
<td>P, C</td>
</tr>
<tr>
<td>9) Flint Icefield</td>
<td>62°10’N, 128°00’W</td>
<td>2290 m (1982)</td>
<td>P, C</td>
</tr>
<tr>
<td><strong>British Columbia</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10) Mt Edziza</td>
<td>57°40’N, 130°40’W</td>
<td>2787 m (1981)</td>
<td>P, C</td>
</tr>
<tr>
<td>11) Tellot Glacier Col</td>
<td>51°25’N, 125°00’W</td>
<td>3020 m (1981)</td>
<td>P, C</td>
</tr>
<tr>
<td><strong>Alberta</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>12) Snow Dome</td>
<td>52°11’N, 117°19’W</td>
<td>3460 m (1984, 86)</td>
<td>P, C</td>
</tr>
<tr>
<td>13) Peyto Glacier</td>
<td>51°39.5N, 116°35’W</td>
<td>2785 m (1986)</td>
<td>P</td>
</tr>
</tbody>
</table>

P = Pit, C = Core (year of sampling in brackets)
Fig. 2. Snow and ice-core analysis results for Seward Glacier (1984): site 8, 1800 m: (a) oxygen-isotope data; S = summer (year in brackets); (b) density of firn; (c) stratigraphy: NS = new snow, bars denote ice; (d) specific electrolytic (liquid) conductivity; (e) pH; (f) nitrate; (g) sulfate and (h) chloride concentrations.

Fig. 3. Snow and ice-core analysis results for Kaskawulsh Glacier Divide (1985): site 7, 2600 m: (a) oxygen-isotope data; S = summer; (b) density; (c) stratigraphy: NS = new snow, bars denote ice; (d) specific electrolytic (liquid) conductivity; (e) pH; (f) nitrate concentration.

Fig. 4. Snow-pit analysis results from King Trench on Mt Logan (1986): site 4, 3360 m: (a) oxygen-isotope data; S = summer 1985; (b) density; (c) specific electrolytic (liquid) conductivity; (d) pH; (e) nitrate and (f) sulfate concentrations.

At King Trench (site 4, 3360 m), a pit dug on 19 May, to the preceding "summer" surface yielded data shown in Figure 4. The $^{18}$O distribution is not "classical" but it confirms the stratigraphic diagnosis of the 1985 balance-year termination, which enables an estimate of the net accumulation for 1985-86 to be determined. There is no evidence of elution in this profile, in which both acid anions vary, with a winter minimum and a "summer" maximum. There is no SO$_4^{2-}$ signal that could be attributed to the eruption of Augustine volcano in March 1986.

At King Col (site 3, 4200 m), a pit dug on 20 May, to a hard surface, provided samples of which the analyses are shown in Figure 5. On the isotopic and stratigraphic evidence, the preceding summer is placed at 140 cm depth. The nitrate shows little modulation and the sulfate shows a spring increase which could be from Augustine. The lower profile tends to suggest some elution; however, this was not seen in the $^{18}$O profile.

On Quintino Glacier (site 5, 2850 m), a pit was dug on 21 May to the preceding summer surface. This yielded data which are shown in Figure 6. An estimate of the 1985-86 net accumulation is 1.0 m w.e. The anion profiles are very similar to those in Figure 4, except for the upper 20 cm, where a sulfate peak is significantly higher than in King Trench. Ice, fog and new snowfall since the King Trench sampling may have contributed to this peak. At 160 cm depth a small sulfate peak is seen. This and the upper peak may be caused by the Augustine volcanic emissions. On 23 May, at King Col, a brown haze was noticed to the northwest in Alaska. This may have been associated with emissions from Augustine volcano or from a forest fire.

By 12 June, a 6.4 m deep pit had been excavated over the 1980 bore-hole site on the NW Col of Mt Logan. Some partial results are plotted in Figure 7, where, according to the $^{18}$O depth relationship and the stratigraphy, the last (net) annual increment is 0.42 m w.e.

It has been established that the isotopic "season" typically follows the true season, with a
Fig. 8. Snow-pit analysis results from Mt Logan (1986): site 2, 5630 m. (a) oxygen-isotope data; (b) stratigraphy; ** = new snow, dashed lines = crusts, ~ = depth hoar; (c) specific electrolytic (liquid) conductivity; (d) pH; (e) nitrate, (f) chloride and (g) sulfate concentrations.

phase shift of up to a few months at this site. The "acidic" section of the core, from 40 to 70 cm depth, corresponds mainly to nitric acid. No positive volcanic signal is seen here, although there are weak increases in sulfate and chloride approximately where the Augustine eruption might be expected, at about 0.5 m depth.

On 13 June, a pit was dug on AINA Peak (site 2, 5630 m), where, according to the data in Figure 8, a possible volcanic (sulfate) peak may be seen, but it does not occur in the spring, where the Augustine eruption signature would be expected. From the NW Col on 16 June, thunder was heard originating from below a 4800 m cloud deck, suggesting that the snow falling at Eclipse might be enriched in nitric acid.

On 29 June, a pit was excavated at Eclipse (site 6, 3017 m) and core recovered to a depth of 13.2 m. Thunder was again heard on 30 June. Snow fell later that day and continued falling until 3 July. Forest-fire smoke originating in the vicinity of Dawson (Fig. 1) was detected on that date. Mt Logan was almost obscured by blue haze on 4 July. The upper limit of the visible haze was estimated at <4000 m. The 30 cm of new snow and the entire pit was sampled (the latter now in duplicate). Analytical results are presented in Figure 9. The upper 10 cm of snow, which fell at the same time as the forest-fire smoke, is relatively acidic (with a pH of 5.2) and the nitrate levels are the highest for the whole year.

Between 70 and 110 cm both a sulfate and a chloride pulse dominate the anion profiles. The species are usually diagnostic of volcanic events (Holdsworth and Peake 1985) and this signature is thus tentatively identified with the Augustine eruption of March 1986 (Kienle and others 1986). The eruption cloud was found to be rich in halides and the transition metals (Symonds and others 1987). Duplicate analyses within this interval of the pit confirm the presence of this major acid peak.

In order to determine whether a relationship exists between the concentration of acid anions species and altitude, or accumulation rate (Herron 1982), the relevant nitrate data from Figures 2, 4, 6, 7, 8, and 9, as well as from Holdsworth and Peake (1985), are plotted in Figure 10a and b. It should be noted that not all data are averaged over the same time span. Earlier data are averaged over intervals of several years, whereas the more recent data are confined to annual or sub-annual intervals. In the extreme case, Seward Glacier is represented by snow from only one storm.

If ionic dilution due to increased precipitation is a valid concept, then, evidently, an equation of the type

$$[C] = [C_0] A^{-\frac{1}{2}}$$

(Herron 1982), where [C] is the concentration of an ionic species in snow accumulating at rate A and [C0] is in constant, can only be applied to Mt Logan (and Greenland data) for A >500 kg m^{-2} a^{-1} (Holdsworth and Peake 1985). For A >500 kg m^{-2} a^{-1}, [C] \approx constant \approx 50 ng g^{-1}. Therefore, the depositional flux (CA) increases directly in proportion to increasing A, which generally corresponds to decreasing altitude. Either the evaporation efficiency of precipitation increases with A, or the air concentration of nitrate is higher at lower altitudes.

Figure 10a does not allow a simple spatial interpretation of the data. On the one hand, if we assume vertical gradients to exist in the nitrate concentration, high AINA Peak point would seem to be consistent with the identification of significantly higher [NO_3]_l levels between about 5 and 6 km (Huerteb and Lazrus 1980); on the other hand, the Mt Logan (ML) data point does not reinforce that interpretation, unless the increase in [NO_3]_l begins above about 5400 m at these latitudes.

Because most of the other sites possess less complete data set than the Yukon sites and the varying degrees of elution, only short summaries of results will be given in most cases.

Northwest Territories

The Flint Icefield site, located about 40 km north-north-east of the Canadian Tungsten Company's mine (Fig.1), possessed a high snow-pack water content and showed extreme 8^18O homogenization below 3 m. The 1981-82 accumulation was ~0.90 m w.e. (up to 10 June). The pH of melt water was measured in the field with a portable pH meter. For the upper 2.25 m the mean pH was 5.43, probably representative of ambient levels. This value may be influenced both by emissions from the mine operation and by the local rock outcrops of dolomite. Below the 1981 (summer) crust, the pH averaged 5.51, indicating the degree of elution after ~1 year.

British Columbia

The Mt Edziza (site 10, 2787 m) snow pack contained liquid water, and seasonal 8^18O variations indicated strong diffusion below a depth of 3 m. Some limited anion measurements showed that SO_4^2- is preferentially eluted with respect to NO_3^- and Cl^- Furthermore, one sample showed high values for all those ions, indicating a (temporary) entrapment.
Tellot Glacier Col (site 11, 3020 m), although a temperate site, showed a fairly well-preserved $^{18}O$ core record but it was difficult to interpret. No anionic data are available but it should be a useful site for some short-term chemical and isotopic studies (Holdsworth 1982).

Alberta

Data from two separate cores obtained in 1984 and 1986 from Snow Dome on Columbia Icefield (site 12, 3460 m) are presented in Figure 11 (Holdsworth and others 1985). These data show that elution occurs with varying degrees of intensity in different years. The upper 2 m of snow show levels of the major anions which are not considered to have been affected by elution. At the other extreme, the section between 8 and 10 m has been subjected to elution, such that, for most of the section, sulfate concentrations are below the detection limit. The nitrate ion shows moderate elution but chloride appears to be unaffected. It is interesting to note that the mean $[Cl^-]$ level for both cores (13.8 ng g$^{-1}$) lies exactly on the theoretical altitude-depletion curve for marine chloride (Herron 1982). Homogenization of the $^{18}O$ values below 8 m is almost complete. At 11.3 m depth the layer was identified and has been assigned to a large forest fire that occurred in August 1971 (Holdsworth and others 1985). The ash occurs in ice which may have impeded subsequent percolation, as suggested by the levels of $[NO_3^-]$ and $[SO_4^{2-}]$ above that layer. A relatively high level of nitrate is seen to be associated with the ash layer. Whether this is the result of a pile-up in the elution process or whether it is a reflection of the original $NO_3^-$ levels is not known. That the latter case may be the more correct one is suggested by the data in Figure 11b. Carbon flakes were found in the samples to a depth of 0.6 m, representing late-summer deposits. Late-summer forest-fire smoke was detected in this region. The late-summer and fall snow may have been reworked, as this is a very windswept site.

The anion analyses of the uneluted 1985-86 winter-spring snow pack in the accumulation zone of Peyto Glacier (site 13, 2785 m) clearly show the winter minimum and a spring maximum in both $[NO_3^-]$ and $[SO_4^{2-}]$.

SUMMARY AND CONCLUSIONS

For the Yukon sites, covering a wide range of altitudes, it is possible to identify an altitude above which reliable sampling from cores on a long-term basis is viable. This level is $\approx$3000 m on exposed snow fields and cols. Some information is, however, available from sites showing elution: first, in extreme cases, the sub-detection limit ionic-concentration data demonstrate that sampling and subsequent analytical procedures do not introduce significant contamination. Secondly, in some cases preferential elution of ionic species can be seen (Davies and others 1982). An elution sequence is given by Brimblecombe and others (1985) which shows that $SO_4^{2-}$ eluted before $NO_3^-$, but this result does not appear to be invariable. In addition, several variations are given within the full sequence of nine ions studied by Brimblecombe and others (1985). The data for Seward Glacier (Fig.2) suggests a partial sequence of $[NO_3^-] > [SO_4^{2-}] > [Cl^-]$ considering only those ions, whereas for Snow Dome (Fig.11) and the Mt Edziza data (not shown), the relative elution sequence is:

$[SO_4^{2-}] > [NO_3^-] > [Cl^-]$ in agreement with Brimblecombe and others (1985). Other ionic and particulate components, and even chemical reactions in the snow pack, may have important effects on the chemistry of the snow and might play a role in determining the diffusion speed of certain ionic species and, hence, their relative elution rate and subsequent removal from a specific location. Insoluble components, such as carbon flakes from forest fires, have been positively identified in the Snow Dome samples. These particles and other unidentified components may play a role in the relative elution rates of ionic species.

Forest-fire smoke fall-out is seen to have a profound effect on the chemistry of snow associated with these events. For the Eclipse site (Yukon) (Fig.9), the specific electrolytic conductivity of this snow (4.7 $\mu$S cm$^{-1}$) was the highest for the whole profile. The nitrate level is high and it is possible that organic acids are also present. On Snow Dome (Alberta), forest-fire fall-out can be indentified positively and associated with elevated levels of nitrate. The likelihood that organic acids or their derivatives may be present in many of the mountain snow-field sites (which are surrounded by forests) is suggested by the work of Irrribarne and Shewchuk (1985). The association of forest fires with lightning storms suggests the possibility that some of the nitric acid present in the snow is derived from the lightning discharges. Extreme forest fires could have long-range effects on remote areas.

The Mt Logan and other Yukon data suggest that a simple interpretation of acid ionic concentrations with respect to accumulation rate and altitude is not yet possible and that a complete interpretation of the aerosol-scavenging process would at least require the use of more long-term data, as well as data from many individual storms at each site.

That the 1986 Augustine volcanic eruption seems to be present only at the Eclipse site and only possibly at one of the others (the NW Col data are not considered to be compelling enough) presents an interesting problem. The aerosols may possibly have been present at the Mt Logan site, but erosion due to the intense local storms may have erased the signature. This effect would be more acute at the higher, more exposed, and lower accumulation-rate sites. Alternatively, and more likely, is the possibility that the eruption cloud may have been confined largely to the lower troposphere and may only have been recorded by the occurrence of precipitation at Eclipse, as an air-mass divergence may form between the Mt Logan and Eclipse sites. Also, since the forest-fire smoke-cloud event witnessed at Eclipse arrived from the north-east during an anticyclonic omega block situation, it is quite possible that the upper Mt Logan sites missed the event altogether, especially if the cloud was confined to the lower troposphere. We have unpublished data which indicate that the Chernobyl nuclear-explosion cloud is identifiable at Eclipse but not on the NW Col of Mt Logan. This event was known to be largely confined to the lower troposphere. The two large $[SO_4^{2-}]$ peaks (associated with minor chloride peaks) seen in the lower part of Figure 8 have not
been explained; they are not seen elsewhere. These data and the data discussed above show that the identification of volcanic events in snow samples even within an area of 3000 km² is not an easy matter.

At the NW Col site on Mt Logan, the annual averages of both NO₃⁻ and SO₄²⁻ still do not differ significantly from pre-1980 volcanically "quiet" period values, which do not show a trend this century (Holdsworth and Peake 1985).

ACKNOWLEDGEMENTS
We thank B Mottle, S Swacha, B Holiday and K Dunn for chemical analyses, and A Williams for field logistic support. Use of the facilities of the Arctic Institute of North America at Lake Kluane and at the University of Calgary are appreciated.

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