

## Isotopic evolution of snowmelt

### 2. Verification and parameterization of a one-dimensional model using laboratory experiments

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[1] Three controlled cold room experiments were conducted to verify and parameterize a one-dimensional (1-D) model that simulates the isotopic composition of meltwater exiting the base of a snowpack. In the model, snow melts at the surface at a constant rate, and water percolates down the column while exchanging isotopically with ice. The effective rate of isotopic exchange and hence the isotopic composition of the melt at a given time is determined by the exchange rate constant  $k_r$ , the height of the original snowpack, the percolation velocity  $u^*$ , and the liquid to ice ratio in the exchange system. The experiments were designed to have different effective rates of exchange by varying the height of the snow column and the melt rate. Fitting the model to each of the experiments yielded  $k_r$  values that fall in a narrow range, 0.14 to 0.17  $\text{hr}^{-1}$ , confirming that  $k_r$  is an intrinsic rate constant for isotopic exchange. Knowing this value is important for developing future models, in which more complicated hydrological conditions are considered. **INDEX TERMS:** 1863 Hydrology: Snow and ice (1827); 1040 Geochemistry: Isotopic composition/chemistry; 1010 Geochemistry: Chemical evolution; **KEYWORDS:** snowmelt, oxygen 18 composition, laboratory experiments, isotopic exchange rate constant

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#### 1. Introduction

[2] Isotopic hydrograph separation has been widely used to study the proportion of different source waters contributing to streamflow, from which water pathways and residence times can be inferred [e.g., *Wels et al.*, 1991; *Buttle and Sami*, 1990]. To determine the contribution of snowmelt to spring runoff, oxygen or hydrogen isotopic compositions of snowmelt, stream water and groundwater are used to separate the hydrograph into new and old water components. During snowmelt, the new water input used for hydrograph separation should be the meltwater exiting the base of the snowpack. The isotopic composition of meltwater is usually assumed to be the average composition of the snowpack, which is often obtained by melting a snow core [*Rodhe*, 1981; *Bottomley et al.*, 1986]. However, the isotopic composition of meltwater varies over time [*Hooper and Shoemaker*, 1986; *Rodhe*, 1998]. Typically the meltwater is initially depleted in  $^{18}\text{O}$  and deuterium (D) relative to the bulk snow and then becomes progressively enriched in  $^{18}\text{O}$

and D through the melting season [*Stichler*, 1987; *Shanley et al.*, 1995; *Taylor et al.*, 2001].

[3] To predict the isotopic evolution of snowmelt, we developed a 1-D model for the isotopic evolution of meltwater [*Taylor et al.*, 2001; *Feng et al.*, 2002]. The model is based on the idea that when snowmelts at the surface, little isotopic fractionation occurs because the entire layer is melted. As this meltwater percolates down the snowpack, however, isotopic exchange takes place between the water and the ice. During this exchange, liquid water becomes depleted in  $^{18}\text{O}$  relative to ice and at equilibrium the  $\delta^{18}\text{O}$  of the water is 3.1‰ lower than that of the ice [*O'Neil*, 1968]. The model has provided insight into the physical mechanisms controlling the isotopic composition of snowmelt. It considers the physical properties of a snowpack (height, permeability, density and wetness) and the kinetics of isotopic exchange between ice and percolating water. The model indicates that the extent of ice-water isotopic exchange increases with the exchange rate constant and the height of the snowpack but decreases with the flow rate of the percolating meltwater.

[4] In our companion paper [*Feng et al.*, 2002], we discussed how the isotopic composition of meltwater is affected by the physical properties of the snow and the melting conditions. In order to extend this model to the field we need to constrain the key parameter in the model, the

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rate constant of the isotopic exchange between ice and water. This parameter can only be determined using controlled melting experiments, in which other physical parameters can be measured and their variations controlled. In addition, modeling data from the controlled experiments provides information about what parameters should be measured to predict temporal and spatial isotopic variations in the field.

[5] In this paper we report on three snowmelt experiments designed to estimate the rate constant of ice-water isotopic exchange. We melted snow columns of various heights using different melt rates, and measured oxygen isotopic compositions of meltwaters. The isotopic trends are fitted by the 1-D model, adjusting the model's parameters to optimize the fit. The rate constant of exchange is then calculated from the fit parameters.

## 2. Cold Room Experiments and Analytical Methods

### 2.1. Experimental Design

[6] While the detailed derivation and discussion of the 1-D model is provided in our companion paper, we list only the nondimensional equations for isotopic ratios to explain the experimental design. Assuming a homogeneous snow column being melted at a constant rate ( $\text{cm hr}^{-1}$  decrease in the snow depth) and ignoring dispersion, the governing equation for water is

$$\frac{\partial R_{\text{liq}}}{\partial t} = -\frac{\partial R_{\text{liq}}}{\partial z} + \psi\gamma(R_{\text{ice}} - \alpha R_{\text{liq}}) \quad (1)$$

and for ice is

$$\frac{\partial R_{\text{ice}}}{\partial t} = \psi(1 - \gamma)(\alpha R_{\text{liq}} - R_{\text{ice}}) \quad (2)$$

where  $R_{\text{liq}}$  and  $R_{\text{ice}}$  are the  $^{18}\text{O}/^{16}\text{O}$  ratio in the water and ice, respectively. The variable  $z$  is dimensionless depth below the snow surface (normalized by the initial depth of the snowpack), and  $t$  is dimensionless time since the onset of melt (normalized by the time that meltwater would take to percolate through the initial depth of the pack). The constant  $\alpha$  is the equilibrium fractionation factor for isotope exchange between ice and water at  $0^\circ\text{C}$ . Let  $a$  and  $b$  be the mass of water and ice, respectively, per unit volume of snow, we define  $f$  to be the fraction of ice participating in the isotope exchange. Therefore the value of  $bf$  is the mass of ice involved in the exchange. The parameter  $\gamma$  is defined as

$$\gamma = \frac{bf}{a + bf} \quad (3)$$

The parameter  $\psi$  is the dimensionless rate of isotopic exchange,

$$\psi = \frac{k_r Z}{u^*} \quad (4)$$

where  $k_r$  is the isotopic exchange rate constant (with dimension of  $\text{time}^{-1}$ ),  $Z$  is the initial snow depth and  $u^*$  is the percolation velocity. If  $k_r$  is constant, we can increase isotopic exchange by either increasing the snow depth or

decreasing the flow velocity because both parameters affect the time of contact between water and ice [Taylor et al., 2001].

[7] Our experimental design entailed obtaining a wide range of  $\psi$  values by melting a short column rapidly and a long column slowly. The parameters  $\psi$  and  $f$  was determined by fitting the model to the laboratory data; we then calculated the isotopic exchange rate constant  $k_r$  using (4).

### 2.2. Cold Room Experiments

[8] The melting experiments were conducted in a  $-1^\circ\text{C}$  cold room at the Cold Regions Research and Engineering Laboratory (CRREL). For each experiment, medium to course-grained natural snow, previously collected outside CRREL and stored in a  $-30^\circ\text{C}$  cold room, was allowed to equilibrate with the ambient temperature in the  $-1^\circ\text{C}$  cold room. We sieved the snow to  $<2$  mm, mixed it thoroughly and took three random samples to test for isotopic homogeneity. We then sieved the snow into a Plexiglas column (90 cm high with a 12.5 cm inside diameter). This Plexiglas column was placed on a plastic perforated disk and funnel. We determined the bulk density of the snow by measuring the volume and weight of the snow in the column.

[9] We used an infrared heat lamp to melt the snow at the top of the column. The lamp was suspended inside the Plexiglas column and moved down frequently so that it remained a fixed distance from the snow surface and melted the snow at a constant rate. The Plexiglas column was wrapped in insulation, a small strip of which could be temporarily removed to observe the snow depth and to adjust the height of the lamp. The melt rate was controlled by the voltage setting of the lamp as well as by the distance of lamp from the snow surface. Meltwater reaching the base of the column flowed through the perforated disk, into the funnel and to a fraction collector through plastic tubing (Figure 1). Heat tape was used to warm the tubing and prevent water from freezing inside the tube. Meltwater was collected in test tubes on a fraction collector that advanced at a set time interval. Our samples allowed us to determine (1) when a tube received meltwater, (2) the flow rate at a given time, (3) the volume of melt recovered as a function of time, and (4) the mass of the recovered melt as a fraction of the total mass of the initial snow.

[10] The three snow columns in experiments 1, 2, and 3 were 18, 38, and 74 cm high, respectively. The corresponding times of melting were 7.25, 72 and 171.5 hours. This gives an average melt rate of 2.5, 0.5, and 0.4  $\text{cm hr}^{-1}$  (Table 1).

[11] The long duration of experiment 3 necessitated that we place the fraction collector in an insulated box. This kept water that occasionally overflowed a tube from freezing onto the mechanism that advanced the tubes. As the insulated box alone did not prevent the water from freezing a light bulb was placed in the insulated box. Initially a 75-watt bulb was used but this overheated the air in the box. A 7.5-watt bulb was substituted and kept the temperature at  $+4^\circ\text{C}$  inside the box. This experimental detail affected the data quality for a short period of this experiment (see 3.3).

### 2.3. Oxygen Isotope Analysis

[12] The water samples were analyzed for  $\delta^{18}\text{O}$  using the method of  $\text{CO}_2$  equilibration [International Atomic Energy



**Figure 1.** Laboratory snow column experimental setup.

Agency, 1981]. The  $^{18}\text{O}/^{16}\text{O}$  ratio was determined using an isotope ratio mass spectrometer, and results were expressed in the  $\delta$  notation as parts per thousand difference relative to Vienna Standard Mean Ocean Water (VSMOW). The precision of the  $\delta^{18}\text{O}$  measurements was 0.1‰ (1 $\sigma$ ).

### 3. Results

#### 3.1. Mass Balance

[13] Mass balance calculations show that 94, 96 and 92% of the water was recovered for experiments 1, 2, and 3, respectively. Some water might have been evaporated from the snow surface during the experiment. These mass losses are within the range found by *Herrmann et al.* [1981] in similar experiments (4 to 13%).

[14] The isotopic mass balance is more difficult to constrain, because we did not analyze the melt collected in every tube. We interpolated the values for samples not

analyzed from the values of the adjacent samples measured for  $\delta^{18}\text{O}$ . The volume-weighted average meltwater  $\delta^{18}\text{O}$  from all three experiments suggests slight  $^{18}\text{O}$  enrichment by evaporation compared to the original snow composition: experiment 1 by 0.16‰, experiment 2 by 0.38‰ and experiment 3 by 0.31‰. In the following analysis we ignore any isotopic change caused by evaporation.

#### 3.2. Discharge

[15] To parameterize the model we need a good estimate of flow rate for each experiment. We obtained this rate from the discharge data measured by the fraction collector, which we plot as specific discharge (water equivalent depth per unit time). In Figure 2, we plotted the percentage of total melt at equally spaced specific discharge intervals for experiments 1 and 3. For experiment 1, 60% of meltwater had a specific discharge rate between 1.2 and 1.6  $\text{cm hr}^{-1}$ . For experiment 3, 69% of meltwater had a specific discharge rate between 0.2 and 0.3  $\text{cm hr}^{-1}$ . The values of 1.4, 0.53 and 0.25  $\text{cm hr}^{-1}$  were used as the model input for experiments 1, 2, and 3, respectively.

#### 3.3. Isotopic Composition of Snowmelt

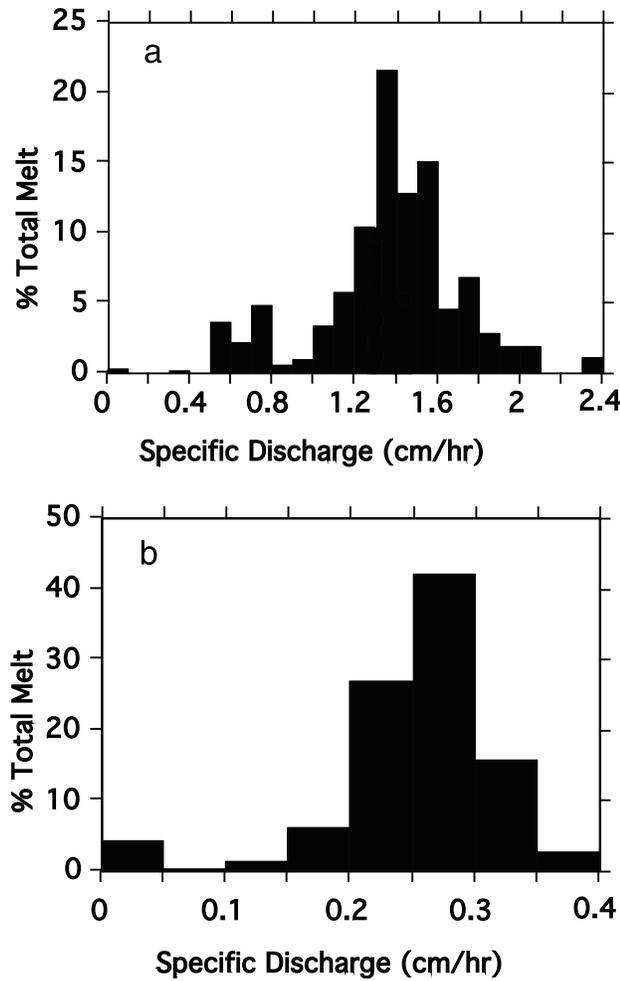
[16] The  $\delta^{18}\text{O}$  of the meltwater samples are plotted against the fraction of the melt relative to the total melt measured by the fraction collector (F). The  $\delta^{18}\text{O}$  values were scaled to plot as the relative difference between each sample and the initial snow by subtracting the snow's average initial isotopic composition from all of the measured values.

[17] In all three experiments,  $\delta^{18}\text{O}$  decreased over roughly the first 10% of the melt (Figure 3). We model this trend by setting the isotopic composition of the initial pore water equal to that of the bulk snow. As this pore water mixes and exchanges with the melt percolating down from the surface we obtain the initial decrease in  $\delta^{18}\text{O}$  seen in the laboratory experiments (see *Feng et al.* [2002] for more discussion). The maximum isotopic depletion in  $^{18}\text{O}$  of the meltwater from the original snow was 0.6‰ for experiment 1, 2‰ for experiment 2 and 1.7‰ for experiment 3. At an F value greater than about 0.1, the  $\delta^{18}\text{O}$  increased with F in all three experiments. However, the  $\delta^{18}\text{O}$  increase follows a linear trend for experiment 1 (except for the last data point), but curved trends for experiments 2 and 3.

[18] In experiment 3 (Figure 3c) a deviation from a smooth trend occurred at  $F \sim 0.2$  (shown by open circles), where the  $\delta^{18}\text{O}$  values are abnormally high. Our records show that these samples were collected when the 75 W bulb

**Table 1.** Laboratory Experiments

| Parameter                                       | Experiment 1    | Experiment 2    | Experiment 3    |
|---|-----------------|-----------------|-----------------|
| Snow height in column, cm                       | 18              | 38              | 74              |
| Average specific discharge, $\text{cm hr}^{-1}$ | $1.28 \pm 0.43$ | $0.58 \pm 0.16$ | $0.24 \pm 0.05$ |
| Specific discharge (used)                       | 1.4             | 0.58            | 0.25            |
| Duration of experiment, hours                   | 7.25            | 72              | 171.5           |
| Time to the first meltwater sample, hours       | 2.5             | 13.5            | 64              |
| Snow height when meltwater first appeared       | 13              | 31              | 55              |
| Lamp-snow distance, cm                          | 20              | 50              | 10              |
| Lamp power setting, V                           | 40              | 30              | 15              |
| Number of water samples collected               | 110             | 137             | 313             |
| Number of samples analyzed                      | 19              | 22              | 21              |



**Figure 2.** Histogram of the percent of total melt release during discrete discharge intervals: (a) specific discharge obtained from fraction collector for experiment 1; (b) specific discharge from experiment 3.

heated the insulated box, containing the fraction collector. Overheating by this bulb might have caused evaporative enrichment of these samples. We exclude them from the modeling calculations.

### 3.4. Model Results

[19] To predict the isotopic composition of snowmelt, we need to solve equations (1) and (2) simultaneously with assigned values of parameters  $\gamma$  and  $\psi$ . Both of these parameters are dependent on water saturation,  $S$ , which is constant at constant melt rate [Feng *et al.*, 2002]. Water saturation is defined as  $S = (S_w - S_i)/(1 - S_i)$ , where  $S_w$  is the total water volume over the pore volume and  $S_i$  is the irreducible water volume over the pore volume. The irreducible water content is assumed to be  $S_i = 0.04$  [Jordan, 1991]. In each experiment, a significant segment of the snow column is melted before the meltwater first appears at the base of the column, and the discharge is relatively constant from this time until the end of the experiment. At the time of the first meltwater appearance, the meltwater must have been held in the unmelted section of the snow column as pore water. We can calculate the

water content  $S$  by assuming that this meltwater is evenly distributed.

[20] The mass of ice and water is related to the water content by the following equations:

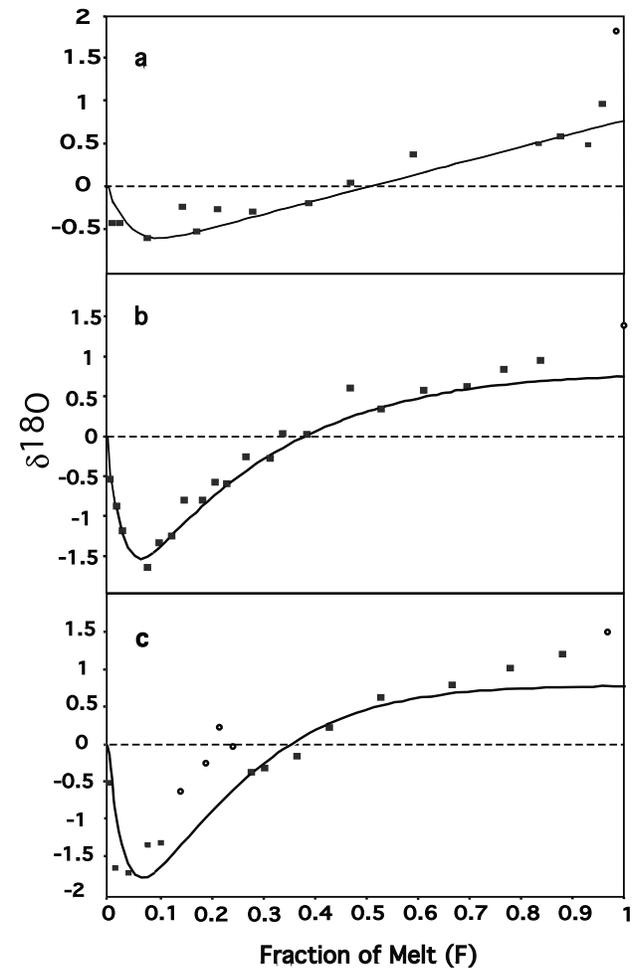
$$a = \phi(1 - S_i)(S + \beta)\rho_{liq} \quad (5)$$

$$b = \phi(1 - S_i)\rho_{ice} \quad (6)$$

where  $\phi$  is the snow porosity,  $\rho_{liq}$  and  $\rho_{ice}$  are the densities of water and ice, respectively, and  $\beta = S_i/(1 - S_i)$ . The porosity can be calculated using the measured initial bulk density ( $\rho_{bulk}$ ), because

$$\rho_{bulk} = \phi S_i \rho_{liq} + (1 - \phi)\rho_{ice} \quad (7)$$

[21] We used the  $\delta^{18}O$  of the bulk snow (the average of the three random samples) as the initial isotopic composition of both the ice and the irreducible water. For each experiment, we searched for the values of  $\psi$  and  $f$  that minimize the sum



**Figure 3.** The  $\delta^{18}O$  values of meltwater samples (points) and model output (line) plotted against  $F$ , the cumulative melt volume divided by the total melt volume: (a) data for experiment 1; (b) data for experiment 2; (c) data for experiment 3. The open circles represent samples that were isotopically enriched by evaporation and which have been excluded from the model calculations. The  $\delta^{18}O$  values were adjusted by subtracting the average isotopic composition of the initial snowpack (now shown by dashed line at  $\delta^{18}O = 0$ ) from all of the measured values.

**Table 2.** Model Parameters Used to Fit Data

| Parameter                                    | Experiment 1            | Experiment 2            | Experiment 3            | Source        |
|--|-------------------------|-------------------------|-------------------------|---------------|
| Bulk density, g cm <sup>-3</sup>             | 0.45                    | 0.43                    | 0.41                    | measured      |
| Average melt rate, cm hr <sup>-1</sup>       | 2.48                    | 0.53                    | 0.43                    | height/time   |
| Porosity                                     | 0.53                    | 0.56                    | 0.58                    | equation 7    |
| Irreducible water content S <sub>i</sub>     | 0.04                    | 0.04                    | 0.04                    | Jordan [1991] |
| Water saturation S                           | 0.31                    | 0.15                    | 0.19                    | calculated    |
| Percolation velocity u*, cm hr <sup>-1</sup> | 7.8                     | 2.7                     | 1.9                     | equation 8    |
| Intrinsic permeability, m <sup>2</sup>       | 2.6 × 10 <sup>-11</sup> | 4.1 × 10 <sup>-11</sup> | 1.7 × 10 <sup>-11</sup> | equation 9    |
| Initial δ <sup>18</sup> O, ‰                 | -17.8                   | -18.7                   | -16.4                   | measured      |
| α  | 1.0031                  | 1.0031                  | 1.0031                  | O'Neil, 1968  |
| f  | 0.9                     | 0.2                     | 0.2                     | optimized     |
| γ  | 0.68                    | 0.44                    | 0.37                    | equation 3    |
| a  | 0.18                    | 0.10                    | 0.13                    | equation 5    |
| b  | 0.43                    | 0.40                    | 0.39                    | equation 6    |
| ψ  | 0.4                     | 2.5                     | 5.5                     | optimized     |
| k <sub>r</sub> , hr <sup>-1</sup>            | 0.17                    | 0.17                    | 0.14                    | equation 4    |

of squares of the differences between modeled and measured isotopic compositions of the melt. All parameters are listed in Table 2.

[22] Figure 3 shows the best fit model curves (solid lines) plotted with the measured data. The model results fit the data fairly well with the exception of the last 5% of the melt, which is more enriched in <sup>18</sup>O than predicted by the model. We suggest that this is an experimental artifact. The last few percent of the snow was usually distributed around the edge of the plastic perforated disk. Without much snow present to absorb the energy from the lamp the temperature inside the column may have increased, enhancing evaporation of the remaining snow. We have indicated these points with circles, instead of squares, and excluded them from the calculations for the best fit. The best fit values of ψ are 0.4, 2.5 and 5.5 for experiments 1, 2, and 3. Using these values and the height of the snow column, the rate constant k<sub>r</sub> is calculated using (4) in which

$$u^* = \frac{Q}{\phi(1 - S_i)(S + \beta)} \quad (8)$$

[Hibberd, 1984]. The calculated k<sub>r</sub> is 0.17 hr<sup>-1</sup> for experiment 1, 0.17 hr<sup>-1</sup> for experiment 2 and 0.14 hr<sup>-1</sup> for experiment 3. The three values are within 15% of the average. The best fit f values are 0.9 for experiment 1 and 0.2 for experiments 2 and 3. These correspond to γ values of 0.68, 0.44 and 0.37, respectively.

## 4. Discussion

[23] Our research objective was to obtain parameters for the physically based model we described in Feng *et al.* [2002]. The model requires that the snow column be homogenous and the melt rate constant. The experiments are designed such that all parameters needed for the model calculations are measured except for two fitting parameters, ψ and f. In this section, we first discuss these fitting parameters and their uncertainties. We then model a set of field observations and discuss measurements needed to extend the model to the field.

### 4.1. Parameters ψ and f

[24] From the optimized values of ψ, we obtained k<sub>r</sub> values that range from 0.14 to 0.17 hr<sup>-1</sup>. This gives an average value of 0.16 ± 0.02 hr<sup>-1</sup>. Even though ψ varies by

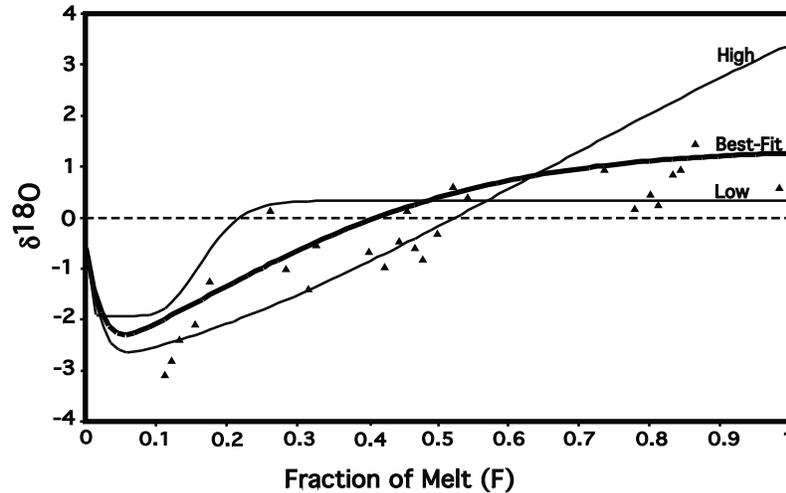
an order-of-magnitude (0.4 to 5.5) among these experiments, the relative standard deviation for the estimated k<sub>r</sub> is only 15%. The success of this parameterization indicates that our model captures the physical processes that control the isotopic composition of meltwater. In addition, knowing the value of k<sub>r</sub> is critical when this model is extended to field conditions. In our model, the parameter ψ is constant because the melt rate is held constant and dispersion is ignored (see equation (6) of Feng *et al.* [2002]). These assumptions may not be valid for a natural snowpack where the melt rate varies. Under such conditions k<sub>r</sub> becomes an independent parameter.

[25] The estimate of parameter f is less certain because we cannot measure either f or γ. An f value of 0.9 was obtained for experiment 1, which had an estimated water content of 31%. experiments 2 and 3, which had water contents of 15 and 19% respectively, have f values of 0.2 (Table 2). This range of f is large considering that the physical properties of snow were similar for all three experiments.

[26] The value of f may increase with the water content in two ways. First, because the snow column is not homogenous in terms of pore size not all pores ‘see’ percolating water. For example, when the water content is low, there may be water only in the small pores. This reduces the effective surface area over which isotopic exchange can occur.

[27] Second, when water wets the snow, metamorphism occurs, because the system reduces its surface energy by increasing its grain size. Recrystallization is one of the mechanisms of isotopic exchange [O'Neil, 1968]. During this process, small ice grains melt completely, without isotopic fractionation, but when water freezes onto larger ice particles <sup>18</sup>O preferentially enters the ice, making the liquid isotopically light. However, the relationship between grain growth and f may not be simple. On the one hand, f should increase with the rate of grain growth because a relatively high mass of snow is involved in the melting-recrystallization process. On the other hand, grain growth enlarges the mean particle size and thus reduces the surface area available for the direct interaction between liquid and ice. The relationship between water content and f will depend on the net result of these two processes.

[28] How the water content controls each of these processes is not known and should be investigated in future studies. Our work suggests that f may not be sensitive to the water content at low saturations (S < 0.2). Our experiment 2 and 3 had S values of 0.15 and 0.19 and they had the same optimized f value (0.2). Experiment 1 was significantly



**Figure 4.** The  $\delta^{18}\text{O}$  values of meltwater samples collected at CSSL (triangles) and model output (lines) plotted against  $F$ , the cumulative melt volume divided by the total melt volume. The thick line is the best fit model output and the thin lines are the model output for the lowest and the highest discharge rates. Only water samples collected after 17 April 1998 are included. The  $\delta^{18}\text{O}$  values were adjusted by subtracting the average isotopic composition (now shown by dashed line at  $\delta^{18}\text{O}=0$ ) of the initial snowpack from all of the measured values.

wetter ( $S = 0.31$ ) and the corresponding  $f$  value (0.9) was considerably higher.

#### 4.2. Modeling the Field Data

[29] Although field conditions often violate some of the assumptions of our model, applying the model to field data may help us to determine the next steps needed to extend this model to natural snowpacks. We used a snowmelt isotopic time series collected during the seasonal melt of a 3.1-meter snowpack at the Central Sierra Snow Laboratory (CSSL) [Taylor *et al.*, 2001]. Figure 4 shows the isotopic composition of meltwater (triangles) collected from 17 April to 25 June of 1998; during this period we measured continuous discharge from the melt pan. The distribution of the specific discharge is shown in Figure 5 and is characterized by three modes. These modes center at about 0.08, 0.4 and 0.8  $\text{cm hr}^{-1}$ , and are referred to as low, medium and high discharge rates. Measured parameters, including the initial height, bulk density, and initial isotopic composition of the snowpack, are listed in Table 3.

[30] We did not measure the intrinsic permeability of the snowpack. We used the average of 6 intrinsic permeability measurements,  $2.2 \times 10^{-9}$ , made previously at CSSL [Colbeck and Anderson, 1982]. The intrinsic permeability,  $k$ , is related to the hydraulic conductivity  $K$  by

$$K = \frac{kg\rho_w}{\mu} \quad (9)$$

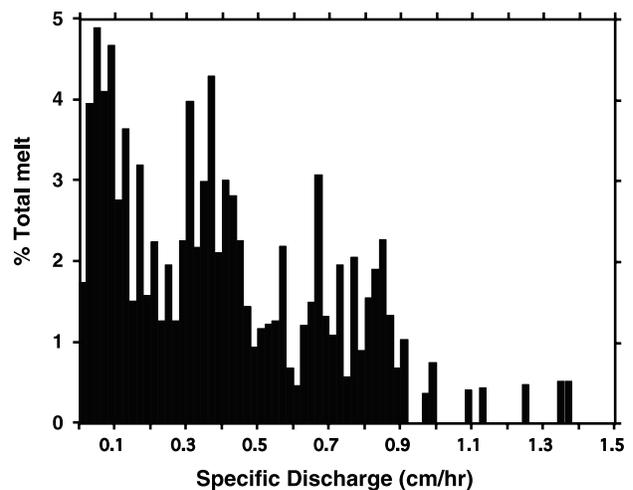
and to  $Q$  by

$$Q = \frac{kg\rho_w S^3}{\mu} \quad (10)$$

where  $g$  is gravitational constant and  $\mu$  is water viscosity. We calculated the water content using (10), and obtained the percolation velocity  $u^*$  from (8). All common parameters and parameters for each discharge mode are listed Table 3.

[31] First, we generated two curves corresponding to the highest and lowest discharge (thin lines in Figure 4). We tuned  $f$  to best bracket the range of the observed  $\delta^{18}\text{O}$  values. The corresponding  $f$  value is 0.1 for the low flow and 0.7 for the high flow. We also obtained the best fit using both  $\psi$  and  $f$  as fitting parameters (thick line). The optimized values are 3 for  $\psi$  and 0.3 for  $f$ .

[32] We make two observations. First, the best fit  $\psi$  value yields a flow rate similar to the highest flow rate, suggesting that conditions experienced during high flow may dominate the isotopic composition of the melt. Second, the measured isotopic variation in the snowmelt is likely caused by melt



**Figure 5.** Histogram showing the percent of total melt release within discrete discharge intervals for data collected at Central Sierra Snow Laboratory. These data include only discharge measurements after 17 April 1998, when continuous flow was measured at the tipping bucket.

**Table 3.** Model Parameters Used to Fit Central Sierra Snow Laboratory Data

| Parameter   | High   | Med.   | Low    | Best Fit | Source                      |
|---|--------|--------|--------|----------|-----------------------------|
| Bulk density, g cm <sup>-3</sup>                        | 0.42   | 0.42   | 0.42   | 0.42     | measured                    |
| Snowpack height, cm                                     | 310    | 310    | 310    | 310      | measured                    |
| Specific discharge, cm hr <sup>-1</sup>                 | 0.8    | 0.4    | 0.08   |          | melt pan                    |
| Porosity  | 0.57   | 0.57   | 0.57   | 0.57     | equation 7                  |
| Irreducible water content S <sub>i</sub>                | 0.04   | 0.04   | 0.04   | 0.04     | Jordan [1991]               |
| Water saturation S                                      | 0.06   | 0.05   | 0.03   | 0.06     | equation 9                  |
| Percolation velocity u*, cm hr <sup>-1</sup>            | 14.8   | 8.4    | 2.2    | 17.6     | equation 8                  |
| Intrinsic permeability, 10 <sup>-9</sup> m <sup>2</sup> | 2.2    | 2.2    | 2.2    | 2.2      | Colbeck and Anderson [1982] |
| Initial δ <sup>18</sup> O, ‰                            | -14.1  | -14.1  | -14.1  | -14.1    | measured                    |
| A   | 1.0031 | 1.0031 | 1.0031 | 1.0031   | O'Neil [1968]               |
| F   | 0.7    | 0.3    | 0.1    | 0.3      | optimized                   |
| Γ   | 0.68   | 0.7    | 0.75   | 0.68     | equation 3                  |
| A   | 0.06   | 0.05   | 0.04   | 0.05     | equation 5                  |
| B   | 0.39   | 0.39   | 0.39   | 0.39     | equation 6                  |
| Ψ   | 3.3    | 5.9    | 23     | 3.0      | optimized                   |
| k <sub>r</sub> , hr <sup>-1</sup>                       | 0.16   | 0.16   | 0.16   | 0.16     | this work                   |

rate variations throughout the melt season. We point out, however, that calculations made using a constant low and high flow are not an adequate way to describe the isotopic variations in the snowmelt, because each δ<sup>18</sup>O value is determined by the melting history prior to that time. Nevertheless, our calculation suggests that changes in the water percolation velocity may be the main source of isotopic variation. To confirm this idea, a model including variable flow rate should be used.

[33] One may model field isotope data by adding the governing isotopic equations to a 1-D mass and energy model, such as SNTHERM [Jordan, 1991]. SNTHERM uses meteorological data to determine the conditions in the snowpack and to predict water flow from the pack. This model calculates the melt rate using the incoming and outgoing radiation data at hourly or shorter time intervals. The model also allows the snowpack to change in height and to melt or freeze depending upon the thermal conditions in the pack. Currently, models such as SNTHERM include more complicated processes than considered in our simple 1-D isotope model. We therefore need to expand our model to include these processes (e.g., refreezing), and verify each refinement using controlled experiments.

## 5. Conclusion

[34] In a cold room, we melted three snow columns of different heights at different rates. The isotopic compositions of the meltwaters were used to parameterize a 1-D model that describes the isotopic evolution of snowmelt. The optimized values for the dimensionless rate constant of isotopic exchange (ψ) gave a consistent value for the exchange rate consistent k<sub>r</sub> = 0.16 ± 0.02 hr<sup>-1</sup>. This value can be used for future applications both in the laboratory and in the field.

[35] The fraction of ice involved in isotopic exchange with water (f) is not as well constrained as ψ. However, our calculations suggest that f may increase with water content. This could result from wet snow metamorphism, in which small snow particles melt and large ones grow. As the grain growth rate increases with increasing water content, more ice would be involved in isotopic exchange with the liquid.

[36] We modeled field data collected at CSSL to help us determine what information we would need to extend this

model to natural snowpacks. We were able to fit the trend of the data using 0.16 hr<sup>-1</sup> for k<sub>r</sub>, 3.0 for ψ and 0.3 for f. This ψ value is close to that calculated for the high flow rate, which suggests that conditions experienced during high flow may dominate the isotopic composition of the melt. Calculations using other flow rates or f values indicate that the measured isotopic scatter in the data set is likely caused by variations of the flow rate. Accurately describing isotopic evolution in the field will require altering the model to allow flow rate to vary with melting conditions.

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