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Isotopic evolution of a seasonal snowcover and its melt by isotopic exchange between liquid water and ice

Jeonghoon Lee^{a,*}, Xiahong Feng^a, Anthony M. Faiia^a, Eric S. Posmentier^a, James W. Kirchner^{b,c,d}, Randall Osterhuber^e, Susan Taylor^f

^a Department of Earth Sciences, Dartmouth College, Hanover, NH 03755, USA

^b Department of Earth and Planetary Science, University of California, Berkeley, CA 94720, USA

^c Swiss Federal Institute for Forest, Snow, and Landscape Research WSL, Birmensdorf, CH-8903 Switzerland

^d Swiss Federal Institute of Technology (ETH), CH-8092 Zürich, Switzerland

^e Central Sierra Snow Laboratory, Box 810, Soda Springs, CA 95728, USA

^f U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH 03755, USA

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ABSTRACT

Understanding an isotopic evolution of a snowpack is important for both climate and hydrological studies, because the snowmelt is a significant component of groundwater and surface runoff in temperate areas. In this work, we studied oxygen and hydrogen isotopic evolution from new snow to snow profile and to meltwater through two winter seasons (1998 and 2001) at the Central Sierra Snow Laboratory, California, USA. The slopes of the δD vs. $\delta^{18}O$ regression for the new snow are similar to that of the global meteoric water line (GMWL) of 8. However, this slope decreases in the snow profile and decreases further in the meltwater. We attribute this systematic slope changes to the isotopic exchange between ice and liquid water that is generated at the snow surface by melting and flows through the snowpack by percolation. A physically-based one-dimensional model, including melting of snow at the surface and isotopic exchange between percolating water and ice, was used to simulate isotopic variation of snowmelt in 2001. A successful simulation was obtained for the δD – $\delta^{18}O$ slope of snowmelt (6.5), which is significantly lower than the slope of the meteoric water line (8.2) defined by the new snow. This result indicates that the liquid water evaporation should not be considered as the only process that yields slopes of the δD vs. $\delta^{18}O$ relationship in surface water and groundwater. The d -excess of the snowmelt is changed from the original snow because of the δD – $\delta^{18}O$ relationship controlled by ice–liquid exchange. With a δD – $\delta^{18}O$ slope less than 8, the d -excess would be anti-correlated with δD or $\delta^{18}O$. The model is also used to examine how isotopic heterogeneity of a snowpack affects the isotopic redistribution in the pore water, ice and meltwater of the snowpack. The results show that isotopic heterogeneity of the snowpack may significantly affect the temporal changes in the δD – $\delta^{18}O$ slopes, and a measured slope at a given time is a combined result of meteorological conditions, which affect both isotopic composition of the original snow and the process of snow metamorphism, and the melting history of the snowpack.

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1. Introduction

Snowmelt is the largest contributor to groundwater recharge in many northern and alpine environments (Koeniger et al., 2008). Understanding the hydrological responses of snowmelt to the watershed is crucial for water resources management because snow dynamics are highly variable in space and time (Lundquist and Cayan, 2002). Stable isotopic measurements have been widely used to study the water cycles, particularly processes related to water movement among

different reservoirs, e.g., atmospheric moisture cycling, evaporation, transpiration, groundwater recharge, and runoff (Unnikrishna et al., 2002; Laudon et al., 2002; Campbell et al., 2002; Taylor et al., 2002a; Liu et al., 2004; Worden et al., 2007; Yuan and Miyamoto, 2008).

One of the isotopic techniques broadly used in isotope hydrology is to examine the slope of the δD vs. $\delta^{18}O$ regression line and d -excess defined as $\delta D - 8 \times \delta^{18}O$. The slope may reveal information about whether water entering the soil, groundwater and lakes has experienced significant evaporation (Blasch and Bryson, 2007; Chowdhury et al., 2008). Typically, soil or lake water evaporation results in a slope less than ~ 8 , the slope of the local meteoric water line. The stable isotope approach is often used for quantifying evaporation, and water balances of lakes and groundwater recharge processes (Grassa et al., 2006; Tsujimura et al.,

* Corresponding author. Now at Jet Propulsion Laboratory, California Institute of Technology, CA 91109, USA. Tel.: +1 818 354 4137; fax: +1 818 354 5148.

E-mail address: jeonghoon.lee@jpl.nasa.gov (J. Lee).

2007; Mayr et al., 2007). The *d*-excess is useful for identifying moisture source regions (e.g., Merlivat and Jouzel, 1979; Johnsen et al., 1989; Feng et al., 2009). Any process that changes δD and $\delta^{18}O$ along a slope different from 8 would cause a change in the value of *d*-excess, and thus a loss or misinterpretation of its source information.

However, processes other than evaporation, such as an isotopic exchange between liquid water and ice or between water vapor and ice may also affect the slope of the δD vs. $\delta^{18}O$ relationship (Taylor et al., 2002a; Earman et al., 2006; Zhou et al., 2008a,b; Lee et al., 2009). Earman et al. (2006) used the δD – $\delta^{18}O$ slope to identify processes (e.g., exchange between snow and water vapor) responsible for alteration of snow isotopic compositions. Zhou et al. (2008a) observed that the δD – $\delta^{18}O$ slope of a glacier decreased with time, and attributed this to thawing and refreezing of pore water that has a smaller δD – $\delta^{18}O$ slope than ice. In a separate contribution, Zhou et al. (2008b) observed lack of change in the δD – $\delta^{18}O$ slope in ice of a glacier, which was interpreted as evidence of preferential flow.

Isotopic variation of snowmelt from a homogenous snowpack under a constant melting rate can be easily predicted (Taylor et al., 2001; Feng et al., 2002). However, the actual isotopic evolution of a snowpack and its melt water is influenced by many other factors including isotopic heterogeneity of the snowpack. Because meltwater is predominantly generated at the snow surface, thus a given mass of meltwater isotopically exchanges with and modifies the solid ice throughout the entire flow path. As a result, the $\delta^{18}O$ (or δD) values, the δD – $\delta^{18}O$ slope, as well as *d*-excess of the snowpack and snowmelt may be influenced significantly by isotopic heterogeneity of the snow column.

Our present work was designed to investigate how the isotopic exchange between liquid and ice influences the isotopic evolution of snow and discharge using both empirical observations and numerical calculations. We measured the isotopic compositions of fresh snow, snowpack profile and snowmelt through two winter seasons at the Central Sierra Snow Laboratory (CSSL), California, USA. A physically-based model by Taylor et al. (2001) and Feng et al. (2002) and isotopic exchange kinetics reported by both Taylor et al. (2002b) and Lee et al. (2009) were used to investigate how snow heterogeneity affects the isotopic evolution of a snowpack.

2. Site information and methods

2.1. Field site

The study was carried out at the CSSL, which is located at 39°22′ 19.5″N, 122°22′ 15″W, at an altitude of 2100 m on the southwest crest of the Sierra Nevada near Soda Springs, California, USA. The average annual precipitation, snowfall, and peak snow depth are 1.3, 10.4, and 2.4 m, respectively. The mean yearly maximum and minimum air temperatures are 26 and –10 °C. On average, the site receives ~80% of its precipitation in the form of snow. Additional information about site conditions has been described in earlier publications (Taylor et al., 2001; Feng et al., 2001; Lee et al., 2008a,b).

The snow laboratory is in a 0.5-hectare clearing in a pine forest. It is instrumented to measure meteorological variables, such as air temperature, precipitation, snow accumulation, snow depth, snow water equivalent (SWE) and shortwave incident and reflected radiation. There are two 6 × 3 m² melt pans (north pan and south pan) that are sloped gently to a corner drain. The discharge from each melt pan is measured by a 4-L tipping bucket attached to a data logger in a hut to which the snowmelt flows underground through 8 m of PVC pipe. An autosampling system for collecting meltwater samples was installed. It intercepted the PVC pipe upstream of the tipping bucket and pumped ~125 mL of water into precleaned plastic bottles on a rotating carousel.

2.2. Sampling

Three types of samples were collected from each of the two winters (winters of 1997–1998 and 2000–2001): new snow (newly precipitated snow), snow profiles and snowmelt. New snow was collected for each of the major storms depositing more than 15 cm of snow (Taylor et al., 2001). Following each storm, a sample was collected with a plastic or Plexiglas corer, melted in a clean plastic bag, and then transferred into a clean plastic bottle. A pit was excavated on April 9 in 1998 and another one on April 1, 2001. Snow profile samples were melted in plastic bags at room temperature, and then transferred to 125 mL plastic bottles. Meltwater was collected with an autosampler throughout the entire winter season (with a few breaks due to instrumental failure). The autosampler was programmed to sample with a frequency determined by the melting rate. During cold periods, it was sampled every 2 h or with every bucket tip, whichever was less frequent. Thus the autosampling frequency varied throughout the sampling period. Sampling procedures and meteorological data for 1998 and 2001 were described in more detail by Taylor et al. (2001) and Lee et al. (2008b), respectively.

2.3. Analytical methods

Samples were analyzed for δD (water samples from both 1998 and 2001) using an on-line chromium reduction system (H/device) (Nelson and Dettnam, 2001), and for $\delta^{18}O$ (water samples only from 1998) using the CO₂ equilibration method with a gas bench (Tu et al., 2001). Both the H/device and the gas bench were interfaced with an isotope ratio mass spectrometer. The D/H and ¹⁸O/¹⁶O ratios were expressed in the δ notation as part per thousand differences relative to the Vienna Standard Mean Ocean Water (VSMOW). The precision of the δD and $\delta^{18}O$ measurements was 0.5‰ and 0.1‰, respectively.

2.4. Numerical model

We use the model described in Taylor et al. (2001) and Feng et al. (2002) and physical parameters by Taylor et al. (2002b) and Lee et al. (2009) to explore the isotopic redistribution of the snowpack. The model assumes a constant melt rate, and incorporates advection of percolating water, ice–water isotopic exchange, but ignores dispersion. The governing equations for the liquid phase and ice are

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

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

where R_{liq} and R_{ice} are the D/H or ¹⁸O/¹⁶O ratio in the liquid and ice, respectively. The variable z is dimensionless depth and t is dimensionless time. The constant a_{eq} is the equilibrium fractionation factor for hydrogen or oxygen isotopic exchange between ice and water at 0 °C. At equilibrium, the $\delta^{18}O$ and δD of the water are expected to be 3.1‰ and 19.5‰ lower than those of the ice, respectively (O'Neil, 1968). The parameter γ quantifies the fraction of ice in the ice–water isotopic exchange system,

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

where a and b are the mass of liquid and ice per unit volume of snow, respectively. The parameter f is the fraction of ice involved in isotopic exchange, which cannot be directly measured in practice. The parameter ψ is the dimensionless rate constant of isotopic exchange,

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

where k_r is the isotopic exchange rate constant (h^{-1}), Z is the initial snow depth (cm), and u^* is the percolation velocity (cm/h). The model has been tested by cold room column experiments (Taylor et al., 2002b) as well as field observations (Taylor et al., 2001; Lee et al., 2009).

3. Results

Fig. 1 shows changes of snowpack depth with time (gray dotted curves) and snowmelt discharge observed at the bottom of the snowpack for the periods from 3/31/98 to 6/8/98, and from 3/31/01 to 5/7/01, respectively. In 1998, snowpack reached a maximum depth of 4 m (SWE = 126.1 cm) on February 22 (Fig. 1a), which was characterized by a large El Niño event (Taylor et al., 2001). In 2001, the maximum snowpack depth was 2.4 m (SWE = 64.8 cm) on March 6 (not shown in Fig. 1b). In addition to the seasonal trend, diel variations of meltwater discharge are apparent in Fig. 1.

The isotopic data for new snow, snow profiles and snowmelt are plotted in Figs. 2–4, respectively. The descriptive statistics are summarized in Table 1. Fig. 2 shows the isotopic compositions of new snow collected in the winters of 1998 and 2001. The most isotopically depleted snow ($\delta^{18}\text{O} = -22.7\text{‰}$, $\delta\text{D} = -173.2\text{‰}$) occurred on March 6 in 1998 and the most isotopically enriched snow ($\delta^{18}\text{O} = -7.5\text{‰}$, $\delta\text{D} = -44.1\text{‰}$) occurred on February 22 in 2001 (Fig. 2). We could not identify the most isotopically depleted or enriched layers in the snowpack (Fig. 3), indicating that isotopic redistribution had occurred due to snow metamorphism and melting (Taylor et al., 2001). However, there is a weak correspondence (increasing or decreasing trend) between the isotopic compositions of the new snow and their composition in the snow profile.

For the winter of 1998 when meltwater sampling had few gaps, a comparison can be made between the new snow and snowmelt. The mean values of $\delta^{18}\text{O}$ and δD did not change significantly from the new snow to the snowmelt, but the standard deviations decreased, indicating that variability of isotopic compositions decreased from new snow to snowmelt ($p = 0.005$). Similar observations were reported previously for both isotopic and chemical variations (Taylor et al., 2001; Unnikrishna et al., 2002; Gurney and Lawrence, 2004; Lee et al., 2008b).

Generally, the meltwater became enriched in ^{18}O and D as the snowpack melted, particularly during the spring melting season

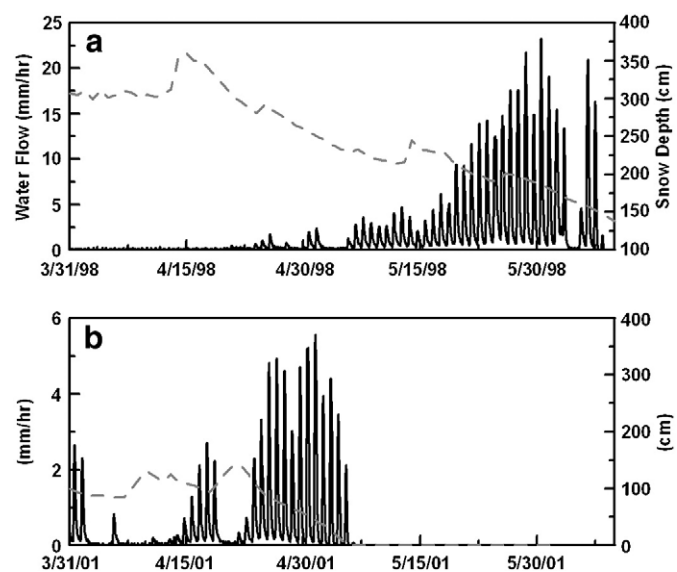


Fig. 1. Change of snowpack depth (dotted gray) and meltwater discharge (black) as a function of time for (a) 1998 and (b) 2001.

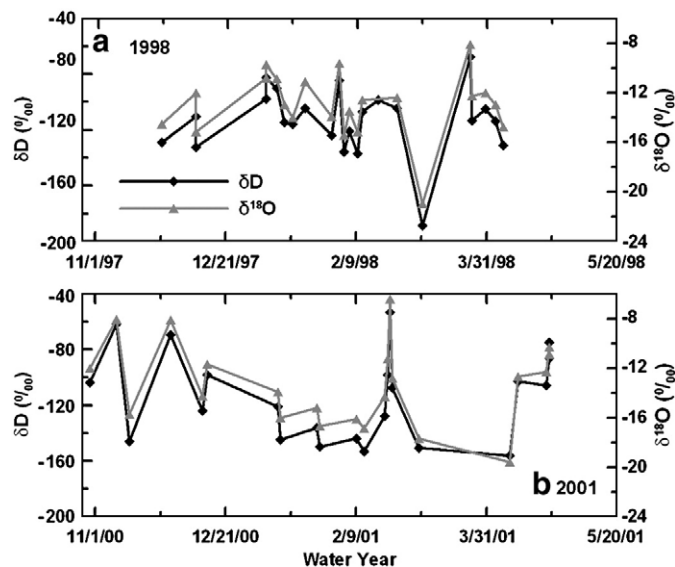


Fig. 2. New snow $\delta^{18}\text{O}$ and δD values for (a) 1998, and (b) 2001.

(Fig. 4) (Taylor et al., 2001). The enrichment trend is gradual in 1998 samples, but more abrupt in 2001 especially for the last 50% of the melt (after April 30).

The δD – $\delta^{18}\text{O}$ diagrams are shown in Fig. 5. The slope of the δD – $\delta^{18}\text{O}$ diagram for new snow is 8.4 in 1998 and 8.2 in 2001, respectively, both being close to the slope 8 of the global meteoric water line (Dansgaard, 1964). From new snow to snow profile and to snow melt, the δD – $\delta^{18}\text{O}$ slope decreases, from 8.4 to 8.1 to 7.1 in 1998 and from 8.2 to 7.2 to 6.5 in 2001. The probability (p) for the slope decreases from new snow to snowpack, and from snowpack to meltwater were 0.173 and 0.018 for 1998 and 0.033 and 0.036 for 2001 (one-tailed). The combined significance (α) of all four decreases in slope (against $H_0 = \text{no decreases}$) was $\alpha \leq 0.0001$ (one-tailed).

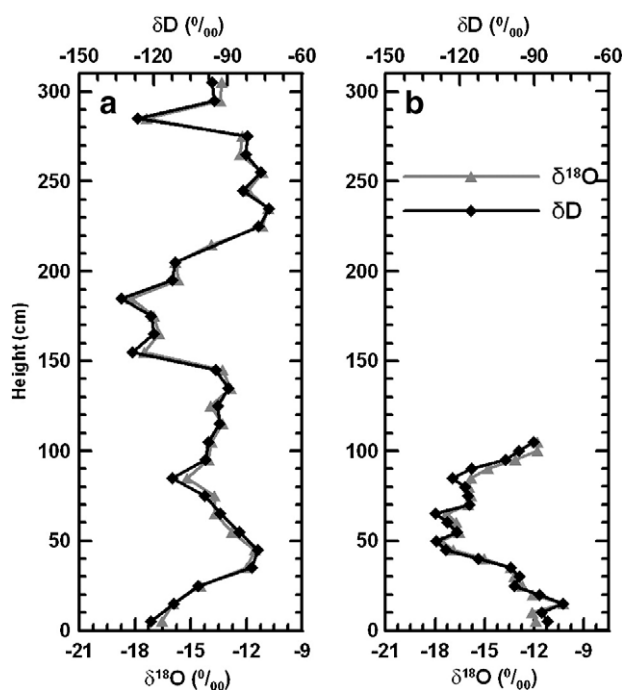


Fig. 3. Snowpack $\delta^{18}\text{O}$ and δD values for snow profiles sampled on (a) April 8, 1998, and (b) April 1, 2001.

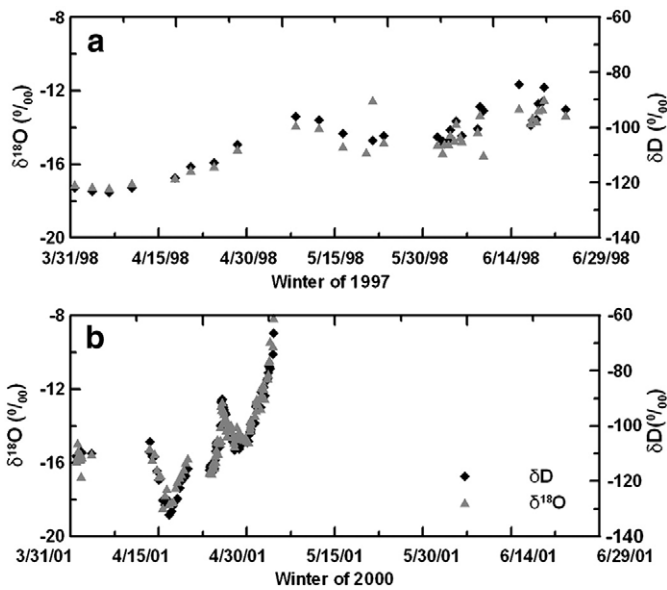


Fig. 4. Snowmelt $\delta^{18}\text{O}$ and δD values for (a) 1998, and (b) 2001.

4. Discussion

Our research objective was to study how the isotopic exchange between liquid water and ice causes an isotopic redistribution from new snow to snowpack and to meltwater. In this section, we discuss the mechanism and pattern of isotopic redistributions using both observed data and model calculations.

4.1. Isotopic redistribution due to isotopic exchange between liquid water and ice

As meltwater percolates through a snowpack, the isotopic exchange takes place between liquid water and ice, which causes isotopic redistribution in a temperate snowpack, such as those at the CSSL. When the top snow layer melts, little isotopic fractionation occurs because the entire layer is transferred to liquid phase (Taylor et al., 2001). As the liquid water percolate through the snowpack, isotopic exchange between liquid and ice occurs, which is associated with isotopic fractionations of both oxygen and hydrogen isotopes (Nakawo et al., 1993; Taylor et al., 2001). The isotopic exchange is controlled by ice–liquid water equilibrium fractionation factor of 3.1‰ for oxygen and 19.5‰ for hydrogen (O’Neil, 1968). As a result, the $\delta^{18}\text{O}$ and δD of snowmelt evolve along a slope less than 8, being close to $19.5/3.1 \approx 6.3$ (Clark and Fritz, 1997; Lee et al., 2009).

This description of the melting–exchange process explains why the δD – $\delta^{18}\text{O}$ slope in our experiments decreased from new snow to snow profiles and to snow melt. Such a systematic evolution of the δD – $\delta^{18}\text{O}$ slope (with time) has been observed by several earlier investigators. Zhou et al. (2008a) observed that the δD vs. $\delta^{18}\text{O}$ slope in firn of an

alpine glacier decreased with time (from June to July) from 10.4 to 8.7. Gurney and Lawrence (2004) also observed that the slope of δD vs. $\delta^{18}\text{O}$ for a snowpack decreased (from April to August) from 7.5 to 6.2, and they attributed this observation to evaporation of liquid water within the snowpack. While some evaporation may be possible, we do not consider it necessary for explaining the observed slope change. Gurney and Lawrence (2004) also reported that the best-fit line for their meltwater observations had a slope of 4.4. This value suggests that at least for the meltwater the δD – $\delta^{18}\text{O}$ slope does not always converge from 8 to the theoretical value of 6.3.

The δD – $\delta^{18}\text{O}$ slope may be affected by processes other than liquid–ice isotopic exchange. Near the surface, snow exchanges with atmospheric water vapor (Earman et al., 2006). At equilibrium, this exchange should yield an ice–vapor relationship of $88.2/11.4 \approx 7.7$ (Merlivat and Nief, 1967; Majoube, 1970) at 0 °C. This process should be of minor influence during the melting season when solar radiation causes relatively intensive melting at the snow surface. Vapor can also be transported through the snowpack when there is a temperature gradient and/or during dry metamorphism. Ice–vapor exchange occurs during these processes. Vapor–ice exchange may be particularly important during the early accumulative phase of the snowpack when the temperature is low and melting is limited. For the study period of this work, we consider this effect to be also minor.

The changes in the δD vs. $\delta^{18}\text{O}$ relationship between snow profiles and snowmelt have not been discussed quantitatively, although the isotopic exchange between different phases of water has been cited as a qualitative explanation. In the following, we use a physically-based model to examine how the ice–liquid isotopic exchange affects the isotopic values, the slope of the δD vs. $\delta^{18}\text{O}$ relationship, and d -excess. We consider both a homogeneous snowpack as well as a snowpack that exhibits vertical heterogeneity.

4.2. Model calculations

In the following calculations, we assumed that the isotopic compositions of liquid water were initially in isotopic equilibrium with ice. In addition, melting was assumed to occur only at the surface (Taylor et al., 2001).

4.2.1. Effect of heterogeneity on snowmelt isotopic compositions

To examine the effect of snowpack isotopic heterogeneity, we constructed several hypothetical snowpacks based on our data collected in the winter of 2001. The $\delta^{18}\text{O}$ and δD values of the snow profile sampled in April 2001 ranged from -7.5% and -44.7% to -19.0% and -160.6% , with mean values of -14.3% and -107.3% , respectively.

We conducted simulations for four snowpacks: (1) a homogeneous snowpack with $\delta^{18}\text{O}$ of -14.3% and δD of -107.3% , respectively; (2) a snowpack with two snow layers of equal thickness, an isotopically depleted surface layer with a $\delta^{18}\text{O}$ value of -16% and δD of -114.9% , and an enriched bottom layer with $\delta^{18}\text{O}$ value of -12.6% and δD of -87.7% ; (3) a snowpack with the stacking opposite to (2), i.e., surface layer being isotopically enriched and bottom layer depleted; and (4) a

Table 1
Results of $\delta^{18}\text{O}$ and δD values (‰) of snow and snowmelt.

Sample type	Mean		Standard deviation		Maximum		Minimum		Number of samples
	$\delta^{18}\text{O}$	δD	$\delta^{18}\text{O}$	δD	$\delta^{18}\text{O}$	δD	$\delta^{18}\text{O}$	δD	
New snow (1998)	-14.3	-101.8	2.7	23.6	-9.1	-58.7	-22.7	-173.2	23
Snowpack (1998)	-14.1	-99.1	2.1	17.1	-10.8	-73.6	-18.2	-133.1	31
Snowmelt (1998)	-14.9	-104.2	1.5	11.9	-11.3	-79.0	-17.3	-124.7	48
New snow (2001)	-14.4	-105.0	3.6	29.8	-7.5	-44.1	-19.0	-160.6	22
Snowpack (2001)	-14.3	-107.3	2.2	16.3	-10.3	-78.3	-17.6	-129.8	21
Snowmelt (2001)	-14.6	-104.5	1.9	12.7	-8.1	-66.4	-18.4	-132.2	115

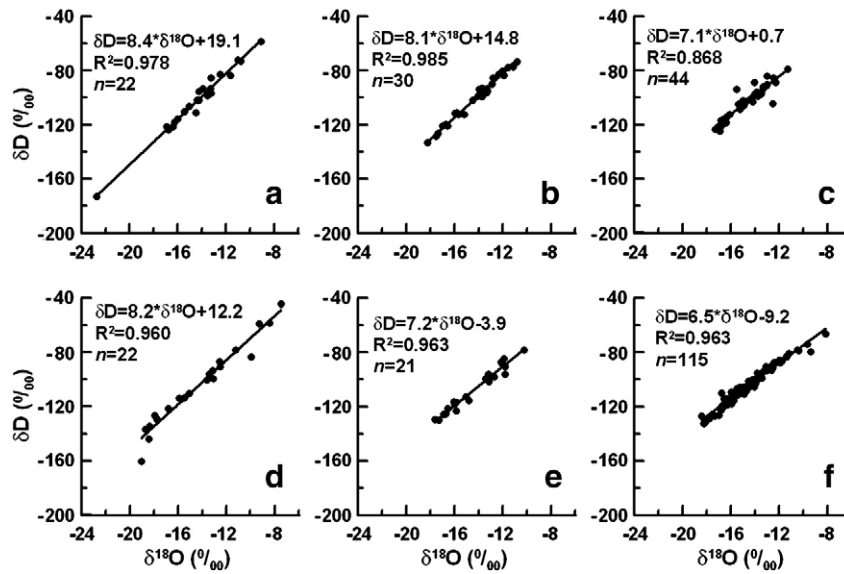


Fig. 5. δD vs. $\delta^{18}O$ plots for (a) new snow, 1998, (b) snowpack, 1998, (c) meltwater, 1998, (d) new snow, 2001, (e) snowpack, 2001, and (f) meltwater, 2001. For each year, the slope decreases from new snow to snow profile, and to meltwater.

snowpack with the same isotopic profile as the one observed on April 1, 2001 (Fig. 3b; slope of the snow profile is 7.2, Fig. 5e). In both (2) and (3), the mean isotopic compositions of the snowpack are the same as in (1), and the two snow layers define a δD - $\delta^{18}O$ slope of 8. Fig. 6 shows the model results for the isotopic compositions of snowmelt plotted as isotopic values against the fraction of the snowpack melted (F).

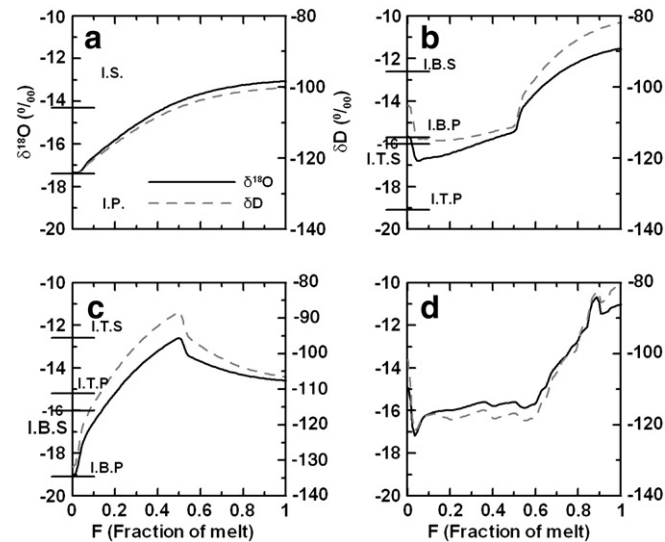


Fig. 6. Evolution of $\delta^{18}O$ and δD values of meltwater as a function of the snowpack fraction melted. A modified version of the model from Taylor et al. (2001) and Feng et al. (2002) was used; two key parameters used in this study are how much ice involved in the isotopic exchange system ($\gamma=0.3$) and the effectiveness of isotopic exchange ($\psi=3$). The physical meaning of these parameters is discussed in the text. (a) Results for Case 1: a homogeneous snowpack with $\delta^{18}O = -14.3\%$ and $\delta D = -107.63\%$. I.S. and I.P. denote isotopic compositions of the Initial Snow and Initial Pore water, respectively. (b) Results for Case 2: a two-layer snowpack with the top layer $\delta^{18}O = -16\%$ and $\delta D = -121.4\%$, and bottom layer $\delta^{18}O = -12.1\%$ and $\delta D = -96\%$. I.B.S., I.B.P., I.T.S., and I.T.P. denote isotopic compositions of the Initial Bottom Snow, Initial Bottom Pore water, Initial Top Snow, and Initial Top Pore water, respectively. (c) Results for Case 3: a two-layer snowpack stacked in with the same two layers in Case 2 but in the opposite order. (d) Results from Case 4: the snowpack with the initial isotopic profile shown in Fig. 3b.

In Case 1 of the isotopically homogeneous snowpack, the isotopic compositions of both oxygen and hydrogen in the snowmelt increase quasi-exponentially (Fig. 6a). This isotopic melting curve is typical of a homogeneous snowpack as discussed by Feng et al. (2002). Melting occurs at the surface without isotopic fractionation, and thus the first meltwater generated from the surface has $\delta^{18}O$ of -14.3% (labeled in Fig. 6a as I.S., i.e., Initial Snow) and δD of -107.3% . The initial pore water is in equilibrium with the snow and has a value of the $\delta^{18}O$ of -17.4% (labeled in Fig. 6a as I.P., i.e., Initial Pore water) and δD of -126.8% , respectively. This initial pore water flows out of the snowpack first, giving the first drop of the discharge of these equilibrium values. As the meltwater percolates down from the surface through the snowpack, it exchanges with the ice, becoming isotopically depleted toward the equilibrium value of $\delta^{18}O = -17.4\%$ and $\delta D = -126.8\%$. In the mean time, this isotopic exchange causes the ice to gain ^{18}O and D , becoming increasingly enriched with time. Therefore, the latter phase of the meltwater is more enriched than the mean isotopic value of the snowpack.

In Case 2 (Fig. 6b), where the top snow layer is isotopically depleted relative to the bottom layer (although with the same mean as in Case 1), $\delta^{18}O$ and δD for the first 50% of the meltwater ($F < 0.5$) first decrease slightly and then increase, but the rate of increase is much slower compared to Case 1. When the melting process reaches the bottom layer ($F = 0.5$), $\delta^{18}O$ and δD increase more rapidly as melting proceeds. This simulation is similar in pattern to that observed by Herrmann and Stichler (1981). The isotopic evolution of Case 2 can be understood as follows using $\delta^{18}O$ as an example. Initially, the pore water at the bottom is in equilibrium with the bottom layer ($\delta^{18}O = -12.6\% - 3.1\% = -15.7\%$). Therefore, the first drop of melt discharge should have the $\delta^{18}O$ value of -15.7% . The upper 50% of the pore water has a $\delta^{18}O$ value of -19.1% . This water exchanges with the lower part of the ice before it reaches the snow base. Before this water reaches equilibrium it should have a value between -15.7% and -19.1% , which explains the initial $\delta^{18}O$ decrease in the first 5% of the melt.

The first meltwater has the isotopic composition of the surface snow layer ($\delta^{18}O = -16.0\%$). The water first exchanges with the upper layer of snow, becoming depleted toward the equilibrium value of -19.1% . It then exchanges with the lower layer, becoming enriched toward the equilibrium value of -15.7% . As a result of exchanging with the isotopically enriched bottom layer, the increase

of the meltwater $\delta^{18}\text{O}$ for the first half of the snowpack is less steep compared to Case 1. In the meantime, when isotopically depleted upper layer meltwater exchanges with the enriched lower layer of snow, the latter (particularly near the top of this layer) would in fact lose ^{18}O to the fluid. This exchange creates a greater isotopic gradient with depth within the lower layer compared to the lower layer in Case 1, which explains why the second half of the meltwater increases in ^{18}O and D more rapidly than the comparable situation in Case 1. This makes sense in terms of mass balance. Since all four cases has the same mean ($\delta^{18}\text{O} = -14.3\text{‰}$), the area enclosed by the isotopic curve and the line $\delta^{18}\text{O} = -14.3\text{‰}$ should add up to zero, i.e., the area above $\delta^{18}\text{O} = -14.3\text{‰}$ and that below it should be equal.

In Case 3, the top layer is isotopically enriched ($\delta^{18}\text{O} = -12.6\text{‰}$) than the bottom layer (-16.0‰). The meltwater $\delta^{18}\text{O}$ increases more steeply than in Case 1 for the first half of the melt until F approaches 0.5, and then it decreases with time through melting of the bottom layer. Initially, the pore water of the upper half of the snowpack has a $\delta^{18}\text{O}$ value of -15.7‰ and the lower half -19.1‰ . Therefore, the $\delta^{18}\text{O}$ of the first discharge is -19.1‰ . When the upper pore water moves to the lower layer of the snowpack, it exchanges with the ice toward the equilibrium value of -19.1‰ . The meltwater first generated from the surface has a $\delta^{18}\text{O}$ value of -12.6‰ . Exchange of this water with the top layer of snow causes it to lose ^{18}O toward the equilibrium value of -15.7‰ , and when the water percolates into the bottom layer, the new equilibrium value becomes -19.1‰ leading to additional exchange and loss of ^{18}O of the meltwater to ice. As a result, the first half of the melt increases in isotopic ratio more rapidly than the comparable situation in Case 1. The isotopic exchange between the meltwater and the bottom half of the snowpack occurs more strongly near the top of the bottom layer, because the isotopic contrast is greatest where the isotopically enriched water ($\delta^{18}\text{O} \geq -15.7\text{‰}$) first encounters the bottom layer ($\delta^{18}\text{O} \geq -16.0\text{‰}$). The isotopic ratios of both liquid and ice continue to change, albeit more slowly, as water continues to flow down through the snowpack. Therefore, while the top isotopically enriched water is being produced by surface melting, the bottom layer of ice gradually develops an isotopic gradient such that $\delta^{18}\text{O}$ decreases with depth. This is why the second half of the meltwater curve has a downward trend as shown in Fig. 6c.

It is interesting that the isotopic curves in Fig. 6d (Case 4) are similar to those in Fig. 6b, which are derived from a snowpack having an isotopically depleted layer stacked on the top of an isotopically enriched layer. Although the actual snowpack corresponding to Case 4 does not have a simple two-layer structure, the top part of the snowpack has relatively low isotopic values, and below 50 cm, the $\delta^{18}\text{O}$ and δD increase to relatively high values. This isotopic distribution in the snow profile explains the significant increases in the snowmelt $\delta^{18}\text{O}$ and δD after April 30, 2001 when the melting surface reached the lower part of the snowpack (Figs. 1b and 4b).

These simulations indicate that the isotopic evolution of snowmelt from an isotopically heterogeneous snowpack may be significantly different from snowmelt from a homogenous snowpack. The isotopic composition of meltwater is affected by its exchange with the entire column of snow, and in return this exchange modifies the remaining snowpack, which controls the isotopic composition of the meltwater at a later time. Note that our model does not consider any potential influence of variable melting rate on the isotopic changes in the snowmelt. This melting effect can be quite significant, particularly when it involves freezing. This effect is evidenced from diurnal isotopic variations observed by Theakstone (2003).

4.2.2. The δD vs. $\delta^{18}\text{O}$ relationship

In each of the four cases discussed above, the model generates a δD vs. $\delta^{18}\text{O}$ slope of the meltwater that is different from 8 (in Case 1) or from the original slope of the snowpack. For the isotopically homogenous snowpack (Case 1), the δD – $\delta^{18}\text{O}$ slope of snowmelt is

5.6, and for the two-layered snowpacks, the δD – $\delta^{18}\text{O}$ slopes are 6.5 and 6.4 for Cases 2 and 3, respectively. Compared to Case 1, the plot is more scattered. For Case 4, the model calculation yields a slope of 6.8, which is slightly higher than but not significantly different from the observed value of 6.5 ($H_0: s_{\text{model}} = s_{\text{observation}}, p = 0.2$) (Fig. 5f).

To assess how the δD vs. $\delta^{18}\text{O}$ slope changes with time we created δD – $\delta^{18}\text{O}$ diagrams for different time periods of a melting process. Table 2 presents the slopes of meltwater for F ranges, from 0 to 0.25, from 0.25 to 0.5, from 0.5 to 0.75 and from 0.75 to 1. For the homogenous snowpack (Case 1), the slope of snowmelt is rather constant through time between 5.5 and 5.8. However, in Case 2 and Case 3, the slopes for meltwater range from 3.7 (Case 2, 25–50%) to 9.7 (Case 3, 75–100%). This result indicates that the slope of the δD vs. $\delta^{18}\text{O}$ relationship of the meltwater from a heterogeneous snowpack may change from one observation period to another. Data from a particular period may define a slope not representative of the meltwater from the entire snowpack, and this slope may either be smaller or greater (although infrequently) than the slope of the original snowpack.

A slightly different presentation, showing the temporal change of the δD – $\delta^{18}\text{O}$ slope in the meltwater, is illustrated by Fig. 7 (as s3 values), which includes the δD – $\delta^{18}\text{O}$ slopes for periods from $F = 0$ to $F = 0.25, 0.5$ and 0.75 , respectively. In Case 2, the δD – $\delta^{18}\text{O}$ slope of snowmelt changes from 3.9 to 6.5 to 5.4 as the fraction of melting (F) increases from 0.25 to 0.5 and to 0.75. In Case 3, the snowmelt slope is less variable, changing from 7.0 to 6.8 and to 6.7. However, these slopes are significantly greater than their Case 1 equivalents of 5.7, 5.8 and 5.8. Again this simulation indicates the effect of isotopic heterogeneity of the initial snowpack on the δD – $\delta^{18}\text{O}$ slope observed during different melting periods. Nevertheless, the calculations only infrequently produce a δD – $\delta^{18}\text{O}$ slope greater than 8, suggesting that the δD – $\delta^{18}\text{O}$ slope is most likely less than 8.

The model can also produce isotopic evolution of ice and pore water in the snowpack, which can help understand observations from studies such as that by Zhou et al. (2008b) who investigated how isotopic compositions of snow layers and pore water in the snowpack evolved during a 10-day period. Fig. 7 also shows the variations of δD – $\delta^{18}\text{O}$ slope in ice (s1) and liquid water (s2) of the snowpack at a given point of time, indicated by $F = 0.25, 0.50$ and 0.75 .

The δD vs. $\delta^{18}\text{O}$ slope is rather constant (between 5.5 and 5.9) for a homogeneous snowpack (Case 1) as F changes with time. All slopes are significantly less than 8 ($p < 0.05$). For a heterogeneous snowpack, slopes are much more variable. In Case 2, the δD vs. $\delta^{18}\text{O}$ slope of ice varied from 11.8 to 3.0 and to 7.2, while the slope of pore water changed from 3.9 to 7.1 to 7.5. Similar variability is shown in Case 3. In addition, the slope of the pore water is not necessarily smaller than the slope of ice. Furthermore, the temporal changes in the δD – $\delta^{18}\text{O}$ slope of pore water and ice for a given pack are not monotonic, and the slope itself is not always less than 8. These simulation results are different from expectations of Zhou et al., 2008b, and demonstrate that snowpack heterogeneity strongly affects the observed δD vs. $\delta^{18}\text{O}$ slope of ice or pore water at different points of time. Interpretation of these slopes cannot be made without considering the entire history of accumulation and melting of the snowpack.

Table 2
Slopes of δD vs. $\delta^{18}\text{O}$ relationship in meltwater from model calculations.

F	(1) Homogeneous (Case 1)	(2) Two layers (Case 2)	(3) Two layers (Case 3)
0–25%	5.5	9.5	7.2
25–50%	5.7	3.7	6.4
50–75%	5.7	7.4	8.9
75–100%	5.8	7.5	9.7

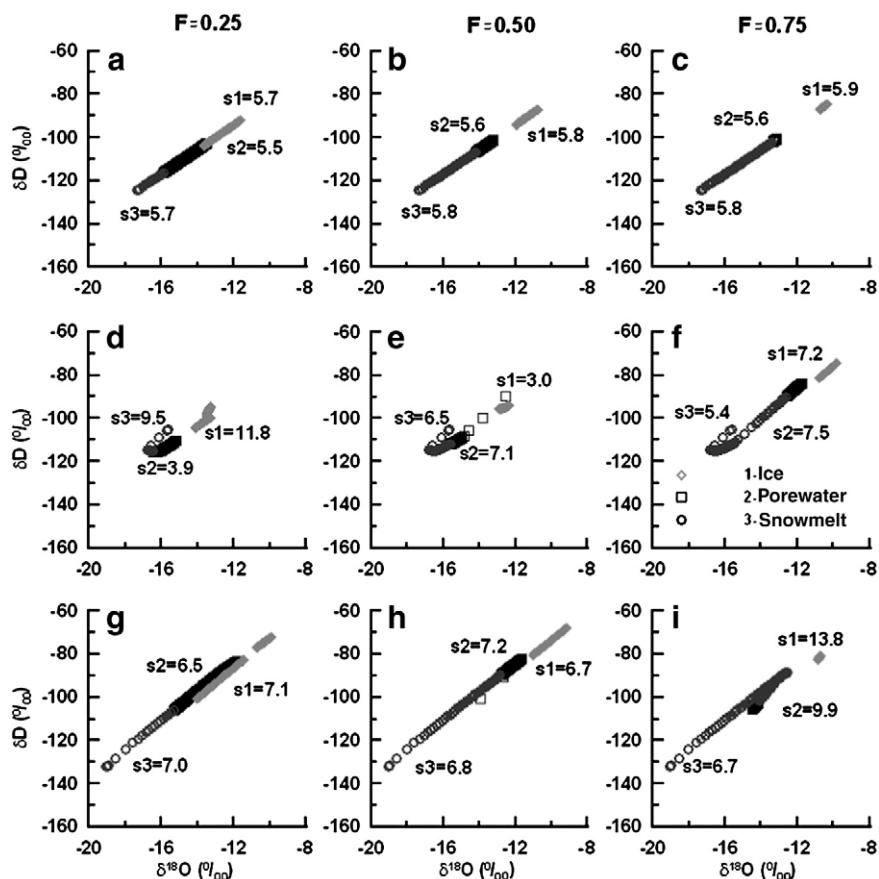


Fig. 7. Variations in the δD – $\delta^{18}O$ slope of ice, pore water and snowmelt discharge. Rows 1 through 3 show results for Cases 1 through 3, and columns 1 through 3 show results for $F=0.25, 0.50$ and 0.75 , respectively. The slopes for ice and pore water vary considerably at different points of observation, and the variation with time is neither monotonic nor consistently below 8. The snowmelt discharge is also significantly affected by snow heterogeneity, which is indicated by differences between Cases 1, 2 and 3, although all δD – $\delta^{18}O$ slopes of meltwater are less than 8.

4.2.3. Deuterium excess (*d*-excess)

The deuterium excess (*d*-excess), defined as $d = \delta D - 8 \times \delta^{18}O$ (Dansgaard, 1964) is often used to infer conditions at the moisture sources of the precipitation (e.g., Merlivat and Jouzel, 1979; Johnsen et al., 1989; Feng et al., 2009). However, this value may be modified by processes after precipitation (Uemura et al., 2008), such as evaporation. Since ice–water exchange follows a δD – $\delta^{18}O$ relationship typically less than 8 in slope, as we discussed in the previous section, snow metamorphism and melting processes should also affect the *d*-excess values of snow profile and snowmelt.

Changes in the *d*-excess are primarily controlled by the δD – $\delta^{18}O$ relationship. Since the slope in this relationship for ice–liquid exchange is less than 8, *d*-excess decreases when δD or $\delta^{18}O$ increases or vice versa. This can be easily seen in all four cases in Fig. 8a as compared with Fig. 6. In a real snowpack, the situation is complicated by the initial *d*-excess values and heterogeneity of the snowpack. For example, in 1998 the snowmelt *d*-excess did not show a significant variation with time (Fig. 8b), even though the δD and $\delta^{18}O$ increased during the melting process (Fig. 4a). This is probably due to the fact that the original new snow had a slope of 8.4 (Fig. 5a), and snow profile had a slope of 8.1 (Fig. 5b). Part of the snow metamorphism occurred when the δD – $\delta^{18}O$ slope was above 8, and thus had an impact to the *d*-excess opposite to our case simulations. Additional complications may also occur locally when δD vs. $\delta^{18}O$ slope is greater than 8 as shown in some examples in Fig. 7. For 2001, the slopes of new snow, snow profile and snowmelt are 8.2, 7.2 and 6.5, respectively. The snowmelt showed a trend of decrease in *d*-excess (Fig. 8c), which is largely consistent with the simulation (Case 4 in Fig. 8a).

5. Conclusion

Stable isotopic compositions of new snow, snowpack and snowmelt from two water years (1998 and 2001) were measured for temporal variation of isotopic compositions of a snowpack and its melt after snow deposition. The mean isotopic values of new snow, snowpack and meltwater were not significantly different, but the standard deviations from the new snow to snowpack and to snowmelt decreased, indicating that the variability of isotopic composition decreases during snow metamorphism and melting. Isotopic data from both years show that the δD vs. $\delta^{18}O$ slopes of new snow are similar to that of the global meteoric water line of 8, and that the δD vs. $\delta^{18}O$ slope of the snow profile is less than that of new snow, and the meltwater slope decreases further.

A one-dimensional model including advection of water melted at the surface of a snowpack at a constant rate and isotopic exchange between liquid water and ice within a snowpack successfully reproduced the δD vs. $\delta^{18}O$ slope (within uncertainty) of the meltwater collected in 2001. This result indicates that the observed slope in the meltwater, which is smaller than the slope of the snowpack that generates the melt, can be largely attributed to melting of snowpack at the surface and the isotopic exchange between the meltwater and ice as water percolates through the snowpack. Slope changes also inevitably result in changes of deuterium excess (*d*-excess). The model calculations also reproduced the decreasing trend in the *d*-excess in 2001.

The model was also used to examine how isotopic heterogeneity of the snowpack affects the isotopic evolution of snowmelt, and the

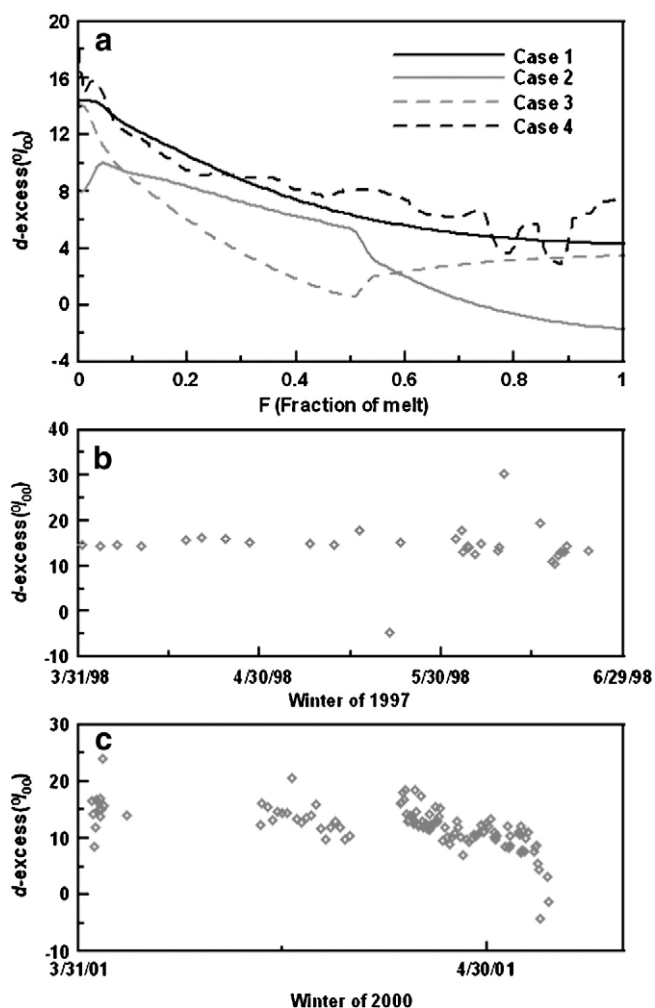


Fig. 8. Variations of d -excess of meltwater for (a) Model results for Cases 1–4, (b) winter 1998, and (c) winter 2001.

evolution of the δD – $\delta^{18}O$ slope in ice and pore water. We draw two conclusions from the model calculations. First, the initial isotopic compositions of a snowpack play an important role in determining the temporal variations of $\delta^{18}O$ or δD of the snowpack and its melt. Consequently, meteorological conditions, which control the initial isotopic compositions of a snowpack, play an important role in determining the evolution of isotopic compositions of the snowpack and its melt, the pattern of which may differ from 1 year to another. Second, slopes of the δD vs. $\delta^{18}O$ relationship in snowmelt may be variable in space and time, depending upon the isotopic stacking of the snow layers and the melting history of the snowpack. Our simulated effect of isotopic heterogeneity on the isotopic evolution of a seasonal snowpack makes it difficult to attribute any observed changes in the δD – $\delta^{18}O$ slope of pore water, ice or meltwater to a single specific process, such as grain growth, vapor–ice exchange, or liquid–ice exchange. Interpretation of isotopic data must consider the effect of isotopic heterogeneity and melting history of the snowpack.

Since the isotopic exchange is controlled by the equilibrium fractionation factors for isotopic exchange between ice and liquid water, the δD vs. $\delta^{18}O$ relationship tends to define a slope that is lower than that of the initial precipitation, with a typical value around 6. Therefore, liquid water evaporation should not be considered as the only cause for the $\delta^{18}O$ vs. δD slope to be lower than that of the meteoric water line.

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References

- Blasch, K.W., Bryson, J.R., 2007. Distinguishing sources of ground water recharge by using δ^2H and $\delta^{18}O$. *Ground water* 45, 294–308.
- Campbell, D.H., Kendall, C., Chang, C.C.Y., Silva, S.R., Tonnessen, K.A., 2002. Pathways for nitrate release from an alpine watershed: determination using $\delta^{15}N$ and $\delta^{18}O$. *Water Resour. Res.* 38 (5), 1052. doi:10.1029/2001WR0005294.
- Chowdhury, A.H., Uliana, M., Wade, S., 2008. Ground water recharge and flow characterization using multiple isotopes. *Ground Water* 46 (3), 426–436.
- Clark, I., Fritz, P., 1997. *Environmental Isotopes in Hydrogeology*. Lewis, New York.
- Dansgaard, W., 1964. Stable isotopes in precipitation. *Tellus* 16 (4), 436–468.
- Earman, S., Campbell, A.R., Phillips, F.M., Newman, B.D., 2006. Isotopic exchange between snow and atmospheric water vapor: estimation of the snowmelt component of groundwater recharge in the southwestern United States. *J. Geophys. Res.* 111, D09302. doi:10.1029/2005JD006470.
- Feng, X., et al., 2001. A study of solute transport mechanisms using rare earth element tracers and artificial rainstorms on snow. *Water Resour. Res.* 37 (5), 1425–1435.
- Feng, X., Taylor, S., Renshaw, C.E., Kirchner, J.W., 2002. Isotopic evolution of snowmelt—1. A physically based one-dimensional model. *Water Resour. Res.* 38 (10), 1217. doi:10.1029/2001WR000814.
- Feng, X., Faiia, A.M., Posmentier, E.S., 2009. Seasonality of isotopes in precipitation: a global perspective. *J. Geophys. Res.* 114, D08116. doi:10.1029/2008JD011279.
- Grassa, F., Favara, R., Valenza, M., 2006. Moisture source in the Hyblean Mountains region (south-eastern Sicily, Italy): evidence from stable isotope signature. *Appl. Geochem.* 21, 2082–2095.
- Gurney, S.D., Lawrence, D.S.L., 2004. Seasonal trends in the stable isotopic composition of snow and meltwater runoff in a subarctic catchment at Okstindan, Norway. *Nord. Hydrol.* 235, 119–137.
- Herrmann, A., Stichler, W., 1981. Isotope input into runoff systems from melting snow covers. *Nord. Hydrol.* 12, 30–318.
- Johnsen, S.J., Dansgaard, W., White, J.W.C., 1989. The origin of Arctic precipitation under present and glacier conditions. *Tellus* 41B, 452–468.
- Koeniger, P., Hubbard, J.A., Link, T., Marshall, J.D., 2008. Isotopic variation of snow cover and streamflow in response to changes in canopy structure in a snow-dominated mountain catchment. *Hydrol. Process.* 22, 557–566.
- Laudon, H., Hemond, H.F., Krouse, R., Bishop, K.H., 2002. Oxygen 18 fractionation during snowmelt: implications for spring flood hydrograph separation. *Water Resour. Res.* 38 (11), 1258. doi:10.1029/2002WR001510.
- Lee, J., Nez, V.E., Feng, X., Kirchner, J.W., Osterhuber, R., Renshaw, C.E., 2008a. A study of solute redistribution and transport in seasonal snowpack using natural and artificial tracers. *J. Hydrol.* 357, 243–254.
- Lee, J., Feng, X., Posmentier, E.S., Faiia, A.M., Osterhuber, R., Kirchner, J.W., 2008b. Modeling of solute transport in snow using conservative tracers and artificial rain-on-snow experiments. *Water Resour. Res.* 44, W02411. doi:10.1029/2006WR005477.
- Lee, J., Feng, X., Posmentier, E.S., Faiia, A.M., Taylor, S., 2009. Stable isotopic exchange rate constant between snow and liquid water. *Chem. Geol.* 260, 57–62.
- Liu, F., Williams, M.W., Caine, N., 2004. Source waters and flow path in an alpine catchment, Colorado Front Range, United States. *Water Resour. Res.* 40, W09401. doi:10.1029/2004WR003076.
- Lundquist, J.D., Cayan, D.R., 2002. Seasonal and spatial patterns in diurnal cycles in streamflow in the western United States. *J. Hydrometeorol.* 3, 591–603.
- Majoube, M., 1970. Fractionation factor of ^{18}O between water vapour and ice. *Nature* 226, 1242.
- Mayr, C., et al., 2007. Precipitation origin and evaporation of lakes in semi-arid Patagonia (Argentina) inferred from stable isotopes ($\delta^{18}O$, δ^2H). *J. Hydrol.* 334, 53–63.
- Merlivat, L., Jouzel, J., 1979. Global climatic interpretation of the deuterium–oxygen 18 relationship for precipitation. *J. Geophys. Res.* 84 (C8), 5029–5033.
- Merlivat, L., Nief, G., 1967. Fractionnement isotopique lors des changements d'état solide-vapeur et liquide-vapeur de l'eau à des températures inférieures à 0 °C. *Tellus* 19, 122–127.
- Nakawo, M., Chiba, S., Satake, H., Kinouchi, S., 1993. Isotopic fractionation during grain coarsening of wet snow. *Ann. Glaciol.* 18, 129–134.
- Nelson, S., Dettman, D., 2001. Improving hydrogen isotope ratio measurements for on-line chromium reduction systems. *Rapid Commun. Mass Spectrom.* 23, 2301–2306.
- O'Neil, J.R., 1968. Hydrogen and oxygen isotope fractionation between ice and water. *J. Phys. Chem.* 72, 3683–3684.
- Taylor, S., Feng, X., Kirchner, J.W., Osterhuber, R., Klaue, B., Renshaw, C.E., 2001. Isotopic evolution of a seasonal snowpack and its melt. *Water Resour. Res.* 37 (3), 759–769.
- Taylor, S., Feng, X., Williams, M., McNamara, J., 2002a. How isotopic fractionation of snowmelt affect hydrograph separation. *Hydrol. Process.* 16, 3683–3690.
- Taylor, S., Feng, X., Renshaw, C.E., Kirchner, J.W., 2002b. Isotopic evolution of snowmelt—2. Verification and parameterization of a one-dimensional model using laboratory experiments. *Water Resour. Res.* 38 (10), 1218. doi:10.1029/2001WR000815.
- Theakstone, 2003. Oxygen isotopes in glacier-river water, Austre Okstindbreen, Okstindan, Norway. *J. Glacio.* 49, 282–298.
- Tsujimura, M., et al., 2007. Stable isotopic and geochemical characteristics of groundwater in Kherlen River basin, a semi-arid region in eastern Mongolia. *J. Hydrol.* 333, 47–57.

- Tu, K.P., Brooks, P.D., Dawson, T.E., 2001. Using septum-capped vials with continuous-flow isotope ratio mass spectrometric analysis of atmospheric CO₂ for Keeling plot applications. *Rapid Commun. Mass Spectrom.* 15, 952–956.
- Uemura, R., Matsui, Y., Yoshimura, K., Motoyama, H., Yoshida, N., 2008. Evidence of deuterium excess in water vapor as an indicator of ocean surface conditions. *J. Geophys. Res.* 113, D19114. doi:10.1029/2008JD010209.
- Unnikrishna, P.V., McDonnell, J.J., Kendall, C., 2002. Isotope variations in a Sierra Nevada snowpack and their relation to meltwater. *J. Hydrol.* 260 (1–4), 38–57.
- Worden, J., Noone, D., Bowman, K., 2007. Importance of rain evaporation and continental convection in the tropical water cycle. *Nature* 445, 528–532.
- Yuan, F., Miyamoto, S., 2008. Characteristics of oxygen-18 and deuterium composition in waters from the Pecos River in America Southwest. *Chem. Geol.* 255, 220–230.
- Zhou, S., Nakawo, M., Hashimoto, S., Sakai, A., 2008a. The effect of refreezing on the isotopic fractionation of melting snowpack. *Hydrol. Process.* 22, 873–882.
- Zhou, S., Nakawo, M., Hashimoto, S., Sakai, A., 2008b. Preferential exchange rate effect of isotopic fractionation in a melting snowpack. *Hydrol. Process.* 22, 3734–3740.