Isotopic changes during the formation of depth hoar in experimental snowpacks

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Abstract—Depth hoar in snow was produced experimentally by imposing a thermal gradient on snow in two different types of experimental apparatus. One experiment was performed in an open-top container in a freezer, five in an apparatus with a closed top. In all six experiments, samples of the snow were analyzed for HDO/H₂O ratios; in two, H₂¹⁸O/H₂¹⁶O ratios were also determined. In all six experiments fractionation was similar. Snow strata that lost mass were depleted in the lighter isotopes, while strata that gained mass were enriched. Results indicate that the isotopic fractionation was the result of diffusion processes as well as change-of-state processes, that there is diffusive mixing of the water molecules on the surfaces of the ice crystals, and that there may be vapor communication over distances larger than one crystal diameter.

INTRODUCTION

DEPTH HOAR IS a type of snow with distinctive crystal shapes (AKITAYA, 1974). It forms in snow with densities less than about 0.3 g cm^{-3} at temperature gradients larger than 1°C cm^{-1}. The high rate of vapor transport forced by the temperature gradient causes the snow to recrystallize entirely in a few days. The snow crystals under these conditions exhibit the skeletal forms characteristic of high growth rates (HOBBS, 1974). These are modified into conical shapes by the fact that the crystals grow on the bottom and sublimate at the top in a process called "hand to hand" by YOSIDA *et al.* (1955).

The micro-structure of the snow can affect the process by affecting the local thermal gradients (SOMMERFELD, 1983; GUBLER, 1985). Such effects may be important in determining the rate of vapor transport of water vapor and of volatile material in snowpacks, and in determining the rate at which depth hoar forms.

During the discussion of the mechanisms of material transport from the bottom to the top of the snowpack, and ultimately to the freezer coils, we will be concerned with the effects of the differing transport mechanisms on the various isotopic forms of water, namely HDO, H₂¹⁶O, H₂¹⁸O. Experimentally, the isotopic ratios

$$\frac{\text{HDO}}{\text{H}_2\text{O}} \quad \text{and} \quad \frac{\text{H}_2^{18}\text{O}}{\text{H}_2^{16}\text{O}}$$

are determined mass spectrometrically and expressed in per mil in delta notation:

$$\delta\text{D or } \delta^{18}\text{O} = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \times 1000$$

where R = ratio of heavy isotopic species to light isotopic species. We will here consider changes in these two δ values, as compared with that in the original snow. In addition, we will also discuss the ratio of the changes in deuterium to the changes in oxygen-18. This latter ratio will be expressed as the "slope of the linear regression line connecting the points in a δD vs. δ¹⁸O plot."

The possibility of fractionation of the light (H₂¹⁶O) and heavy (HDO, H₂¹⁸O) molecules during the metamorphism of snow suggested that measurements of δD and δ¹⁸O of snow might provide information on the mechanism of depth-hoar formation. If a strict crystal-to-crystal movement of material occurred, there could be no change in the isotopic composition of the snow. After a period of time, the entire mass of the lower crystal would be deposited on the lower side of the next crystal above it. If the isotopic composition of the snow changed, an alternative theory of depth-hoar formation would be needed. The changes in these ratios compared to the original snow give information on the transport processes.

Because the vapor pressure of the lighter molecule H₂¹⁶O is higher than that of the heavier molecules H₂¹⁸O and HDO, the vapor will be enriched in the light molecules relative to the solid in equilibrium with it. This difference in vapor pressure results in the vapor being lower in δD by 122 per mil and in δ¹⁸O by 11.8 per mil at 0°C, and by 160 per mil and 13.4 per mil at −20°C (FRIEDMAN and O'NEIL, 1977). This process will result in a slope of 10 to 13 for a δD vs. δ¹⁸O plot of samples of the vapor, or from the solid condensed from it. During a Rayleigh distillation process it is assumed that, at any

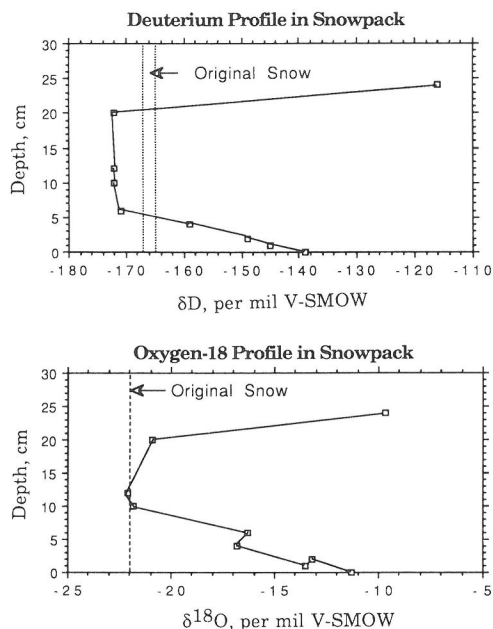FIG. 1. Isotopic profiles of δD (top) and $\delta^{18}O$ (bottom) for the open-box experiment.

instant of time, the vapor is in isotopic equilibrium with the condensed phase that is emitting the vapor.

We performed a simple experiment in which the vapor coming off snow was collected on a surface cooled by dry ice. Isotopic analysis showed that the vapor had 110 per mil less deuterium than the snow from which it sublimed, yielding a fractionation factor of 1.11. MOSER and STICHLER (1970) obtained a fractionation factor of 1.10 to 1.11 for a similar study. In both experiments the period of time that the sublimation occurred was short, and therefore the process studied was probably a transient-state study. A basic question is whether fractionation occurs in the steady state. If temperature gradient metamorphism is strictly "hand to hand," no change in composition would occur. After a period of time the entire mass of the lower crystal would be deposited on the lower side of the crystal above it. For this process to be effective in the steady state, the solid phase must be mixed. Because self-diffusion in ice is about 1/1000 as rapid as molecular diffusion in the vapor, the amount of isotopic separation due to vapor pressure differences between the isotopic molecules will be greatly reduced from the values of approximately 130 per mil for deuterium and 12 per mil for oxygen-18 that would be expected if the molecules in the solid mixed rapidly.

The existence of a quasi-liquid film on the surface of snow crystals at temperatures above −30°C has

been postulated and can help explain the existence of isotopic fractionation during the sublimation of snow. Even though this process results in only a small isotopic fractionation, the cascading of many such change-of-state events, as the vapor travels vertically through the snowpack, might result in relatively, large isotopic changes, with slopes of the δD vs. $\delta^{18}O$ plots having values greater than five.

A discussion of isotopic fractionation caused by diffusion is given in the companion paper (FRIEDMAN et al., this volume).

EXPERIMENTS

Both undisturbed and sieved snow were exposed to temperature gradients. At the initiation and at times during the course of each experiment, a vertical series of samples was taken and analyzed for δD by the method described by WOODCOCK and FRIEDMAN (1963) and for $\delta^{18}O$ by the technique of O'NEIL and EPSTEIN (1966). The deuterium results are precise to ±1 per mil, while the $\delta^{18}O$ analyses are precise to ±0.2 per mil.

Open box experiment

An open-top box 25 × 25 × 25 cm was constructed from 50 mm thick styrofoam. This was placed on a heat source maintained at −1.2°C in a freezer at −24°C and filled with snow. The temperatures at four different levels were monitored with thermistors. The lower 15 cm of snow had a gradient of 1.05°C cm⁻¹ while the upper 10 cm had a lower gradient of about 0.80°C cm⁻¹. The nonlinearity of the gradient was probably the result of air being able to mix into the upper layer of the open box. After the experiment proceeded for 31 days, the false front of the container was removed, the first 50 mm of snow in a plane parallel to the front was discarded to eliminate border effects, and samples were taken for isotopic analysis.

The average density of the snow increased from 0.14 to 0.19 g cm⁻³ during the 31-day duration of the study. There was a 276 g (about 10%) loss of total mass from the container to the freezer walls, which is equal to a layer of water 2 mm deep. Most of the lower 30–50 mm of the original snow was lost by sublimation into the upper part, and adhesion to the walls of the box prevented settling. The results of the isotopic analyses are shown in Fig. 1. Frost collected from the freezer walls was 10 per mil lower in δD than the original snow.

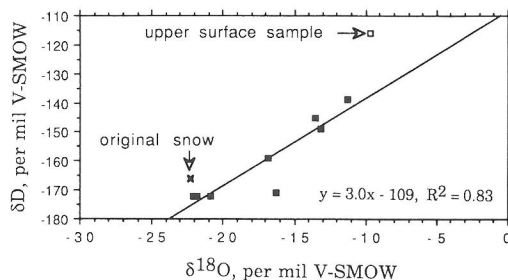A plot of δD vs $\delta^{18}O$ (Fig. 2) has a slope of three in

FIG. 2. Plot of δD vs. $\delta^{18}O$ for the open-box experiment.

contrast to the slope of about 10 to 13 to be expected if the mass-transport process took place under an equilibrium Rayleigh distillation process. This is in agreement with the results of SOMMERFELD *et al.* (1987).

Closed box experiments

An apparatus similar to that described in SOMMERFELD (1983) was constructed. This apparatus housed ten poly-ethylene bags of snow of dimensions $30 \times 30 \times 10$ cm. A special lid had ten aluminum blocks that fitted into the bags with a clearance of less than 3 mm. The lid was pro-vided with a circulating coolant to maintain its temperature at about $-15°C$. The bottom surface of the apparatus was a heated plate whose temperature was controlled between -1 and $-2°C$. The entire apparatus was insulated with 100 mm of styrofoam and was placed in a cold room maintained at $-10°C$. The lid was allowed to settle with the upper surface of the snow to limit sublimation losses from the samples and to maintain a more uniform thermal gradient. The thermal gradient was monitored by six ther-mocouples placed in a central bag. The boundary tem-peratures were controlled to $±0.1°C$. The resulting gra-dients were almost linear and constant with time (SOM-MERFELD, 1983).

January, 1987. Ten bags were placed in the apparatus on January 8, 1987. Nine samples of the original snow were analyzed to determine the variability of the original snow. They showed a range in δD of -176 to -194, and in $\delta^{18}O$ of -22 to -26. The variability in these samples was much larger than in the snow used in the open box experiment described above.

The experiment was conducted for 13 days at an average gradient of $0.5°C$ cm^{-1}. Samples for isotopic analysis were taken on January 11 and January 21. During this time the density increased from 0.220 to 0.242 g cm^{-3}. Quali-tatively, the lower portion of the snow was about 7 per mil higher in δD and about 3 per mil higher in $\delta^{18}O$ than the average at the end of the experiment.

The slope of the δD vs. $\delta^{18}O$ plot should not be affected by the original variability in either isotopic species. There is relatively little scatter in this plot in Fig. 3, and the slope decreased from 4.9 for the original snow to 4.2 and 3.7 for the two sample dates, in agreement with the results of the open box experiments and with SOMMERFELD *et al.* (1987). The low value of 4.9 for the initial snow samples is the result of metamorphism that occurred before the snow was collected for the experiments.

February, 1987. A second set of samples was collected on February 18, 1987. They were placed in the apparatus under a thermal gradient of $0.45°C$ cm^{-1} for 28 days. During this period the density of the samples increased from 0.279 to 0.308 g cm^{-3}. Samples for analysis of δD were removed on February 23, March 3, 10, and 17. Al-though the scatter in the data is large, the lower 5 cm show an increase in δD associated with mass loss, and the upper part shows a somewhat smaller decrease associated with mass gain.

March, 1987. A third experiment was initiated on March 23, 1987, and terminated 50 days later. The initial density was 0.200 g cm^{-3} which increased to 0.254 g cm^{-3} at the end of the experiment. The temperature gradient averaged $0.595°C$ cm^{-1} throughout the experiment.

There is somewhat less scatter in this set of samples than in the previous set, but the variation in isotopic com-position was still high. Here there is a clear increase in δD
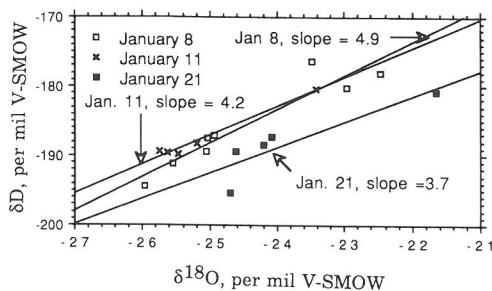

FIG. 3. Plot of δD vs. $\delta^{18}O$ for the closed-box experi-ments, January 1987.

in the lower 5 cm and a smaller decrease in the upper 15 cm.

February, 1988. An attempt was made to eliminate the natural variability of the snow by mixing a sample of snow and sieving into the sample bags. This experiment was initiated on February 12, 1988, and terminated on March 9. During this 25-day period, the density of the snow in-creased from 240 to 251 kg m^{-3} under a thermal gradient of $54°C$ m^{-1}.

Samples were collected for δD analysis at the initiation, and on February 25 and March 3. Samples from three bags were taken at selected levels for isotopic analysis. Each set of three samples from each level was combined for the analysis in an attempt to further reduce the variability. Fractionation was similar to that observed in the February 1987 experiment but the measurements showed less scatter as expected.

March, 1988. The last experiment was initiated on March 14 and run to April 13, 1988. Sieved snow was used and densities and thermal gradients were essentially identical to those of the previous experiment. Samples were taken for analysis at the initiation and on April 4 and April 13, again combining samples from three bags for each level. The lower 5 cm became significantly enriched in deuterium while the upper 15 cm became depleted.

DISCUSSION

Clearly, fractionation of the isotopic species oc-curred in the open-box experiment. The bottom 5 to 10 cm of the snow was depleted in the lighter species as the snow sublimated from the lower to the upper crystals. The upper 5 cm of the snow was also depleted in the lighter species. We verified that this was caused by sublimation and deposition of vapor to the freezer walls, where the deposited ice was enriched in the lighter species.

The results from the 1987 series of experiments with a closed-top apparatus were less clear. Appar-ently, the snow used in the open-top experiment was unusually uniform in isotopic composition. The large variability in isotopic composition of the snow in 1987 made interpretation difficult when the re-sults were plotted on coordinates similar to those of the open-box experiment. Two problems were associated with this variability: (1) the initial sam-

ples, and probably most of the other samples, had initial vertical gradients in isotopic composition; and (2) the average isotopic compositions among the samples varied significantly. However, the curves seemed to show depletion of the lighter species at the bottom and enrichment of the lighter species at the top, similar to the results of SOMMERFELD *et al.* (1987). To test this impression we assumed that the average isotopic composition of each bag would not change during the course of the experiment because with the closed top, very little mass is lost. We calculated the difference between the average for each sample and the average composition of the bottom 5 cm and of the top 15 cm. If our impression is correct, then the difference for the lower layer should increase with time as the lighter isotopic species is depleted and the δ values should become increasingly negative with time. The results are shown in Table 1. In each case, the regression line is consistent with isotopic fractionation. The correlation is better in some experiments than others where there is large scatter. In the 1988 experiments, the snow was mixed and sieved to make it more homogeneous, which improved the results.

COMPARISON WITH NATURAL SNOWPACK

In a companion paper in this volume, FRIEDMAN *et al.* describe the results of isotopic measurements carried out on natural snowpacks. The snowpack that most closely resembled our experimental snowpack is their "plastic-pack." This snowpack was deposited on soil that had been covered with a plastic sheet to prevent the transfer of moisture from the ground to the snowpack. However, the plastic sheet did not prevent the formation of a temperature gradient in the snow caused by the transfer of heat from the soil to the snow above it.

The plastic-packs from Fairbanks, Alaska, in both 1985 and 1986, developed a characteristic depth-hoar profile. However, the slope of the δD vs. $\delta^{18}O$ plot gave values of 8 and 11, in contrast to the value of 3 from the experimental snowpack.

This difference might be explained by the greater length of time that the natural packs were exposed to a temperature gradient (~ 150 days), as compared to the 31 days for the experimental pack. This would allow additional time for diffusion in the solid to increase the efficiency of the Rayleigh process, which, in turn, would increase the slope. Another factor might be the differences in temperature as well as thermal gradient between the experimental and natural snowpack.

Table 1. Slopes of the regression lines of the δD vs. $\delta^{18}O$ plots for experiments of 1987–1988

Experiment	0–5 cm		5–20 cm	
	Slope	R^2	Slope	R^2
January 1987	0.24	0.86	−0.14	0.59
February 1987	0.15	0.28	−0.06	0.14
March 1987	0.25	0.89	−0.12	0.64
February 1988	0.12	0.97	−0.04	0.64
March 1988	0.18	0.99	−0.18	0.99

The upper surfaces of the natural and experimental packs show very different isotopic changes. This can be explained by several factors, including the very different relative humidity (rH) of the two environments. The removal of material to the freezer coils would tend to reduce the rH to low values, in contrast to the natural environment, where the rH would have been high. The high rH, combined with the fact that the water vapor in the air would have an isotopic composition in equilibrium with that of the snow, would act to reduce the change in isotopic composition at the top of the natural pack.

The interchange between water vapor in the atmosphere and the natural snowpack would be an important factor in maintaining an equilibrium slope of about ten. In the absence of this interchange in the experimental pack, kinetic processes would tend to predominate, yielding lower slopes for the δD vs. $\delta^{18}O$ plot.

CONCLUSIONS

The fact that fractionation is observed within the body of the snow shows that vapor transport in snow under a thermal gradient involves processes other than "hand to hand" sublimation. Because diffusion in the solid is slow, it is unlikely to be important in the time scale of these experiments. However, ice is known to exhibit surface premelting at temperatures above −10°C and perhaps to temperatures as low as −30°C (HOBBS, 1974). The quasi-liquid layer on the surface of ice is mobile and exhibits chemical characteristics similar to those of liquid water (CONKLIN *et al.,* 1989; SOMMERFELD *et al.,* 1991). Diffusion within this layer could mix the upper parts of the ice crystals, where sublimation occurs. Thus, the quasi-liquid layer would make the substrate appear more like a liquid than a solid for the water molecules. The resulting slopes of the δD vs. $\delta^{18}O$ plots are 3 to 4, within the range that EHHALT and KNOTT (1964) and CRAIG and GORDON (1965) predicted for evaporation from the liquid.

Another possible explanation for the observed fractionation is diffusion in the vapor, where the communication distance is several crystal diameters. This would allow fractionation because of the different gas diffusion rates of the different isotopic species. For this mechanism, the ratio of the separation factors would be about two.

We speculate that both mechanisms are important. The fact that the δD vs. $\delta^{18}O$ plot has a slope of three to four argues that the quasi-liquid layer is important. In addition, the fact that sieved snow fractionates at about the same rate as natural snow indicates that the micro structure of the snow is not of primary importance in the fractionation process. On the other hand, the top layers of the snow were at $-10°C$ or colder where the thickness of the quasi-liquid layer is very reduced (HOBBS, 1974). The fact that the fractionation in the upper layers is not much different than in the warmer lower layers indicates that a mechanism not involving the quasi-liquid layer is also active.

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