

## Isotopic mass fractionation of snow due to depth hoar formation

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**Abstract:** To clarify the isotopic changes ( $\delta D$  and  $\delta^{18}O$ ) of snow due to depth hoar formation, large temperature gradients were imposed on snow samples using a closed and insulated box for several days.  $\delta D$  and  $\delta^{18}O$  increased in the high temperature region where sublimation enriched heavy  $H_2O$ , and decreased in the low temperature region where light  $H_2O$  was concentrated. Isotope diagrams of the data showed slopes of 2.4-4.9, which indicated that isotopic fractionation on sublimation depends on the kinetic isotope effect. It was also suggested that the transfer coefficient of water vapor in snow increases slightly due to convection; and the changes of isotopic profiles depend primary on the snow density as it affects permeability to vapor diffusion.

### 1. Introduction

It is well known that ice cores contain various paleoenvironmental signals of high resolution. Since the isotopic composition of oxygen and hydrogen in snow deposited in polar regions depends primary on the condensation temperature of water vapor in the atmosphere, numerous studies have been done on converting the measured isotope records into past temperature changes. In addition, the evaporation process of water vapor in moisture sources regions (Johnsen *et al.*, 1989) and the transportation process poleward from an ocean source (Kato and Higuchi, 1979) also affect isotopic composition in snow. Recently, these isotopic exchange processes have been considered in general circulation models (GCMs) and promising results have been reported by researchers (*e.g.* Jouzel *et al.*, 1997; Armengaud *et al.*, 1998).

On the other hand, it has been an object of study for a long time that the profile of isotopic composition changes in deposited snow. Qualitatively, a "smoothing effect" of isotopic stratification exists in porous firn and obliterates seasonal variations after deposition (Dansgaard *et al.*, 1973), complicating the use of stable water isotopes as paleothermometers. Johnsen (1977) experimentally obtained a diffusion length of 0.07-0.08 m of ice from  $\delta^{18}O$  profiles in Greenland and Antarctica, and proposed a technique of 'deconvolution' of the isotope signal. Whillians and Grootes (1985) noted that the smoothing rate strongly depends on temperature and density of the firn.

Thus, to interpret the stable isotope signals in a snow and ice core, it is essential to inquire into the quantitative details of isotopic changes according to vapor transport in the deposited snow. A high temperature gradient is often found near the snow surface,

where the temperature field is highly fluctuating due to exposure to the ambient air temperature, producing faceted and depth hoar crystals beneath the snow surface (Akitaya and Shimizu, 1987; Colbeck, 1989; Fukuzawa and Akitaya, 1993; Birkeland, 1998). Since these hoar crystals are formed by vapor transport, the profile of isotopic composition in snow easily and rapidly changes due to sublimation. Satow and Watanabe (1985) imposed a thermal gradient on a snow sample which included an ice crust and discussed some patterns of profile changes in  $\delta^{18}\text{O}$ . Sommerfeld *et al.* (1991) also executed similar experiments and pointed out that the communication distance of water vapor is several crystal diameters. Friedman *et al.* (1991) investigated isotopic changes of deposited snow due to its metamorphism in Alaska for 9 years.

In this paper, we would like to report how the profiles of the isotopic composition of oxygen and hydrogen in snow changed quantitatively, under the condition of large temperature gradient.

## 2. Experimental methods

The device is a closed and insulated box 240 mm in length, 270 mm in width and 150 mm in height constructed from 50 mm thick Styrofoam (Fig. 1). The cold room and the heater unit controlled temperatures of both cooling and heating plates made of aluminum, respectively. The temperatures of the top and the bottom were monitored with thermocouples.

We suppose that the isotopic composition in the snow specimen was uniform since the snow, composed of rounded grains sampled at Nakayama Pass in Hokkaido, was sifted through a sieve (aperture: 1.7 mm), stirred thoroughly and then put in the box. The density of the snow specimen before imposing a temperature gradient was about  $3.8 \times 10^2 \text{ kg m}^{-3}$ .

In order to check the effects of gravity and temperature on the changes of isotopic profiles, four runs were executed as summarized in Table 1. The upper and lower temperatures fluctuated (root mean square:  $\pm 0.4^\circ\text{C}$ ) due to the temperature control system of the cold room. The snow specimens were subjected to a large temperature gradient for 11 days and changed to “hard depth hoar” (Akitaya, 1974). After these experiments, about 0.05 m of snow in a plane parallel to the inside wall was removed to

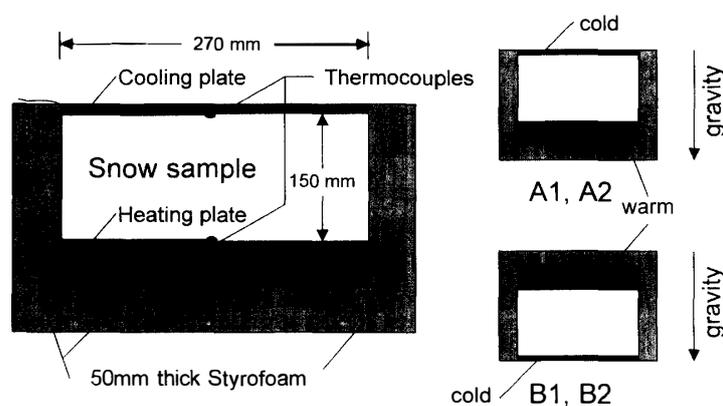


Fig. 1. Illustration of the apparatus (left) and its positions in each run No. (right).

Table 1. Summary of the temperature environment.

Run No.	Mean temperature		Mean temperature gradient (°C m <sup>-1</sup> )
	upper part (°C)	lower part (°C)	
A 1	-15.7	-2.9	85
B 1	-3.5	-17.3	92
A 2	-18.6	-12.6	40
B 2	-12.3	-19.2	46

eliminate border effects, and 15 samples for isotopic analysis ( $\delta\text{D}$  and  $\delta^{18}\text{O}$ ) were taken by cutting the snow specimens horizontally 0.01 m in thickness. The analyses of stable isotopes were carried out for the melted samples;  $\delta\text{D}$  was determined with a mass spectrometer (Finnigan MAT252) of the Department of Environmental Science and Technology, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, and  $\delta^{18}\text{O}$  was determined with a mass spectrometer (Finnigan MAT250) of the Laboratory of Cryosphere Variation, Institute for Hydrospheric-Atmospheric Sciences of Nagoya University. The analytical errors of  $\delta\text{D}$  and  $\delta^{18}\text{O}$  are  $\pm 0.2\text{‰}$  and  $\pm 0.1\text{‰}$ , respectively.

### 3. Results

Figure 2 shows a vertical thin section (about 0.5 mm in thickness) of the snow specimen (A1: 70–80 mm in depth) by the aniline method (Kinosita and Wakahama, 1960). Cup-shaped and striated depth hoar crystals were well developed downward, whereas the upper part of the crystals had a smooth face due to sublimation. This photograph indicates that water vapor in the specimen moved upward macroscopically.

The results of the isotopic analyses are shown in Fig. 3.  $\delta\text{D}$  and  $\delta^{18}\text{O}$  increased in the high temperature region, in contrast to a decrease in the low temperature region. Large changes were seen only in the top and the bottom layers. The isotopic profiles of  $1\text{--}14 \times 10^{-2}$  m in specimen height seemed to shift slightly from the initial value; they are due to the errors of the initial values, which were obtained from only one sample for each specimen before these experiments. Qualitatively, these tendencies can be understood as follows: the so-called “hand to hand” process of vapor transport (Yosida *et al.*, 1955) formed depth hoar crystals on one side of a snow particle and concentrated light  $\text{H}_2\text{O}$  there conversely, sublimation (evaporation) occurred on the other side which became enriched with heavy  $\text{H}_2\text{O}$ . As a result, the isotope profiles did not change except in the top and the bottom layers, where water vapor is only added or lost macroscopically.

Comparing A1 and A2, and B1 and B2, respectively, the isotopic changes of the former are larger than those of the latter. This is because the temperature gradients of the former are twice those of the latter as we have seen in Table 1. In addition, the changes in the high temperature region are larger than those at low temperature. For example, in A1,  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of the bottom layer increased 1.3‰ and 4.7‰, respectively, in contrast, those of the top layer decreased 0.5‰ and 0.7‰, respectively. Assuming that the temperature profiles were linear, we can safely say that the vapor density



Fig. 2. A thin section of a snow specimen (A1) composed of depth hoar crystals.

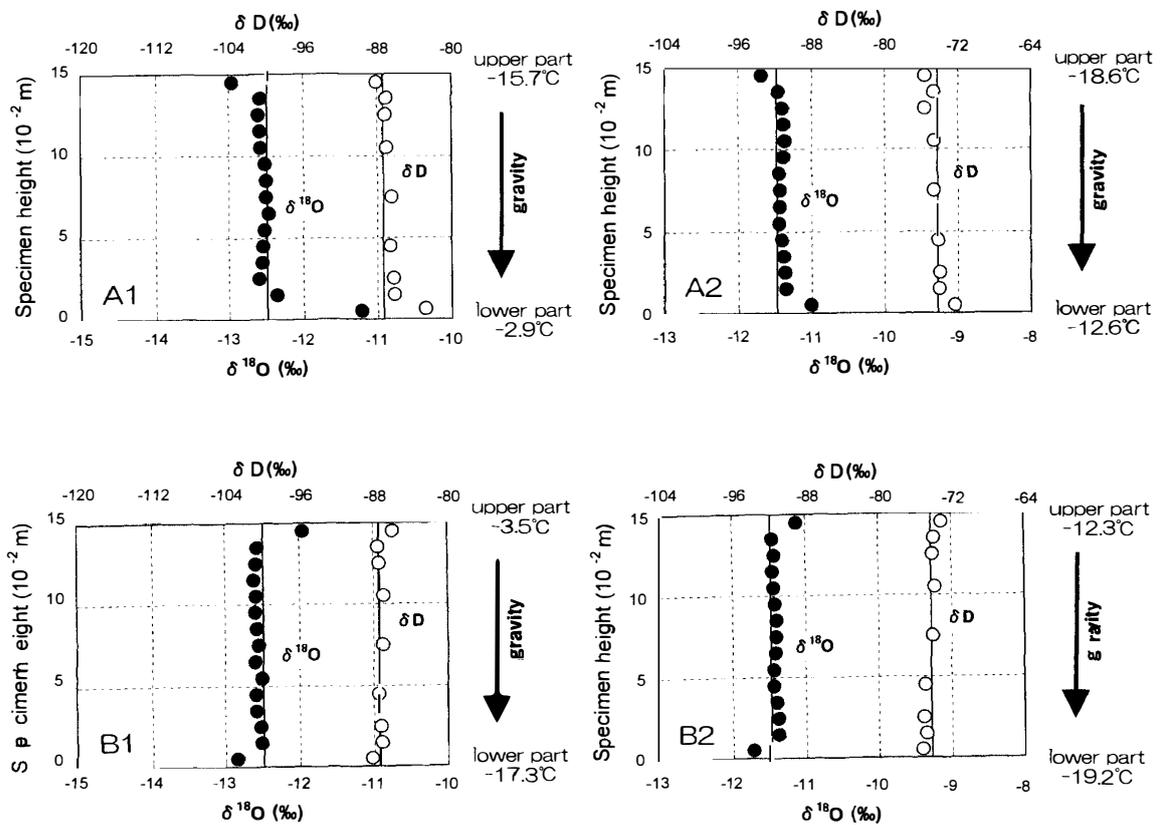


Fig. 3. Isotopic profiles of  $\delta D$  and  $\delta^{18}O$ . Solid lines show the initial conditions.

gradient in the high temperature region was larger than that at low temperature according to the saturated vapor pressure.

On the other hand, the changes of isotopic composition in A1 and A2 are larger than those of B1 and B2, respectively; the conditions of the temperature and temperature gradient are almost the same nevertheless. The most likely explanation is that the air in the pore space of snow is unstable and convection may occur in experiments A1 and A2, while the air is stable and the water vapor must diffuse by self diffusion in experiments B1 and B2. Hence, these results indicate that the transfer coefficient of water vapor in the snow structure pore space increases slightly due to convection.

Figure 4 shows the relation between  $\delta^{18}\text{O}$  and  $\delta\text{D}$ . A plot of  $\delta\text{D}$  versus  $\delta^{18}\text{O}$  has a slope of 3.1 as A1, 2.4 as B1, 4.9 as A2 and 3.1 as B2, in contrast to the slope of 8 for the meteoric water line. These slopes are also lower than the slope of about 10 to 13 to be expected if the mass-transport process takes place under an equilibrium Rayleigh distillation process (Sommerfeld *et al.*, 1991). The value of 3.1 in A1 agrees well with the value of 3.0 obtained by Sommerfeld *et al.* (1991), of which conditions of temperature and temperature gradient are almost the same. Compared with the results of A1 and A2, the slope of A1 is smaller than that of A2, while the slope of B1 is smaller than that of B2. This is mainly because the amount of vapor transfer in A1 and B1 was larger than that of A2 and B2, respectively. However, it remains unsettled why the slope of B1 is smaller than that of A1, and why the slope of B2 is smaller than that of A2.

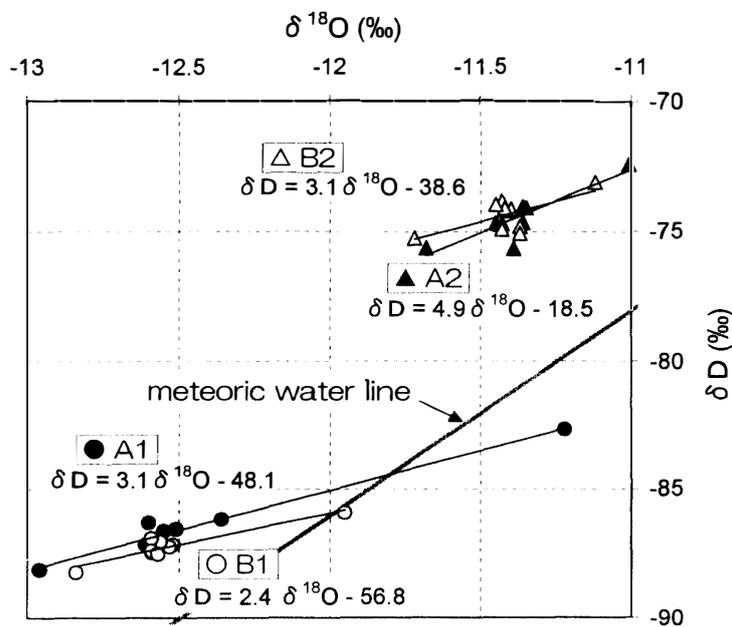


Fig. 4.  $\delta\text{D}$  plotted against  $\delta^{18}\text{O}$ . Thin lines show the regression lines of each run, and the thick line shows the meteoric water line ( $\delta\text{D} = 8\delta^{18}\text{O} + 10$ ).

#### 4. Discussion

Dansgaard (1964) introduced an effective fractionation factor which depends on the evaporation rate, and noted that the slope becomes small (about three) for fast

evaporation due to a kinetic effect. Sommerfeld *et al.* (1991) pointed out that the quasi-liquid layer on the ice surface would make the substrate appear more like a liquid than a solid to the water molecules. In our experiment, the slopes of the relation between  $\delta^{18}\text{O}$  and  $\delta\text{D}$  are much smaller than those of the meteoric water line in Fig. 4, just as in Dansgaard's report. Therefore, it is reasonable to conjecture that a kinetic effect plays an important role on the sublimation process from ice to vapor, as well as on the evaporation process from water to vapor.

As we have mentioned in the introduction, Johnsen (1977) reported that the diffusion length of the annual  $\delta^{18}\text{O}$  cycle is 0.07–0.08 m, from the results of ice core analyses, whether the annual  $\delta^{18}\text{O}$  cycle is obliterated or not. In contrast, Whillians and Grootes (1985) concluded from their numerical model and theory that the smoothing rate is strongly dependent on temperature and density of the firn. In order to discuss the mean diffusion length of water vapor in snow, we would like to compare with the result of Sommerfeld *et al.* (1991) and that of this study (A1), as shown in Table 2. Experimental periods are almost the same between them. The snow density and the temperature gradient of this study are both about 1.7 times larger than those of Sommerfeld *et al.* (1991), respectively, whereas the changes of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of this study are less than those of Sommerfeld's result. Hence, it is likely that the effect of snow density on permeability of water vapor is more effective in changing  $\delta^{18}\text{O}$  than the effect of vapor pressure gradient as a driving force of vapor transport.

Table 2. Comparison of this study and the results of Sommerfeld *et al.* (1991).

	Sommerfeld <i>et al.</i> (1991)	This study (A1)
Experimental period (day)	13	11
Snow density ( $\text{Mg m}^{-3}$ )	0.23	0.38
Temperature gradient ( $^{\circ}\text{C m}^{-1}$ )	$5 \times 10^1$	85
The change of $\delta^{18}\text{O}$ (‰) (at the part of high temperature)	3	1.3
The change of $\delta\text{D}$ (‰) (at the part of high temperature)	7	4.7

## 5. Conclusion

Snow samples were subjected to thermal gradient in a closed and insulated box.  $\delta\text{D}$  and  $\delta^{18}\text{O}$  increased in the high temperature region where sublimation enriched heavy  $\text{H}_2\text{O}$ , and decreased in the low temperature region where light  $\text{H}_2\text{O}$  was concentrated, as depth hoar crystals formed in the specimens. In contrast, these profiles did not change greatly except in the top and bottom layers, and it can be expressed as a “hand to hand” process of vapor transport. The transfer coefficient of water vapor in snow seemed to increase slightly due to convection. Finally, it was suggested that the changes of isotopic profiles depend primarily on the snow density as it affects the permeability of vapor diffusion.

The questions which we must consider next are as follows: how the stable isotopes distribute in a snow grain, and how the heavy  $\text{H}_2\text{O}$  exists on the ice surface where sublimation is predominant, including the effect of quasi-liquid layer on an ice surface.

In addition, two points need to be clarified quantitatively, how the sublimation rate depends on the slope of the relation between  $\delta D$  and  $\delta^{18}O$ , and how temperature and snow density depend on the mean diffusion length of water vapor.

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