

## DOES SNOW HAVE ION CHROMATOGRAPHIC PROPERTIES ?

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### ABSTRACT

In this study we investigate whether or not grains of metamorphosed snow (ice crystals) can act as a chromatographic column selectively adsorbing and retaining inorganic ions. The chromatographic process has been proposed as a potential mechanism to explain the preferential elution of inorganic ions observed in water from melting snowpacks. Experiments were conducted using a 1.8-cm-diameter by 30-cm-long Pyrex glass column filled with frozen droplets and natural snow grains. Deionized water and solutions containing known dilute concentrations of sulfate, nitrate and chloride were then slowly allowed to flow down through the column and the eluant was collected in 1-mL aliquots. An experiment specifically designed to detect chromatographic effects showed all three species appeared at the bottom of the column simultaneously, indicating that ice surfaces exhibit no preferential affinity for these anions.

### INTRODUCTION

When a snowpack melts, the concentration of solutes in the resulting meltwater is not constant but varies with time: the initial 30% of meltwater contains 50-80% of the total solutes (Johannassen et al., 1975; Johannassen and Henriksen, 1978). This phenomenon, colloquially called "acid flush" because nitric and sulfuric acids are major constituents in the initial meltwater, has been known for over a decade and is now technically referred to as "fractionation."

Another more recently discovered process that occurs in melting snowpacks is that of "preferential elution" or temporal ion differentiation within the highly concentrated or fractionated initial snowpack meltwater. That is, not all ions are enriched to the same extent and some ions elute or are removed sooner than others. This process was first reported by Davies et al. (1982) and has been extensively investigated experimentally by Brimblecombe, Tranter, Davies and co-workers since then. Although the specific order of elution varies with the age of the snow and its chemical composition, generally  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  appear in meltwater fractions before  $\text{Cl}^-$ . The exact cause of preferential elution is still poorly understood. One proposed explanation is that there may be chromatographic effects when meltwater percolates downward through a snowpack (Tranter et al. 1986). In other words the snowpack itself acts as an ion chromatograph with ice grains selectively retaining and retarding the elution of certain ions (e.g.,  $\text{Cl}^-$ ) over others (e.g.,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ ). It is well known that solid surfaces (metal, plastic and glass) can sorb molecular vapors and ions from air and aqueous solutions. The extent and strength of this sorption depends upon the physical and chemical properties of both the adsorbed species and the substrate. As a substrate, snow can sorb molecular vapors such as  $\text{SO}_2$  and  $\text{NO}_x$  from the atmosphere (Valdez et al., 1987). In this study we investigate the probability of metamorphosed snow grains (ice crystals) acting as a chromatographic column selectively adsorbing and retaining inorganic ions.

### EXPERIMENTAL

The flow of spring meltwater through metamorphosed snow grains was simulated using a 1.8-cm-diameter by 30-cm-long glass column filled with natural snow grains or frozen deionized water drops (Fig. 1). The column was made by replacing the stopcock of a Pyrex 100-mL burette with a plastic three-way valve. Teflon tubing attached the valve to the glass column. A 5-cm<sup>3</sup> plastic Luer-Lok (Becton Dickinson) syringe was connected to the horizontal port of the three-way valve. The vertical path of the three-way valve transferred aliquots of the column eluant to a collection vial (1.5-mL, Perkin-Elmer sample cup).

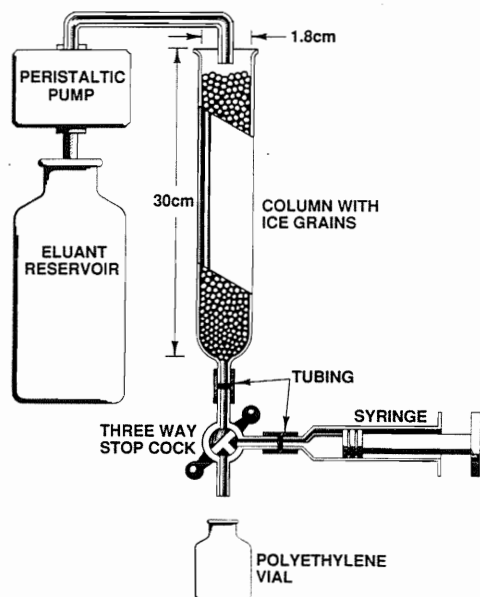


Figure 1. Schematic of apparatus used for chemical elution experiments. Not to scale.

Table 1. Bulk ionic composition of homogenized natural snow used for chemical elution experiment.

Ion	Concentration (mg/L)
H <sup>+</sup>	0.022 (pH = 4.7)
Na <sup>+</sup>	0.31
K <sup>+</sup>	0.017
Ca <sup>2+</sup>	0.058
Mg <sup>2+</sup>	0.0095
Cl <sup>-</sup>	0.52
NO <sub>3</sub> <sup>-</sup>	1.1
SO <sub>4</sub> <sup>2-</sup>	0.51

Table 2. Composition of solution used to prepare synthetic snow grains.

Ion	Concentration (mg/L)
H <sup>+</sup>	0.1 (pH = 4.0)
Cl <sup>-</sup>	0.50
NO <sub>3</sub> <sup>-</sup>	6.2
SO <sub>4</sub> <sup>2-</sup>	5.0

Table 3. Composition of eluant solution used for anion chromatographic experiment.

Ion	Concentration (mg/L)
H <sup>+</sup>	0.01 (pH = 5.0)
Cl <sup>-</sup>	0.10
NO <sub>3</sub> <sup>-</sup>	1.0
SO <sub>4</sub> <sup>2-</sup>	1.0

The column was filled with one of the following packings: natural snow grains, frozen solution drops, or frozen deionized water drops. Compositions of the natural snow samples and the solution used for the frozen drops are given in Tables 1 & 2, respectively. Artificial ice beads were made by freezing approximately 10- $\mu$ L drops of deionized water (Milli Q, Millipore Corp.) or deionized water spiked with chloride, nitrate and sulfate (Table 2). The water droplets were frozen on polyethylene sheets in a Class 100 clean air station located inside a coldroom at -12°C. The frozen hemispherical drops weighed an average 6.4 mg, loss of mass being attributed to evaporation.

Deionized water or deionized water spiked with chloride, nitrate and sulfate concentrations representative of precipitation (Table 3) were employed as column eluents.

All labware was washed with soap and water and then rinsed several times with deionized water in a Class 100 clean air station.

Analytical standards for the determination of Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> were prepared from NaCl, KNO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (Baker, reagent grade). The concentration of the working standards and the determination of pH was verified daily by the analysis of the National Institute of Science and Technology simulated rain water reference standards SRM-2694 I&II.

Analyte concentrations were determined by using flame (FAA) and graphite furnace atomic absorption (GFAA) spectrophotometry, ion chromatography and pH measurement. The small (1-mL) aliquot restricted analysis volumes to less than 200  $\mu\text{L}$  per instrumental technique.

Anions were determined with a Dionex Model 2010i ion chromatograph, equipped with a HPICE-AS3 separator column, AFS 1-2 anion fiber suppressor and 50- $\mu\text{L}$  sample loop. The eluant was 3 mM  $\text{NaHCO}_3$ /2.4 mM  $\text{Na}_2\text{CO}_3$  and the regenerate was 25 mN  $\text{H}_2\text{SO}_4$ , flowing at 2.9 mL/min and 3.0 mL/min, respectively.

The determination of ammonium ion was also performed by ion chromatography. For this analysis a HPIC CS-1 separator column, CFS 1-2 cation fiber suppressor, and 100- $\mu\text{L}$  loop were employed. The eluant was 7.5 mM  $\text{HCl}$ , with a flow rate of 2.3 mL/min, and the regenerate was 0.04 M  $\text{Ba}(\text{OH})_2$ , with a flow rate of 3.0 mL/min.

Hydrogen ion concentrations were established with a MI-410 micro-combination pH electrode (Microelectrodes, Inc.). Quiescent 100- $\mu\text{L}$  aliquots were measured after the electrode was calibrated with low ionic strength buffers (Orion).

Sodium concentrations were determined by FAA with a Perkin-Elmer Model 403 spectrophotometer. To reduce the sample volume 100  $\mu\text{L}$  aliquots were injected into a conical vial before aspiration into the burner chamber.

Potassium, calcium and magnesium were determined by GFAA with the same spectrophotometer and a Perkin-Elmer Model 2200 heated graphite atomizer.

#### Experimental Method

Column elution experiments were conducted within a Class 100 clean air station in a coldroom at 0°C. At the start of an experiment the aqueous solutions passed onto the columns were 2°C. Eluant solution flow of approximately 0.5 mL/min onto the column was metered with a peristaltic pump (Buchler Instr.). The eluant (deionized water or deionized water spiked with dilute acids and salts) appeared to wet the surface of all the column packing. Column eluant was removed by suction created by the syringe. Volumes ranging between 200 and 500  $\mu\text{L}$  were pulled off the column through the three-way valve into the section of tubing attached to the syringe. The three-way valve was then turned so this aliquot could be pushed into a collection vial. Once the vial contained 1 mL it was removed and emptied into a 7.5-mL CPE polyethylene bottle. The collection vials were rinsed with deionized water between samples. After eluant flow onto the column was stopped only a single additional aliquot could be obtained. The column packing surface areas for the natural snow grains and the frozen droplets were approximately  $1.4 \times 10^3$  and  $1.0 \times 10^3$   $\text{cm}^2$ , respectively. Column retention volumes were about 4.5 mL for the snow grains and 3 mL for the frozen droplets. If we assume uniform coverage of the column packing, the wetted surface was approximately 3  $\mu\text{m}$  thick.

#### RESULTS AND DISCUSSION

Three different types of column elution experiments were conducted for this study using (1) natural snow grains and deionized water, (2) frozen solution drops and deionized water and (3) frozen deionized water drops and synthetic salt solutions.

For the first experiment the column was filled with approximately  $2 \times 10^4$  natural snow grains (1-2 mm) collected in March 1987 from a rural snowpack in Hanover, New Hampshire. The bulk chemical composition of this snow, as determined by triplicate analysis after homogenization, is given in Table 1. Deionized water was applied (0.5 mL/min) to the top of the column and 1-mL aliquots of eluant were collected at the bottom. Concentrations of cations (Fig. 2) and anions (Fig. 3) are as much as 4.5 times higher in the initial eluant than in the bulk snow itself. Divalent ions (calcium, magnesium and sulfate) are fractionated to a greater extent than univalent ions. The high initial concentration aliquots decrease exponentially and appear to stabilize after the eighth aliquot. The concentration of the least fractionated ion, chloride, shows the smallest change and was always less than the bulk snow concentration, partially because of dilution by the deionized water.

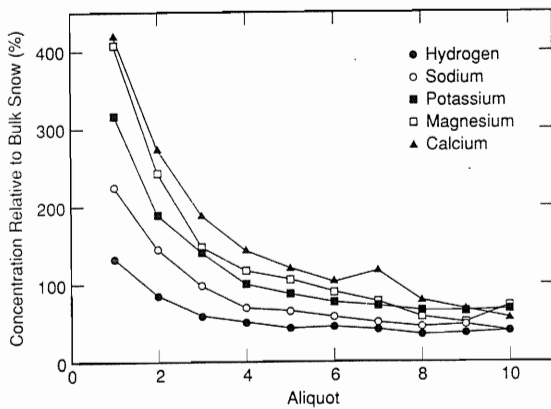


Figure 2. Cation concentrations in sequential aliquots for natural snow elution. Concentrations have been normalized to bulk snow concentrations.

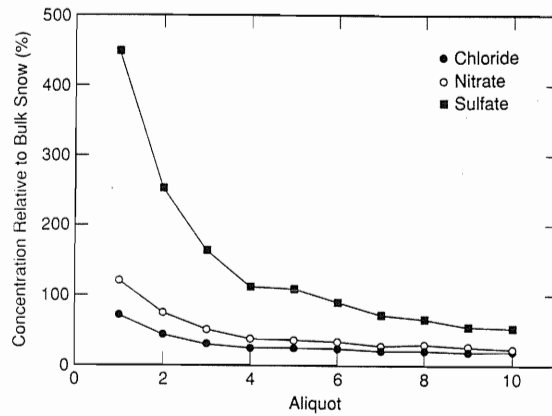


Figure 3. Normalized anion concentrations in sequential aliquots for natural snow elution.

Other ions were also diluted by the eluant, reducing their concentrations so that the actual enrichment (fractionation) would have been quite higher if the snow grains were allowed to melt naturally. Using deionized water for elution reduced the time of the experiment from an estimated 10-12 hours to about 30 minutes. Of the five cations studied, hydrogen ion shows the least relative enrichment (Fig. 2). Thus, the term "acid flush" is somewhat misleading since other constituents are also fractionated and to a greater degree.

Figures 2 and 3 show the effects of chemical fractionation but preferential elution is not readily apparent. Ionic ratios (Fig. 4) show the early elution of sulfate, and to a lesser degree nitrate, relative to chloride. Notice that the ratios plotted in Figure 4 have been normalized to the corresponding ratios in the bulk snow so that even with the high enrichments (fractionation) of initial aliquots, sulfate and nitrate appear earlier (elute earlier or preferentially) than chloride.

As an indirect check on the accuracy of our analytical methods and to determine if we measured all major constituents present in the snow, anion/cation ratios were calculated and are plotted in Figure 5. Ideally, this ratio should be unity for ionic balance and electroneutrality. Generally, the ratio is near unity but with a slightly decreasing trend from 1.1 for the first aliquot to about 0.8 for the tenth aliquot. While some of the deviation could be due to experimental error ( $\pm 5\%$  for each ion) this effect would be random and would not be expected to produce an apparently steady trend. Alternatively, since the ratio decreases with aliquot, an unanalyzed cation may be present later in the

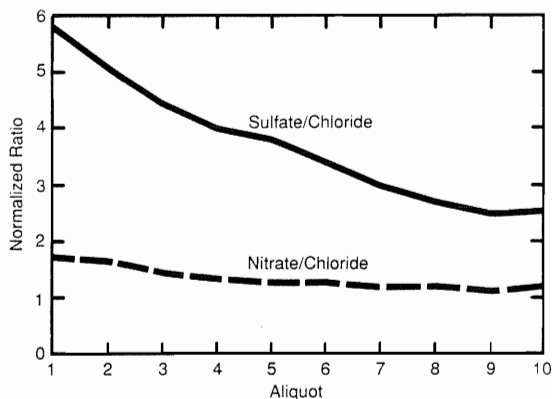


Figure 4. Normalized  $\text{SO}_4^{2-}/\text{Cl}^-$  and  $\text{NO}_3^-/\text{Cl}^-$  ratios in sequential aliquots for natural snow elution.

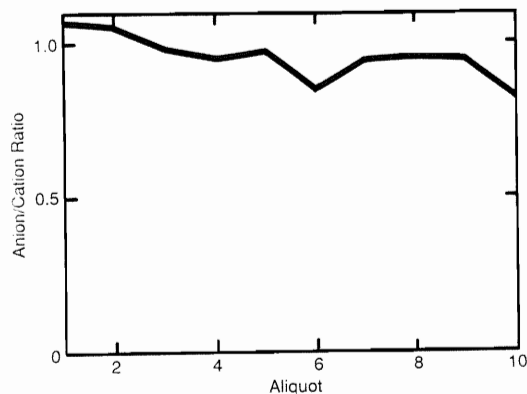


Figure 5. Ion balance for natural snow elution. Anion/cation ratios were calculated from summed concentrations in  $\mu\text{eq/L}$ .

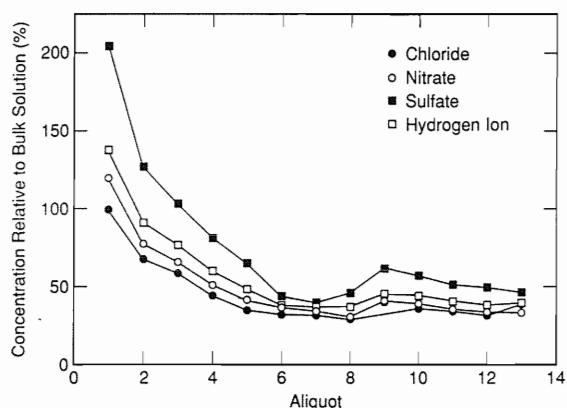


Figure 6. Normalized anion concentrations in sequential aliquots for elution from frozen solutions drops.

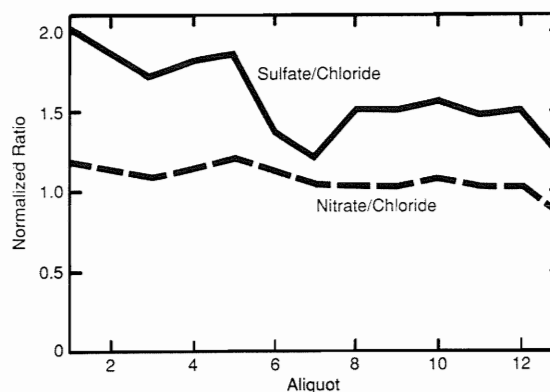


Figure 7. Normalized  $\text{SO}_4^{2-}/\text{Cl}^-$  and  $\text{NO}_3^-/\text{Cl}^-$  ratios in sequential aliquots from frozen solution drops.

elution sequence. An obvious choice of cation would be  $\text{NH}_4^+$ , but the concentrations we determined were too low to explain the observed differences. This decreasing anion/cation ratio has also been observed in natural snow samples by others and has been tentatively attributed to dissolved forms of organic carbon (M. Tranter, Univ. of Southampton, UK, personal communication).

To simulate the fractionation and preferential elution processes in the laboratory, we prepared a synthetic metamorphosed snow grains by freezing a solution containing the ions and concentrations shown in Table 2. These anion levels are typical of acid snow for the northeast United States. The column was filled with approximately 5000 frozen hemispherical droplets of this solution and, as with the natural snow grains in the previous experiment, eluted by slowly passing deionized water downward. Concentrations in the eluant (Fig. 6) are initially high (2-fold for  $\text{SO}_4^{2-}$ ) and decrease rather rapidly as elution progresses. The fact that the relative chloride concentration in the first aliquot is 100% (i.e., the same as the bulk snow) is fortuitous and simply indicates that any fractionation present was offset by dilution with the deionized water used for elution. Again, fractionation (Fig. 6) and preferential elution (Fig. 7) are occurring but to a smaller extent than in natural snow grains; e.g., for  $\text{SO}_4^{2-}$  only a 2-fold enrichment is present for the frozen solution drops instead of the 6-fold enrichment over bulk for natural snow.

From the previous two experiments it was not possible to distinguish if the observed preferential elution was caused by an actual chromatographic sorption mechanism or if it was due to the fact that the initial meltwater from ice grains surfaces had a different composition than the later melting and eluting inner grain material as has been recently proposed by Brimblecombe et al. (1987, 1988). The third type of elution experiment was designed specifically to determine whether or not snow has ion chromatographic properties. This experiment was essentially the reverse of the second experiment: instead of percolating distilled water through frozen solution drops, a synthetic solution representative of natural precipitation (composition given in Table 3) was allowed to flow through a column of frozen distilled water drops.

Results of this experiment are shown in Figure 8 for the three anions studied. As in any chromatographic analysis, the column was first conditioned with carrier liquid, in this case deionized water. The synthetic snow solution was treated as would a "sample" in standard chromatographic analysis, "injected" and then allowed to flow downward through the column. Sample flow onto the column occurred between collection of the fourth and fifth aliquot as indicated by the arrow on the abscissa. After a short period of sample application the eluant was then switched back to deionized water (second arrow on abscissa of Fig. 8). The high concentration of chloride in the first aliquot was due to a small but finite amount of impurity ( $2.2 \mu\text{g Cl}^-/\text{L}$ ) in the deionized water used to prepare the frozen droplets used in the column. Chloride in the deionized water was excluded as the drop freezes and is forced to the surface. Then, when deionized water flowed over the frozen droplet in the column, the chloride near or on the surface was released first. Shortly after the synthetic snow solution was applied, concentrations of all three anions rose

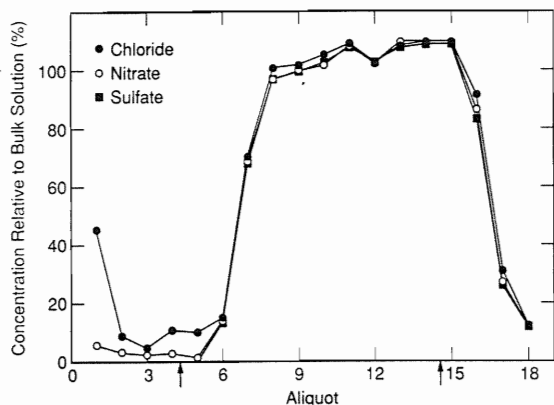


Figure 8. Normalized anion concentrations in sequential aliquots for chromatographic experiment using frozen deionized water drops. Arrows on abscissa indicate the beginning and the end of application of synthetic snow solution.

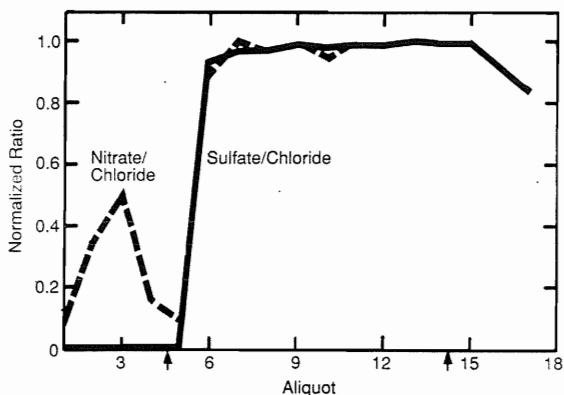


Figure 9. Normalized  $\text{SO}_4^{2-}/\text{Cl}^-$  and  $\text{NO}_3^-/\text{Cl}^-$  ratios in sequential elution aliquots for chromatographic experiment where synthetic snow solution was allowed to flow over frozen distilled water drops. Arrows on the abscissa are the same as for Figure 8.

simultaneously to that of the bulk solution and remained at this level through succeeding aliquots until they decreased to background levels once deionized water was reapplied. Throughout the experiment all normalized concentrations paralleled each other very closely and were even superimposed for many of the aliquots.

Normalized ionic ratios (Fig. 9) were constant and essentially unity throughout the duration of the experiment when synthetic solution was applied. All three ions eluted simultaneously (i.e., no preferential elution), indicating that sorptive chromatographic effects are absent for these three anions.

If it is not chromatographic, what, then, is the cause of preferential chemical elution in snowpack meltwater? Previously, Tsiouris et al. (1985) observed preferential chemical elution from snow grains that had been aged for one year in a coldroom. But the same snow sample showed no preferential chemical elution when it was originally collected. This indicates to us that preferential elution is related to processes occurring during snow metamorphosis. We hypothesize that selective exclusion of ions during grain growth, whether occurring in a coldroom or natural snowpack, produces mature snow grains that have enriched chemical concentrations on the surface compared to the interior. Although growth of snow grains occurs from the vapor state (no melting is required) the exclusion of ionic salts is analogous to the rejection of ions from a slowly freezing salt solution. Because different ions are excluded with different efficiencies, the ionic ratio in the surface portion of the grains is different from that within the grain interior and the bulk snow itself. Generally, sulfate salts are less soluble and more efficiently excluded than the more soluble chlorides (Gross 1968). Both fractionation and the order of preferential chemical elution are consistent with this hypothesis. The composition of snow meltwater has been modelled in terms of the mixing of two different solutions: a highly concentrated surface brine and a more dilute solution from grain interiors (Brimblecombe et al. 1988). While this model is also useful, the snow metamorphic process is a major mechanism strongly influencing both fractionation and preferential chemical elution. Future efforts toward a better understanding to these two processes should focus upon the simultaneous physical and chemical changes taking place during snow metamorphosis.

## CONCLUSIONS

The initial fractions of meltwater from natural snow have ionic concentrations that are two to six times higher than that of the bulk snow from which they originate. Initial fractions of meltwater from frozen solution droplets also contain higher concentrations than the bulk solution from which they are prepared, but these fractions are two to three times less concentrated than comparable fractions from natural snowmelt. During controlled laboratory experiments ice grains did not exhibit any chromatographic sorption for  $\text{Cl}^-$ ,  $\text{NO}_3^-$  or  $\text{SO}_4^{2-}$ , indicating that the preferential chemical elution observed in snowpack meltwater is not due to an ion chromatographic process.

#### REFERENCES

- Brimblecombe, P., S.L. Clegg, T.D. Davies, D. Shooter, and M. Tranter (1987) Observation of the preferential loss of major ions from melting snow and laboratory ice. Water Resources, Vol 21, pp. 1279-1286.
- Brimblecombe, P., S.L. Clegg, T.D. Davies, D. Shooter, and M. Tranter (1988). The loss of halide and sulfate ions from melting ice. Water Resources, Vol 22, pp. 693-700.
- Davies T.D., C.E. Vincent and P. Brimblecombe (1982) Preferential elution of strong acids from a Norwegian ice cap. Nature, 300, pp. 161-163.
- Gross, G.W. (1968) Some effects of trace inorganics on the ice/water interface. Trace Inorganics in Water, 153rd ACS Symposium, Miami, FL, American Chemical Society, 73, pp. 27-97.
- Johannessen, M., T. Dale, E.T. Gjessing, A. Henriksen, and R.F. Wright (1975) Acid precipitation Norway: The regional distribution of contaminants in snow and chemical processes during snowmelt. Proceedings of Isotopes and Impurities in Snow and Ice, Grenoble, 1975, Int. Ass. Sci. Hydrol. Publ., 118, pp. 116-120.
- Johannessen, M. and A. Henriksen (1978) Chemistry of snow meltwater: changes in concentration during melting. Water Resources Research, 14, pp. 615-619.
- Tranter, M., P. Brimblecombe, T.D. Davies, C.E. Vincent, P.W. Abrahams and I. Blackwood (1986) The composition of snowfall, snowpacks and meltwater in the Scottish highlands - evidence for preferential elution. Atmospheric Environment, 20, pp. 517-525.
- Tsiouris, S., C.E. Vincent, T.D. Davies and P. Brimblecombe (1985) The elution of ions through field and laboratory snowpacks. Annals of Glaciology, 7, pp. 196-201
- Valdez, M.P., Bales, R.C., D.A. Stanley and G.A. Dawson (1987) Gaseous deposition to snow 1. Experimental study of SO<sub>2</sub> and NO<sub>2</sub> deposition. Journal of Geophysical Research, 92, pp. 9779-9787.

