

# 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. Initial 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 initial runoff water ion concentrations might 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 formation of basal ice during snowmelt. Meltwater samples were collected throughout melt from within the snowpack using an extraction tube; runoff water was collected at the base. All samples were analysed for major anions and cations. Results showed that formation of basal ice layers can sometimes enrich the initial 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. Enrichment was greatest with the rapid formation of a thick basal ice layer. The implications are that basal ice formation alters 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. Copyright © 2008 John Wiley & Sons, Ltd.

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## 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 the individual ions lack ability to become incorporated into the crystal lattice of ice (Davies *et al.*, 1987). The ability is related to the hydrated radii of the ion and capability to form hydrogen bonds. For instance, ions such as Na<sup>+</sup> and Cl<sup>-</sup> are incorporated more readily into the ice crystal lattice than are NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>. These excluded ions can be readily mixed with percolating meltwater, enhancing initial meltwater ion concentrations.

Studies have shown an initial two- to seven-fold enrichment in ion concentrations in the meltwater released at the base of the snowpack compared to the bulk composition of the parent snowpack (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. Most of the enrichment occurs

during the first 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, runoff, 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<sup>-2</sup> s<sup>-1</sup>], can be approximated as:

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

where  $\rho_i$  and  $\rho_s$  are the respective densities of the basal ice and the snowpack [kg m<sup>-3</sup>],  $\lambda$  is the latent heat of fusion [333 kJ kg<sup>-1</sup>], and  $dz/dt$  is the rate of ice growth [m s<sup>-1</sup>] (Woo and Heron, 1981).

Basal ice layers have been observed in both glacial environments, where they are referred to as superimposed ice (e.g. Wakahama *et al.*, 1976), and in non-glacial environments (e.g. Woo *et al.*, 1982; Marsh and Woo, 1984; Stein *et al.*, 1994). Several studies have looked

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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  $\text{NO}_3^-$  concentrations as the percentage of concrete frost in a boreal forest watershed increased to 75%. Concrete frost was assumed to be associated with basal ice formation. However, to the knowledge of the authors, no laboratory studies have examined the influence of basal ice layer formation on runoff chemistry.

The objective of this article 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 forms 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 (50 mm diameter) was placed with its base  $\sim 30$  mm above the slit opening for extraction of meltwater before basal ice contact [snowmelt water (SW)]. The half-pipe covered a tenth of the base area. The base consisted of a metal plate, which was underlain by a cooling system that was connected to a temperature-controlled refrigerated bath (RTE-DD8, Neslab). The entire apparatus was tilted  $8^\circ$  so that meltwater drained freely into collectors.

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 min by a Campbell Scientific Canada 23X datalogger.

Inside surfaces of the box, i.e. base and sides, 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.

Experiments were carried out in a temperature-controlled cryospheric environmental laboratory. The room contained a dual refrigerating system (Heatcraft, BZ series) with stable cooling capacity from  $+7.5$  to  $-30^\circ\text{C}$  ( $\pm 2^\circ\text{C}$ ) and is sealed to prevent contamination of samples from dust and air particulates.

Three experiments were conducted using snow from a site located within the limits of Saskatoon, Saskatchewan, Canada, a city of just over 200 000 with a cold continental climate and little industry (experiment 1), and two sites located in rural areas 15 km outside of city limits (experiment 2 and 3), in a hay meadow. Snow used in experiment 1 and 2 was collected 2–3 days after each precipitation event, but metamorphism was not pronounced. Fresh snow, collected  $<12$  h after a precipitation event, was used in experiment 3 (Table I). In all experiments, the snow was composed of loose 1–2 mm crystals. The chemical compositions of the parent snow were dominated by  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  (Table II).

To homogenize the snowpack, the snow was sieved with an 8 mm mesh [high density polyethylene (HDPE)]. The depth of the snowpack was  $\sim 0.45$  m at the beginning of the experiments, giving a total snow volume of  $0.15\text{ m}^3$  within the box. The initial densities of the snowpacks were  $\sim 350\text{ kg m}^{-3}$  in the first experiment,  $\sim 410\text{ kg m}^{-3}$  in the second, and  $\sim 215\text{ kg m}^{-3}$  in the third. The snow was then left to reach thermal equilibrium; room temperature was  $-2^\circ\text{C}$  and coolant temperature was set at  $-5^\circ\text{C}$ ,  $-4^\circ\text{C}$ , and  $-3^\circ\text{C}$  in each experiment, respectively. Once thermal equilibrium was reached, the room temperature was increased to  $+5^\circ\text{C}$ . Small adjustments ( $\pm 3^\circ\text{C}$ ) 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.

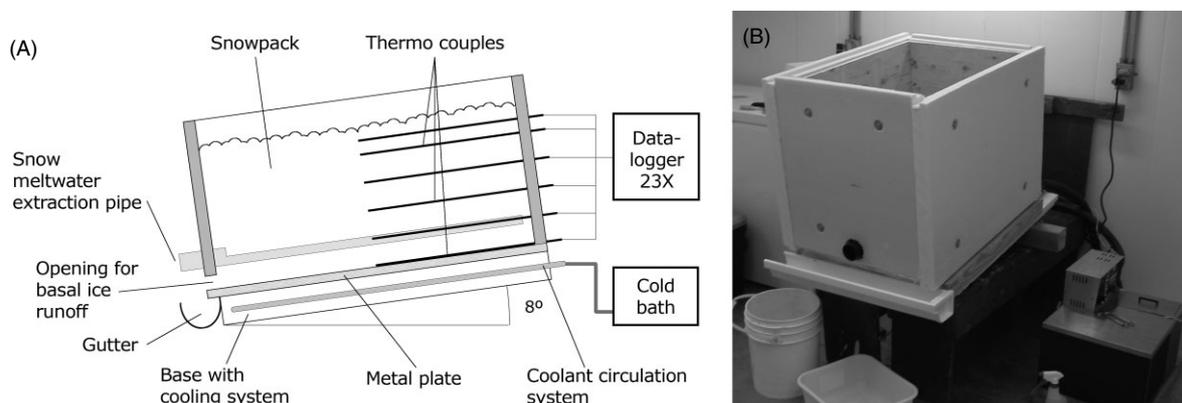


Figure 1. (A) Schematic drawing of the experimental box and its instrumentation (not to scale). (B) The actual box placed in the temperature-controlled room

Table I. Summary of snow and melt conditions for each experiment

Experiment		1	2	3
Snow	Origin	Within city	Rural area	Rural area
	Age [days]	2–3	2–3	< 0.5
Initial snow depth [m]	—	0.45	0.46	0.46
Initial snow density [kg m <sup>-3</sup> ]	—	~350	~410	~215
Temperature [°C]	Room	+5	+5	+5
	Coolant, initially	-5	-4	-3
	Base of snowpack (average)	-2	-0.5	-0.2
Experiment duration [days]	—	6.2	11.3	5.1
Timing of sample collection [days after initiation]	Runoff water, BW	2.9	1.7	1.0
	Meltwater, SW	3.9	5.8	3.2
Basal ice thickness [mm]	—	80	40	30

Table II. Ion concentrations [ $\mu\text{eq l}^{-1}$ ] in the parent snowpacks

Experiment	H <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Charge balance
1	0.009	12.7	11.5	0.7	16.2	5.5	6.2	22.8	73.7	+0.67
2	0.077	25.3	35.4	4.0	26.3	15.1	11.0	30.9	84.5	+0.44
3	0.428	9.8	11.5	n.d.	13.8	3.1	8.4	25.0	13.0	+0.49

n.d., not detected.

For the duration of melt, changes in snow depth and the volume of melt and runoff water eluted from the box were observed. On the basis of this, estimates of snow water equivalent (SWE) could be made since direct measurements would cause disturbance of the snowpack. Experiments were terminated once the depth of the snowpack had decreased by >55%. At this point, melting from the sides of the box was pronounced, revealing a direct view of the basal ice.

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

All water samples were filtered through 0.4  $\mu\text{m}$  nucleopore filter paper. Most samples were filtered immediately. The rest were kept at  $-20^\circ\text{C}$  until filtration took place. 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); reporting detection limit was 2.8  $\mu\text{eq l}^{-1}$ . Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used for SO<sub>4</sub><sup>2-</sup> analysis; reporting detection limit was 2.1  $\mu\text{eq l}^{-1}$ . Standard analytical methods according to American Public Health Association (APHA) were used for Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> (Eaton and Franson, 2005). Analyses of Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup> were done with atomic absorption spectroscopy (SpectrAA 220, Varian). Detection sensitivity for distilled deionized water was found to be  $\pm 0.5 \mu\text{eq l}^{-1}$  for Na<sup>+</sup>,  $\pm 1.8 \mu\text{eq l}^{-1}$  for K<sup>+</sup>,  $\pm 1.1 \mu\text{eq l}^{-1}$  for Mg<sup>2+</sup>, and  $\pm 3.4 \mu\text{eq l}^{-1}$  for Ca. Samples analysed for cations were acidified with H<sub>2</sub>SO<sub>4</sub> to pH = 2 to limit further chemical reactions. Nitrate and NH<sub>4</sub><sup>+</sup> concentrations were determined using standard colorimetric method on a Technicon AutoAnalyzer II; detection limits were 0.5  $\mu\text{eq N l}^{-1}$  for

NO<sub>3</sub><sup>-</sup> and 1.0  $\mu\text{eq N l}^{-1}$  for NH<sub>4</sub><sup>+</sup>. Duplicate runoff water and meltwater samples were used for QA/QC; ~10% of total number of samples collected. If they were not within  $\pm 15\%$  of any measured parameter, samples were reanalysed. Ion charges were not balanced for all samples as all major ions were not analysed and carbonate species might have been present at the pH range (6.3–8.2) encountered (e.g. Maupetit and Davies, 1991). In-between filtering and analyses, samples were stored at  $-20^\circ\text{C}$ .

## RESULTS

The three experiments differed with respect to snowpack density, melt rate, and temperature at the base of the snowpack (Table I). 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  $\sim 56 \text{ kg m}^{-3} \text{ d}^{-1}$ . This experiment showed the lowest average melt rate (3.6 mm d<sup>-1</sup>), the coldest base conditions, and the smallest cumulative reduction in SWE (7.4 mm) of all the experiments. The greatest daily melt rate was observed in experiment 2 at 17.6 mm d<sup>-1</sup>. Average melt rate was 6.8 mm d<sup>-1</sup> resulting in a cumulative loss of 25.4 mm SWE, the greatest of all experiments. The density increase rate in experiment 2 was about one-fifth of the other experiments;  $\sim 11 \text{ kg m}^{-3} \text{ d}^{-1}$ . In experiment 3 the rate of increase in density was almost the same as in experiment 1;  $\sim 50 \text{ kg m}^{-3} \text{ d}^{-1}$ . The average melt rate was the highest observed (7.8 mm d<sup>-1</sup>) and the total change in SWE was about half that of experiment 2; 13 mm.

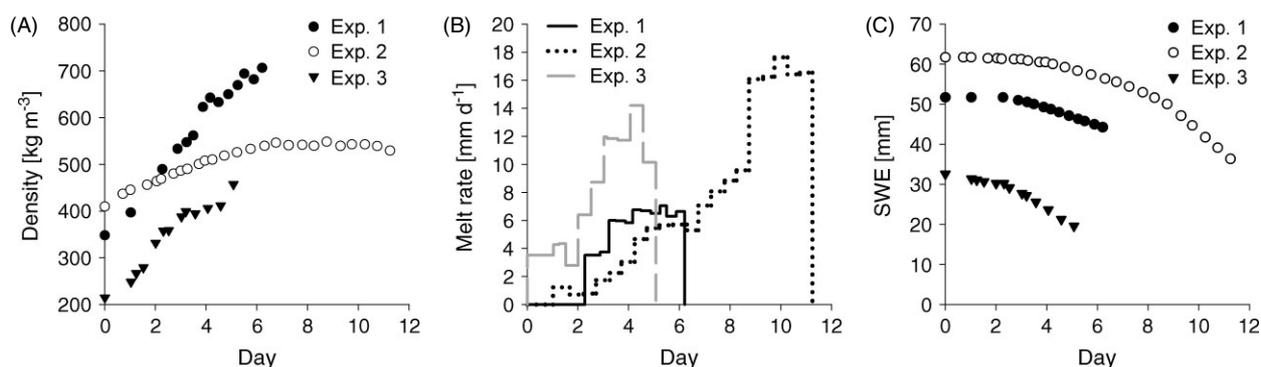


Figure 2. Variation in snowpack density (A), melt rate (B), and snow water equivalent, SWE (C), during melt

The average base temperature throughout melt was  $-2^{\circ}\text{C}$  in experiment 1,  $-0.5^{\circ}\text{C}$  in experiment 2, and  $-0.2^{\circ}\text{C}$  in experiment 3 (Table I). This range was chosen as it represents a range of melt period soil temperatures observed in many seasonally frozen soils.

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

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 first BW was collected after  $\sim 3$  days in experiment 1,  $\sim 2$  days in experiment 2, and  $\sim 1$  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 (Table I). A reason for this delay could be that the SW extraction tube was snow-filled and so had to be saturated and melting before it could transmit water for collection outside the box. It is also possible that the preferential flow paths provided water to the base before they intersected with the extraction tube. However, with a 10% collection area the extraction tube likely received preferential flow path water at most times. Total melt period was shortest for experiment 3 ( $\sim 5$  days) followed by experiment 1, which lasted  $\sim 6$  days. In experiment 2, the snow melted over  $\sim 11$  days.

The ion concentrations in the BW and SW were normalized to the corresponding ion concentration in the parent snowpack. This was done to minimize the influence that difference in origin of the snowpack and therefore parent snow composition may have on the results. The normalized value is the concentration factor, CF (Johannessen and Henriksen, 1978), and shows enriched conditions when  $\text{CF} > 1$  and depleted conditions when  $\text{CF} < 1$ .

The variations in CF during melt for both BW and SW are shown in Figure 3. General for all experiments were that BW showed more irregular curves than SW. The figure also shows that the CFs for the BW were predominantly greater than or similar to the SW; most significant in experiment 1 but also for most ions in experiment 2. The variations in  $\text{H}^+$  concentrations showed contrasting behavior compared to the other ions. The only distinct differences between the CFs of BW and SW were observed in experiment 1. In experiment 2 and 3 similar CFs were observed for both BW and SW throughout melt; for the majority of the melt period, the CF was less than 1, increasing to just above 1 by the end of the melt. The curves for  $\text{NO}_3^-$  and  $\text{NH}_4^+$  showed an irregular CF evolution in experiment 1. In experiment 2 and 3 the variations in CFs corresponded more with the behavior of most other ions. For most ions, the greatest CFs were obtained within the initial third of the melt period. Table III shows that, in general, the greatest CFs were obtained in experiment 1 and the lowest values in experiment 3. Most of these maximum CFs are within the range of values reported in previous studies ( $\text{CF} = 2\text{--}10$ ; e.g. Tranter, 1991); however, CFs  $> 20$  have also been reported.

Normalizing the ion concentration in the BW with the corresponding concentration in the SW ( $\text{BW}/\text{SW} = \text{enrichment ratio}$ ) indicates the relative enrichment of runoff water. If the enrichment ratio is  $> 1$  then BW is enriched, if the enrichment ratio is  $< 1$  then BW is depleted, compared to the SW. Figure 4 shows the variations in the enrichment ratio throughout melt for each ion. A total of 24 samples were suitable for calculating the enrichment ratio for the nine ions. A total of 10 ratios were undefined and so not plotted in Figure 4 since either the BW or SW had an ion concentration equal to zero. The range of enrichment ratio observations for an individual ion in Figure 4 indicates the change in ratio during melt.

Experiment 1 showed the least variation in enrichment ratio throughout melt for all ions. The enrichment ratio for the  $\text{H}^+$  concentration indicated depletion ( $\sim 0.5$ ) whilst that for the other ions indicated enrichment ( $\sim 2$ ). The greatest scatter in the ratio was observed in experiment 2, where it initially increased and then decreased. Only  $\text{SO}_4^{2-}$  showed continuous enrichment throughout

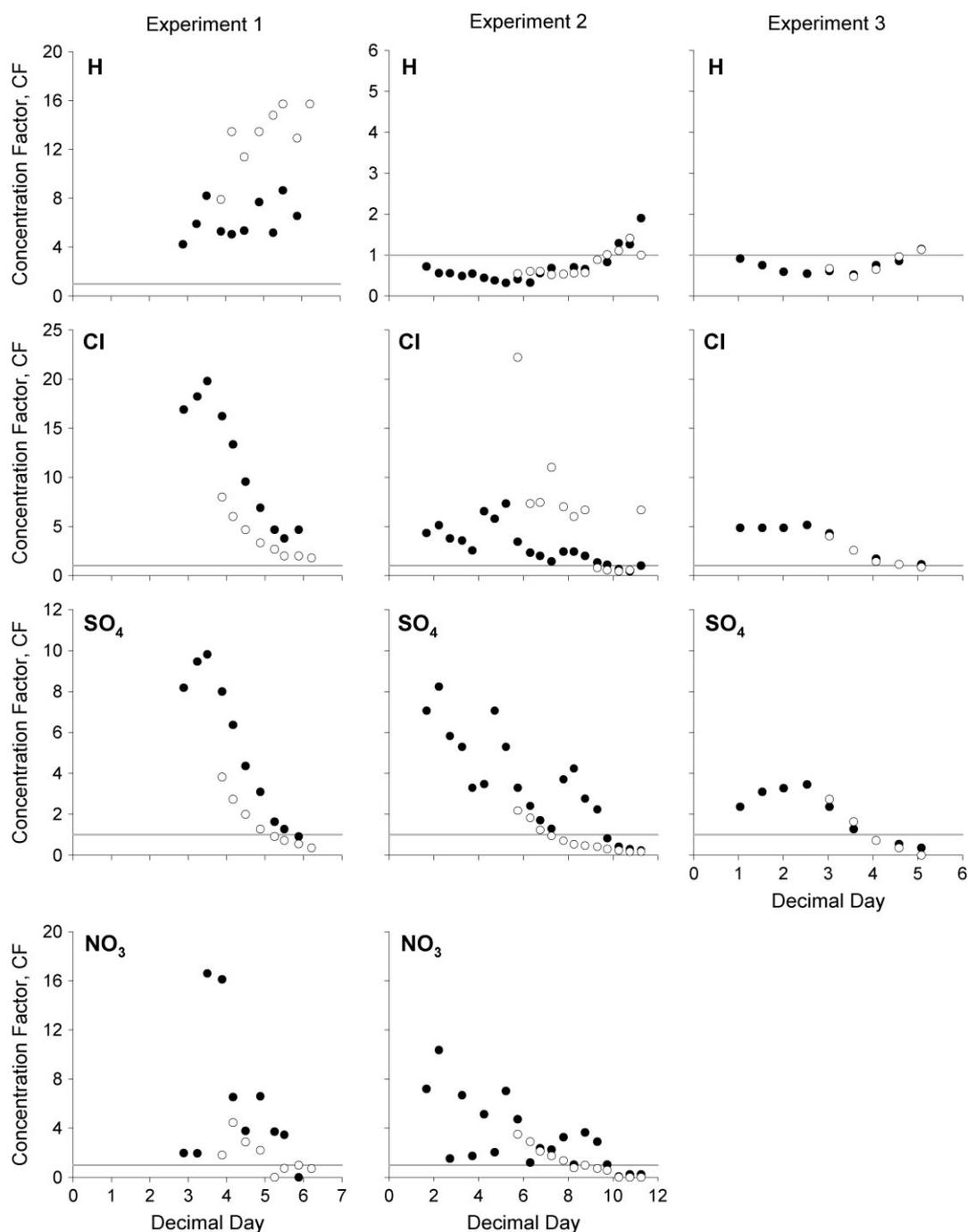


Figure 3. Fractionation curves showing change in concentration factors, CF, during melt for runoff water (BW, closed circles) and the snowpack meltwater (SW, open circles). The horizontal grey line represents  $CF = 1$

melt. In the last experiment (3), the enrichment ratio was very close to 1 during the whole melt period. Small variations in ratio were seen for  $H^+$ ,  $Cl^-$ ,  $SO_4^{2-}$ ,  $NO_3^-$ , and  $NH_4^+$ ; for the rest of the ions, the ratio increased slightly over time.

The mean difference between the CF for BW and SW is given in Table IV; both for each ion and overall (simple average of all ions) for each experiment. Positive values indicate enriched runoff water compared to meltwater. Positive differences were found for  $SO_4^{2-}$ ,  $NO_3^-$ ,  $NH_4^+$ , and  $Ca^{2+}$  in all three experiments. Generally, the largest mean differences in CF were observed for the individual

ions in experiment 1. The mean differences in experiment 3 were all close to zero, indicating similar concentrations in both runoff water and meltwater.

The dispersion of mean differences for each ion and overall, by experiment, is shown in Table V; the dispersion was calculated as root mean square deviation, (RMSD). For the individual ions, the greatest RMSD values were observed for  $H^+$  (2.1),  $SO_4^{2-}$  (1.4),  $NO_3^-$  (4.6), and  $NH_4^+$  (5.1) in experiment 1,  $Cl^-$  (5.2),  $K^+$  (8.6), and  $Mg^{2+}$  (0.8) in experiment 2, and  $Ca^{2+}$  (2.3) in experiment 3. Generally, experiment 3 showed the least dispersion ( $<1$ ).

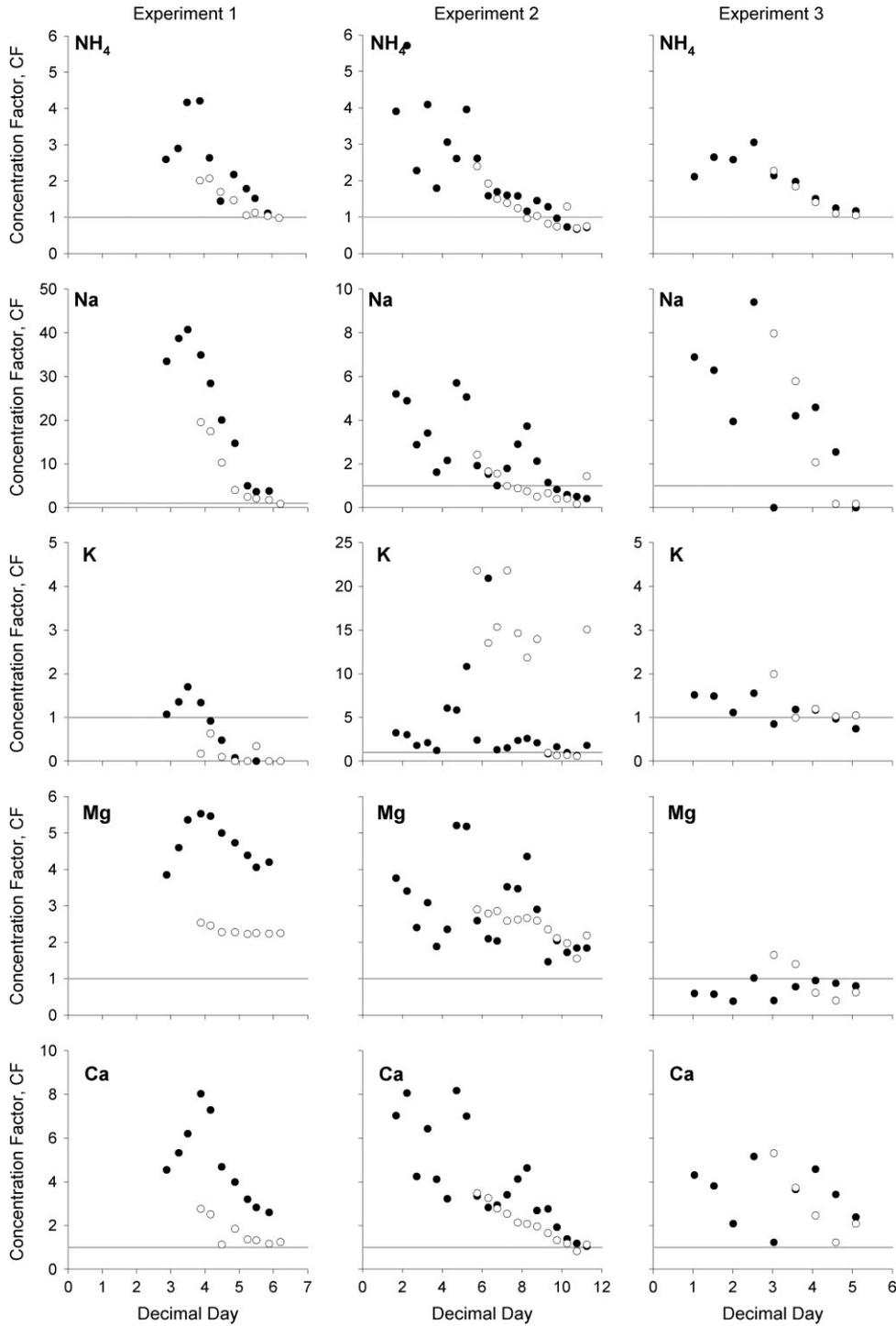


Figure 3. (Continued)

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

Experiment		CF, H <sup>+</sup>	CF Cl <sup>-</sup>	CF SO <sub>4</sub> <sup>2-</sup>	CF NO <sub>3</sub> <sup>-</sup>	CF NH <sub>4</sub> <sup>+</sup>	CF Na <sup>+</sup>	CF K <sup>+</sup>	CF Mg <sup>2+</sup>	CF Ca <sup>2+</sup>
1	BW	8.7	19.8	9.8	16.6	4.2	40.7	1.7	5.5	8.0
	SW	15.7	8.0	3.8	4.5	2.1	19.5	0.6	2.5	2.8
2	BW	1.9	7.3	8.2	10.4	5.7	5.7	20.9	5.2	8.2
	SW	1.4	22.2	2.2	3.5	2.4	2.4	21.8	2.9	3.5
3	BW	1.1	5.1	3.5	n.a.	3.1	9.4	1.6	1.0	5.2
	SW	1.1	4.0	2.7	n.a.	2.3	8.0	2.0	1.7	5.3

n.a., not applicable.

ION ENRICHMENT OF SNOWMELT RUNOFF WATER

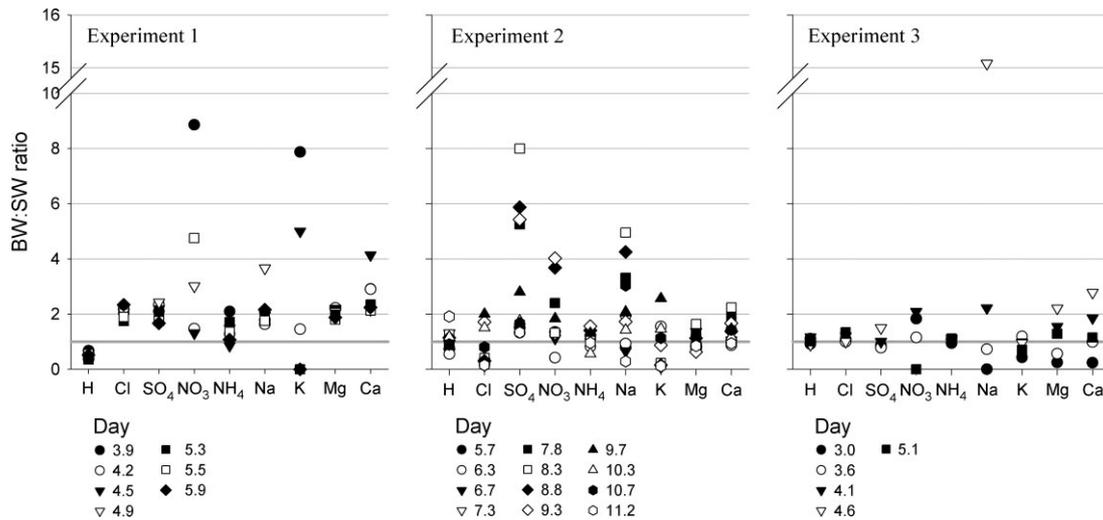


Figure 4. Variation in the ion ratio between runoff water, BW, and snow meltwater, SW

Table IV. Mean differences between CF values for runoff, BW, and meltwater, SW, in each experiment. Positive values refer to BW generally being enriched compared to the SW; negative values the opposite

Experiment	H <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Overall
1	-6.6	4.3	1.9	3.9	0.6	7.6	0.2	2.4	2.9	1.9
2	0.1	-4.7	1.2	0.7	0.1	0.6	-7.6	0.1	0.7	-1.0
3	0.0	0.2	0.0	0.0	0.1	-1.0	-0.3	-0.2	0.1	-0.1

Table V. Calculated root mean square deviation for the differences between CF values for runoff, BW, and meltwater, SW, in each experiment

Experiment	H <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Overall
1	2.1	2.4	1.4	4.6	0.7	5.1	0.4	0.4	1.5	4.5
2	0.3	5.2	1.2	1.1	0.3	1.1	8.6	0.8	0.8	4.5
3	0.1	0.1	0.3	n.a.	0.1	3.8	0.5	0.7	2.3	1.6

n.a., not applicable.

After termination of the experiment, the residual snow was removed from the box exposing the basal ice layer. The thickness of the basal ice varied from 80 mm in the first experiment to respectively 40 and 30 mm in the following two experiments (Table I). Analyses of the chemical composition of the ice layers were not possible as the experimental setup did not allow its intact removal without contamination.

DISCUSSION

The influence of a 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 BW were compared to ion concentrations in meltwater without BW. The results showed that contact with the basal ice layer sometimes enriched the ion concentrations in runoff water compared to fractionation happening solely within the snowpack; especially during the initial half of melt.

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 soil 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 acts analogous to a switch in the flow pathway, 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); in this case,

further ion-concentration enrichment is possible. Thus frozen soils with variable infiltrability 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. Preferential flow paths (or finger flow) initially feed 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 ( $-2^{\circ}\text{C}$ ) and grew the thickest basal ice layer (80 mm). The base temperatures were higher in the other two experiments ( $\sim -0.5^{\circ}\text{C}$ ) and their basal ice layers were approximately half that of experiment 1 (30–40 mm). These basal ice layers all 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 rates. The delay between initial runoff water and initial meltwater was believed to be a function of the ability of extraction tubes to transmit meltwater to the front of the box, 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 is probably a function of the flow rate, base temperature, and the rate of growth of the basal ice layer. In the first experiment, the basal ice increased in thickness throughout melt, causing continuous ion exclusion and thereby enrichment of the runoff water. In the warmer experiments (experiment 2 and 3), the basal ice layer stopped growing during melt. The undulating pattern of the runoff ion concentrations in experiment 2 is thought to be a result of the basal ice layer growth having reached a limit. 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 runoff water enrichment in experiment 3 is most likely explained by a late formation of the basal ice layer.

The CFs of both BW and SW were greatest in experiment 1 and lowest in experiment 3 (Table III). CF peaked early in melt and then decayed exponentially with time (Figure 3). CF for BW usually peaked after the first few samples during each experiment. Extrapolating the SW CF observations backward to the first observations sometimes resulted in correspondence between these extrapolations and the BW CF values. The delay in peak and possible commonality of first ion concentrations may

provide some evidence of ion uptake early in the basal ice formation. However, further investigations are required of this mechanism. For instance, an alternative explanation for this delayed peak in CF could be that the initial water released at the base of the box originated primarily from relatively dilute preferential flow (Marsh and Pomeroy, 1999), whereas matrix flow dominated by the time the meltwater collection was possible using the collection tubes.

Overall the CF for SW showed little scatter. However, the BW CF showed abrupt increases in enrichment followed by concentrations that were slightly depleted or equal to the meltwater. The exception was in relatively cold experiment 1 where BW remained enriched compared to SW throughout melt.

Preferential flow is normally depleted compared to matrix flow (Marsh and Pomeroy, 1999), SW was likely to have been dominated by matrix flow and basal ice formation was dominated by preferential flow. If the basal ice did not influence the BW chemistry, then the enrichment ratio would be less than 1. However, 81% of the 63 enrichment ratios in experiment 1 were enriched compared to meltwater; only  $\text{H}^+$  was consistently depleted. Average enrichment was near 2.0 overall for experiment 1. In experiment 2, 61% of the 108 ratios were enriched with an overall average enrichment of  $\sim 1.5$ ; 38% of the ratios were depleted or near 1. The enrichment ratios in experiment 3 showed an enrichment for 56% of the 45 ratios, with an overall average enrichment of  $\sim 1.2$ ; 40% were depleted. That the enrichment ratios were near to or greater than 1 and hence overcame depletionary effects due to preferential flow demonstrates the substantive effect of BW in enhancing concentrations of runoff water compared to the meltwater leaving the snowpack.

The mean difference between the CFs for BW and SW support the observations from the enrichment ratios (Table IV). For experiment 1, the only negative mean difference was found for  $\text{H}^+$ ; thus the overall mean difference is positive. A negative overall mean difference was observed for experiment 2 even though a majority of the ions showed positive values. This was caused by the large negative values for  $\text{Cl}^-$  and  $\text{K}^+$ , which were a result of the depletion of BW compared to SW. This behavior is believed to be associated with road salt contamination of snow used in this experiment with higher than natural concentrations of  $\text{Cl}^-$  and  $\text{K}^+$ . Excluding  $\text{Cl}^-$  and  $\text{K}^+$  from the calculation of the overall mean difference in experiment 2 reveals a positive tendency and the overall mean difference becomes equal to 0.5. In experiment 3, the mean differences were all close to zero indicating similar concentrations in both BW and SW, which correspond with the observations shown in Figure 3.

The overall dispersion of the difference between CF in the BW and SW, calculated as RMSD, was 4.5 for each of experiments 1 and 2 (Table V). These values were strongly influenced by the behavior of  $\text{NO}_3^-$  (RMSD = 4.6) and  $\text{Na}^+$  (RMSD = 5.1) in experiment 1 and  $\text{Cl}^-$  (RMSD = 5.2) and  $\text{K}^+$  (RMSD = 8.6) in experiment 2. In experiment 3 most ions had RMSD

<1 with the overall dispersion value (1.6) strongly influenced by  $\text{Na}^+$  (RMSD = 3.8) and  $\text{Ca}^{2+}$  (RMSD = 2.3). In all three experiments approximately half the ions had dispersion values <1, but  $\text{NH}_4^+$  and  $\text{Mg}^{2+}$  were the only ions for which all dispersion values were <1. No ion showed high dispersion values in all three experiments. The results from considering statistical dispersion are consistent with the trends observed from the enrichment ratios, in that experiment 1 runoff water was most enriched, with lower enrichment for experiment 2 and little enrichment for experiment 3. In all measures the enrichment and degree of difference between snowmelt water and runoff water increased with increasing thickness of basal ice layer and decreased with increasing basal temperature during melt. This suggests that the thickness of the basal ice layer and the rapidity of its formation may have an important role in regulating runoff water ion concentrations.

### CONCLUSIONS

The experiments showed that the formation of an ice layer at the base of a snowpack was associated with a compositional change in the runoff water chemistry. During the initial melt period, runoff basal ice contact water was most often enriched compared to snowmelt water collected before surface contact. This enrichment can be attributed to ion exclusion during refreezing of meltwater into basal ice. The enrichment effect was most pronounced with the rapid formation of a thick basal ice layer early in melt under relatively cold experimental conditions and was small to negligible when basal ice growth was slow and later in melt under relatively warmer experimental conditions.

Since basal ice formation only occurs with restricted infiltration, the occurrence of basal ice not only enriches some runoff water ion concentrations but is associated with low infiltrability such that almost all meltwater ion flow is to runoff. This will have a strong effect not only on peak concentrations, but on ion pathways and loading to aquatic ecosystems. Because of these features, basal ice formation should be recognized as having an important role in meltwater chemistry and the disposition of snowmelt ions to the non-snow environment.

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