

Isotopic evolution of snowmelt

1. A physically based one-dimensional model

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Received 27 July 2001; revised 8 June 2002; accepted 20 June 2002; published 31 October 2002.

[1] The $^{18}\text{O}/^{16}\text{O}$ ratio of snowmelt from a seasonal snowpack typically increases with time as the melting process progresses. This temporal evolution is caused by isotopic exchange between liquid and ice as meltwater percolates down the snow column. Consequently, hydrograph separations of spring runoff using the bulk snow composition as the new water end-member will be erroneous. Accurate determinations of the new water input should take into account the temporal variation of the snowmelt. Here we present a one-dimensional (1-D) physically based model for the isotopic evolution of snowmelt. Two parameters, the effective rate of isotopic exchange between water and ice and the ice to liquid ratio of the exchange system, are important for controlling the range and temporal pattern of the isotopic variation in snowmelt. For all plausible values of these parameters the modeled isotopic signature of snowmelt changes by 1–4‰ as snowmelt progresses. These isotopic shifts will affect the results of hydrograph separations. *INDEX TERMS:* 1863 Hydrology: Snow and ice (1827); 4870 Oceanography: Biological and Chemical: Stable isotopes; 3210 Mathematical Geophysics: Modeling; *KEYWORDS:* snowmelt, oxygen isotopes, modeling, spring runoff

Citation: Feng, X., S. Taylor, C. E. Renshaw, and J. W. Kirchner, Isotopic evolution of snowmelt, 1, A physically based one-dimensional model, *Water Resour. Res.*, 38(10), 1217, doi:10.1029/2001WR000814, 2002.

1. Introduction

[2] Subsurface flow paths affect many watershed processes, including flood generation [e.g., *Beven and Kirkby*, 1979; *Bonell*, 1993], contaminant transport [e.g., *Kirchner et al.*, 2000; *Larsson et al.*, 1999], soil gas emission fluxes [e.g., *Li et al.*, 1992], and rates of chemical weathering [*Engstrom et al.*, 2000] and acid neutralization [e.g., *Bishop et al.*, 1990]. Subsurface flow paths and residence times of water are commonly inferred from stream hydrograph separations of individual precipitation or snowmelt events [e.g., *Hooper and Shoemaker*, 1986; *McDonnell et al.*, 1991; *Obradovic and Sklash*, 1986; *Cooper*, 1998; *Soulsby et al.*, 2000; *Wels et al.*, 1991]. This technique assumes that the stream discharge during and shortly after a rain or snowmelt episode can be separated into a few (typically two or three) contributing sources, e.g., groundwater (old water) and event water (or new water). Oxygen or hydrogen isotopes of water are widely used for hydrograph separations because these elements are components of water and can be considered conservative over the time-scale of concern.

[3] In the case of hydrograph separation of spring runoff, the “new water” end-member is often assumed to have a constant $\delta^{18}\text{O}$ value equal to the average $\delta^{18}\text{O}$ of the

snowpack [*Bottomley et al.*, 1986; *Rodhe*, 1981]. However, both laboratory and field investigations [e.g., *Herrmann and Stichler*, 1981; *Taylor et al.*, 2001] have shown that the $\delta^{18}\text{O}$ value of snowmelt does not equal the $\delta^{18}\text{O}$ of bulk snow. Instead, the snowmelt is typically ^{18}O -depleted early in the melt season and becomes gradually enriched in ^{18}O as melting proceeds. This isotopic evolution results from isotopic exchange between water and ice as water percolates down the snow column. At equilibrium, the $\delta^{18}\text{O}$ of water is 3.1‰ lower than that of ice [*O’Neil*, 1968], so the initial snowmelt leaving the pack has a lower $\delta^{18}\text{O}$ value than the bulk snow. As melting progresses, the remaining pack becomes increasingly enriched in ^{18}O and, consequently, so does the corresponding melt. Because the isotopic composition of snowmelt is usually not the same as the isotopic composition of the bulk snow, hydrograph separations based on the $\delta^{18}\text{O}$ of the bulk snow will be in error [*Feng et al.*, 1998]. This interaction between ice and water may also affect the isotopic compositions of glaciers that experience some degree of melting in the summer. Understanding and quantifying the isotopic alteration in ice through ice-water exchange is important for climatic studies using ice cores.

[4] Although the qualitative description of isotopic exchange between liquid water and ice is straightforward, a quantitative description of this process is necessary if the isotopic compositions of snowmelt or glaciers are to be predicted. Such a quantitative description must include the effects of the physical properties of the snowpack, including its depth, porosity, and permeability. *Búason* [1972] pre-

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sented the first model describing the isotopic variability of snowmelt. His model considers the rate of water percolation and kinetics of ice-water exchange, but assumes that the isotopic exchange reaction occurs between water and the bulk ice rather than between the water and the ice surface. We [Taylor *et al.*, 2001] recently have described an alternative model, which quantifies the surface area using a parameter that allows only a fraction of the ice to interact with the liquid water. In this contribution, we refine our model and systematically discuss the parameters controlling the $\delta^{18}\text{O}$ of snowmelt during the process of melting, particularly those parameters controlling the isotopic exchange between the fluid and solid phases. In a companion paper [Taylor *et al.*, 2002], we measure the important physical constants for the ice-water exchange kinetics using controlled experiments. We will focus our discussion to modeling snowmelt from seasonal snowpacks, but the physical model can be extended to describe the effect of melting on the isotopic variations of glaciers.

2. Physically Based 1-D Model

2.1. Governing Equation for Water Percolation in Snow

[5] We assume that the snowpack is homogeneous. Water percolation in snow is usually described by a reduced form of Richards' equation [Colbeck, 1972; Hibberd, 1984],

$$\frac{\partial S}{\partial t^*} = -\frac{K}{\phi(1-S_i)} \frac{\partial S^n}{\partial z^*} \quad (1)$$

where ϕ is porosity of snow, t^* and z^* are dimensional time and depth below the snow surface, K is hydraulic conductivity of the snowpack at saturation, and S is the effective water saturation, which is related to the total water saturation S_w (water volume/pore volume) and irreducible water saturation S_i (irreducible water volume/pore volume) as

$$S = \frac{S_w - S_i}{1 - S_i} \quad (2)$$

K is hydraulic conductivity of the snowpack at saturation, and is determined by water density, ρ , gravitational acceleration, g , and water viscosity, μ as

$$K = \frac{\rho kg}{\mu} \quad (3)$$

The parameter n relates the percolation velocity u^* to the saturated hydraulic conductivity and effective saturation through the constitutive relation [Hibberd, 1984]

$$u^* = \frac{K}{\phi(1-S_i)} \frac{S^n}{S+\beta} \quad (4)$$

where $\beta = S_i/(1-S_i)$. In this work n is taken to be 3, following Colbeck [1972].

[6] Equation (1) is in the form of the well-known kinematic wave equation. Solutions to this equation break down at a saturation wave front, which must be treated separately.

If we define the wave front as the location where the fluid volume flux increases abruptly, then the wave front propagates at a velocity η^* given for ripe snow by [Hibberd, 1984]

$$\eta^* = \frac{K}{\phi(1-S_i)} \frac{S_+^n - S_-^n}{S_+ - S_-} \quad (5)$$

where S_+ and S_- are the saturation values directly behind and preceding the wave front.

2.2. Governing Equations for Isotope Ratios of Water and Ice

[7] The $^{18}\text{O}/^{16}\text{O}$ ratio of the liquid phase (R_{liq}) is controlled by advection, dispersion, and ice-water isotopic exchange. In contrast, the $^{18}\text{O}/^{16}\text{O}$ ratio of ice (R_{ice}) is only controlled by its isotopic exchange with the liquid. The standard governing equations for R_{liq} and R_{ice} are,

$$(S+\beta) \frac{\partial R_{\text{liq}}}{\partial t^*} = -\frac{\partial [u^*(S+\beta)R_{\text{liq}}]}{\partial z^*} + \frac{\partial}{\partial z^*} \cdot \left[(S+\beta)D^* \frac{\partial R_{\text{liq}}}{\partial z^*} \right] + k_r \gamma (S+\beta) (R_{\text{ice}} - \alpha R_{\text{liq}}) \quad (6)$$

$$\frac{\partial R_{\text{ice}}}{\partial t^*} = k_r (1-\gamma) (\alpha R_{\text{liq}} - R_{\text{ice}}) \quad (7)$$

where D^* is the dispersion coefficient, k_r is the ice-water isotope exchange rate constant, and α is the equilibrium fractionation factor for oxygen isotope exchange between ice and water at 0°C . The isotopic exchange is assumed to be first order with respect to the volume concentration of ^{18}O in both the liquid and the ice [Criss *et al.*, 1987; Feng and Savin, 1993]. This is equivalent to saying that the rate of isotope exchange is proportional to the distance ($R_{\text{ice}} - \alpha R_{\text{liq}}$) of the system from ice-liquid equilibrium ($R_{\text{ice}} - \alpha R_{\text{liq}} = 0$). The parameter γ is used to quantify the fraction of ice in the ice-water isotopic exchange system,

$$\gamma = \frac{bf}{a+bf} \quad (8)$$

where a and b are the mass of water and ice per unit volume of snow,

$$a = \phi(1-S_i)(S+\beta)\rho_{\text{liq}} \quad (8a)$$

$$b = (1-\phi)\rho_{\text{ice}} \quad (8b)$$

with ρ_{ice} and ρ_{liq} being the density of ice and liquid water, respectively. The parameter f denotes the fraction of ice involved in isotopic exchange; f will depend on the size distribution and surface roughness of the ice grains, the accessibility of the ice surface to the infiltrating water, the extent of solid diffusion within the ice, and the degree of melting and refreezing at the ice surface. In practice, these microscopic variables cannot be directly measured, and f is treated as a tuning parameter.

[8] In this paper we only consider a simple flow condition: a ripe snowpack melting at a constant rate. Under

this condition, the water saturation S and flow velocity u^* are constant and equation (6) becomes

$$\frac{\partial R_{\text{liq}}}{\partial t^*} + u^* \frac{\partial R_{\text{liq}}}{\partial z^*} = \frac{\partial}{\partial z^*} \left[D^* \frac{\partial R_{\text{liq}}}{\partial z^*} \right] + k_r \gamma (R_{\text{ice}} - \alpha R_{\text{liq}}) \quad (9)$$

We further assume that dispersion is not significant, i.e., $D^* = 0$. Equation (9) then reduces to

$$\frac{\partial R_{\text{liq}}}{\partial t^*} + u^* \frac{\partial R_{\text{liq}}}{\partial z^*} = k_r \gamma (R_{\text{ice}} - \alpha R_{\text{liq}}) \quad (10)$$

2.3. Nondimensional Equations

[9] For discussion and comparison purposes, it is convenient to nondimensionalize the governing equations. We define nondimensional depth z and time t , by normalizing by the initial depth of the snowpack, Z , and the time it takes percolating water to traverse that distance:

$$z \equiv \frac{z^*}{Z} \quad \text{and} \quad t \equiv \frac{t^* u^*}{Z} \quad (11)$$

Equations (1), (4), (5), (10) and (7) become

$$\frac{\partial S}{\partial t} + \frac{n(S + \beta)}{S} \frac{\partial S}{\partial z} = 0 \quad (12)$$

$$u = 1 \quad (13)$$

$$\eta = \frac{\eta^*}{u^*} \quad (14)$$

$$\frac{\partial R_{\text{liq}}}{\partial t} + \frac{\partial R_{\text{liq}}}{\partial z} = \psi \gamma (R_{\text{ice}} - \alpha R_{\text{liq}}) \quad (15)$$

$$\frac{\partial R_{\text{ice}}}{\partial t} = \psi (1 - \gamma) (\alpha R_{\text{liq}} - R_{\text{ice}}) \quad (16)$$

where

$$\psi = \frac{k_r Z}{u^*} \quad (17)$$

The dimensionless constant ψ quantifies effectiveness of the isotopic exchange. While k_r should be constant, one can increase the extent of ice-water exchange by either increasing the snow depth or decreasing the flow velocity, both of which increase the time of contact between ice and water.

2.4. Solution for a Constant Melt Rate

[10] Our solution procedure is as follows: We first solve the flow equation (12) assuming that initially the snow column is ripe [Colbeck, 1976] and at the irreducible saturation level. At $t = 0$, S at the surface is increased from zero to S_0 and kept at this value for the entire experiment. Therefore the initial and boundary conditions are

$$S(0, z) = 0 \quad (18)$$

$$S(t, z_s) = S_0 \quad (19)$$

where z_s represents the snow surface. Because the snowpack is melting from the top, the surface boundary moves downward. The melt rate V_m^* is defined as the rate at which the snow depth decreases. It is related to the water saturation by,

$$V_m^* = \frac{u^* \phi S_w}{(1 - \phi) \frac{\rho_{\text{ice}}}{\rho_{\text{liq}}} + \phi S_w} = \frac{u^* \phi (1 - S_i) (S_0 + \beta)}{(1 - \phi) \frac{\rho_{\text{ice}}}{\rho_{\text{liq}}} + \phi (1 - S_i) (S_0 + \beta)} \quad (20)$$

The corresponding nondimensional melt rate V_m is

$$V_m = \frac{\phi (1 - S_i) (S_0 + \beta)}{(1 - \phi) \frac{\rho_{\text{ice}}}{\rho_{\text{liq}}} + \phi (1 - S_i) (S_0 + \beta)} \quad (21)$$

[11] The sudden increase of water saturation at $t = 0$ at the snow surface creates a wave-front. Preceding the wave-front, $S = 0$ and behind it, $S = S_0$. Therefore using (4), (5) and (14), the velocity of the wave-front propagation η is

$$\eta = 1 + \frac{\beta}{S_0} \quad (22)$$

Note that β is greater than zero and thus $\eta > u = 1$, i.e., the wave-front travels faster than the water itself.

[12] With the given boundary and initial conditions, the solution for (12) is a constant $S = S_0$ behind the wave-front (Figure 1). This solution suggests that, with a constant water saturation, the water percolation velocity (u^*) is constant for a homogenous snowpack (equation (4)). Thus we can use (10) and (7) (or the nondimensional equations (15) and (16)) as governing equations to solve for the isotopic ratios of water and ice during the melting process.

[13] The initial isotopic ratio of ice is assumed to be the isotopic ratio of the bulk snow before melting, R_0 , i.e.,

$$R_{\text{ice}}(0, z) = R_0 \quad (23)$$

This is valid because the initial water content is very low (assumed to be $S_i = 0.04$ in this work). R_{ice} is the isotope ratio of the fraction (f) of the ice that participates in the isotopic exchange with the water (and therefore evolves over time); the isotope ratio of the rest of the ice is assumed to remain constant at R_0 . The initial $^{18}\text{O}/^{16}\text{O}$ ratio for the irreducible water in snow is difficult to constrain. Two end-member values are (1) the upper bound which is identical to that of ice and (2) the lower bound that is in isotopic equilibrium with the ice (3.1‰ lower than the $\delta^{18}\text{O}$ of ice). In nature the actual value will probably lie between these end-members, and will depend on the history of snow metamorphism prior to the onset of continuous melting. Here we assume that the initial isotopic ratio of the liquid is the same as that of the bulk snow, that is

$$R_{\text{liq}}(0, z) = R_0 \quad (24)$$

This assumption yields solutions that resemble our experimental observations and some of our field data [Taylor et al., 2001, 2002], but it is not necessarily valid for all snowpacks. However, using the lower bound assumption

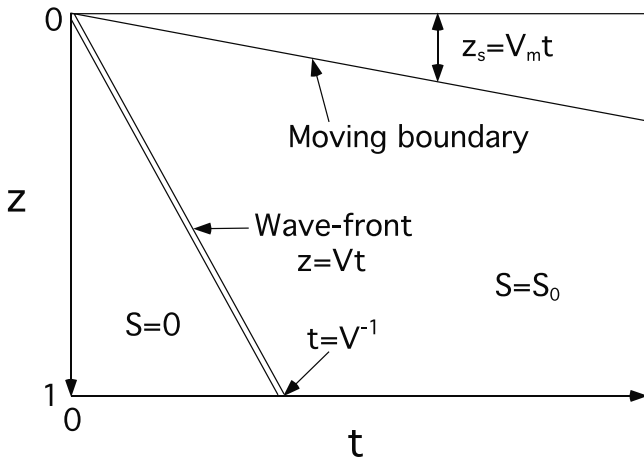


Figure 1. Solution for equation (12). Water saturation at the surface increases abruptly at $t = 0$ from $S = 0$ to $S = S_0$ and kept at that level until the snowpack is all melted. The abrupt increase in saturation creates a wave front that travels with a velocity V . The double line shows the position of the wave front. Before the wave front reaches the bottom ($t < V^{-1}$), the solution is $S = 0$ preceding the front and $S = S_0$ behind it. At $t > V^{-1}$, $S = S_0$ everywhere. The snow surface moves down at a velocity V_m because of melting.

would only affect the isotopic composition of the early melt (first 10%).

[14] The boundary condition for R_{ice} is that R_{ice} at z_s ($z_s = tV_m$)

$$R_{ice} = R_{ice}(t, z_s) \quad (25)$$

R_{liq} at the boundary is the isotopic ratio of the meltwater generated at z_s . It has three components, 1) the pore water, 2) the ice that has undergone isotopic exchange with the liquid, and 3) the ice not participating in the isotopic exchange and thus still having the original isotopic composition. Therefore, at the surface,

$$R_{liq} = \frac{a}{a+b} R_{liq}(t, z_s) + \frac{bf}{a+b} R_{ice}(t, z_s) + \frac{b(1-f)}{a+b} R_0 \quad (26)$$

[15] Equations (15) and (16) are solved numerically using the initial and boundary conditions given by (23), (24), (25) and (26). Constants used for the calculations are listed in Table 1.

3. Results and Discussion

[16] This simple physically-based 1-D model has shown promise in our earlier work [Taylor *et al.*, 2001], and its validity is further tested in our companion paper [Taylor *et al.*, 2002]. Our goal in this paper is to discuss the factors controlling the isotopic evolution of snowmelt and the physical significance of the model parameters. We also make predictions for field observations given a possible range of snow properties and melting conditions. Finally, we describe the implications for hydrograph separation.

3.1. Effective Rate of Isotopic Exchange

[17] It is not trivial to evaluate the contribution of the individual physical parameters because of the many inter-

relationships among them. Equations (15) and (16) indicate that the change of the isotopic ratios in meltwater and ice are controlled by two nondimensional constants, ψ and γ . The parameter ψ quantifies the effectiveness of isotopic exchange, which increases with increasing depth of the snowpack and with decreasing velocity of water percolation. The parameter γ (and more directly f) is a measure of how much ice is involved in the isotopic exchange with the liquid phase. Both ψ and γ are dependent upon the physical properties of snowpack and its melt rate. We first discuss how the characteristics of the solution for equations (15) and (16) are controlled by ψ and γ , and then we examine how ψ and γ are related to the physical properties of snow.

[18] Figure 2 illustrates how the $\delta^{18}O$ of meltwater evolves over time for different values of ψ and γ . The values of other constants and parameters are listed either in Table 1 or in the caption. The isotopic value in the diagrams is defined as $(R_{liq}(t, 1)/R_0 - 1)1000$, i.e., it is the relative difference from the original bulk snow. The dashed horizontal line at $\delta^{18}O = 0$ indicates the composition of the original snow. The vertical lines in Figure 2 are drawn at the 0.1 melt fraction. The initial $^{18}O/^{16}O$ ratio of the pore water is assumed to equal that of the bulk snow. This assumption may not be appropriate for all snowpacks. Thus the first 10% of the melt composition observed in the field may not resemble the trend here. For example, if the initial pore water were assumed to be in isotopic equilibrium with the bulk snow, the meltwater $\delta^{18}O$ would start at -3.1‰ and rise monotonically throughout the simulation.

[19] Figure 2 shows that the meltwater $\delta^{18}O$ trend may be curved, changing rapidly during the early melt and more slowly toward the end. Other solutions show more or less linear trends throughout the entire melting process (except for the initial transient). Roughly speaking, one can see that a curved trend usually occurs when ψ is relatively large and f is relatively small (γ is small).

[20] One fact to keep in mind is that snow is very permeable, and thus the water content is typically low (5–10% of pore volume [Colbeck and Anderson, 1982]). Therefore the liquid fraction is a small proportion of the bulk snow. For example, given a saturation of $S = 0.1$, an irreducible water content $S_i = 0.04$ and a porosity of 0.5 the liquid water is 12.9% of the total mass of the system. If f is 0.3, the liquid to exchangeable ice ratio (a/bf) is about 0.5. Therefore even with a relatively low f , there is sufficient mass of ice to exchange with the liquid. In the discussions below, we will use the following terms to describe the various components of the system. We define bulk snow as the total system that includes both liquid and solid phases ($a + b$). Exchangeable ice refers to the fraction of ice that interacts with the liquid water (bf), and the remaining ice, $b(1 - f)$, is referred to as nonexchangeable ice. Bulk ice refers to the total ice (b).

[21] Consider an extreme case with a large value of ψ (e.g. a very long snow column and very slow fluid velocity) and a relatively small value of f . Initially, at the snow surface, meltwater and the exchangeable ice both equal the bulk snow, i.e., 3.1‰ out of equilibrium from each other. Since ψ is large, the exchange is substantial, making the melt considerably depleted in ^{18}O when it approaches the base of the snowpack. One can see from Figure 2a that the maximum depletion of the early melt increases with increasing ψ . This exchange causes the

Table 1. List of Symbols

Symbol	Description	Units	First Used in Equation
α	equilibrium oxygen isotope fractionation factor between ice and water (=1.0031)		(6)
a	mass of liquid water	g/cm ³	(8)
b	mass of ice	g/cm ³	(8)
β	$S_i/(1 - S_i)$		(4)
D^*	dispersion coefficient	cm/s	(6)
f	fraction of ice involved in exchange		(8)
g	gravitational acceleration (=980)	cm/s ²	(3)
k	intrinsic permeability	cm ²	(3)
K	hydraulic conductivity	cm/s	(1)
k_r	isotope exchange rate constant	s ⁻¹	(6)
n	exponent (=3)		(1)
ρ_{ice}	density of ice at 0°C (=0.917)	g/cm ³	(8)
ρ_{liq}	density of water at 0°C (=1)	g/cm ³	(9)
γ	fraction of liquid (=a/bf)		(6)
R_{ice}	¹⁸ O/ ¹⁶ O ratio of ice exchanging with the liquid		(6)
R_{liq}	¹⁸ O/ ¹⁶ O ratio of pore water		(6)
R_0	Initial ¹⁸ O/ ¹⁶ O ratio of the bulk snow		(23)
S	effective water saturation $(S_w - S_i)/(1 - S_i)$		(1)
S_i	irreducible water content: irreducible volume of water over pore volume		(2)
S_w	total water content: total water volume over the pore volume		(2)
t^*	time	s	(1)
t	dimensionless time		(11)
u^*	water velocity	cm/s	(4)
u	dimensionless velocity		(13)
μ	viscosity of water at 0°C	dyne-s/cm ²	(3)
V_m^*	melt rate	cm/s	(20)
V_m	dimensionless melt rate		(21)
z^*	depth	cm	(1)
z	dimensionless depth		(11)
Z	total depth of the snow pack	cm	(11)
z_s	dimensionless depth of snow surface (=tV _m)		(25)
ϕ	porosity		(1)
ψ	dimensionless parameter (=k _r Z/u*)		(15)
η^*	wave velocity	cm/s	(5)
η	dimensionless wave velocity		(14)

liquid water and the exchangeable ice to adjust to equilibrium values relative to each other (~3‰ difference). Because only a small proportion of ice changes its isotopic composition (f is small), the $\delta^{18}\text{O}$ of the bulk ice does not change significantly. With time, the newly generated meltwater at the surface approaches a constant isotopic value, and so does the exchangeable ice. These two phases are related by $\alpha R_{liq} \approx R_{ice}$, under which condition the exchange reaction reaches steady state, and the $\delta^{18}\text{O}$ of the meltwater becomes a horizontal line. Such a system produces a curved trend in the isotopic evolution.

[22] The other extreme scenario is when f is large (e.g., close to 1) and ψ is relatively small (e.g., short column and high fluid velocity). Two things happen in this case; (1) the ratio of liquid to the exchangeable ice (a/bf) is small, and therefore the ice phase does not change its isotopic composition as much as the liquid phase, and (2) the newly generated meltwater at the snow surface has the isotopic composition similar to the exchangeable ice below the surface and thus is always out of equilibrium with the ice by about 3‰. This constant difference between liquid and ice results in a constant slope of the $\delta^{18}\text{O}$ curve, and therefore a straight line trend.

[23] The intermediate situations between these two end-member cases produce shapes that vary in curvature and slope. Both curved and linear trends have been observed in field and laboratory experiments [Arnason, 1969; Herrmann and Stichler, 1981; Maulé and Stein, 1990; Shanley

et al., 1995; Taylor *et al.*, 2001]. Particularly, in a series of cold room experiments we conducted melt experiments using snow columns of different heights and various melt rates [Taylor *et al.*, 2002]. We observed a linear isotopic trend for a short column melted at a relatively high rate (small ψ), and curved trends for experiments with long columns and/or slow melt rates. We were able to describe the experimental results using this 1-D model, which suggests that the model incorporates the essential physics of the system.

3.2. Effect of Snow Properties and Melt Rate

[24] Both ψ and γ are functions of snow properties. The parameter ψ is directly related to the depth of snow and water percolation velocity (equation (17)). The parameter γ is determined by snow porosity, intrinsic permeability and melt rate (equations (3), (4) and (20)). The melt rate determines the liquid water content which, in turn, affects the liquid to ice ratio by changing the values of a (equation (8a)). The grain size distribution of the snowpack affects the surface area of the snow and, therefore the fraction of ice participating in the isotope exchange (f). As a result of these intricate relationships, ψ and γ are not independently variable. In general, as the melt rate increases, the meltwater percolation velocity increases, and thus ψ decreases. At a high melt rate, the ratio of liquid to ice ($a:b$) is relatively high due to a high water content. If f is independent of snow wetness, γ decreases with increasing melt rate. However,

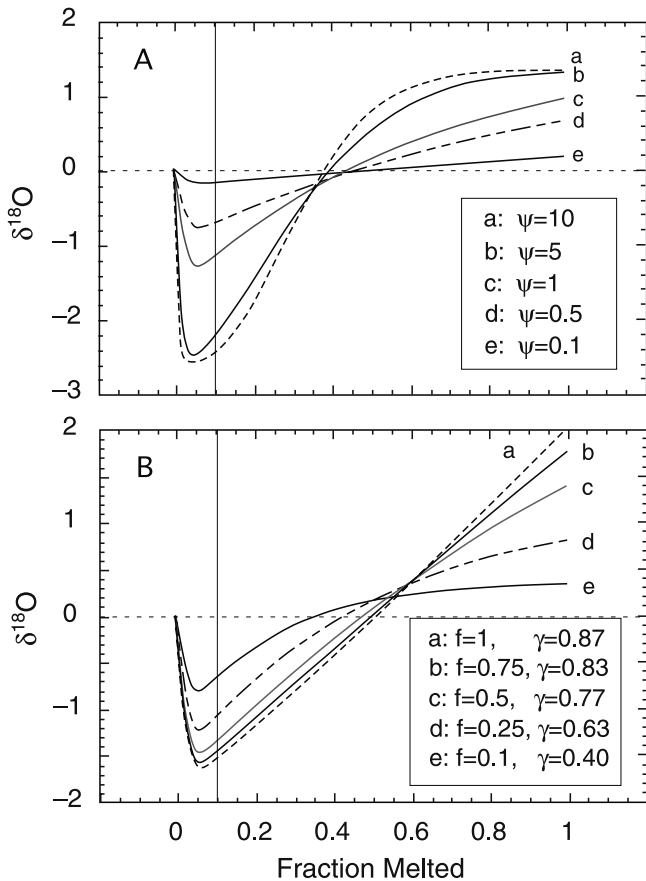


Figure 2. Solutions for equations (15) and (16) expressed as the $\delta^{18}\text{O}$ value relative to the initial $^{18}\text{O}/^{16}\text{O}$ ratio of the bulk snow. (a) Solutions for different ψ values at fixed $f = 0.3$ ($\gamma = 0.67$). (b) Solutions for different f (and therefore different γ) at fixed $\psi = 1$. Other parameters are the same for all simulations: $\phi = 0.5$, $S_i = 0.04$, and $S = 0.1$. Values of physical constants are listed in Table 1. Dashed horizontal lines indicate the isotopic composition of the initial snow. A vertical line is drawn at 10% melt fraction to indicate that the $\delta^{18}\text{O}$ of the earlier melt is affected by the chosen initial isotopic ratio of the pore water and may not resemble the experimental observations.

water content may also affect the rate of recrystallization of ice grains [Colbeck, 1986]. Recrystallization occurs in wet snow because the system tends to reduce surface energy by increasing the grain size. Recrystallization is one of the mechanisms of isotopic exchange [O'Neil and Taylor, 1967]. During this process, ice grains of small sizes are melted completely without isotopic fractionation, but when water recrystallizes onto large ice particles ^{18}O preferentially enters the solid phase, making the liquid isotopically light. Therefore increasing the melt rate may also cause f and, consequently γ to increase (for more discussion, see Taylor et al. [2002]).

[25] Figure 3 shows a number of model results for a typical range of field conditions. Two intrinsic permeability values, 1×10^{-8} and $1 \times 10^{-9} \text{ m}^2$, were used [Jordan et al., 1999; Wankiewicz, 1978]. The high end of the melt rate (V_m^*) is taken to be about 2.5 cm/hr, which was the highest

instantaneous melt rate recorded at Central Sierra Snow Laboratory, Soda Spring, California in spring 1998. Parameters not listed inside Figure 3 are held constant for all runs and the values are listed in the figure caption. In Figure 3a, f equals 0.2 for all runs. Figure 3b compares two curves with identical parameterization (high melt rate) except that the f value is 0.2 for one curve and 0.5 for the other, simulating the possibility that f may increase with water content.

[26] In general, for a given intrinsic permeability, a slow melt rate tends to yield a curved isotopic trend and relatively large isotopic differences between the early and late meltwaters. In contrast, a fast melt rate produces a linear (or less curved) isotopic trend and a smaller isotopic range. This observation is consistent with the earlier discussion about the dependence of the solution of (15) and (16) on the parameterization of ψ and γ . Other things being equal, the low melt rate corresponds to a high value of ψ and therefore more rapid exchange and a greater isotopic range.

[27] Figure 3b shows that if the f value increases with wetness, the range of isotopic variation would be greater and the trend more linear compared to the case where the f value is constant. An application of the model to our experimental data [Taylor et al., 2002] indicates a positive relationship between f and S . A more complete exploration of this relationship is still needed before the model can be extended to describe the isotopic evolution of natural snowpacks.

3.3. Implications for Uncertainties of Hydrograph Separation

[28] Figures 2 and 3 show that the $\delta^{18}\text{O}$ of the early melt of a snowpack may be as much as 2‰ lower (or more depending upon the initial conditions) than that of the initial bulk snow. Therefore using the bulk snow as the new water end-member in a hydrograph separation of spring runoff may not be accurate. While a full discussion of this problem will be presented in a separate contribution (S. Taylor et al., How uncertainties in the isotopic composition of snowmelt affect hydrograph separation, submitted to *Hydrological Processes*, 2002), we use one example to demonstrate the point.

[29] Figure 4a shows the hydrograph and the δD variations of Mink Brook stream water sampled at Etna, New Hampshire during the spring runoff of 1998. The observation was made in hydrogen isotopes and we assume here that each per mil change in $\delta^{18}\text{O}$ is equivalent to 8‰ change in δD . The new water fractions of the hydrograph are shown in Figure 4b. Two calculations are compared. In the first calculation (circles), the bulk snow δD value before melting started was used as the new water end-member. In the second calculation (diamonds), the δD is assumed to have varied during the melting process. We also assume that melting occurred evenly during Julian days 84–104, and that the new water isotopic composition evolved following the curve b in Figure 3a. During this time period, there was a small storm on April 1–2 (Julian days 91–92), bring 16mm of rain with a δD value of -54‰ . There is no obvious indication of this storm in the stream hydrograph, and we ignored it in our calculation. About 10% error would be introduced if the δD of the bulk snow were used for the

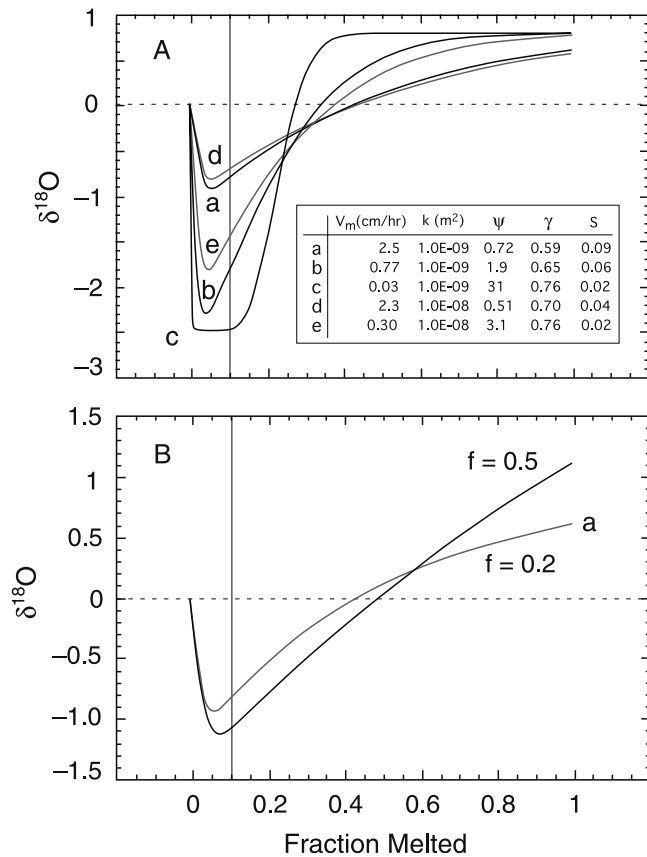


Figure 3. Solutions for equations (15) and (16) for snowpacks of different intrinsic permeabilities and melt rates. (a) Comparison of different runs at constant $f = 0.2$ but different melt rates and permeabilities (and therefore different ψ and γ). (b) Comparison of two curves that have different f values but identical parameterizations otherwise. Parameters not shown inside Figure 3 are the same for all runs: $\phi = 0.5$, $S_i = 0.04$, $k_r = 0.15 \text{ hr}^{-1}$, and $Z = 100 \text{ cm}$. Values of physical constants are listed in Table 1.

new water composition, with overestimates of the new water fraction for the early phase of the melting process and underestimates for the late phase. In this example, the isotopic composition of the bulk snow before melting is about -100‰ , which is about 20‰ different from the δD of the base flow. If the difference were smaller, the error in the hydrograph separation using the bulk snow would be greater.

4. Conclusion

[30] A physically based 1-D model of isotopic evolution of snowmelt from a seasonal snowpack is described. This model assumes 1) that snow is melted at the surface at a constant rate, 2) that isotopic transport is through advection only (dispersion is ignored), and 3) that isotopic exchange occurs between percolating water and ice. Two nondimensional parameters, the effectiveness of exchange (ψ) and the ice-to-liquid ratio of the exchange system (f), are shown to be important for controlling the shape and range of the isotopic variations of snowmelt. These two parameters are determined by snow properties, such as grain size distribution, porosity, permeability and wetness, as well as the rate

of melting. For a given snowpack with a fixed set of properties, the isotopic melt curve is largely controlled by the melt rate. In general, a fast melt rate tends to yield a linear isotopic trend and slow rate a curved one.

[31] The total isotopic variation through the melt season ranges from 1‰ to 4‰ for $\delta^{18}\text{O}$, depending upon the melt conditions. These variations are sufficient to cause errors in hydrograph separations, and this model should be useful for improving their accuracy. With proper parameterizations, this model may be used for continuous hydrograph separations or incorporated into more sophisticated mass and energy snowmelt models, such as SNTHERM (developed by Jordan [1991]). The physical process of ice–water exchange may also be important for the isotopic compositions of melting glaciers. With modifications and proper parameterizations, this model could be used to quantify the isotopic variations in glaciers, which is important for climate studies of ice cores.

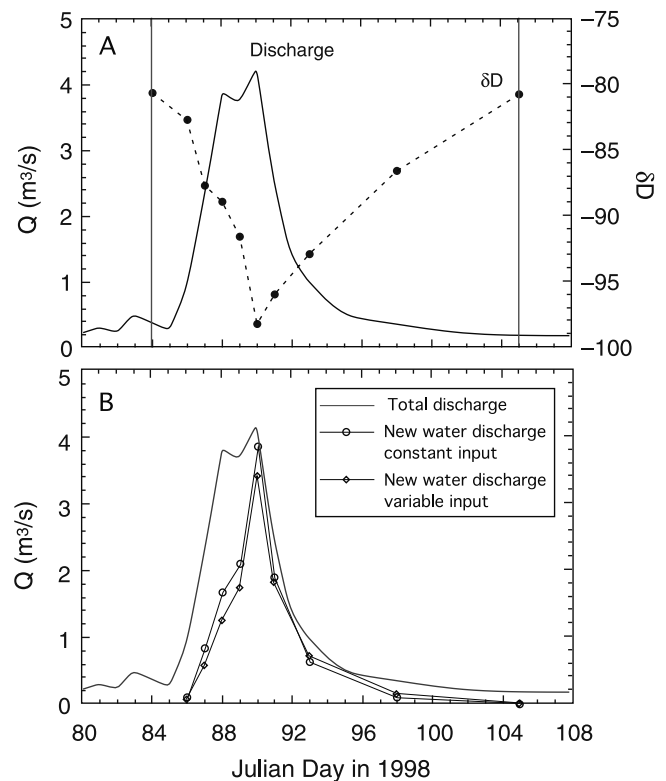


Figure 4. Hydrograph separations using a constant isotopic composition versus the isotopic composition that evolves during the melting process. Data are collected from Mink Brook, Etna, New Hampshire. (a) The hydrograph and the δD variations for the spring runoff of 1998. (b) Comparison of fractions of new water for two hydrograph separations. Circles are calculated assuming a constant value of -100‰ (measured for the bulk snow before melting near the sampling site) as the δD of the new water input. Diamonds are calculated using the curve b in Figure 3a as the δD of the meltwater input. It is assumed that the melting process occurred evenly between Julian days 85–104, and the $\delta^{18}\text{O}$ values in Figure 3a are converted to δD using the ratio of 1:8‰.

[32] **Acknowledgments.** Support for this work comes from the NSF grants ATM-9628759, EAR-9903281 and EAR-9814121 and Department of the Army (AT-24 Snow Ice and Frozen Ground Program).

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