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Preferential exchange rate effect of isotopic fractionation in a melting snowpack

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Abstract:

Stable isotope exchange processes between solid and liquid phases of a natural melting snowpack are investigated in detail by separating the liquid water from snow grains at different depths of the snowpack and collecting the bottom discharge using a lysimeter. In the melting–freezing mass exchange process between the two phases, the theoretical slope of the δD–δ^{18}O line for newly refrozen ice is calculated to be nearly that of pore water. However, based on observations of the isotopic evolution and snow grain coarsening of the snowpack, it is demonstrated that the slope of the δD–δ^{18}O line for newly refrozen ice is equal to that of the original ice. This is proved to be due to preferential water flow in the snowpack, which leads to relatively more deuterium and less oxygen-18 in the mobile water than the immobile water because of the kinetic effect. Higher mass exchange rate in the mobile water region results in excess deuterium in the bulk refrozen ice, compared with the fractionation of uniform fractionation factors and exchange rate. This effect, which is termed the 'preferential exchange rate effect of isotopic fractionation', is shown to be larger in the lower part than the upper part of the snowpack. Copyright © 2008 John Wiley & Sons, Ltd.

KEY WORDS snowpack; isotopic fractionation; preferential water flow; snowmelt

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INTRODUCTION

Stable isotope studies of oxygen and hydrogen have made important contributions in meteorological, hydrological and environmental fields. The concentrations of deuterium and oxygen-18 in present-day precipitation have been shown to display high correlation with surface air temperature, relative humidity of the atmosphere, and amount of precipitation (Dansgaard, 1964; Yurtsever and Gat, 1981; Rozanski *et al.*, 1993). These meteorological/environmental relationships with the concentrations of deuterium and oxygen-18 have been used in numerous studies aimed at reconstructing past climates from various environmental archives, such as ice cores, lacustrine deposits, tree cellulose, and others (Johnsen *et al.*, 1989; Edwards, 1993; Gasse and van Campo, 1994; Thompson *et al.*, 2000; Ferrio and Voltas, 2005). The variations of isotopic ratios in surface waters and groundwaters are used for hydrograph separation and for estimating a series of hydrological parameters, including rate of groundwater recharge, flow paths, and particle velocities and transit times along various parts of the water flow through a catchment (Rodhe, 1998). In water cycles, isotopic fractionation takes place during phase change, which is highly complicated (Dansgaard, 1964; Cooper, 1998; Ingraham, 1998). The isotopic applications thus rely heavily on the understanding of the fractionation processes between phases under different conditions. Snowpack, glacier and ice cap, the main environmental components at high altitudes and latitudes, play an important role in the water cycles. During the period of snow storage there will be little or no water input to the ground. The groundwater reservoir will gradually decline by draining to the stream, whose discharge recedes corresponding to the falling groundwater level and flow. During snowmelt the groundwater reservoir recovers and stream discharge may reach its annual peak by contributions from groundwater as well as overland flow (Rodhe, 1998). Therefore, the isotopic fractionation processes proceeding in or at these water reservoirs, have received much attention from scientists and many studies have been carried out on them (Cooper, 1998; Stichler and Schotterer, 2000). However, there still remain many questions to be answered because of the complexity of the processes under varying conditions (Cooper, 1998; Rodhe, 1998; Stichler and Schotterer, 2000).

The empirical isotopic composition line (the linear relation between δD and δ^{18}O) or the meteoric water line (Craig, 1961) and the deuterium excess, which is defined as $d = \delta\text{D}-8\delta^{8}\text{O}$, are commonly used as indicators of water vapour source, humidity of the source, and kinetic conditions (Dansgaard, 1964; Jouzel *et al.*, 1982; Armengaud *et al.*, 1998) in isotope hydrology, modern environmental studies and palaeoclimatic reconstructions by ice core. While extensive investigations have been conducted

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on the meteoric water line for precipitation (Clark and Fritz, 1997; Ingraham, 1998), few have been reported on the evolution of the line after snow deposition, especially during snowmelt. Most investigations have dealt with only one kind of isotope, mainly oxygen-18. Work was presented recently on the change of the δD–δ^{18}O line and the deuterium excess of melting snowpack (Zhou *et al*., 2008). In that work, the slope of the δD–δ^{18}O line for the liquid phase was found to be lower than for the solid phase of the snowpack. This causes the slopes to become lower and lower as the diurnal melt–freeze episodes cycle throughout the melting season, which is clearly demonstrated in the glacier firn. However, some of the isotopic processes behind the findings are still unclear. For example, how does water percolation affect interphase isotopic exchange in the snowpack? Why does the slope for the solid phase remain larger than for the liquid water? Addressing these issues, this paper examines the isotopic processes within a melting snowpack and demonstrates the effect of preferential water flow on these processes.

METHODS

The fieldwork was conducted at the Snow Melting Research Station of Hokkaido University, Moshiri (44°23′N, 142°17′E), in the northern part of Hokkaido, Japan from February to April 1998. The data used in this analysis were obtained mainly between 2 and 14 April, when the snowpack was midway through the melting period and its thickness decreased from 105 cm to 46 cm because of melting. Successive snow pits were dug and the entire depth profile at 4-cm increments was sampled most days within a plain plot. Each sample was *in situ* (in pit) centrifuged with a hand-driven centrifuge to separate liquid water from snow grains, and then the separated water and snow grains were sampled separately. A portion of each separated snow grain sample was subjected to water content measurements using an Akitaya calorimeter (Institute of Low Temperature Science, Hokkadio University). The centrifuge essentially includes two cylinder-shaped polythene boxes each 9·5 cm in height and 9 cm in diameter. The central part of the inner cover of each box was cut so that a cup-shaped mesh could be fitted into it. Snow samples were then put into the mesh for centrifuging. The snow sampler and the mesh were cooled in wet snow before use. Based on a large number of pre-experiments, the centrifugal time interval for a single sample was restricted to 30 s to ensure minimum melt and effective separation. The setup was tested for a series of isotope determinations by comparing each of the measured isotopic ratios of non-separated wet snow with the calculated value of the corresponding sample, which was obtained using the water content data of the non-separated snow and separated snow grains, and the isotopic ratios of the separated snow grains and water. No melting effect was detected in these tests. Grain photos of each sample were taken using a camera with a magnifying lens. A 90×90 cm^2 lysimeter, which had been installed for many years, was used to continuously collect the bottom discharge of the snowpack.

All the samples were analysed for their oxygen-18 and deuterium ratios (with an accuracy of $\pm$0·1‰ for δ^{18}O and $\pm$1·0‰ for δD) at the Hydrospheric Atmospheric Research Center, Nagoya University, Japan. The grain size of each sample was manually measured using the photographs.

ISOTOPIC FRACTIONATION AND δD–δ^{18}O LINE

Isotopic results for the snowpack

When snow grains and liquid water co-exist, mass exchange occurs between the two phases, with large grains growing at the expense of small ones (Raymond and Tusima, 1979). In accordance with the phase change, isotopic fractionation takes place and causes enrichment of ^{18}O in the solid phase, which has been demonstrated by experiment (Arnason, 1969; Nakawo *et al*., 1993), model calculations (Buason, 1972; Taylor *et al*., 2001, 2002; Feng *et al*., 2002) and field observations (Stichler *et al*., 1981; Suzuki, 1993). Figure 1 shows the isotopic data of separated snow grain and pore water samples for 4 days. The isotope values of the pore water, except for two or three samples, are lower than those of the corresponding snow grains. This is invariably true for data obtained on other days, and indicates the rapid isotopic fractionation between percolating meltwater and snow grains (Zhou *et al*., 2001). When these isotopic data are plotted on a δD–δ^{18}O diagram for each day (Figure 2), it is found that all the slopes of the regression lines for liquid phase are lower than those of the corresponding regression lines for solid phase (Zhou *et al*., 2008). Figure 2 (solid lines) presents three of these δD-δ^{18}O diagrams using

Table I. Slopes of the regression lines (δD versus δ^{18}O) for the observed data of the snowpack on different days. Also shown are the standard errors and R^2 values

Date	4–2	4–4	4–6	4–8	4–9	4–10	4–11	4–12	4–14
Solid phase	6·9	6·8	6·9	6·7	6·8	6·6	6·7	6·4	6·5
Standard error	0·90	0·79	0·57	0·42	0·46	0·48	0·58	0·42	0·95
R^2	0·81	0·89	0·92	0·96	0·96	0·95	0·94	0·97	0·87
Liquid phase	4·7	5·1	5·2	4·9	4·9	4·9	4·5	4·3	4·7
Standard error	0·75	0·40	0·36	0·39	0·64	0·35	0·84	1·20	1·16
R^2	0·74	0·92	0·94	0·93	0·85	0·96	0·78	0·65	0·73

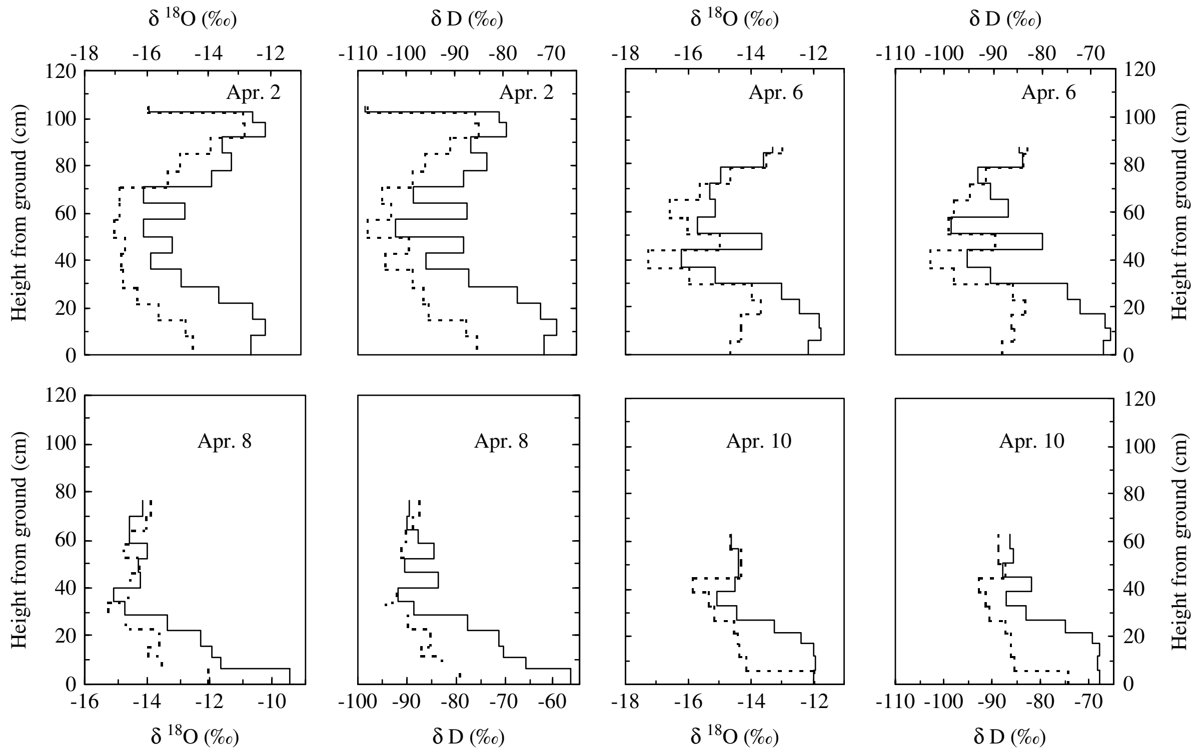

Figure 1. Isotopic evolution of the snowpack, showing $\delta^{18}O$ and δD profiles for both solid (solid line) and liquid (broken line) phases

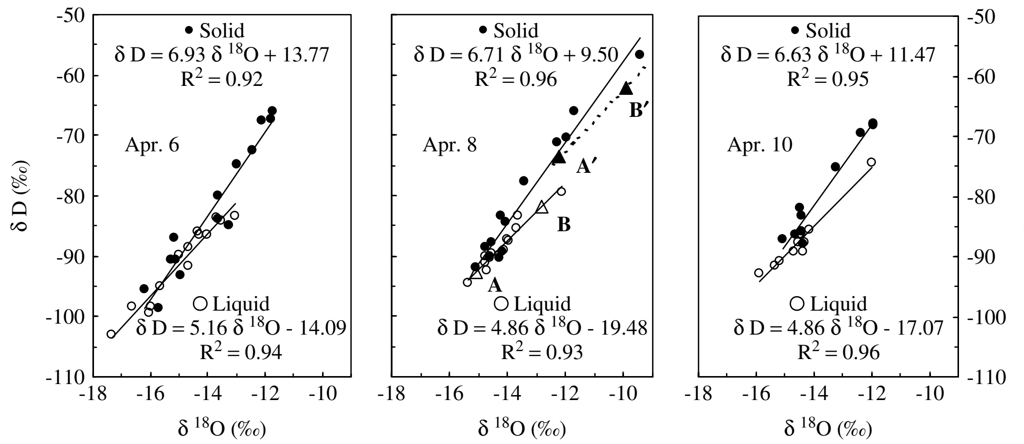

Figure 2. δD–$\delta^{18}O$ diagrams for both solid and liquid portions of the snowpack on three days. Regression lines and equations are shown. The theoretical line (broken, 8 April) is also shown for the newly refrozen ice under equilibrium fractionation. Points A and B (open triangles, 8 April) are on the line and for pore water at two depths. Points A′ and B′ (filled triangles) are, correspondingly, for the newly refrozen ice at the two depths. See text for details

corresponding data sets displayed in Figure 1. Table I lists the slopes and their standard errors for each of the two phases and their differences for each of the observational days. It can be seen in the table that the slopes for solid and liquid show a slight decreasing trend with time, with the former fluctuating in the range 6·9–6·4 and the latter, 5·2–4·3. *t*-tests were carried out on the data and they show that there are no distinct differences between the regression lines for the solid phase at the significance level 0·05 (Zhou *et al.*, 2008). This means that the slope changes for the solid phase are negligible in the period, or that melting of the snowpack has no clear impact on the δD–$\delta^{18}O$ line for the solid phase. However, at a significance level of 0·05, *t*-tests show clear differences between some regression lines for the liquid phase. As a whole, the differences between the lines for the liquid are indistinct in the periods of 2–10 April and 11–14 April, but distinct between these two periods, which indicates an overall slight decrease in the slope of the liquid phase throughout the whole period.

Isotopic processes within melting snowpack

Within a melting snowpack, the isotopic ratio ($^{18}O/^{16}O$ or D/H) of ice is controlled only by its isotopic exchange with liquid water. In contrast, the isotopic ratio of the liquid phase is controlled by advection, dispersion, and

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ice–water isotopic exchange. Based on these processes, Feng *et al*. (2002) proposed a one-dimensional model that simulates the isotopic composition of meltwater exiting the base of a snowpack. The model, which was verified and parameterized by laboratory experiments (Taylor *et al*., 2002), assumes that the snowpack is homogeneous and melts at a constant rate. However, a natural snowpack like the Japanese one is heterogeneous and the liquid water in the snow is viewed to be in different pools or flow paths. This is termed the preferential water flow (Harrington and Bales, 1998; Feng *et al*., 2001). Adding to this, the melt rate of the snowpack is changing daily and seasonally (Zhou *et al*., 2008). The model thus needs to be further developed and parameterized to capture the more complicated isotopic processes involved in the mass exchange within a natural melting snowpack.

Instead of modelling, we directly analyse the δD–δ^{18}O lines of the snowpack. First, consider fractionation in the refreezing process of pore water for the whole snowpack. In Figure 2 (8 April), Points A $({R_A}^o, {R_A}^d)$ and B $({R_B}^o, {R_B}^d)$ $({R_A}^o, {R_B}^o$ and ${R_A}^d, {R_B}^d$ are oxygen-18 and deuterium ratios for the two points respectively, similarly for Point A' and B' below), on the regression line, are for the pore water at two depths of the snowpack. Points A' $({R_{A'}}^o, {R_{B'}}^d)$ and B' $({R_{B'}}^o, {R_{B'}}^d)$ are for the newly refrozen ice onto large grains at the two depths. Suppose α_d and α_o are the fractionation factors for deuterium and oxygen-18, respectively and S_{liq} is the slope of the δD-δ^{18}O line for liquid phase, then

$$S_{liq} = \frac{{R_B}^d - {R_A}^d}{{R_B}^o - {R_A}^o} \qquad (1)$$

and the slope, for the newly refrozen ice onto large grains, S_{ice} is:

$$S_{ice} = \frac{{R_{B'}}^d - {R_{A'}}^d}{{R_{B'}}^o - {R_{A'}}^o} = \frac{\alpha_d({R_B}^d - {R_A}^d)}{\alpha_o({R_B}^o - {R_A}^o)} = S_{liq}\frac{\alpha_d}{\alpha_o} \qquad (2)$$

For α_d and α_o values in isotopic equilibrium (1·0212 and 1·00291 respectively, Lehmann and Siegenthaler, 1991), $S_{ice} = 1{\cdot}018 S_{liq}$. In non-equilibrium, α_d, α_o and the $\frac{\alpha_d}{\alpha_o}$ ratio are a little lower than in equilibrium, which can be calculated from the data by Souchez and Jouzel (1984). Therefore, the slope for the newly refrozen ice should nearly equal the slope for the liquid whether the fractionation is in equilibrium or not. Further, suppose C_1 and C_2 are the intercepts of the lines for the liquid phase and the newly refrozen ice respectively, then:

$$C_2 = \alpha_d(C_1 + 1) + S_{liq}\left(\frac{\alpha_d}{\alpha_o} - \alpha_d\right) - 1 \qquad (3)$$

Based on Equations (2) and (3), the line for the newly refrozen ice on 8 April, under equilibrium fractionation, is shown in Figure 2 (broken line). Thus the lines under non-equilibrium states are situated in between the equilibrium line and the line for the liquid.

The amount of refrozen ice in the observational period is then estimated. According to the daily measurements of snow grain size (Hashimoto *et al*., 2002; Zhou *et al*., 2003), the mean grain volume of a layer on 8 April had increased to 2·2–6·3 times that on 27 March. Calculations show that the exchange of mass between solid and liquid phases is between $1{\cdot}4 \times 10^{-2}$ and $7{\cdot}33 \times 10^{-2}$ g cm^{-3} day^{-1} (Hashimoto *et al*., 2002). Assuming the same grain-coarsening rate in the period 8–14 April, for which grain size measurements were not performed, the mean grain volume of a snow layer increased on 14 April to 2·4–3·8 times that on 2 April. The grain coarsening also means some smaller grains were disappearing owing to the melt (Raymond and Tusima, 1979), and thus the number of grains progressively becomes less. Therefore, for the grains appearing on 14 April, the mean grain volume increase in a layer is less than 2·4–3·8 times that seen on 2 April. The assumed grain-coarsening rate for the period 8–14 April is largely underestimated because the averaged discharge rate in the period was measured to be 1·69 times that of the period between 27 March and 8 April. Since the dry density (density excluding liquid water) of the bulk snow was measured to have increased by only 0·02 g cm^{-3} from 1–8 April, and showed no clear increase from 8–14 April (Zhou *et al*., 2003), this higher water flow rate means higher water content and higher grain coarsening rate, which will be explained later. Based on the daily frequency distributions of grain size of the snow layers (Hashimoto *et al*., 2002; Zhou *et al*., 2003), it is estimated that, for the bulk snow on 14 April, the amount of ice refrozen since 2 April accounts for at least 46% of the total ice amount, and the quantity of original ice from 2 April being at most 54% of it. Using these ratios and adopting the slope values 4·9 (the averaged value 4·8 for pore water times the factor 1·018) and 6·9 for the refrozen and original ice respectively, the slope for the solid phase of the bulk snow on 14 April, is calculated to be 6·0. This value is the mass-weighted average of the slopes of the two lines because the combination of two linear lines definitely yields a new linear line having an average slope. The grain coarsening difference of the snow layers would result in a deviation of the averaged slope, which is estimated to be $\pm$0·2 by comparing the results of applying both uniform and different measured refrozen/original ice mass ratios to the snow layers of each day using the measured isotopic profiles. While the value 6·0 is already lower than the observed lowest value 6·4, the calculations have not included the above-mentioned refreezing effect (the whole surface layer (less than 20 cm) was observed to refreeze on most nights), although this effect was indistinct (Zhou *et al*., 2008). However, in the above analysis, the slope changes of the solid phase are demonstrated to be negligible during the whole period. Therefore, the slope, for the newly refrozen ice onto larger grains in the ice–water exchange process, is not nearly equal to the slope for the pore water, but much larger and equal to that for the solid phase. This means that excess or extra deuterium, relative to oxygen-18, is exchanged to the refrozen ice, and that this process is more effective in the lower part than the upper part of the snowpack because the isotopic ratios

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of the lower profile are generally larger than those of the upper profile (Figure 1). This also indicates that the deuterium exchanges faster or has a larger exchange rate than oxygen-18, since it cannot be explained by the fractionation effect (whether it is kinetic or not) alone as above.

PREFERENTIAL EXCHANGE RATE EFFECT OF ISOTOPIC FRACTIONATION

In general, there is no reason to consider differing exchange rates for deuterium and oxygen-18 if the isotopes are homogeneously distributed in pore water (the diffusion difference between deuterium and oxygen-18 is negligible in fractionation (Nakawo *et al.*, 1993)). Fortunately, a melting snowpack, being similar to other porous media, contains waters with different flow rates containing different solute concentrations. These waters can be simply divided into mobile and immobile waters (Harrington and Bales, 1998; Feng *et al.*, 2001). Although the definition of mobile and immobile waters is somewhat vague, the discharge can undoubtedly be regarded as mobile water. Figure 3 shows the differences among the isotopic ratios of discharge, bottom pore water and ice grain samples. It is clear that the isotopic ratio for the pore water is intermediate, smaller than that for the ice grains, but larger than that for the discharge. As the pore water includes both mobile and immobile waters, the concentration for the immobile water must be between the concentrations for the pore water and ice grains. These differences clearly indicate the existence of mobile and immobile waters, and the significance of water flow rate for the isotopic composition of the waters, which, in spite of being physically modelled (Harrington and Bales, 1998; Feng *et al.*, 2001), has not been demonstrated directly and isotopically like this. Since water flow rate is determined by water saturation (Colbeck, 1972), water saturation in the mobile region is higher than the immobile region where water is immobile or nearly immobile. A higher water saturation means higher water content because mobile water channels connect around, and intercross with, immobile water pores, and thus they share a unit snow volume having the same dry density. These observations show that, for snow layers with differing water contents, the grain coarsening rate increases with increasing water content (Zhou *et al.*, 2003), which is equivalent to saying that the mass exchange rate in the region of high water content is larger than in the region of low water content. Hence, the larger exchange rate occurs in the mobile phase. As equilibrium fractionation occurs under conditions of very slow freezing and complete mixing of the bulk water (Dansgaard, 1964; Lehmann and Siegenthaler, 1991), the isotopic fractionation in the immobile region, if not at equilibrium, is closer to the equilibrium state than the mobile region. Then, by the mass-dependent isotope fractionation effect (Dansgaard, 1964), which can be observed in the data of Souchez and Jouzel (1984), the fractionation factor ratio $\frac{\alpha_d}{\alpha_o}$ for the mobile region is smaller than for the immobile region, and then the oxygen-18 relative to deuterium is more depleted in the mobile water than in the immobile water. Figure 4 presents all the isotope data for both discharge (as mobile water) and pore water (as a mixture of mobile and immobile waters) in the period from 2–9 April. Although the data for the pore water are somewhat scattered owing to the fractionation differences in the snowpack (Figure 5) and also because of the isotopic changes within the snowpack over time, it is still shown that, in the common range of the two regression lines, the discharge contains more deuterium or less oxygen-18 than the pore water as a whole. It should be pointed out that the pore water samples were obtained at the time of high flow rates (so that enough sample water could be separated), and as such more deuterium was expected. However, the discharge water, while being continuously collected by the lysimeter, was sampled only twice on most days, and thus was a mixture of water at different flow rates. This explains why the two regression lines are very near. When the isotope-depleted water percolates downward, its oxygen-18 is further depleted relative to deuterium, and thus its deuterium relatively increases. This is demonstrated by Figure 5, which shows the isotopic compositions of pore water in the surface and bottom layers (both are about 25–30 cm thick) for all of the observational days. While the slopes of the two regression lines are essentially the same, the deuterium concentration of pore water in the bottom layer is 2‰ higher than in the surface layer. More deuterium in the mobile water and a larger exchange rate in the mobile region would inevitably result in excess or surplus deuterium being exchanged to the bulk refrozen ice, compared with the fractionation of a uniform $\frac{\alpha_d}{\alpha_o}$ ratio and exchange rate in the whole snowpack. This effect is intensified with increasing depth because of the relatively increasing deuterium concentration in the mobile water. As the lower profile generally has higher isotopic ratios (Figure 1), the slope for the newly refrozen ice becomes much larger than for the pore water. Since this effect originates from the difference in the exchange rate between mobile and immobile water regions, here it has been termed the 'preferential exchange rate effect of isotopic fractionation'. This effect should occur at varying levels of intensity in snowpacks during melt periods because the water flow rate, water saturation or content, the extent of the mobile water region and the exchange rate are different from place to place.

It is noted that in Figure 5 the two lines are essentially parallel. Theoretically, if one ignores the isotopic dispersion in the snowpack (Feng *et al.*, 2002; Taylor *et al.*, 2002), the slopes of the two lines could be slightly different depending on the differences between layers of the snowpack in the $\frac{\alpha_d}{\alpha_o}$ ratio of the mobile region, the volume ratio of mobile water to immobile water, and the state of mobile–immobile isotopic exchange (especially the exchange difference between oxygen-18 and deuterium). The difference in the slopes of the two lines

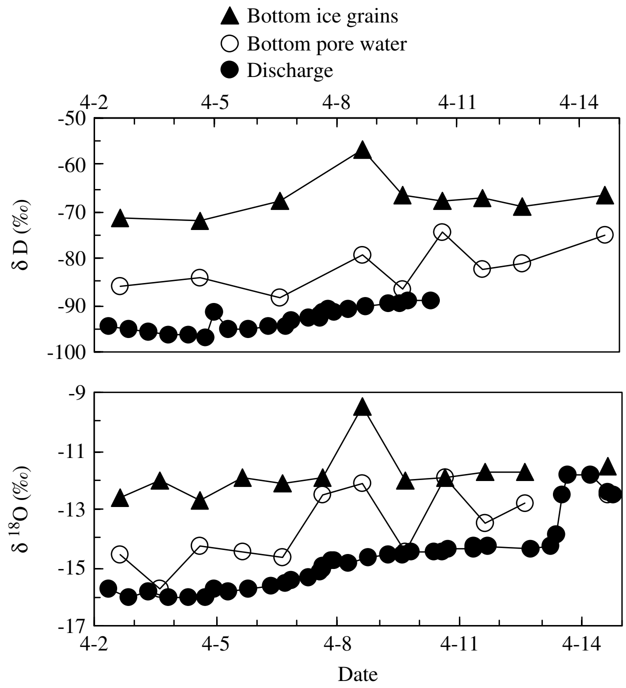

Figure 3. Isotopic variations of bottom ice grains and pore water, and discharge of the snowpack

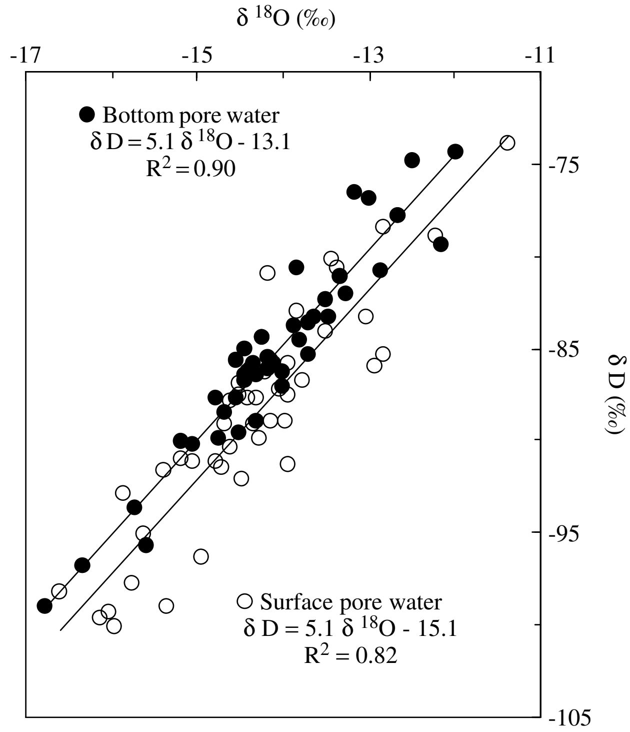

Figure 5. The δD–δ^{18}O plot for pore water in the surface and bottom layers of the snowpack (2–14 April). The respective standard errors for slopes of the lines of surface pore water and of bottom pore water are 0·36 and 0·26

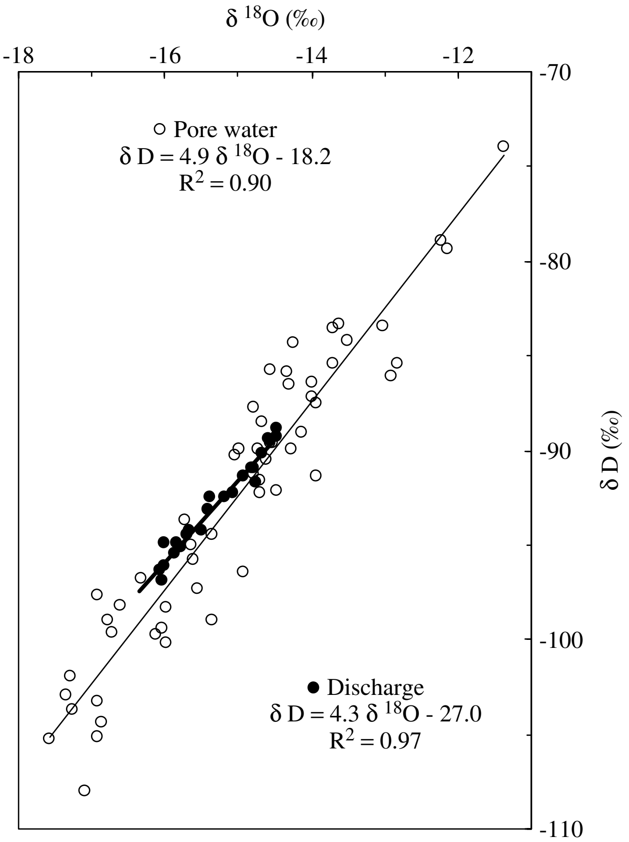

Figure 4. The δD–δ^{18}O plot for pore water and discharge of the snowpack (2–9 April). The respective standard errors for slopes of the pore water and of the discharge are 0·22 and 0·17

would also depend on the structure of the snow layers. This is rather complicated and a more sophisticated model, similar to that of Feng *et al.* (2001) or Harrington and Bales (1998), would need to be developed. However, the identical slope of the lines for the surface and bottom layers indicates that the impact of all these factors is negligible in the snowpack as a whole.

CONCLUSIONS

The existence of preferential water flow in melting snowpack has been demonstrated isotopically and directly. Preferential water flow produces different water saturation of pores, snow water contents and water flow rates, which result in differences in isotopic fractionation and mass exchange rate. The isotopic fractionation in the immobile water region, if not at equilibrium, is closer to the equilibrium state than that in the mobile water region. Because of this difference, by the mass-dependent isotope fractionation effect, the mobile water relatively has more deuterium and less oxygen-18 than the immobile water. When the meltwater percolates downward through the snow column, its oxygen-18 is further depleted relative to deuterium, so that its deuterium, relatively, increases. As the water content and thus the inter-phase mass exchange rate are higher in the mobile region than in the immobile region, excess or surplus deuterium is exchanged into the bulk refrozen ice, compared with the fractionation of uniform fractionation factors and exchange rate. This effect, which is termed the 'preferential exchange rate effect of isotopic fractionation,' is intensified with increasing depth because of the relatively increasing deuterium concentration in the mobile water, and thus results in a much higher slope of the $\delta D-\delta^{18}O$ line for the newly refrozen ice, compared with the theoretical slope, which nearly equals the slope for the pore water.

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REFERENCES

Armengaud A, Koster RD, Jouzel J, Ciais P. 1998. Deuterium excess in Greenland snow: analysis with simple and complex model. *Journal of Geophysical Research* **103**(D8): 8947–8953.

Arnason B. 1969. The exchange of hydrogen isotopes between ice and water in temperate glaciers. *Earth and Planetary Science Letters* **6**: 423–430.

Buason T. 1972. Equation of isotope fractionation between ice and water in a melting snow column with continuous rain and percolation. *Journal of Glaciology* **11**(63): 387–400.

Clark ID, Fritz P. 1997. *Environmental Isotopes in Hydrogeology*. Lewis Publishers: Boca Raton.

Colbeck SC. 1972. A theory of water percolation in snow. *Journal of Glaciology* **11**(63): 369–385.

Cooper LW. 1998. Isotopic fractionation in snow cover. In *Isotope Tracers in Catchment Hydrology*, Kendall C, McDonnell JJ (eds). Elsevier Science BV: Amsterdam, The Netherlands; 119–136.

Craig H. 1961. Isotopic variations in meteoric waters. *Science* **133**: 1702–1703.

Dansgaard W. 1964. Stable isotopes in precipitation. *Tellus* **16**(4): 436–468.

Edwards TWD. 1993. Interpreting past climates from stable isotopes in continental organic matter. In *Climate Change in Continental Isotopic Records*, Geophysics Monographs Series, Vol. 78, Swart PK, Lohmann KL, McKenzie J, Savin S (eds). AGU: Washington DC; 333–343.

Feng X, Kirchner JW, Renshaw CE, Osterhuber RS, Klaue B, Taylor S. 2001. A study of solute transport mechanisms using rare earth element tracers and artificial rainstorms on snow. *Water Resources Research* **37**(5): 1425–1435.

Feng X, Taylor S, Renshaw CE, Kirchner JW. 2002. Isotopic evolution of snowmelt: 1. A physically based one-dimensional model. *Water Resources Research* **38**(10): 1217, doi: 10·1029/2001WR000814.

Ferrio JP, Voltas J. 2005. Carbon and oxygen isotope ratios in wood constituents of *Pinus halepensis* as indicators of precipitation, temperature and vapour pressure deficit. *Tellus* **57B**: 164–173.

Gasse F, Campo EV. 1994. Abrupt, post-glacial climate events in West Asia and North Africa monsoon domains. *Earth Planetary Sciience Letters* **126**: 435–456.

Harrington R, Bales RC. 1998. Modeling ionic solute transport in melting snow. *Water Resources Research* **34**(7): 1727–1736.

Hashimoto S, Zhou S, Nakawo M, Sakai A, Ageta Y, Ishikawa N, Narita H. 2002. Isotope studies of inner snow layers in a temperate region. *Hydrological Processes* **16**: 2209–2220.

Ingraham NL. 1998. Isotopic variations in precipitation. In *Isotope Tracers in Catchment Hydrology*, Kendall C, McDonnell JJ (eds). Elsevier Science BV: Amsterdam, The Netherlands; 87–118.

Johnsen SJ, Dansgaard W, White JWC. 1989. The origin of Arctic precipitation under present and glacial conditions. *Tellus* **41B**: 452–468.

Jouzel J, Merlivat L, Lorius C. 1982. Deuterium excess in an East Antarctic ice core suggests high relative humidity at the oceanic surface during the last glacial maximum. *Nature* **299**(5885): 688–691.

Lehmann M, Siegenthaler U. 1991. Equilibrium oxygen- and hydrogen-isotope fractionation between ice and water. *Journal of Glaciology* **37**(125): 23–26.

Nakawo M, Chiba S, Satake H, Kinouchi S. 1993. Isotopic fractionation during grain coarsening of wet snow. *Annals of Glaciology* **18**: 129–134.

Raymond CF, Tusima K. 1979. Grain coarsening of water-saturated snow. *Journal of Glaciology* **22**(86): 83–105.

Rodhe A. 1998. Snowmelt-dominated systems. In *Isotope Tracers in Catchment Hydrology*, Kendall C, McDonnell JJ (eds). Elsevier Science BV: Amsterdam, The Netherlands; 391–433.

Rozanski K, Araguas-Araguas L, Gonfiantini R. 1993. Isotopic patterns in modern global precipitation. In *Climate Change in Continental Isotopic Records*, Geophysics Monographs Series, Vol. 78, Swart PK, Lohmann KL, McKenzie J, Savin S (eds). AGU: Washington DC; 1–36.

Souchez RA, Jouzel J. 1984. On the isotopic composition in δD and $\delta^{18}O$ of water and ice during freezing. *Journal of Glaciology* **30**(106): 369–372.

Stichler W, Rauert W, Martinec J. 1981. Environmental isotope studies of Alpine snowpack. *Nordic Hydrology* **12**: 297–308.

Stichler W, Schotterer U. 2000. From accumulation to discharge: modification of stable isotopes during glacial and post-glacial processes. *Hydrological Processes* **14**: 1423–1438.

Suzuki K. 1993. Oxygen-18 of snow meltwater and snow cover. *Seppyo* **55**(4): 335–342 (in Japanese with English summary).

Taylor S, Feng X, Kirchner JW, Osterhuber R, Klaue B, Renshaw CE. 2001. Isotopic evolution of a seasonal snowpack and its melt. *Water Resources Research* **37**(3): 759–769.

Taylor S, Feng X, Renshaw CE, Kirchner JW. 2002. Isotopic evolution of snowmelt: 2. Verification and parameterization of a one-dimensional model. *Water Resources Research* **38**(10): 1218, doi: 10·1029/2001WR000815.

Thompson LG, Yao T, Mosley-Thompson E, David ME, Henderson KA, Lin P-N. 2000. A high-resolution millennial record of the South Asian monsoon from Himalaya ice cores. *Science* **289**: 1916–1919.

Yurtsever Y, Gat JR. 1981. Atmospheric waters. In *Stable Isotope Hydrology: Deuterium and Oxygen-18 in the Water Cycle*, Technical Report Series, Vol. 210, Gat JR, Gonfiantini R (eds). International Atomic Energy Agency: Vienna; 103–142.

Zhou S, Nakawo M, Hashimoto S, Sakai A, Narita H, Ishikawa N. 2001. Isotopic fractionation and profile evolution of a melting snowcover. *Science in China* (Series E) **44**: (Supplement): 35–40.

Zhou S, Nakawo M, Hashimoto S, Sakai A, Narita H, Ishikawa N. 2003. Densification and grain coarsening of melting snow. *Chinese Journal of Polar Science* **14**(1): 12–23.

Zhou S, Nakawo M, Hashimoto S, Sakai A. 2008. The effect of refreezing on the isotopic fractionation of melting snowpack. *Hydrological Processes* **22**(6): 873–882. DOI: 10.1002/hyp.6662.