Ion Enrichment of Snowmelt Runoff Water
Caused by Basal Ice Formation

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ABSTRACT

Once meltwater reaches the base of a snowpack it can infiltrate the underlying stratum, runoff, or refreeze and form a basal ice layer. Basal ice formation is most common early in melt over saturated or very cold frozen soils. Meltwater becomes enriched in ion concentrations compared to the parent snow due to ion fractionation during thaw and percolation through the snowpack. If ion exclusion occurs during basal ice formation, further enrichment of runoff water ion concentrations can occur. The influence of basal ice formation on runoff water chemistry was examined by comparing ion concentrations in runoff water that had sustained basal ice contact, to meltwater before basal ice contact. A series of experiments, involving melting a snowpack in a large insulated box over a cold impermeable substrate in a temperature-controlled room, were carried out. A cooling system at the chemically inert base ensured frozen conditions during snowmelt. Meltwater samples were collected throughout melt from within the snowpack using an extraction tube, and runoff water was collected at the base. All samples were analyzed for major anions and cations. Results showed that formation of basal ice layers enriched the runoff water compared to meltwater before basal ice contact. Ion concentrations in basal ice contact runoff water were up to sixteen times greater than those in no-contact meltwater; however, on average, basal ice contact runoff water showed 1.5 times the ion concentrations of the no-contact meltwater. The implications are that basal ice formation will act to strongly alter both meltwater ion pathway and concentration. When no basal ice is present, enhanced infiltration of meltwater ion load can cause relatively dilute runoff water. When basal ice is present all meltwater runs off and further ion concentration enrichment occurs.

Keywords: basal ice; super-imposed ice; snow chemistry; runoff; frozen ground; enhanced infiltration

INTRODUCTION

Snowpack metamorphism and refreezing of meltwater within the snowpack relocates incorporated ions to quasi-liquid layers on the grain surface and between grains (Colbeck, 1981). This partitioning, or ion exclusion, occurs because of the individual ions lack of ability to become incorporated into the crystal lattice of ice (Davies *et al.*, 1987). The ability is related to the ion's hydrated radii and capability to form hydrogen bonds. For instance, ions such as Na^+ and Cl^- are incorporated more readily into the ice crystal lattice than NO_3^- and SO_4^{2-}. These excluded ions can be readily mixed with percolating meltwater, enhancing initial meltwater ion concentrations.

Studies have shown an initial 2- to 7-fold enrichment in ion concentrations in the meltwater released at the base of the snowpack compared to the bulk composition of the parent snowpack

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(Johannessen and Henriksen, 1978). A typical ion elution curve shows initial enrichment followed by a rapid decrease until the meltwater is depleted relative to the parent snowpack (e.g. Johannessen and Henriksen, 1978); this is referred to as ion fractionation. Studies have shown that the depletion occurs after approximately one-third of the total melt period. Fractionation is influenced by ion distribution within the parent snowpack, melt-freeze cycles, rain-on-snow events, snow depth, and preferential flow through the snowpack (e.g. Colbeck, 1981; Davies *et al.*, 1982; Marsh and Pomeroy, 1999). Consequently, snow meltwater chemistry may be strongly influenced by processes occurring weeks or months prior to melt (Cragin *et al.*, 1996).

Once the meltwater reaches the base of a snowpack it can infiltrate the underlying stratum, run off, or pond. Ponding occurs when melt rates exceed infiltration rates and may result in the formation of a basal ice layer if there is sufficient heat flow into the soil (Woo and Heron, 1981). The rate of heat released by the growth of the basal ice layer, Q [kg m^{-2} s^{-1}], can be approximated as:

$$Q = (\rho_i - \rho_s)\lambda \cdot \frac{dz}{dt}$$
(1)

where ρ_i and ρ_s are the respective densities of the basal ice and the snowpack [kg m^{-3}], λ is the latent heat of fusion [333 kJ kg^{-1}], and dz/dt is the rate of ice growth [m s^{-1}] (Woo and Heron, 1981).

Basal ice layers have been observed in both glacial environments, where it is referred to as superimposed ice (e.g. Wakahama *et al.*, 1976), and non-glacial environments (e.g. Woo *et al.*, 1982; Marsh and Woo, 1984; Stein *et al.*, 1994). Several studies have looked at the importance of basal ice formation on meltwater routing in both environments (e.g. Wakahama *et al.*, 1976; Jones and Pomeroy 2001). The influence that a growing basal ice layer has on runoff chemistry was inferred by Jones and Pomeroy (2001) as they observed considerable increases in NO_3^- concentrations as the percentage of concrete frost in the watershed increased to 75%. However, to the knowledge of the authors, no laboratory studies have presented the influence that a growing basal ice layer has on runoff chemistry.

The objective of this paper is to identify, in a controlled setting, whether meltwater flow in contact with a basal ice layer becomes enriched in ion concentrations compared to meltwater, which has no contact with a basal ice layer. It is hypothesized that ion exclusion takes place during basal ice formation and that an enriched brine will be present at the basal ice surface, which mixes with meltwater in contact with it.

METHODOLOGY

An insulated box, with a cooling system at the base, was used to control snowmelt and basal ice formation (Figure 1). Expanded polystyrene plates were used as insulation. The front of the box had a slit along the base for collection of runoff water, which had sustained basal ice contact (BW). An acrylonitrile butadiene styrene (ABS) half-pipe was placed with its base ~30 mm above the slit opening for extraction of meltwater before basal ice contact (SW). The half-pipe covered a tenth of the base area. The base consisted of an inert metal plate, which was underlain by a cooling system that was connected to a temperature controlled refrigerated bath (RTE-DD8, Neslab). The whole setup was tilted 8º.

Variations in snowpack temperature were measured using thermocouples (TC; type-E and -T); they were placed at the base and 10, 20, 30, 40, and 45 cm above the base. A TC (type-K) was used to measure the temperature of the coolant. Temperatures were samples every 10 s; averaged temperatures were recorded every 15 minutes by a Campbell Scientific Canada 23X datalogger.

Materials that did not have a chemically inert surface were covered by polyethylene to avoid contamination. All materials used were cleaned thoroughly with deionized distilled water (DDI). Plastic gloves were worn at all times to prevent contamination.
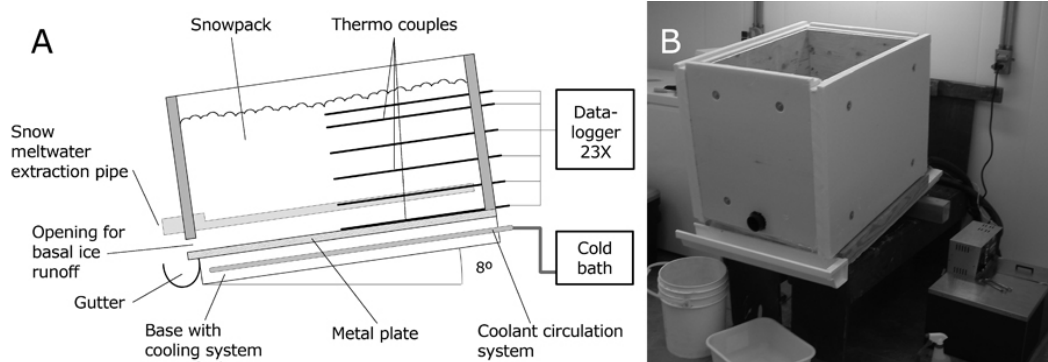
Figure 1. A) Schematic drawing of the experimental box and its instrumentation (not to scale). B) The actual box placed in the temperature controlled room.

Three experiments were conducted using snow from a site located within city limits (experiment 1) and two sites located in rural areas (experiment 2 and 3). The snow used in experiment 1 and 2 was a few days old, but metamorphism was not pronounced. Fresh snow was used in experiment 3. In all experiments, the snow was composed of loose 1-2 mm crystals. The chemical compositions of the parent snow were dominated by magnesium and calcium (Table I).

To homogenize the snowpack, the snow was sieved with an 8 mm mesh (HDPE). The depth of the snowpack was 0.45 m, giving a total snow volume of 0.15 m^3 within the box. The densities of the snowpacks were ~350 kg m^{-3} in the first experiment, ~410 kg m^{-3} in the second, and ~215 kg m^{-3} in the third. The snow was then left to reach thermal equilibrium; room temperature was –2 ºC and coolant temperature was set at –5 °C, –4 °C, and –3 °C in each experiment, respectively. Once thermal equilibrium was reached, the room temperature was increased to +5 ºC. Small adjustments of the coolant temperature were made throughout the experiment to ensure formation of basal ice. These adjustments were made based on the TC readings at the base of the snowpack.

During melt, water samples (BW and SW) were collected simultaneously twice a day. Minimum sample size was 60 ml due to analytical methods.

All water samples were stored cold until filtered through 0.4 µm Nuclepore filter paper. Prior to filtration, pH was measured using an Orion 290A meter with an Orion low maintenance triode. Chloride was measured using ion chromatography (Dionex ICS 2000); detection limit was 0.1 mg l^{-1}. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used for SO_4^{2-} analysis; detection limit was 0.1 mg l^{-1}. Standard analytical methods according to American Public Health Association (APHA) were used for Cl^- and SO_4^{2-} (Eaton and Franson, 2005). Analyses of Na^+, K^+, Mg^{2+}, and Ca^{2+} were done with atomic absorption spectroscopy (SpectrAA 220, Varian). Detection limits were 0.25 mg l^{-1} for Na^+, 1.0 mg l^{-1} for K^+, 0.15 mg l^{-1} for Mg^{2+}, and 2.0 mg l^{-1} for Ca. Samples analyzed for cations were acidified with H_2SO_4 to pH 2 to limit further chemical reactions. Blind samples for QA/QC, ~10% of total number of samples collected, comprised of duplicate runoff water and meltwater samples. If they were not within ± 15% of any measured parameter, samples were reanalyzed. Ion balances were not assessed as analyses of NO_3^- and NH_4^+ could not be done. In-between filtering and analyses, samples were stored at –20 ºC.

Table 1. Ion concentrations [µeq l^{-1}] in the parent snowpacks.

Exp. #	H^+	Cl^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}
1	0.009	12.7	11.5	5.5	6.2	22.8	73.7
2	0.077	25.3	35.4	15.1	11.0	30.9	84.5
3	0.428	9.8	11.5	3.1	8.4	25.0	13.0

RESULTS

The three experiments differed with respect to snowpack density, melt rate, and temperature at the base of the snowpack. In all of the experiments both density and melt rate increased as melt progressed (Figure 2). The greatest increase in snowpack density was observed in experiment 1 with ~56 kg m^{-3} d^{-1}. This experiment showed the lowest average melt rate (5.9 mm d^{-1}) and smallest cumulative reduction in snow water equivalent, SWE (7.4 mm) of all the experiments. The greatest daily melt rate was observed in experiment 2 at 17.6 mm d^{-1}. Average melt rate was 7.7 mm d^{-1} resulting in a cumulative loss of SWE of 25.4 mm, the greatest of all experiments. The increase in density for experiment 2 was about a fifth of the other experiments; ~11 kg m^{-3} d^{-1}. In experiment 3 the rate of increase in density was almost the same as in experiment 1; ~50 kg m^{-3} d^{-1}. The average melt rate was the highest observed (8.2 mm d^{-1}) and the total change in SWE was about half that of experiment 2; 13 mm. The average base temperature throughout melt was –2 ºC in experiment 1, –0.5 ºC in exp. 2, and –0.2 ºC in exp. 3.

The timing of when the first water was present for collection varied between experiments. Snowpack structure causes instability of the meltwater wetting front, which results in formation of flow fingers and preferential flow paths within the snowpack (Wankiewicz, 1979). The flow fingers are an important mechanism for rapid delivery of meltwater to the bottom of the snowpack while it is still below 0 ºC (Woo *et al.*, 1982). The ion mass flux in these flow fingers are higher than that in the matrix flow (Marsh and Pomeroy 1999); implying that basal ice will be primarily comprised of enriched water from matrix flow.
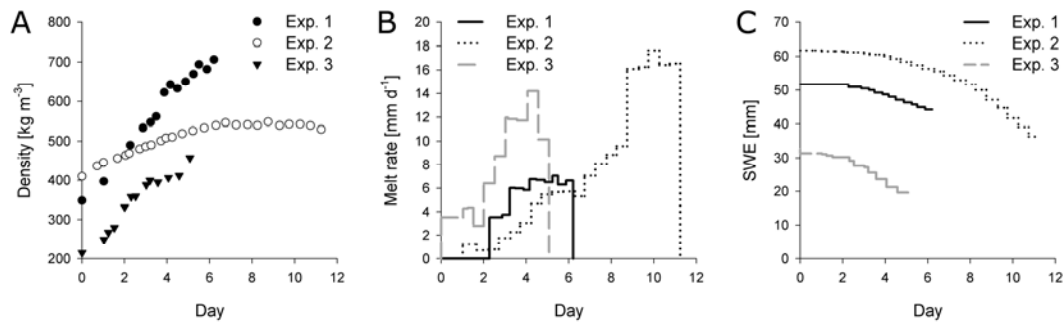

Figure 2. Variation in snowpack density (A), melt rate (B),
and snow water equivalent, SWE (C), during melt.

In each of the experiments runoff water with basal ice contact (BW) was collected at the base before meltwater with no basal ice contact (SW) was present for collection. The reason being that flow fingers did not often intersect with the SW extraction pipe. The first BW was collected after 3 days in experiment 1, 2 days in experiment 2, and 1 day in experiment 3. SW was collected 1-4 days after the initial BW sample; after 1 day in experiment 1, 4 days in experiment 2, and 2 days in experiment 3. Total melt period was shortest for experiment 3 (5 days) followed by experiment 1, which lasted 6 days. Experiment 2 melted over approximately 11 days.

The ion concentrations in the BW and SW were normalized to the corresponding ion concentration in the parent snowpack. The normalized value is the concentration factor, CF (Johannessen and Henriksen, 1978), and shows enriched conditions when CF>1 and depleted conditions when CF<1.

Examples of the variation in CF during melt for both BW and SW are shown in Figure 3. Only the curves for SO_4^{2-} and Ca^{2+} are shown as Cl^-, Na^+, K^+, and Mg^{2+} showed similar trends; just different CFs. General for all experiments were that BW showed more irregular curves than the SW; additionally, the CFs for the BW were predominantly greater than or similar to the SW. The variations in H^+ concentrations were not as distinct as for the other ions, showing similar CFs for

both BW and SW throughout melt; for the majority of the melt period CF was less than 1, increasing to just above 1 by the end of the melt.

For most of the ions, the greatest CFs were obtained within the initial third of the melt period. Table II shows that in general the greatest CFs were obtained in experiment 1; the lowest values were obtained in experiment 3.

Normalizing the ion concentration in the BW with the corresponding concentration in the SW indicates whether the BW is enriched (>1) or depleted (<1) compared to the SW. Figure 4 shows the variations in BW:SW ratio throughout melt for each ion. The vertical spread of the points indicates if the ratio changes throughout melt; little spread indicates little variation.

Experiment 1 showed the least variation in ratio throughout melt for all ions. Generally, the BW contained half the H^+ concentration of the SW and at least double the concentration for the rest of the ions. Greater scatter in the ratios were observed in experiment 2, where the ratios initially increased and was followed by a decrease. Only SO_4^{2-} showed continuous enrichment throughout melt. In the last experiment, the ratios were very close to 1 during the whole melt period. Very little variations were seen for H^+, Cl^-, and SO_4^{2-}; for the rest of the ions, the ratio increased throughout time.

After termination of the experiment, the residual snow was removed from the box exposing the basal ice layer, BI. The thickness of the BI varied from 80 mm in the first experiment to respectively 40 and 30 mm in the following two experiments.
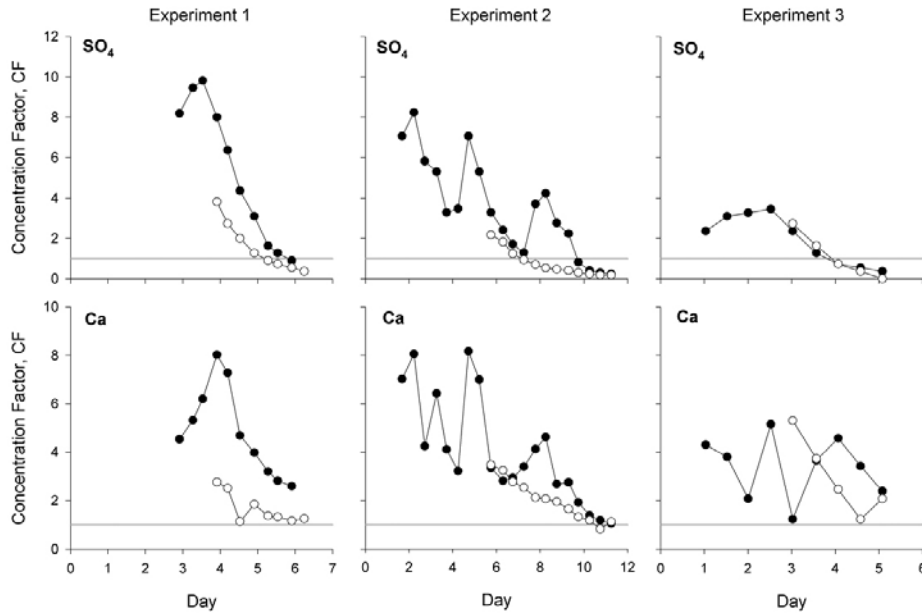

Figure 3. Fractionation curves showing change in concentration factors, CF, during melt for the major ions SO_4^{2+} and Ca^{2+} in the runoff water (BW, closed circles) and the snowpacks meltwater (SW, open circles). The gray horizontal line represents CF=1.

Table 2. The greatest concentration factors, CF [(µeq l^{-1}) (µeq l^{-1})$^{-1}$], in the runoff water, BW, and meltwater, SW, for each ion in each experiment.

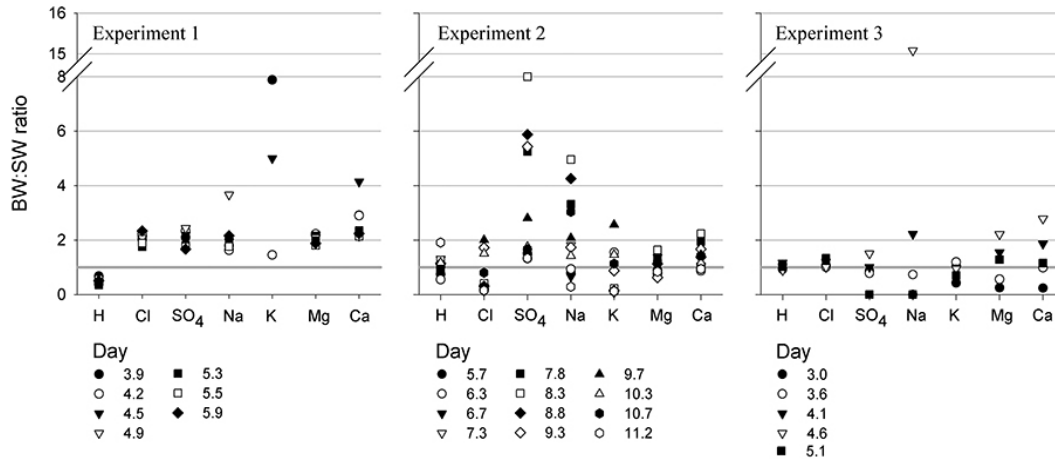| Exp. #		CF H$^+$	CF Cl$^-$	CF SO$_4^{2-}$	CF Na$^+$	CF K$^+$	CF Mg^{2+}	CF Ca^{2+}
1	BW	8.7	19.8	9.8	40.7	1.7	5.5	8.0
	SW	15.7	8.0	3.8	19.5	0.6	2.5	2.8
2	BW	1.9	7.3	8.2	5.7	20.9	5.2	8.2
	SW	1.4	22.2	2.2	2.4	21.8	2.9	3.5
3	BW	1.1	5.1	3.5	9.4	1.6	1.0	5.2
	SW	1.1	4.0	2.7	8.0	2.0	1.7	5.3

Figure 4. Variation in the ion ratio between runoff water, BW, and snow meltwater, SW.

DISCUSSION AND CONCLUSION

The influence of a growing basal ice layer on runoff chemistry was examined through three snowmelt experiments differing in snowpack density, melt rate, and basal cooling conditions. Ion concentrations in runoff water that had sustained basal ice contact were compared to ion concentrations in meltwater without basal ice contact. The results showed that contact with a basal ice layer enriched the ion concentrations in the runoff water compared to fractionation happening solely within the snowpack.

Based on the soil surface infiltrability of frozen ground three infiltration regimes have been defined (Gray *et al.*, 1985): 'unlimited infiltrability' where all water released at the soils surface infiltrates; 'limited infiltrability' where a partitioning of the water between infiltration and surface runoff takes place; and 'restricted infiltrability' where infiltration is negligible and water in excess ends up as runoff or evaporates. Formation of a basal ice layer will act almost as a switch, causing an unlimited or limited infiltrability regime to become a restricted infiltrability regime. Consequently, the implications of basal ice formation are that it will not only alter the flow path but also the concentration of the ion load released from the snowpack. When no basal ice is present and infiltration is limited, but not restricted, a non-linear relationship between meltwater ion load and infiltration rate into frozen soil results in enhanced infiltration, which causes a dilution of the runoff water (Lilbæk and Pomeroy, 2007). When basal ice is present, infiltration is restricted and all meltwater runs off (e.g. Jones and Pomeroy, 2001) and further ion concentration enrichment occurs. Thus, surfaces with variable infiltrability of frozen soils may exhibit great variance in soil and flow path chemistry during snowmelt.

The experiments exhibited a large variation in the timing of water collection. This was believed to be a result of variations in initial snowpack density, melt rate, flow paths, and base temperature. Finger flow initially feeds the base of the snowpack with meltwater (e.g. Wankiewicz, 1979), where it refreezes and basal ice is formed. The base temperature influenced the thickness of the growing ice layer. Experiment 1 had the coldest base temperature throughout melt (–2 ºC) and grew the thickest basal ice layer (80 mm). The base temperatures were higher in the other two experiments (~ –0.5 ºC) and their basal ice layers were approximately half that of experiment 1 (30-40 mm). These basal ice layers compare to those found in nature (Woo *et al.*, 1982; Marsh and Woo, 1984).

At some point, refreezing of meltwater releases enough latent heat to increase the temperature of the surrounding snow to the melting point and runoff initiates. The combination of the thick basal ice layer, high initial snowpack density, and slow average melt rate in experiment 1 resulted in a later collection of initial runoff water compared to the other experiments. The small variation in timing between experiment 2 and 3 was probably a result of similar base temperatures and melt

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rates. The delay between initial runoff water and initial meltwater was believed to be a function of the arrival of the matrix flow to the lower part of the snowpack and the thermal state of the basal ice.

The scatter observed in the runoff water ion concentrations are probably a function of the flow rate and the rate of growth of the basal ice layer. In the first experiment, the basal ice was assumed to increase in thickness throughout melt, causing continuous ion exclusion and thereby enrichment of the runoff water. At some point during melt, the thickness of the basal ice layer approaches a limiting value; increasing rate of meltwater supply to the base is the reason for this (Wakahama *et al*., 1976). The wavy behaviour of the runoff ion concentrations in experiment 2 are thought to be a result of the basal ice layer having reached its limiting thickness. At this stage the basal ice layer may alternate between enriching the runoff water due to refreezing of percolating meltwater and diluting it as a result of melting of the ice layer itself causing the runoff water to have ion concentrations close to those in the meltwater itself. The lack of enrichment in experiment 3 can be explained by a late formation of a basal ice layer so that the initial water samples were not affected by basal ice layer growth. In general, it was found that the surface of the basal ice was enriched in Cl^-, K^+, and Ca^{2+}, and depleted in Na^+ and Mg^{2+}.

The degree of enrichment of both runoff water and meltwater compared to the parent snowpack were greatest in experiment 1; lowest concentration factors were obtained in experiment 3. The ion fractionation curves decayed exponentially throughout melt, showing the highest concentrations during the initial part of the melt. Overall, little scatter were observed for the meltwater curves. The runoff water curves, however, showed abrupt increases in enrichment followed by concentrations that were slightly depleted or equal to the meltwater; except in experiment 1. Based on the BW:SW ratio, 84% of the compared samples in experiment 1 showed an enrichment of the runoff water compared to the meltwater; only the ratios for H^+ showed depleted conditions. Average enrichment showed twice the ion concentration in the runoff water compared to the meltwater. In experiment 2, 55% of the samples were enriched and 40% were depleted; average enrichment was ~1.5. The BW:SW ratios in experiment 3 showed enrichment for the cations as melt proceeded, but little for the anions. Still, 46% of the samples were enriched, showing an average enrichment of ~1.3; 37% were depleted.

In conclusion, the experiments showed that ion exclusion does take place during basal ice formation, enhancing the enrichment of the runoff water. The degree of enrichment increases with the rate of growth of the basal ice layer.

ACKNOWLEDGMENTS

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