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The effect of refreezing on the isotopic composition of melting snowpack

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Abstract:

The isotopic composition of solid and liquid portions of natural melting snowpack is investigated in detail by the separating of liquid water from snow grains at different depths of the snowpack. The slope of the δD–δ^{18}O line for the liquid phase is found to be lower than for the solid phase. This is proved to be due to the isotopic fractionation occurring in the melt–freeze mass exchange within the snowpack. Melting of the snowpack has no clear impact on the δD–δ^{18}O line for the solid phase, but the slope of the δD–δ^{18}O line for the liquid shows an overall slight decrease in the melting period. When the snowpack is refrozen, the refreezing process would inevitably cause the slope of the solid phase to decrease because of the discrepancy between the slopes of the two phases. Thus the slope of the solid would become lower and lower as the diurnal melt–freeze episodes cycle throughout the melting season. This effect is then demonstrated by looking into the isotopic composition changes of glacier firn. The extent of the effect depends on the snowpack properties and environmental conditions. The slope changes also result in a decreasing trend in deuterium excess. Copyright © 2007 John Wiley & Sons, Ltd.

KEY WORDS ice core; snowpack; refreezing; isotopic composition

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INTRODUCTION

Ice core research has greatly contributed to the study of climate change over recent decades (e.g. Dansgaard *et al*., 1985, 1993). Stable water isotopes (δ^{18}O, δD) preserved in ice cores can be used as proxy temperature indicators, for dating, and by measuring the deuterium excess, for tracing the water vapour source of precipitation (Jouzel *et al*., 1982; Armengaud *et al*., 1998). These methods, however, are more problematic when applied to cores taken from areas of high melt because melting can introduce time gaps, cause isotopic fractionation, and remove good seasonal signals making time-scales difficult or impossible to evaluate (Koerner, 1997). Unfortunately, many studies have not given due consideration to melt effects on the derivation of time-scales or the interpretation of ice-core chemistry and stable-isotope ratios (Koerner, 1997). This highlights the need for a better understanding of the metamorphosing processes of melting snowpacks, especially in the context of the isotopic processes. This need is greatly reinforced by the isotope hydrological applications in temperate regions, where snowmelt can account for the majority of the water added to a catchment and often causes the largest annual stream discharge event (Rodhe, 1998). One of the most important applications is the two-component isotopic hydrograph separation that partitions runoff water into event and pre-event water sources, and thus contributes to flood prediction and water resource management. While this technique has been used extensively in a number of areas (Taylor *et al*., 2002a), the large variation in snowmelt isotopic composition, caused by fractionation during melting, has impeded an accurate separation of stream-flow during spring flood episodes (Laudon *et al*., 2002). Although recent studies have been carried out on modelling the isotopic evolution of snowmelt (Taylor *et al*., 2001, 2002b; Feng *et al*., 2002), there remain many questions to be answered on the isotopic processes of melting snowpack (Cooper, 1998).

When snow grains and liquid water co-exist at 0 °C, 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 are demonstrated by experiments (e.g. Arnason, 1969; Nakawo *et al*., 1993), model calculations (e.g. Buason, 1972; Feng *et al*., 2002) and field observations (e.g. Stichler *et al*., 1981; Suzuki, 1993). Many investigations have been carried out on how melt and isotopic fractionation change the isotopic profile of a snowpack (e.g. Suzuki, 1993; Taylor *et al*., 2001; Hashimoto *et al*., 2002; Unnikrishna *et al*., 2002). These investigations, which were conducted generally by digging successive snow pits, have demonstrated conspicuous isotopic fractionation between the solid and percolating liquid phases and its influence on the

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isotopic evolution of the snowpack. In most of these studies, however, analysis was limited only to oxygen-18 (^{18}O) and the fractionation differences for deuterium were ignored. Also, the sampling intervals between successive snow pits were long, usually varying from 1 week to more than 1 month, which would cause much environmental and metamorphosing information to be lost.

In a previous study (Hashimoto *et al.*, 2002), the difference of the δD–δ^{18}O relationships between precipitation and snowpack was found, but further analysis was not performed. This paper presents two separate series of observational results. One from a seasonal snowpack and another from the firn of a glacier. The evolution of isotopic composition for both snow grains and percolating water in wet snow and its freezing effect on firn are examined. Although the fieldwork on the seasonal snowpack was carried out together with the previous work (Hashimoto *et al.*, 2002), the data of the δ^{18}O–δD relationships are totally different from the previous ones. The data used in the present study include two sets of the solid and liquid phases of wet snow, but the previous data were an independent set which were derived from the samples of bulk snow containing both snow grains and liquid water. Only 3 days of δ^{18}O data for both solid and liquid phases shown in the previous paper are used in this study.

METHODS

The fieldwork was conducted at two separate sites. One at a seasonal snowpack in Japan and another at a glacier in China. The Japanese site was the Snow Melting Research Station of Hokkaido University, Moshiri (44°23′N, 142°17′E), in the northern part of Hokkaido. The snowpack at the Japanese site was as thick as 180·1 cm on 14 February 1998 and its recorded lowest temperature was −17·3 °C on 7 February 1998. The observations were made from February to April 1998. The data used in this analysis were obtained mainly between 2 and 14 April 1998. The snowpack began to melt in the last 10 days of March. The fieldwork included the following tasks. (1) Inserting eight temperature sensors into the snowpack at different heights to automatically record the temperature variations throughout the whole fieldwork period. (2) Digging successive snow pits most days within the plain plot of the station and sampling snow at 4 cm intervals continuously from the surface to the bottom of the pit wall using a $4 \times 6 \times 7$ cm^3 sampler. (3) *In situ* (in pit) separating of liquid water from snow grains with a hand-driven centrifuge and then sampling the separated water and snow grains separately. A portion of each separated snow grain sample was subjected to water content measurements using an Akitaya Calorimeter. The centrifuge essentially includes two cylinder-shaped polythene boxes with 9·5 cm in height and 9 cm in diameter of the cross section. A cup-shaped mesh was fitted onto the inner cover of each box. Snow samples were 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 the isotopic ratio of the non-separated wet snow with that of the separated snow from the same well-mixed sample. The isotopic ratio of the separated snow was obtained using the water content data of the non-separated wet snow and the isotopic ratios of the separated snow grains and water. No melting effect was detected in these tests. (4) Continuously collecting the bottom discharge using a 90×90 cm^2 lysimeter. (5) Continuously collecting precipitation. (6) Measuring snow water content at different heights with a dielectric moisture meter (Denoth moisture meter) made by Innsbruck University, Austria. (7) Taking grain photos of each sample using a camera with a magnifying lens. The grain size of each sample was measured manually using the photos. (8) Collecting meteorological data including radiation, air temperature, humidity, and wind velocity using an automatic station.

The work in China was carried out at 7-1 Glacier in the Qilian Mountains, at the north-east rim of Qinghai-Tibetan Plateau between June and July 2002. The pit site was 4860 m a.s.l., about 200 m higher than the multiple-year equilibrium line altitude (ELA) of the glacier. The thickness of firn was 83 cm on 16 June 2002 and it decreased to 20 cm on 17 July 2002 because of melting. The tasks were similar to the above-mentioned work in Japan, but the liquid–solid separation was not performed and no lysimeter was available. Also, the interval between each successive snow pit was longer (6–7 days).

All the samples were analysed for their oxygen-18 and deuterium ratios (with an accuracy of ±0·1‰ for δ^{18}O and ±1·0‰ for δD) at the Hydrospheric Atmospheric Research Centre, Nagoya University, Japan.

ISOTOPIC FRACTIONATION AND SLOPE OF ISOTOPIC COMPOSITION LINE

Isotopic results for the snowpack

Figure 1 presents 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 the data obtained on other days, and indicates the rapid isotopic fractionation between percolating meltwater and snow grains (Zhou *et al.*, 2001). Figure 2 shows the isotopic composition of two phases for 9 days including the 4 days from Figure 1. It can be seen, from Figure 2, that all slopes of the isotopic composition line for snow grains are larger than for interstitial water, with the former being about 6·4–6·9 and the latter, 4·3–5·2.

Although the slope of the solid phase shows a slight decreasing trend from 6·9 on 2 April to 6·5 on 14

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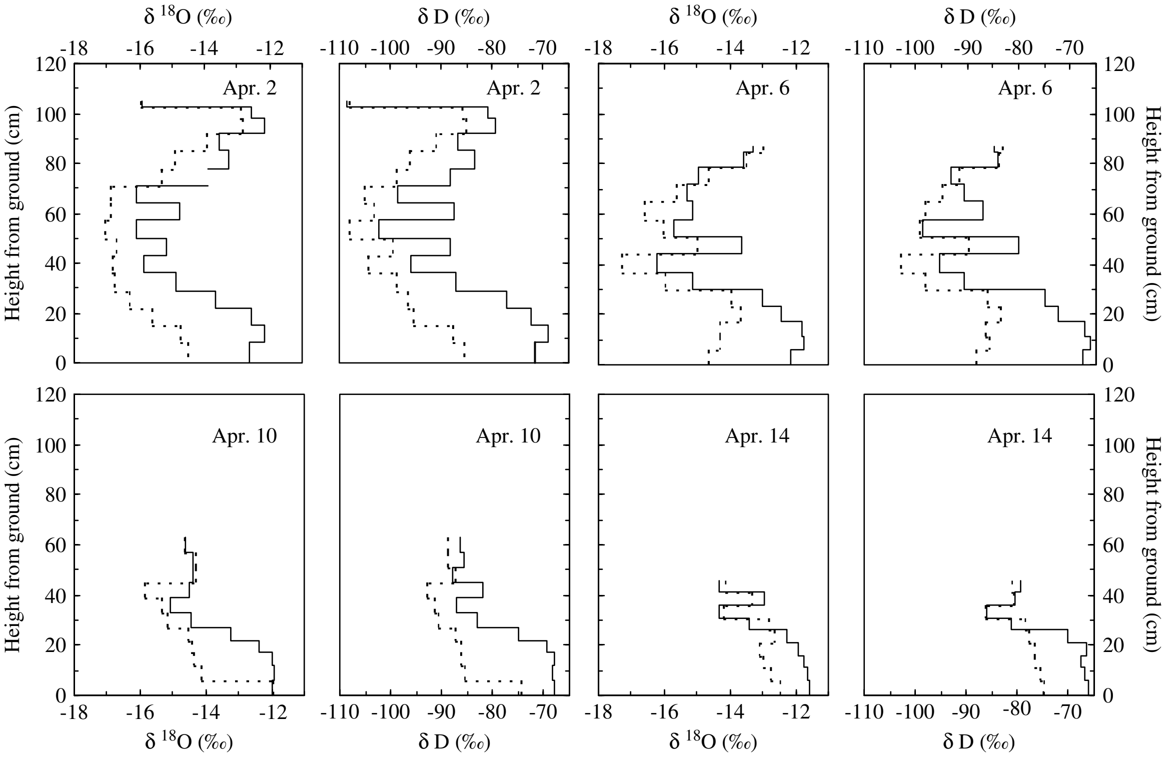

Figure 1. Isotopic evolution of the snowpack, showing δ^{18}O and δD profiles for both solid (solid line) and liquid (broken line) phases

April (Figure 2), these changes are small. Thus, t-tests were carried out and show that there are no distinct differences between the regression lines for the solid at the significance level of 0·05. 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–δ^{18}O line for the solid phase. The slope variations for the liquid phase in the period (4·3–5·2) are a little larger than for the solid phase. Thus, t-tests show clear differences between some regression lines for the liquid at the significance level of 0·05. As a whole, the differences are indistinct in the periods of 2 to 10 April and 11 to 14 April, but distinct between these two periods. This indicates an overall slight decrease for the slope of the liquid phase in the whole period.

Evaporation and isotopic composition

Two major processes may modify the isotope distribution in the melting snowpack and control the δD–δ^{18}O slopes of percolating meltwater. One is the evaporation or sublimation at the snow surface; another is the melt–freeze mass exchange between the solid and liquid phases. The negligible change of the slope for the solid phase indicates that these two major processes have little impact on it in the period studied. Nevertheless, the slopes for interstitial water, shown in Figure 2, are well within the typical range of the evaporation line, which is generally close to five (Gonfiantini, 1986). Further analyses, however, show that these slope values cannot be a result of the evaporation effect. Table I presents the isotopic data for each surface sample of the 9 days shown in Figure 2. It can be seen that most of the isotopic ratios for liquid phase are very close to the corresponding isotopic ratios for the solid phase, and the differences between them are within the accuracy of the measurements. Yet, several pairs have larger differences, for example, the ones for 4 April. However, when looking at the deuterium excess, which is defined as $d = \delta\text{D}-8\delta^{18}\text{O}$ and used as an index for non-equilibrium conditions (Dansgaard, 1964), it is found that all the differences of the deuterium excess ($d_s - d_l$) between the two phases for a single day, are well within the precision of the calculations

Table I. Comparison of isotopic data between solid and liquid phases of the surface samples

		2 April	4 April	6 April	8 April	9 April	10 April	11 April	12 April	14 April
δ^{18}O(‰)	Solid	−15·89	−12·16	−13·27	−14·20	−14·20	−14·63	−14·57	−14·94	−14·31
	Liquid	−15·98	−11·36	−13·03	−13·94	−13·81	−14·69	−13·85	−14·54	−14·15
δD(‰)	Solid	−108·49	−79·80	−84·86	−89·20	−87·02	−86·50	−85·52	−88·63	−79·51
	Liquid	−108·22	−74·00	−83·41	−87·50	−86·72	−89·10	−83·02	−86·87	−81·05
$d_s - d_l$(‰)[a]		−0·99	0·59	0·47	0·37	2·83	2·16	3·27	1·49	2·78

[a] The values of d_s and d_l are for deuterium excess ($d = \delta\text{D}-8\delta^{18}\text{O}$) for solid and liquid phases, respectively.

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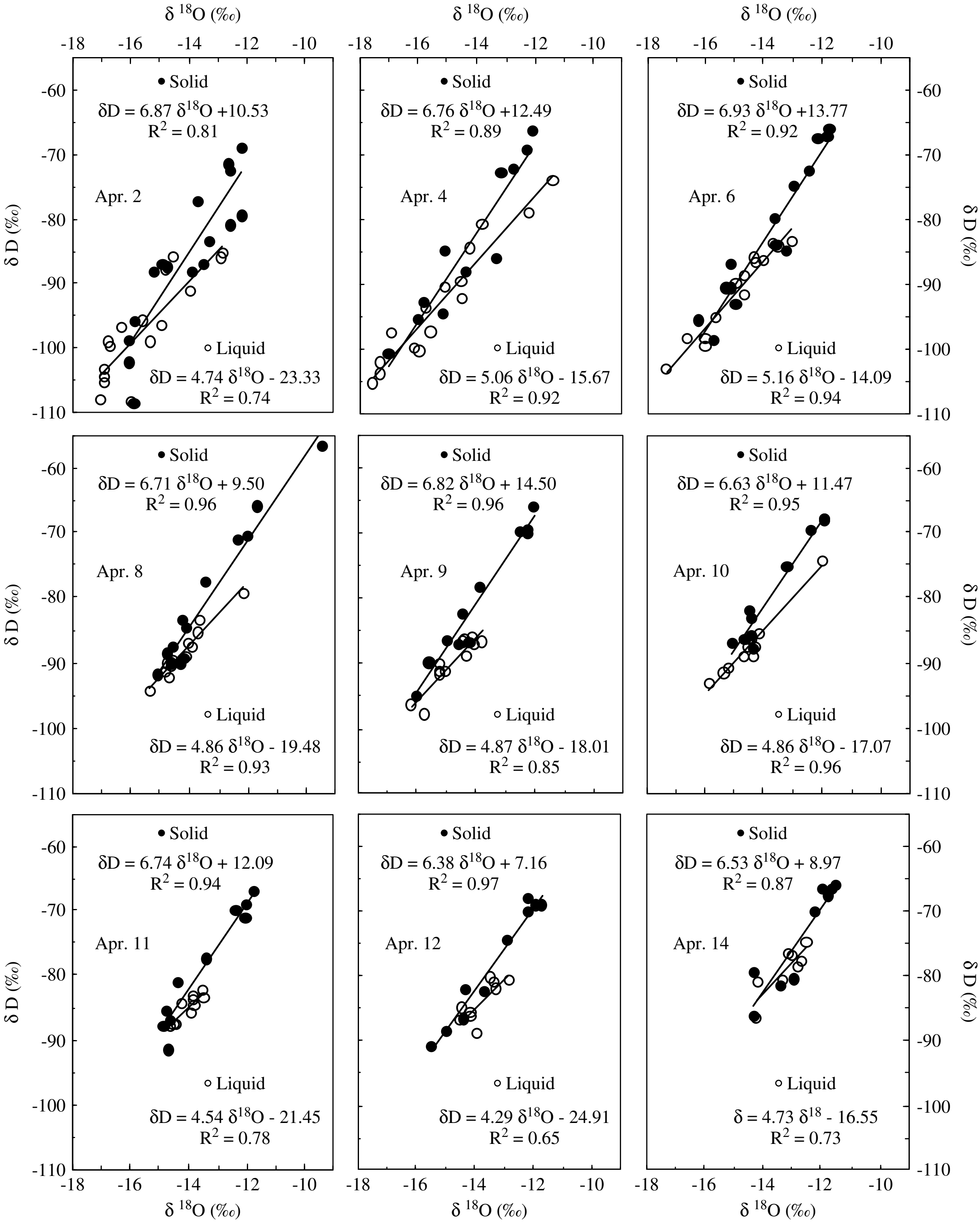

Figure 2. δD–δ^{18}O diagrams for both solid and liquid portions of the snowpack in the observational days. Regression lines and equations are shown

(d_s–d_l = ±3·6‰). This indicates that the evaporation or sublimation also has little impact on the δD–δ^{18}O slopes for infiltrating meltwater. Even if the impact were not negligible, its direct effect would be limited to the surface because internal fractionation would prevent the preservation of the evaporation line. Therefore, it is the isotopic fractionation that determines the slope of the liquid phase. This conclusion is similar to that reached by Taylor *et al.* (2001) and modelled by Feng *et al.* (2002).

Evaporation effect on the isotopic composition of water is well understood (Craig *et al.*, 1963; Dansgaard, 1964). The influence of sublimation on the isotopic composition of snow is also documented (Sommerfield *et al.*, 1991; Stichler *et al.*, 2001), but restricted to a snow depth of 7 cm only (Stichler *et al.*, 2001). The intensity of these effects is dependent on variable conditions such as air temperature, relative humidity and wind speed. The sublimation is the strongest during daytime

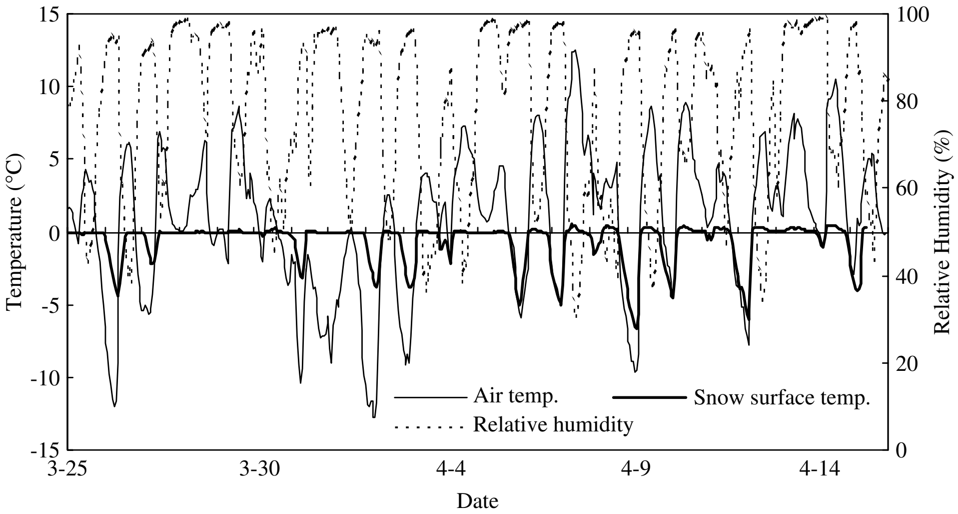

Figure 3. Diurnal variations of air temperature, snow temperature at 0 cm depth and relative humidity of the snowpack during the observational period

due to the highest moisture deficit of the ambient air accompanied by high snow surface temperature (Stichler *et al.*, 2001). For the snowpack in Japan, the records of snow temperature and snow water content indicate that the whole snowpack did not become isothermal (ice grains and water co-exist) until 20 March. The period of 2 to 14 April belonged to the middle melting season. Figure 3 shows the air temperature, relative humidity and snow surface (0 cm deep) temperature variations from 25 March to 15 April. It is seen that most of the daily largest temperatures are higher than 5 °C. The relative humidity also shows diurnal variations with the lower values appearing in the daytime. These conditions favour evaporation loss of water. Evaporation loss, from 25 March to 15 April, was calculated to be 2·1 mm (Zhou *et al.*, 2000) using the meteorological data and empirical formulas (Ishikawa, 1994). This value compares with those of Baldwin and Smith (1989), who obtained a total evaporation amount of 8·6 mm between January and March of 1971 and 3·3 mm in April 1971 from another snowpack. Evaporation loss was therefore far smaller than the total snowmelt of 393 mm obtained by the lysimeter in the same period. Hence the evaporation rates were considerably smaller than the melting rates at the snow surface, which can be seen from the discharge rate variations shown in Figure 4 [bottom melting of the snowpack totalled 3·5 mm in the period (Zhou *et al.*, 2000) and thus was negligible]. This explains why the evaporation or sublimation has little impact on the slopes for solid and liquid phases.

Isotopic fractionation effect

Within the melting snowpack, significant melting–freezing mass exchange occurs. According to the daily measurements of snow grain size (Zhou *et al.*, 2003; Hashimoto *et al.*, 2002), the mean grain volume of a snow layer increased by 1·2–5·3 times from 27 March to 8 April. Calculations show that the exchange of mass, between the solid and liquid phases, is between $1{\cdot}4 \times 10^{-2}$ and $5{\cdot}07 \times 10^{-2}$ g cm^{-3} per day (Hashimoto *et al.*, 2002). If there is no isotopic fractionation in the refreezing process of pore water, then the isotopic values should remain on a line with the same slope irrespective of its phase because melting occurs without fractionation (Jouzel and Souchez, 1982). Hence the large discrepancies between slopes of solid and liquid phases, shown in Figure 2, clearly demonstrate the isotopic fractionation occurring in the refreezing process. The physical processes associated with the fractionation, however, are rather complicated and different for solid and liquid phases. The isotopic ratio (^{18}O/^{16}O or D/H) of ice (R_{ice}) is only controlled by its isotopic exchange with liquid water. In contrast, the isotopic ratio of the liquid phase (R_{liq}) is controlled by advection, dispersion, and ice–water isotopic exchange. The standard governing equation of a one-dimensional model for the solid phase (Feng *et al.*, 2002) is:

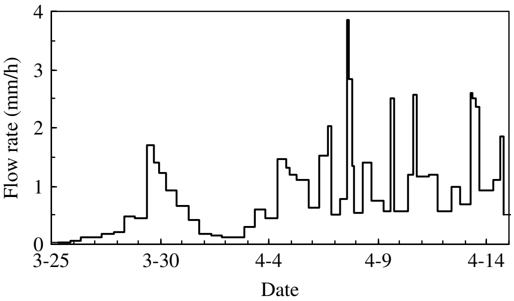

Figure 4. Diurnal discharge variations of the snowpack

$$\frac{\partial R_{\mathrm{ice}}}{\partial t} = k_r(1-\gamma)(\alpha R_{\mathrm{liq}} - R_{\mathrm{ice}}) \qquad (1)$$

and assuming the snowpack is homogeneous and melts at a constant rate, the equation for the liquid phase is:

$$\frac{\partial R_{\mathrm{liq}}}{\partial t} = -u\frac{\partial R_{\mathrm{liq}}}{\partial z} + \frac{\partial}{\partial z}\left[D\frac{\partial R_{\mathrm{liq}}}{\partial z}\right] + k_{\mathrm{r}}\gamma(R_{\mathrm{ice}} - \alpha R_{\mathrm{liq}}) \qquad (2)$$

where, t is time, k_r is the ice–water isotope exchange rate constant, γ is the ratio of ice involved in isotopic exchange to the total mass of pore water and the ice involved, α is the fractionation factor for oxygen/hydrogen isotope exchange between ice and water, u is the percolation velocity, z is depth below the snow surface, and D is the dispersion coefficient. The dispersion term in Equation (2) is demonstrated to be not significant, i.e. $D = 0$ (Feng *et al.*, 2002; Taylor *et al.*, 2002b). Comparing the two equations, it is clear that, unlike the solid phase, the isotopic composition change of the liquid is related not only to the parameters (k_r, γ and D) but also to the water flow rate (u), which shows large daily variations (Figure 4). This may explain why there are some distinct changes between the regression lines for the liquid phase, but not for the solid in the observational period (Figure 2), although the parameters are considered to be also associated with snow properties including the water flow rate (Feng *et al.*, 2001, 2002; Taylor *et al.*, 2001, 2002b). The fractionation factor (α) also affects the slopes of the regression lines, although the differences of its values between equilibrium (Lehmann and Siegenthaler, 1991) and non-equilibrium conditions (Souchez and Jouzel, 1984) are small, and the effective isotopic fractionation observed is often close to experimentally determined values (Cooper, 1998). However, how the parameters, the water flow rate and the fractionation factor control the δD–δ^{18}O lines of the two phases, especially the line of the liquid phase, needs complete numerical calculations, which is beyond the scope of this paper. Moreover, Feng *et al.*'s (2002) model is based on the assumptions of a homogeneous snowpack and a constant melt rate. A natural snowpack like the one in Japan, however, is heterogeneous that the liquid water in snow is viewed to be in different pools or flow paths, which is termed the preferential water flow (Harrington and Bales, 1998a,b; Feng *et al.*, 2001). The melt rate is also changing daily and seasonally (Figure 4). The model thus needs to be further developed and parameterized to capture the more complicated isotopic processes involved in the mass exchange within natural melting snowpack.

REFREEZING EFFECT ON THE SLOPE OF ISOTOPIC COMPOSITION LINE

Mechanism of the refreezing effect

A snowpack experiences diurnal melt–freeze episodes (melting during daytime and refreezing at night) during the melting season. Since the isotopic compositions and the δD–δ^{18}O line slopes of the two phases are different (Figures 1 and 2), the freezing process would change the slope of the solid phase if the whole snowpack is refrozen. This process can be explained by Figure 5. In Figure 5, the two lines, Ls and Ll, as those shown in Figure 2, denote the isotope data of a day for solid and liquid phases respectively. The slopes for Ls and Ll are S_s and S_l, respectively. The values A and A' are two data points, respectively, for the solid and liquid portions of a snow sample from the depth profile of a melting snowpack. So are B and B'. The values R^o and R^d are oxygen-18 and deuterium ratios, respectively. The isotopic ratios at the four points ($R^o{}_{1-4}$ and $R^d{}_{1-4}$) are shown in Figure 5. Suppose the whole snowpack is refrozen at the moment when its water content is r by weight. The results of A and A' then join to point A'', and B and B' join to B''. Thus, A'' ($R^o{}_5$, $R^d{}_5$) and B'' ($R^o{}_6$, $R^d{}_6$ are then on the line for the refrozen snowpack, Lr. Thus the slope of Lr, S_r is:

$$S_r = \frac{R^d{}_5 - R^d{}_6}{R^o{}_5 - R^o{}_6} = \frac{S_s(1-r)(R^o{}_1 - R^o{}_2) + S_l r(R^o{}_3 - R^o{}_4)}{(1-r)(R^o{}_1 - R^o{}_2) + r(R^o{}_3 - R^o{}_4)} \tag{3}$$

Since $S_s > S_l$, $R^o{}_1 - R^o{}_2 > 0$ and $R^o{}_3 - R^o{}_4 > 0$, then $S_s > S_r > S_l$. This clearly demonstrates that the refreezing process inevitably causes the slope of the solid phase to decrease. The new slope, however, should be just slightly lower than the original slope of the solid because the water content is limited. The largest averaged water content for the snowpack (Figure 6), which was obtained during the whole period, was 14·5% by weight at about 14:00 on 7 April when the discharge rate was the largest (Figure 4). Figure 6 also shows the density and water content profiles for the snowpack in Japan on 8 April. The water content was measured in the morning when the discharge rate was during its lowest period of the day. The averaged water content of the profile was 8·3% by weight, corresponding to a water saturation of 0·08, which was close to the minimum water saturation of 0·07 (Colbeck, 1974). Suppose the whole snowpack is refrozen, using the data shown in Figures 2 and 6 for 8 April, the new slope for the solid is then calculated [by regression, not Equation (3)] to be 6·66, 0·05 lower than the pre-refreezing value of 6·71. However, if the same observed isotopic and density data of 8 April is used, but the largest water content value of 14·5% is uniformly adopted, then the calculated new slope is 6·58, 0·13 lower than the old value. Similarly, using the observed density data and the water content values which are also

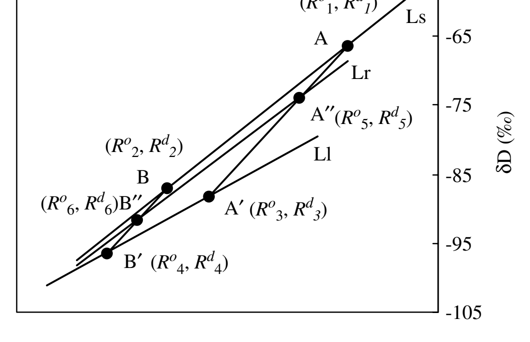

Figure 5. Schematic figure showing the mechanism of the refreezing effect on the decreasing slope of the δD–δ^{18}O line for the melting snowpack. See text for details

approaching the minimums, and supposing the snowpack is refrozen, the calculated new slopes of the solid are 6·70 and 6·35 respectively for 11 and 12 April, a little lower than the old slopes (6·74 and 6·38). These differences between the old and new slopes are a little smaller than the actual ones because the separated samples of ice grains, of which the old slopes of the solid are derived from the isotopic data, were measured to have a water content of 2–4% corresponding approximately to an average saturation of 0·023. Therefore, as the diurnal melt–freeze process cycles during the melting season, the slope of the solid phase would become increasingly lower.

Refreezing effect on the snowpack and glacier firn

The refreezing effect, corresponding to the daily melt–freeze extent and the environmental conditions (e.g. bottom conditions of snow), is different during different periods and for different snowpacks. For the snowpack in Japan during the observational period of 2 to 14 April, the daily freezing depths were recorded to be no deeper than 20 cm, and no freezing occurred at all during some nights, which can be seen from the snow surface (0 cm depth) temperature variations (Figure 3). Hence, the refreezing effect is not immediately obvious. As indicated earlier, the decreasing of the slope for the solid phase is indistinct in this period.

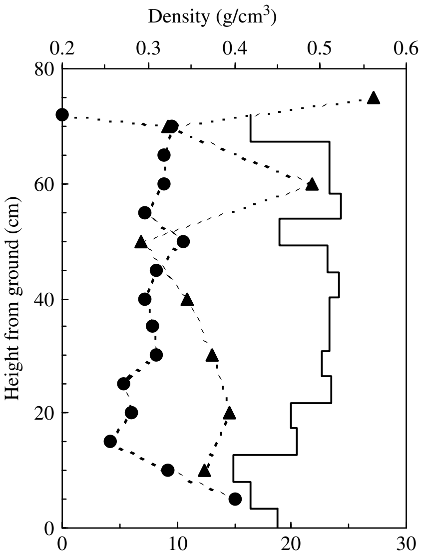

Figure 6. Depth profile of the largest average water content of the snowpack (triangles) during the whole observational period. Also shown are the profiles of water content (dots) and density (solid line) observed on 8 April

Differing from the snowpack, the slope decrease of the δD–$\delta^{18}O$ line for firn of the glacier in China is clear, which is shown by Figure 7. It can be seen that, with the exception of 5 July, as the melt proceeds the

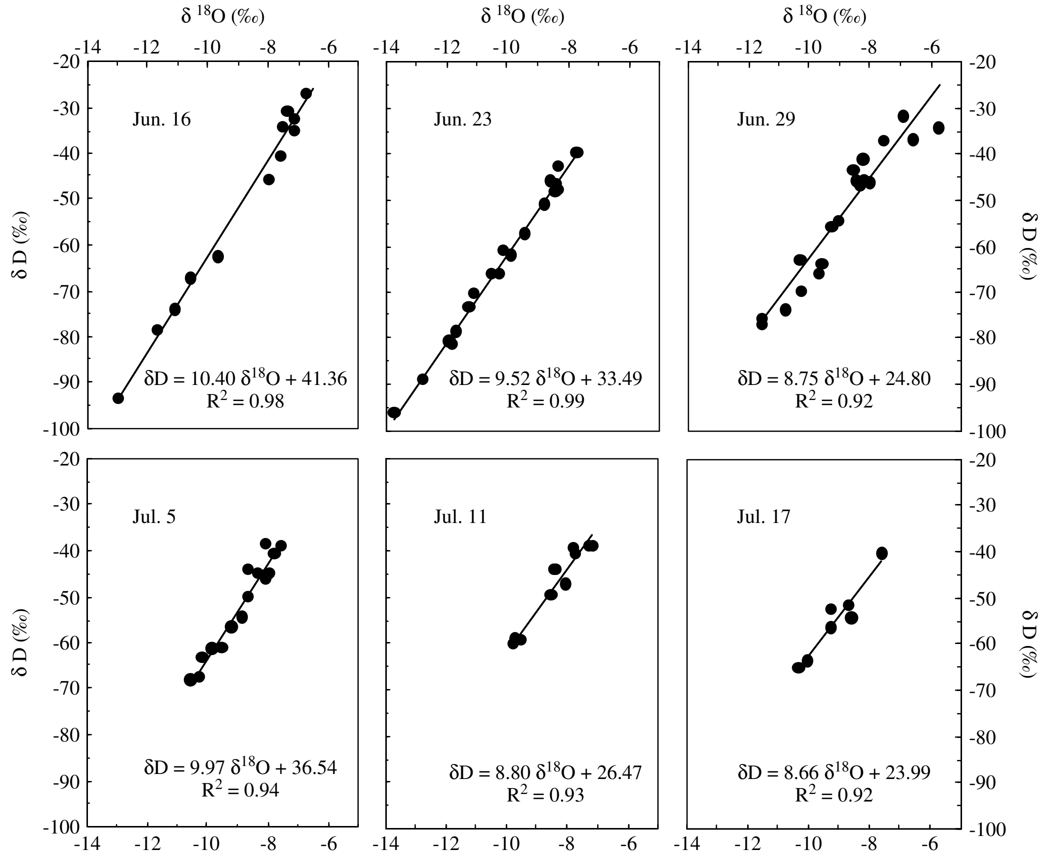

Figure 7. δD–$\delta^{18}O$ diagrams for the firn of the glacier, showing the slope changes

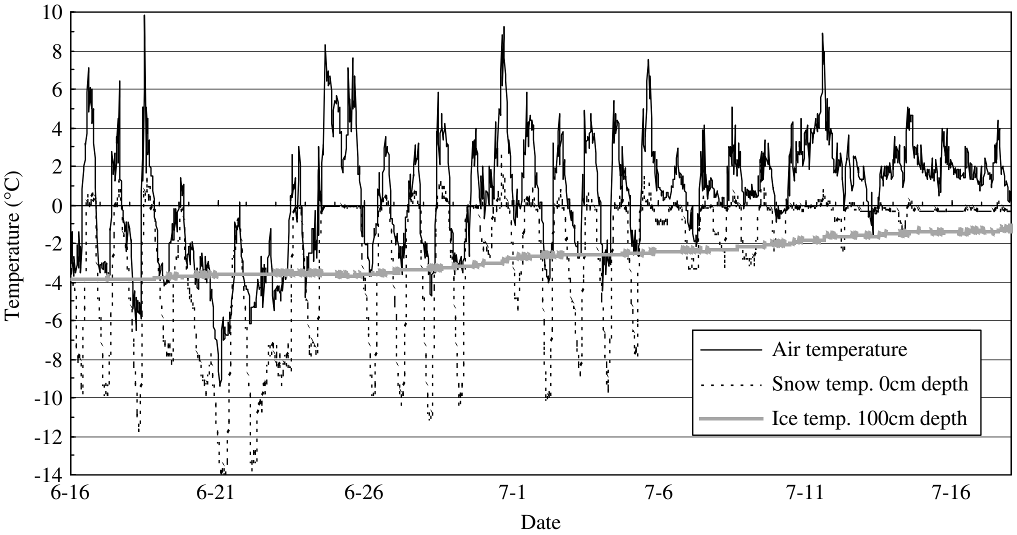

Figure 8. Diurnal variations of air temperature, snow and ice temperature at two depths from the firn surface of the glacier. The depths were measured on 15 June when the sensors were buried

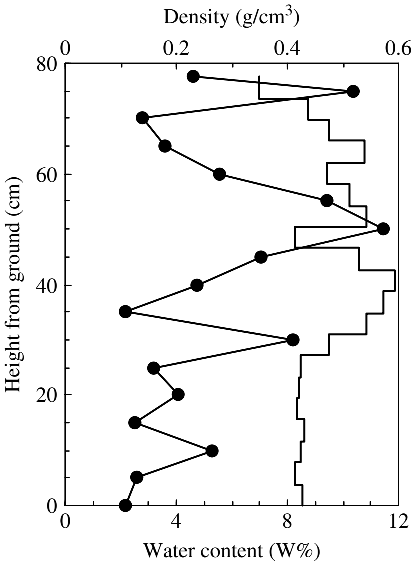

Figure 9. Depth profiles for water content (dots) and density (solid line) of the glacier firn observed on 29 June

slope decreases. Nevertheless, the slope decrease rate seems to be different during different periods. Early in the melting season, from 16 to 29 June, the slope decrease rate was approximately 0·13 per day on average. Midway through the melting season, from 11 to 17 July, there was no clear slope decrease, which was confirmed by the *t*-test between the two regression lines at the significance level of 0·05. The inconsistency of 5 July may be due to the fact that there was a well-developed impermeable ice layer in the middle of the pit wall that day. The ice layer preserved the isotopic concentrations beneath it. Regressions give slopes of 10·2 and 9·2 for the snow samples beneath and above the ice layer, respectively. The differences of slope decrease rate should be due to the different meteorological conditions and vertical snow temperature gradients in different periods. Figure 8 shows the air temperature, firn surface temperature (0 cm depth) and ice temperature variations. The ice temperature sensor was placed at the depth of 100 cm from the firn surface on 15 June when the firn thickness was 85 cm. It is shown that the air temperature varied much more abruptly and largely before 5 July than after 5 July, and that the firn surface temperature was much lower than 0 °C during most nights before 5 July, but at about 0 °C after 5 July. The ice temperature increased during the whole period. Based on these data and comparing them with those shown in Figure 3 (corresponding to 0–20 cm refreezing depths), it is determined that all the firn layer or a large portion of it was refrozen during most nights before 5 July, but not after 5 July when freezing occurred only at its bottom and surface. Figure 9 shows the density and water content profiles of the firn on 29 June (at 14 : 30). Comparing Figure 9 with Figure 6, it is clear that, while the bulk densities of the two profiles are essentially the same, the averaged water content of the firn profile is 3% lower than that of the snowpack profile. Hence, if the whole firn layer is refrozen, the slope decrease of the solid phase (S_s—S_r) would be a little lower than that for the snowpack on 8 April (0·05), assuming the same ice–water isotopic relationships as those shown in Figures 1 and 2 for the snowpack (i.e. $\Delta S = S_s$—S_l is identical, and isotopic concentrations of pore water are lower than those of corresponding snow grains). However, the observed average slope decrease rate (0·13 per day) is much higher than the value of 0·05, and matches the value for the snowpack refrozen at the time of the largest water content. Since the total melt amount of the firn is estimated to be about 280 mm from 16 June to 17 July, the average melt rate of the firn is lower than that of the snowpack (393 mm in 21 days). It is unlikely that the average water content for the firn was much larger than for the snowpack. In fact, the averaged water content of the firn on 29 June (Figure 9) was the largest obtained in the period of the high decrease rate of the slope (16–29 June). Therefore, the high decrease rate of the slope indicates that there was extra water refrozen in the firn. This is demonstrated by the fact there were five ice layers in the profile of 23 June, but only two in that of 16 June. The formation of ice layer is a process of refreezing. When the daily surface melting begins and meltwater percolates downward, because of the abrupt and significant increase of air temperature and the larger snow temperature gradient, the temperature below the firn surface is still under the melting point and thus some percolating water is refrozen. The larger refrozen amount in the firn can be seen from the density changes. From 16 June to 5 July, the averaged density of the firn changed from 0·41 to 0·48 g cm^{-3}, but that of the snowpack in Japan varied from 0·46 to 0·48 g cm^{-3}, showing no clear increasing trend (Zhou *et al.*, 2003). For the period between 5 and 17 July, the situation was similar to that of the snowpack in Japan, and the main portion of the firn layer was not refrozen, which is estimated from Figure 8. Hence the refrozen effect cannot be detected clearly.

Refreezing effect on deuterium excess

According to the definition of the deuterium excess ($d = \delta D - 8\delta^{18}O$), slope changes would inevitably result in changes of the deuterium excess. This can be explained by Figure 5. Suppose d_1 and d_2 are the deuterium excesses for the data points A and A'', respectively, i.e. the solid portion before and after freezing, then the deuterium excess change is:

$$d_2 - d_1 = (1 - r)[8(R^{o}{}_1 - R^{o}{}_3) - S_{AA'}(R^{o}{}_1 - R^{o}{}_3)] \tag{4}$$

where $S_{AA'}$ is the slope of the line AA'. Generally, $R^{o}{}_1$—$R^{o}{}_3 > 0$ (Figure 1), thus d_2—$d_1 < 0$ when $S_{AA'} > 8$, and vice versa. This indicates that the refreezing process may cause a decrease or an increase of deuterium excess depending on the difference of the isotopic compositions between the two phases before freezing. Figure 10 shows the temporal deuterium excess changes for two bottom snow layers, one (20 cm thick) from the firn, another (46 cm thick) from the snowpack (the solid phase). Although the changes are in a similar range of about five, the snowpack layer exhibits larger variability, while the firn layer shows a more steady decrease in deuterium excess.

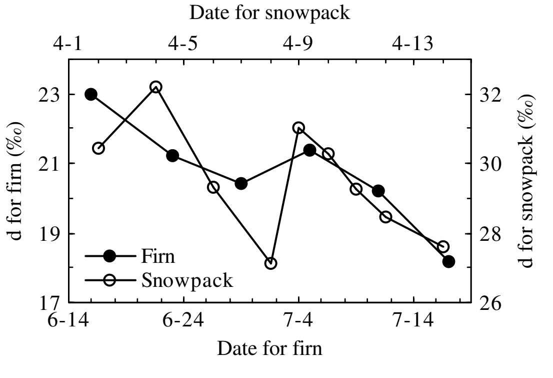

Figure 10. Temperal deuterium excess (d) changes of two bottom snow layers. One (20 cm thick) from the firn, and another (46 cm thick) from the seasonal snowpack

CONCLUSION

The slope of the δD–$\delta^{18}O$ line for the liquid phase of a melting snowpack is found to be lower than for the solid phase. Melting of the snowpack has no clear impact on the δD–$\delta^{18}O$ line for the solid phase, but the slope of the δD–$\delta^{18}O$ line for the liquid shows an overall slight decrease in the melting period. The discrepancy between the slopes of the two phases is due to the isotopic fractionation occurring in the melt–freeze mass exchange within the melting snowpack, and will cause the slope of the solid phase to decrease with increasing numbers of the diurnal melt–freeze cycles throughout the melting season. The value of slope decrease reaches 1·7 for the firn of the glacier in the observational period. However, the decrease rates and extents of the slope depend on the variations in meteorological conditions and snow properties. While the decrease rate is large for the glacier firn early in the melting season (0·13 per day on average), the slope decrease for seasonal snow and for the firn in the middle melting season is indistinct. Slope changes also result in changes of deuterium excess. Although the deuterium excess changes essentially depend on the difference between the isotopic compositions of the two phases before freezing, and thus may be different in snowpacks, the observations show a decreasing trend in deuterium excess with decreasing slopes. The decrease value of deuterium excess is about 5‰ for a firn layer of the glacier in the whole observational period. Given the common use of the isotopic composition line and the deuterium excess as indicators of water vapour source, humidity of the source, and kinetic conditions in ice core research and isotope hydrology, the findings may be important in paleoclimatic reconstructions and modern environmental studies. However, further work must be done to quantify the changes in slope and deuterium excess as a result of variable meteorological and climatic conditions.

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