

Honor Paper Award

**Effects of Crystal Metamorphosis on the
Elution of Chemical Species From Snow**

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ABSTRACT

Columns of fresh snow were aged in a -20°C coldroom with an imposed thermal gradient of approximately $36^{\circ}\text{C}/\text{m}$ for periods of one to eight weeks. Deionized distilled water was then passed through a column of this aged snow and the eluate collected in sequential aliquots for determination of H^+ , Cl^- , NO_3^- and SO_4^{2-} . Concentrations of these ions in the eluate show that both fractionation (higher concentrations in initial aliquots) and preferential elution (greater enrichment of SO_4^{2-} relative to Cl^-) in melting snow are strongly influenced by snow metamorphic processes.

INTRODUCTION

Recent field and laboratory experiments (Davies et al. 1982, Tranter et al. 1986, Brimblecombe et al. 1987, 1988) have shown that the release of inorganic ions from a melting snowpack is not uniform with time: initial meltwater contains higher concentrations than the bulk or latter portions, a phenomenon known as fractionation (Johannessen et al. 1975, Johannessen and Henriksen 1978). Moreover, some ions, e.g. SO_4^{2-} , are released sooner than others, e.g., Cl^- . This phenomenon is commonly referred to as preferential chemical elution (Davies 1982). One explanation proposed by Tranter et al. (1986) for preferential chemical elution is that the snowpack acts as a chromatographic column, selectively adsorbing and slowing the release of certain ions (Cl^-) in the percolating meltwater over others (SO_4^{2-}). Recently, Hewitt et al. (1989) conducted experiments to specifically test this theory. They allowed solutions of known dilute ion concentrations to flow down through a column of frozen deionized water droplets (ice grains) and collected the eluate in sequential aliquots. If ice grains show preferential affinity for inorganic ions, then strongly sorbed ions would appear in later eluate fractions than would weakly sorbed ions. However, all three species measured Cl^- , NO_3^- and SO_4^{2-} , eluted simultaneously, indicating that snow and ice surfaces do not exhibit chromatographic behavior. Consequently, preferential chemical elution observed in melting snowpacks is not a result of chromatographic effects or selective ion retention during meltwater percolation.

Another mechanism proposed by Hewitt et al. (1989) is that preferential chemical elution in snowpack meltwater is a result of preferential ion exclusion from snow grains during snow metamorphosis. When snow undergoes

metamorphosis, some large ice crystals grow larger at the expense of smaller ones (Colbeck 1987). While these grains are growing, chemical constituents are being excluded/incorporated into the ice crystal with different efficiencies. This produces mature snow grains that possess nonhomogeneous distributions of ions. As a result, when a snowpack containing these mature grains melts, ions are released or elute sequentially with time, and the resulting elution order is related to the exclusion efficiency of different ions imposed by the metamorphic growth process.

In this study we present results of experiments conducted to evaluate the effects of snow metamorphosis and the resultant snow crystal habit upon elution chemistry. Columns of aged snow were washed with deionized distilled water and the eluate was collected. This directly simulated the removal of ions from metamorphosed snow grains by rainwater percolation through a snowpack, and was also analogous to percolation of snow meltwater itself.

EXPERIMENTAL

All plastic, glass, and stainless steel laboratory utensils used for snow collection, grain growth, sample storage and analysis were thoroughly cleaned as described previously (Hewitt et al. 1989).

Snow Collection

Snow was collected on 22 January 1990 after an overnight precipitation event from the center of a half-acre field near our laboratory. The fresh snow layer, consisting of a mixture of submillimeter needles and irregular crystals, was scooped into a clean plastic bag. Prior to setting up the grain growth columns, the collected snow was placed in an insulated box and stored under isothermal conditions for nine days in a -20°C coldroom.

Grain Growth Column and Temperature Gradient Apparatus

The four grain growth columns consisted of 1-mm-thick butyrate plastic cylindrical tubes of 3.7-cm O.D \times 55-cm length with fitted polyethylene end caps. These columns were filled after mechanically mixing the snow and passing it through a 18-mesh polypropylene sieve. Using a large funnel we poured the desegregated snow crystals into the growth columns, which were agitated while filling to facilitate uniform packing. The snow transfer operation was performed at the opening of a clean air station housed in a coldroom at -2.2°C . Four columns were sequentially filled as described above to a 50-cm depth, resulting in densities of $0.18 \pm 0.01 \times 10^3 \text{ kg/m}^3$. Additionally, three subsamples of the sieved snow were collected for determinations of bulk snow chemical composition.

Once filled the grain growth columns were taken to a -20°C coldroom and placed in the insulated temperature gradient apparatus (Fig. 1). This apparatus positioned the columns at equal distances from the walls and from one another inside a 20-cm-I.D. cardboard tube. The space between the four cylindrical cavities was filled with urethane foam insulation covered at both ends with rigid Styrofoam insulation. Once all four grain growth columns had been fitted into the cavities of the grain growth apparatus, a plastic bag was put over the top of the cardboard tube to protect against particle contamination, and additional fiberglass insulation (9 cm thick \times 56 cm wide) was wrapped three times around the vertical walls.

The grain growth apparatus was positioned on an aluminum plate, 0.6 cm thick \times 20 cm O.D. Centered below the aluminum plate and on top of a large rectangular 5-cm-thick Styrofoam board was a thin ($\approx 1.0\text{-mm}$ \times 18-cm O.D.) heating pad. Current to the heating pad was controlled with a rheostat. The temperature of the aluminum plate was

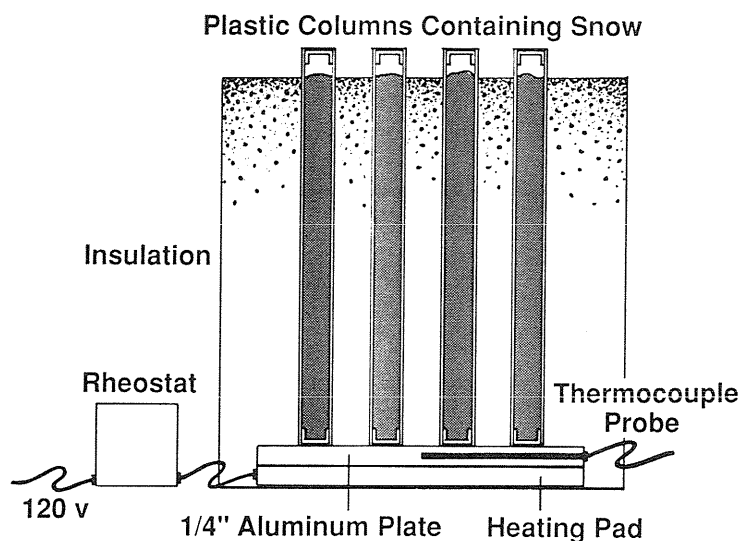


Figure 1. Schematic drawing (not to scale) of experimental arrangement used for aging snow. The base of the columns was maintained at -2°C with a heating pad while the top of the columns was at the temperature of the coldroom, -20°C .

monitored with a 9-cm-long, 3-mm-diameter needle probe thermocouple that fit snugly into a hole drilled radially into the plate. Throughout the grain growth experiment, the rheostat was set to maintain a temperature of $-2 \pm 1^{\circ}\text{C}$ within the aluminum plate, thus creating a temperature gradient between the top and bottom of the snow grain growth columns of approximately $36^{\circ}\text{C}/\text{m}$. Temperature readings were taken at least daily. Individual snow grain growth columns were removed after each treatment period of 7, 14, 28, and 56 days, and a placebo column of identical dimensions filled with loosely packed fiberglass insulation was inserted into the vacant cavity to maintain thermal balance.

Column Elution

Once a grain growth column had been removed from the temperature gradient apparatus, it was placed on a clean polyethylene sheet inside a clean air station within the -20°C coldroom. Taking precautions not to disturb the fused snow grains, we cut the column into two sections with a razor knife, resulting in a lower 15-cm portion (bottom 1/3) that had been in contact with the aluminum plate and the upper 35 cm (top 2/3) portion. The length of the bottom column (15 cm) was based on the snow packing density required to provide the necessary 30 g of snow grains needed to perform an elution experiment (Hewitt et al. 1989). The snow from each section was then transferred to polyethylene bottles. The bottle containing snow from the bottom 15 cm was shaken to desegregate the fused grains. Subsamples of these dispersed snow grains were taken for microscopic crystal identification and for bulk snow chemical determinations. Most of the remainder was used for the elution experiments. Basically elution experiments were conducted by slowly applying distilled deionized water dropwise onto the top of the snow columns, allowing it to percolate down through the snow grains and collecting the emerging water in sequential 1-mL aliquots. Ionic concentrations on some of these aliquots are lower than in the original bulk snow because of dilution by the applied deionized water. For more complete details of the elution setup and operation, refer to Hewitt et al. (1989).

Figure 2. Original snow used for metamorphosis/elution experiments consisting of 0.1- to 0.3-mm rounded crystals. Rounding of fresh snowflake arms and angularities occurred during isothermal storage at -20°C for several days.

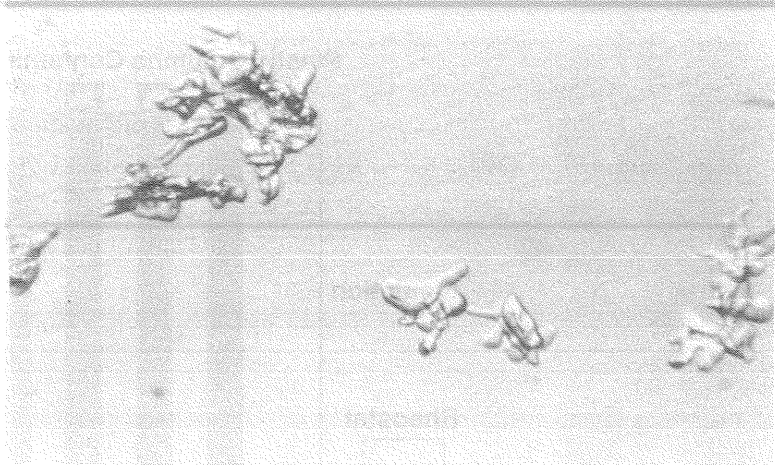


Figure 3. Snow crystals aged for one week with an imposed temperature gradient of $38^{\circ}\text{C}/\text{m}$. Sample taken from bottom third of column 1. Crystals are larger (0.2–0.4 mm) than original snow and have developed some angularity.

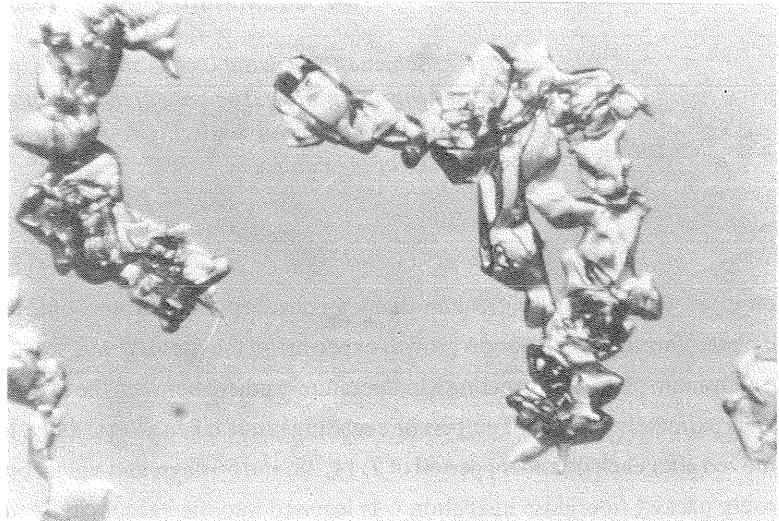
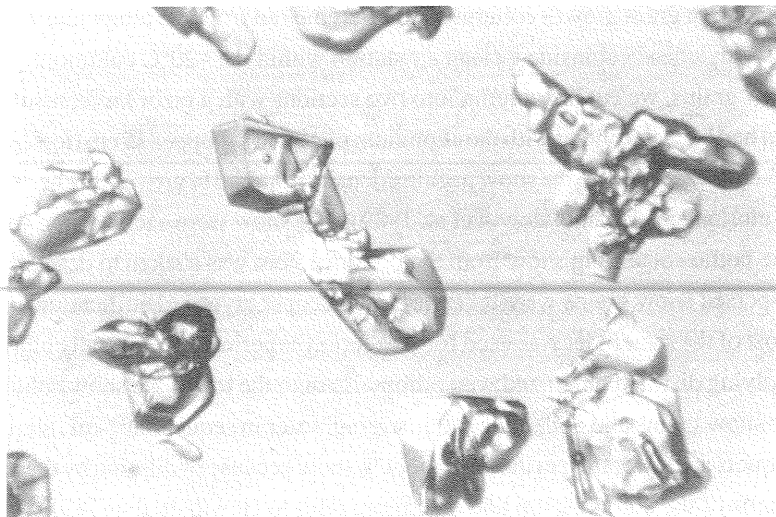


Figure 4. Snow crystals aged for two weeks. Sample taken from bottom third of column 2. Crystal size ranges from 0.5 to 0.7 mm.



RESULTS

Figures 2–6 show the effect of aging (metamorphosis) upon the snow crystals. The original starting material (Fig. 2) for the experiment consisted of small (0.1- to 0.3-mm) crystals and crystal fragments whose apexes became slightly rounded during the time between sample collection and experiment initiation due to higher vapor pressure at sharp curvatures (Kelvin effect). After one week of aging with an imposed $36^{\circ}\text{C}/\text{m}$ temperature gradient (Fig. 3), crystals in the bottom of the column had developed some angularity and grown to 0.2 to 0.4 mm, while after two weeks (Fig. 4) crystal growth was more extensive (0.5 to 0.7 mm) and the crystals were angular with hexagonal plates beginning to appear. After four weeks (Fig. 5) crystals were much larger (≈ 1 mm), faceted, and beginning to sinter. The final sampling, taken after eight weeks (Fig. 6), contained large (up to 3 mm), sintered, highly faceted crystals, many of which were hexagonal and cup-shaped, similar to depth-hoar.

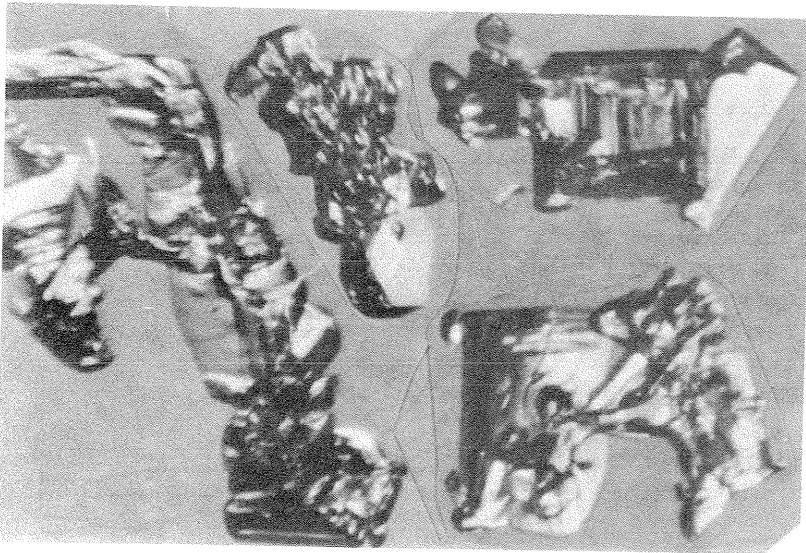


Figure 5. Snow crystals aged for four weeks. Sample taken from bottom third of column 3. Crystals are larger (up to 2 mm), sintered and faceted.

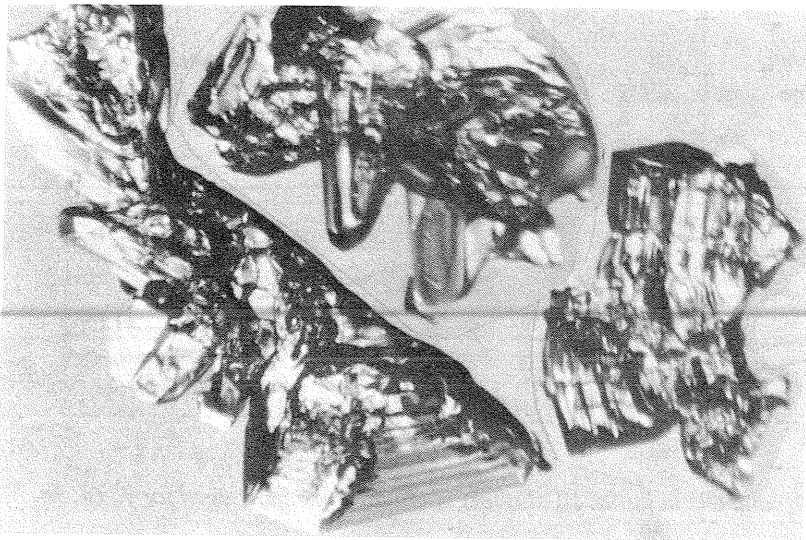


Figure 6. Snow crystals aged for eight weeks. Sample taken from bottom third of column 4. Crystals are as large as 3 mm, sintered and highly faceted. Many hexagonal, cup-shaped, faceted, depth-hoar crystals are present, like the one in the lower center of photo.

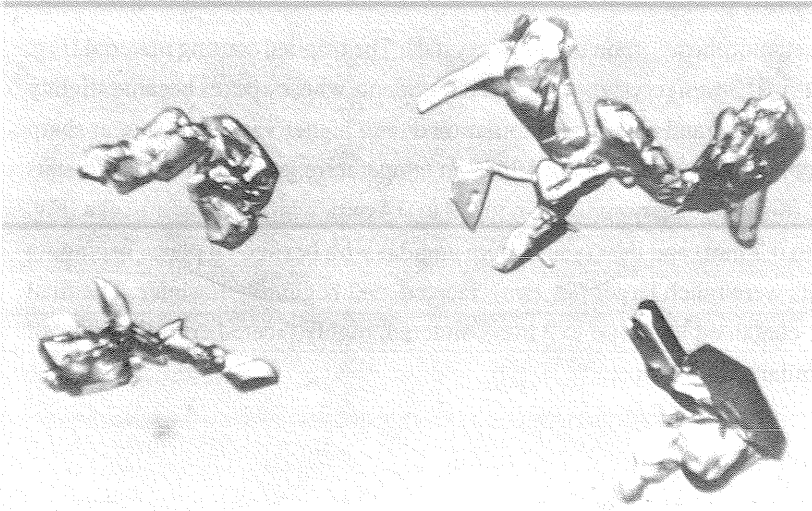


Figure 7: Snow crystals aged for eight weeks. Crystals are from top two-thirds of column 4. Crystals are 0.3–1 mm in size and some faceting (see hexagonal plate in lower right) is apparent, although most crystals are rounded due to the slower growth rates because of the lower temperature in the upper section of the column. This material is similar in appearance to that present in the bottom third of column 1 (see Figure 2).

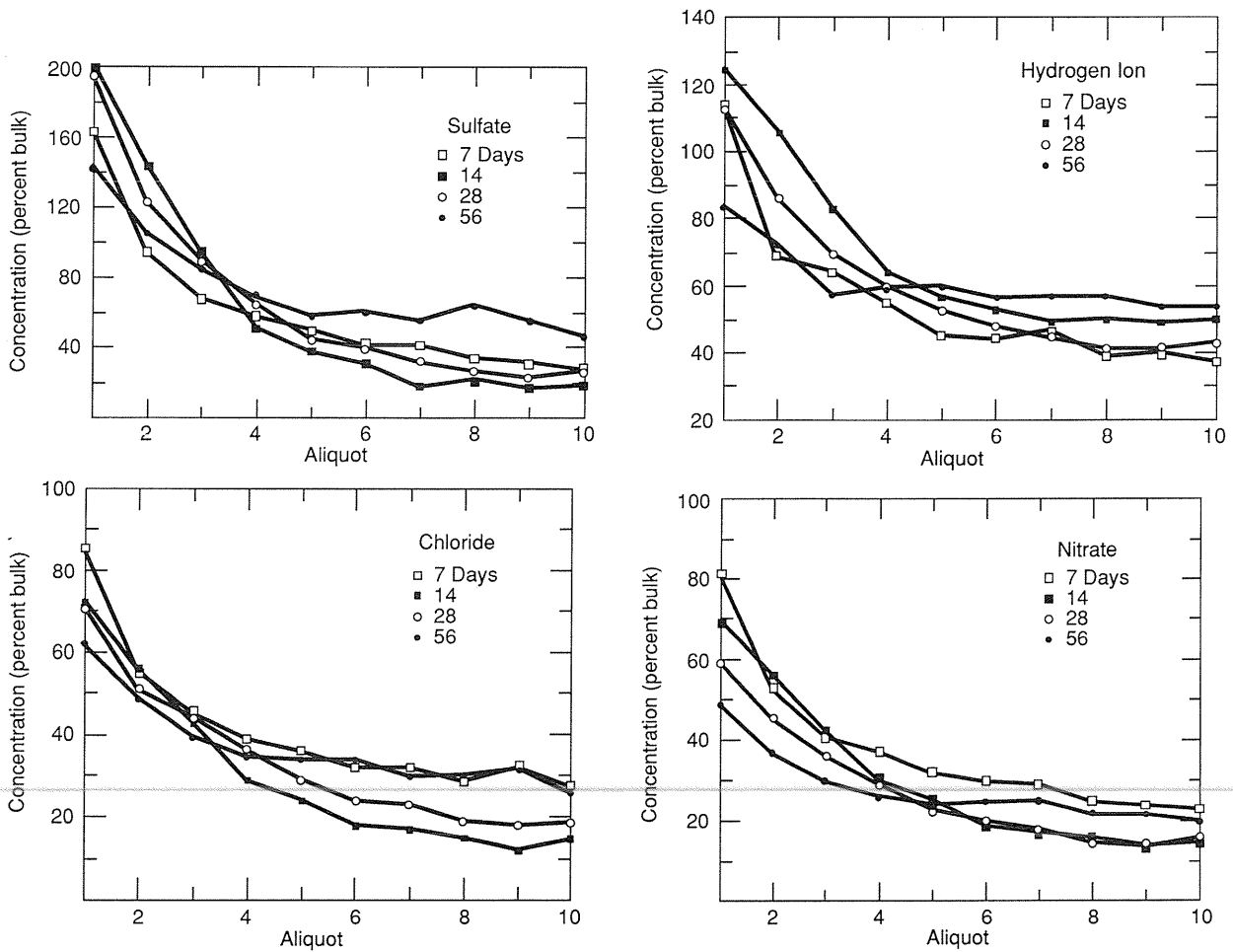


Figure 8: Concentrations of SO_4^{2-} , H^+ , NO_3^- and Cl^- in initial 10 aliquots of eluant from snow aged for 7, 14, 28, and 56 days.

To show the effect of temperature upon crystal growth, the top two-thirds of column 4 was sampled (Fig. 7). While this material was under the same temperature gradient as that in the bottom third of the column, the average temperature was -14°C (compared to -5°C for the bottom third). The crystals are smaller (0.3–1 mm) and, while some faceting is apparent, most are rounded because of the slower growth rates resulting from the lower temperature in the upper section of the column. This material is similar in appearance to that present in the bottom third of column 1 (see Fig. 2).

While the snow crystals are undergoing the above metamorphic physical changes, concurrent chemical changes are taking place as well. Figure 8 shows sulfate, hydrogen, nitrate and chloride ion concentrations in sequential elution aliquots for the snow crystals aged in columns. The aging times of 1, 2, 4, and 8 weeks are the same as those for the crystal in the photographs of Figures 3 through 6.

DISCUSSION

Chemical fractionation (higher ionic concentrations in initial meltwater aliquots) and preferential elution (some ions are enriched more than others) are readily apparent in Figure 8. Our explanation, suggested earlier (Hewitt et al. 1989) is that both these phenomena result from ion exclusion during snow grain metamorphosis. Figure 9 shows this concept schematically. Assume that initially (time t_1) all crystals have similar solute distributions (represented by shading). As the snowpack ages and large grains grow at the expense of smaller ones (Colbeck 1987) the concentration of impurities increases for the smaller grains (time t_2) until they have completely dissipated (time t_3), leaving their impurities upon the surfaces of the mature grains. At the same time, the larger grains are growing, selectively rejecting/incorporating chemical species within the newly developed layers of ice lattice. Of course, not all the small grains disappear completely and at any given time the snowpack or column has a variety of grain sizes and impurity distributions. But the overall trend is an exclusion of impurities from snow grain interiors to their surfaces. The extent of this exclusion, or conversely inclusion within the growing ice grain matrix, depends upon the chemical species or ion; i.e., it is preferential. The process is analogous to the exclusion of ions from a freezing salt solution: less soluble salts, such as sulfates, are more

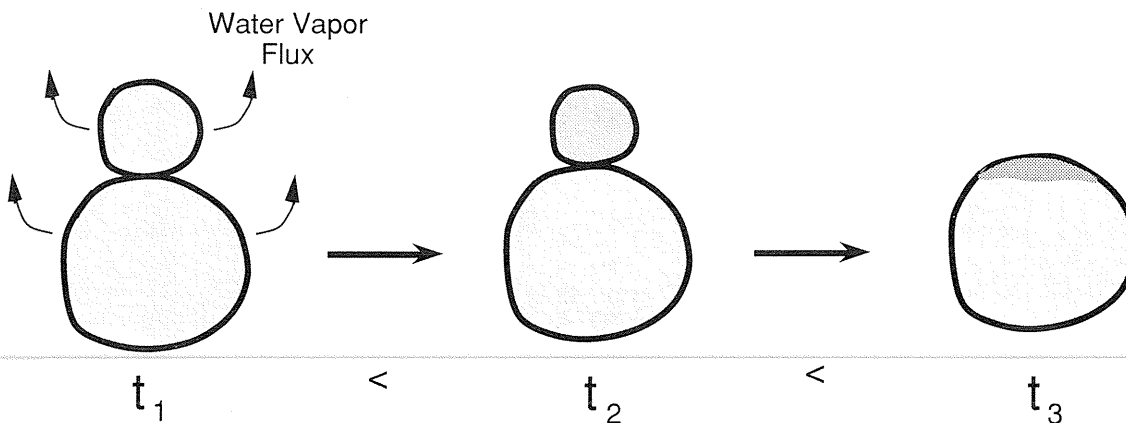


Figure 9: Theoretical depiction of chemical changes occurring during snow metamorphosis. Initially (time t_1) assume all snow grains have similar solute concentrations (represented by shading). As large grains grow and small grains dissipate, solutes within the smaller grains (time t_2) become concentrated. At time t_3 , some small grains have disappeared, leaving their solute load upon the surface of the larger grains.

efficiently excluded than more soluble chlorides (Gross 1968). Accordingly, a mature or well-metamorphosed snow grain (Fig. 10) would have higher SO_4^{2-} concentrations and $\text{SO}_4^{2-}/\text{Cl}^-$ ratios on the surface than within the interior. The more efficiently excluded ions are more highly enriched on the snow grain surfaces and thus appear sooner and in higher concentrations in the eluate water.

Preferential exclusion should also result in changing eluate ionic ratios with time. This is manifested most clearly for the $\text{SO}_4^{2-}/\text{NO}_3^-$ ratios (Fig. 11) which increase progressively as the snow age increases.

Average ratios of the three anions for the first five eluate aliquots are given in Table 1. The normalized $\text{SO}_4^{2-}/\text{NO}_3^-$ ratio increases from 1.8 for snow aged 7 days to 2.8 for the same snow aged for 56 days, indicating that SO_4^{2-} is excluded more efficiently than NO_3^- . The average normalized $\text{SO}_4^{2-}/\text{Cl}^-$ ratio increases from 1.7 to 2.5 between 7 and 28 days but then drops to 2.1 for the 56-day-old snow. This indicates that at least initially, SO_4^{2-} is excluded more efficiently than Cl^- . But why the drop in the $\text{SO}_4^{2-}/\text{Cl}^-$ ratio between 28 and 56 days? It is not caused by higher Cl^- levels since concentrations of this ion in the eluate aliquots (Fig. 8d) decrease. Also the average normalized $\text{NO}_3^-/\text{Cl}^-$ ratio remains constant between 28 and 56 days and in fact does not deviate appreciably from unity for the four aging periods. A closer look at the ionic concentration curves in Figure 8 reveals that the degree of fractionation does not increase with sample

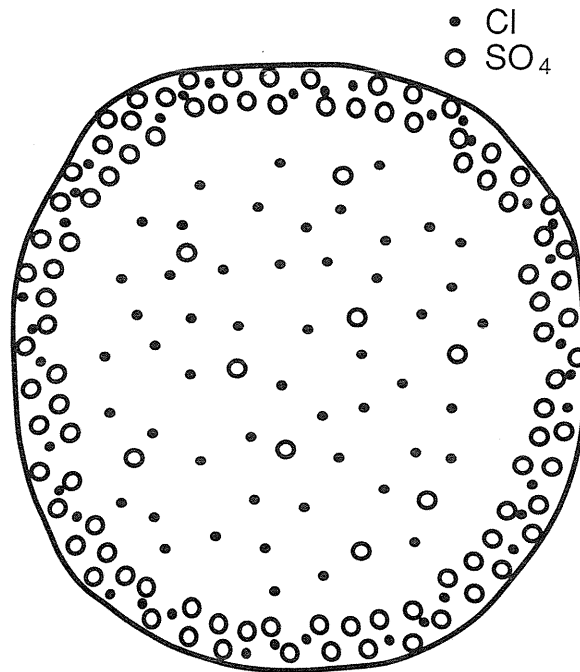


Figure 10: Hypothetical distribution of solute (SO_4^{2-} and Cl^- only) within a mature aged snow grain. The selective exclusion/retention of chemical species during metamorphosis results in snow grains with enriched surface concentrations, especially of insoluble ions such as SO_4^{2-} .

Table 1. Average normalized ionic ratios for initial meltwater aliquots.

Normalized Ratio	Age (days)			
	7	14	28	56
$\text{SO}_4^{2-}/\text{NO}_3^-$	1.8	2.4	2.7	2.8
$\text{SO}_4^{2-}/\text{Cl}^-$	1.7	2.4	2.5	2.1
$\text{NO}_3^-/\text{Cl}^-$	0.9	1.0	0.8	0.8

age for all ions. For the initial aliquots, SO_4^{2-} concentrations increase from 7 to 14 days, show little change between 14 and 28 days, and are lower at 56 days. So the lower $\text{SO}_4^{2-}/\text{Cl}^-$ ratio at 56 days could be attributed to lower SO_4^{2-} concentrations. Now the question becomes: why do SO_4^{2-} concentrations decrease at 56 days and, further, why do they remain stable instead of increasing between 14 and 28 days? An influential factor, we believe, is the type and shape of the snow crystals themselves. At 28 and 56 days (Fig. 5 and 6) the snow crystals are not just larger but highly faceted and sintered as well. During metamorphosis, impurities are excluded from/included within the crystals to a different extent depending on the final crystal shape. It is reasonable to expect that percolating water would rinse surface impurities from highly structured, sintered, depth-hoar-type crystals less rapidly and less efficiently than from rounded

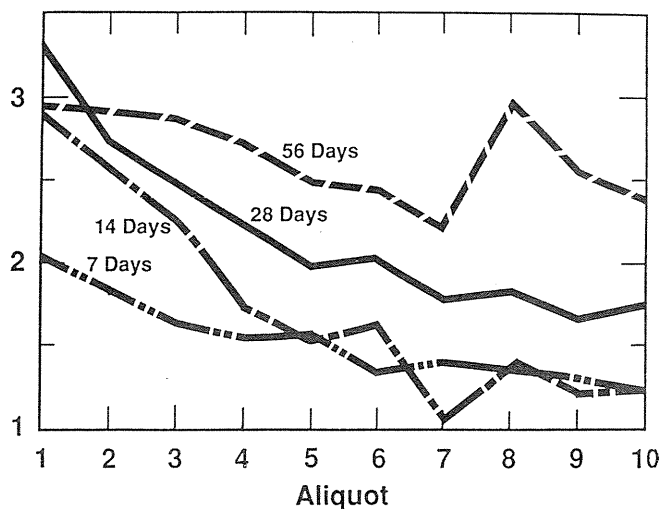


Figure 11: Individual normalized (to bulk snow) $\text{SO}_4^{2-}/\text{NO}_3^-$ ratio for initial ten elution aliquots. This ratio increases with snow age due to more efficient exclusion of SO_4^{2-} than NO_3^- (or conversely less efficient inclusion of SO_4^{2-} than NO_3^- within the ice crystal lattice) during snow crystal growth.

individual crystals. Thus, in cases where a snowpack is dominated by sintered depth-hoar crystals, solute release is retarded and initial chemical concentrations are lower. The chemical elution curves in Figure 8 are in accord with this explanation: between the 28- and 56-day-old snow where the degree of faceting and sintering is moderate to heavy, eluate concentrations in the initial aliquots remain level or decrease.

CONCLUSIONS

Preferential chemical elution during snowpack melting is strongly influenced by preferential chemical exclusion during snow crystal growth. Less soluble chemical impurities, such as sulfates, are excluded more efficiently and appear sooner and in higher concentrations than more soluble species, such as chloride. Snow crystal habit also influences the chemical release. The elution order and degree of fractionation is therefore "predetermined" before spring melt begins. Future work on physical and chemical changes during snowpack metamorphosis should focus upon the effect of different crystal types and growth rates upon the degree of fractionation in eluting meltwater.

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