DISSERTATION

DEUTERIUM AND SNOW HYDROLOGY

Submitted by
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WE HEREBY RECOMMEND THAT THE DISSERTATION PREPARED UNDER OUR SUPERVISION BY CLARK HENRY JUDY ENTITLED DEUTERIUM AND SNOW HYDROLOGY BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

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ABSTRACT

DEUTERIUM AND SNOW HYDROLOGY

HDO samples from natural and laboratory snowpacks show that snowpack metamorphism can reduce the initial variability in the HDO content of snow. Field studies in Colorado indicated melt water percolation reduced the variability from a spread of -229‰ to -106‰ relative to Standard Mean Ocean Water for fresh snow to a spread of -182‰ to -158‰ for the snowpack in the middle of the melt period. Further studies in the laboratory indicated that isotopic fractionation and vapor transport occurring during depth hoar formation may homogenize the lower part of the snowpack before melt occurs. The homogenization of the HDO content of the snowpack would reduce the problems involved in following snowmelt through the hydrologic system.

Preliminary studies indicated three unexpected results. No clear relationship was found between the HDO content of fresh snow and altitude. Fractionation did occur during sublimation from a snow surface. Depth hoar formation appeared to occur because of a continuous diffusion of material, not exclusively by a crystal-to-crystal transfer of mass.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

The objective of this study is to investigate the feasibility of using HDO (water with a heavy hydrogen atom) as a tracer in snow hydrology studies. As this study is exploratory in nature, several questions are asked with the thought that the information obtained could provide a base for future studies of greater detail. An attempt was made to collect the minimum amount of samples that would produce useable results. The expense of analysis for the isotope content of the samples, relative to the value of the information obtained, was always considered.

The problem of investigating the use of HDO as a tracer in snow hydrology studies might be developed as follows:

1. Do individual storms have a unique HDO content?
2. What is the consistency of the HDO content of a given storm in relation to location, elevation, and major physiographic barriers?
3. How does the metamorphism of the snowpack influence the HDO content of the snow?
4. Depending upon 1-3 above, can melt water be traced through the soil profile?
5. Depending upon 1-4 above, can soil water be traced as it becomes part of the streamflow?

This study will be concerned mainly with parts one and three. Part two should be developed with the aid of a meteorologist, as a knowledge of the movement of the air mass before it reaches the mountains and while it is over the mountains would be important. Work on parts four and five would be justified if it was believed that snowmelt could be identified as a separate component in the soil moisture system.

The questions given greatest emphasis in this study are:

1. How much variation is there in the HDO content of different snow storms at a given location in the Rocky Mountains?
2. Does snow metamorphism cause a homogenization of the HDO content of the snowpack?
3. If there is homogenization, what are the processes involved?
4. What equipment, procedures, and ideas might be of use in future studies?

As the results of each step were unknown, when the study plan was written, some flexibility was built into the study.

The need for the above information is basic to the overall problem. If HDO is to be used as a tracer in snow hydrology, information about the input is needed. We must know how uniform the HDO content of the snow is, and if this HDO content is changed before or during the melt period. The literature gives hints about the answers, but nothing definite. Nearly all the work with heavy water and snow has been directed towards dating the layers of the firn within glaciers. Two papers concerned with the annual snowpack have been presented since the completion of this study (Moser & Stichler, 1970, and Dincer et al., 1970).

These papers will be commented upon during the discussion of the results of this study.

There may also be some indirect benefits occurring from the study. Information obtained about the processes of snow metamorphism may be applied by persons studying the melt rates of snow, avalanche control, the internal energy balance of the snowpack, and other phenomena.

The first part of the study was carried out at Pingree Park, a valley at an elevation of 2700 meters on the eastern slope of the Rocky Mountains in northern Colorado (41° N latitude, 106° W longitude). A sample of new snow was taken whenever possible after each major snowfall, and a pit dug to obtain data on the development of the snowpack profile. At the beginning and near the end of the melt period a vertical series of samples was taken from the pit wall to indicate any change in the HDO content of the snow caused by metamorphism or melt water percolation.

As it was difficult to determine what effect, if any, depth hoar formation (the development of large, delicate crystals in the lower part of the snowpack) had on the homogenization of the snowpack, it was decided to conduct a laboratory study on this phase of snow metamorphism. Snow of a known HDO content was placed under a temperature gradient in a freezer. After allowing about one month for depth hoar formation to take place, a systematic set of samples of the snow was taken so any change in the HDO content of the snow could be detected.

To complement the two major parts of the study, two short experiments were run. The changes in the HDO content of the snow with elevation during a single storm were determined for a transect over the continental divide. And, the fractionation between HDO and H_2O during sublimation was measured. These experiments were considered preliminary in nature because they were done to provide a feel for the changes in the HDO content of the snow that might occur. They should be repeated so there is additional data to back up the results obtained.

CHAPTER II

LITERATURE REVIEW

Isotopes, atoms of the same element having different atomic masses, have been utilized as tracers in physical processes and chemical reactions since their discovery in the 1930's. The similarity of the isotope to the most prevalent form of the element allows it to follow a similar process or reaction path. The differences in mass permit the detection and measurement of the isotope.

Heavy water is a term sometimes used to describe that part of water which is not H_2O but an isotopically heavier form of it. These non-typical forms of water show excellent possibilities for use as tracers as there would be no problems trying to obtain uniform mixing of an introduced material and the water being traced.

Rankama (1963) lists the relative abundance of hydrogen and oxygen atoms as follows:

$H = 99.9844\%$
$D = 0.0156\%$

$O^{16} = 99.7590\%$
$O^{17} = 0.0374\%$
$O^{18} = 0.2039\%$

H^3 (T or tritium) is not listed as it is a radioactive isotope with a half-life of 12.26 years. H^2 (deuterium) is commonly designated by a D. There are also several more isotopic forms of oxygen, most of them radioactive and with half-lives of less than one day.

Water may be any combination of the above mentioned isotopes; H_2O, H_2O^{18}, HDO, and H_2O^{17} being the most common. These isotopic forms of water occur naturally. HTO also occurs naturally in limited amounts, but most HTO used in scientific investigations is a by-product of bomb tests and other nuclear projects. Dansgaard (1964) summarizes much of the work that has been done with H_2O^{18} in precipitation, and Friedman et al. (1964) review the work with HDO.

Each form of water has a different vapor pressure (page 73 of the appendix). This causes a fractionation of the light and heavy components to occur during evaporation, condensation, and sublimation. Several papers giving details on how the atmospheric processes affect the HDO and H_2O^{18} content of precipitation are: Ambach et al. (1968); Bleeker, Dansgaard, and Lablans (1966); Dansgaard (1953, 1954, and 1964); Ehhalt et al. (1963); Eriksson (1965); Isono et al. (1966); Lorius (1963); Matsuo and Friedman (1967); and O'Neil and Epstein (1966).

The activities of the different forms of water are not related directly to the square roots of the masses of the molecules as classic physical chemistry might imply. What is called a kinetic effect (Thatcher, 1967) prevails. Apparently the difference in nuclear spins between H and D (Fast, 1962) causes the thermodynamic properties of HDO to be affected more than those of H_2O^{18}.

Temperature is an important factor in determining the areal variations in the isotopic content of precipitation. Dansgaard (1954) gives five factors that affect the H_2O^{18} content of precipitation:

A. Temperature of the precipitation
B. The origin of the vapor
C. The condensation temperature
D. Cooling since the start of condensation
E. Evaporation during falling.

Facy et al. (1963) quote Botter, Lorius, and Nief (1961) as having determined that the temperature and the pressure of the atmosphere are important.

Vapor pressure differences are the basis for the fractionation which causes variations in the isotopic content of precipitation. The vapor pressure ratios (eg.; V.P. H_2O/V.P. HDO) between the different types of molecules are temperature dependent and are modified by changes in temperature, which in turn may be caused by changes in elevation or characteristics of individual storms.

Snow has a lower HDO content than rain, it occurs at a lower temperature than rain. Whatever the exact process, we receive a varied HDO input with snow. Snow has from 10 to 23 percent less HDO than ocean water. Rain usually has 0.5 to 9 percent less HDO than ocean water.

The isotope content of precipitation is often expressed as a per mil deviation relative to Standard Mean Ocean Water (SMOW) (Craig, 1961a). Snow could be expected to have a deuterium content between -100‰ SMOW and -230‰ SMOW.

Snow on the ground undergoes several changes involving melting, freezing, and vapor exchange which may modify the isotopic content of the snowpack. This metamorphism of the snowpack is described by Sommerfeld and LaChapelle (1970). It may be divided into three stages.

Destructive metamorphism; the plates, needles, and other original forms of snow become rounded grains of ice. During this phase the entire layer of snow involved becomes more dense.

Constructive metamorphism; the rounded grains of ice are transformed into complex crystals with a definite plate like structure. These crystals may develop into a honeycomb like structure in the lower part of the snowpack and are commonly referred to as depth hoar.

Melt metamorphism; the melt water flowing through the snowpack brings the snow to an isothermal (0° C) condition and breaks down the more delicate crystal structures.

A fourth stage, pressure metamorphism, must be considered when one is concerned with the formation of glaciers.

Depth hoar has been defined by Giddings and LaChapelle (1962) as the condition of snow when the initial snow grains have been replaced by crystals deposited from vapor movement. This vapor movement is caused by a temperature gradient within the snowpack. There may also be other contributing factors, as Yosida (1955) found that the vapor flux in snow is four to five times that occurring in air at the same temperature.

The literature contains no reference to the possible fractionation of HDO and H_2O during depth hoar formation. Ragotzkie and Friedman (1965) state that, "Sublimation does not produce fractionation of D_2O and H_2O molecules, since the process is sort of a layer-by-layer removal of matter..." But, this does not rule out changes in HDO content during depth hoar formation that are caused by diffusion or partial sublimation. Epstein et al. (1965) related depth hoar to layers with a higher H_2O^{18} content than the rest of the snow. A preliminary study by Benson (personal communication, 1968) indicated an enrichment and possible fractionation of HDO during depth hoar formation.

Dansgaard (1961) made the following observations about the H_2O^{18} content of snow:

A. Seasonal variations in glaciers are preserved for hundreds of years in layers averaging about 30 cm. thick.

B. There is no enrichment during evaporation from ice.

C. Enrichment is significant for evaporation from wet snow only.

D. Fractionation is possible but not probable in dry snow during vapor exchange between solid states.

The last point concerns the process of depth hoar formation, but gives us no further information. Points B and C seem to indicate little enrichment of the snow surface during the winter but some enrichment of the surface during spring melt.

Sharp, Epstein, and Vidzunas (1960) state that the refreezing of melt water and rain is important in the enrichment and homogenization of H_2O^{18} within the unmelted snow. Macpherson and Krause (1967) found that the percolating melt water tends to homogenize the H_2O^{18} content of snow. While the above references concern H_2O^{18} not HDO, they appear to be supported by the results of a laboratory study by Arnason (1969a). He allowed a column of snow to melt at the top and collected the water that had percolated through the snow. The drain water had 8‰ less HDO than the snow, which would indicate that an isotopic exchange occurs between the ice and water and may be an important factor in the homogenization of snow.

The above papers about isotopes and snow have been concerned with snow as a contribution to glacial ice, not with an annual snowpack. But, the stages of metamorphism previous to firnification are nearly identical for both types of snowpacks.

CHAPTER III

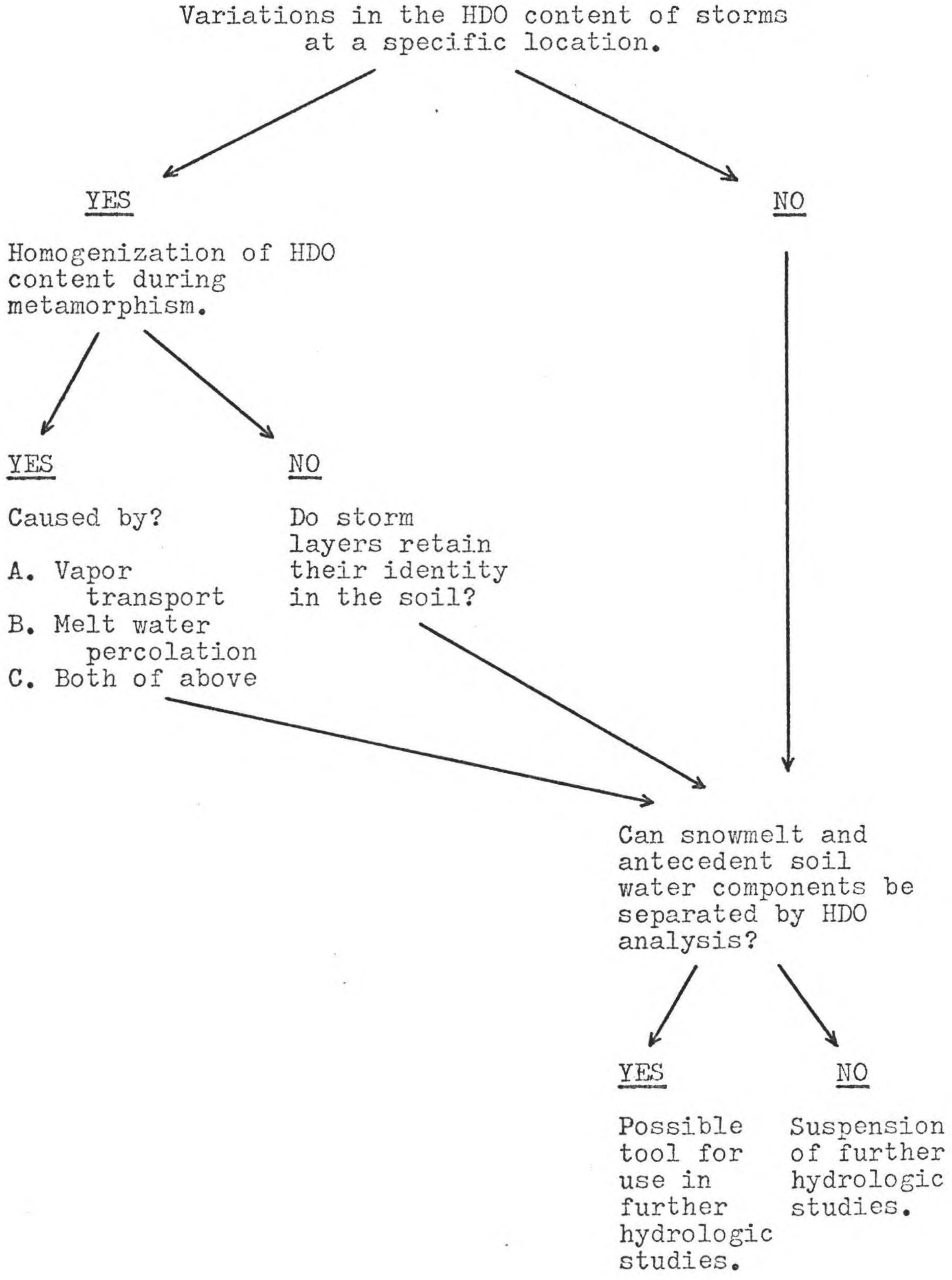
DEUTERIUM VARIATIONS IN AN ANNUAL SNOWPACK

The isotopic fractionation occurring between H_2O, HDO, and H_2O^{18} during evaporation and condensation causes a variation in the relative amounts of these isotopic forms of water in precipitation. This study was designed to determine the isotopic variation of snow at a specific location in the Rocky Mountains and to follow the changes in the original isotope content caused by the metamorphism of the snowpack. The information will be used to detect potential problems associated with the use of deuterium as a natural label in snowmelt runoff studies.

Friedman et al. (1964) mention several aspects of HDO which suggest that one would find a variation in the HDO content of different storms at a given location, and that there are processes (as fractionation between H_2O and HDO during evaporation and freezing) by which snowpack metamorphism might change the HDO content of the original snow.

The fractionation between H_2O and HDO during freezing has been measured by several people. Arnason (1969b) presents a summary of previous work as well as data on an experiment in which he determined that ice would contain

Figure 1. Flow chart for HDO variations in an annual snowpack.



1.0208 ± 0.0007 times as much HDO as the water it was frozen out of.

Arnason (1969a) also noted in another study that a recrystalization followed by an isotopic exchange between ice and water must be an important factor in the homogenization process. The observations of Sharp, Epstein, and Vidzunas (1960) and Macpherson and Krause (1967) that melt water is important in the homogenization of the snowpack lend strength to the theory of isotopic exchange during the percolation of melt water or rain.

Vapor transport is another possible means of homogenization of the HDO content of a snowpack. Epstein et al. (1965) reported that layers of depth hoar had a higher isotope content then the rest of the snow.

As very little was known about the HDO content of seasonal snowpacks when this study was started, a flow chart (figure 1) was set up to guide the progress of the research.

PROCEDURE

During the 1967-1968 snow year, samples of fresh snow were taken whenever possible after each major snowfall at Pingree Park. Pits were dug in a 15 by 25 meter opening in the lodgepole pine (Pinus contortus) forest to obtain data on the development of the snowpack profile. Colored threads were used to identify the surface of the snow at various stages during the study period.

Figure 2. The Pingree Park snowpack profile on March 30, 1968. The threads marking the different layers of snow are barely visible. The thin black object is a ball point pen used for a size reference.

Figure 3. The Pingree Park snowpack profile on May 3, 1968. Two threads are still visible in the snow. The other threads have been suspended from the shovel handle. The 500 cc CRREL density tube and weighing apparatus are below and in front of the shovel handle.

At the beginning and near the end of the melt period a vertical series of samples was taken from the pit wall, an attempt being made to sample the parts of the snowpack which could be related to the earlier samples of new snow. The threads marking the layers of snow are barely visible in figure 2, which shows the snowpack profile on March 30. The snowpack profile of May 3 is shown in figure 3, as is the 500 cc CRREL snow tube used to take density measurements.

The snow samples were placed in widemouth glass jars, capped, and allowed to melt. Then the samples were transferred to smaller screw capped glass bottles. These bottles were sealed with paraffin to insure against accidental opening or evaporation until laboratory analyses were made.

The water samples were converted to hydrogen gas and analyzed for their deuterium content on a mass spectrometer by the procedure described by Friedman (1953). The measurements were reported as the per mil deviations relative to SMOW (Standard Mean Ocean Water). Laboratory measurements are precise to the nearest per mil.

RESULTS

The results of the laboratory measurements are listed in table 1. A recording rain gage equipped with an Alter shield, located on the valley floor about 100 meters from the study site, gave the dates and amounts of precipitation for the storm events. The data are presented with the newest snow at the top of the table to coincide with the

TABLE 1. Date and Water Equivalent for Each Storm during the 1967–1968 Snow Year at Pingree Park, Colorado (deuterium concentration relative to SMOW is given for each storm sampled and for the profile samples)

		‰ D relative to SMOW		
Date	Precipitation, mm	New Snow	Profile 3–30–68	Profile 5–3–68
1968				
4–27	3.8			
4–21	2.5			
4–17	22.9	−124		
4–7	7.6			
		−177		
4–3	14.0			
3–26	6.6			
3–20	10.2			
3–17	.8			
3–14	3.0	−116		
3–10	8.4			
3–7	.8			
3–2	1.8			
			170*	
2–27	2.0			
		−156		
2–24	9.1		−169	
2–20	5.8	−213		
2–12	10.7	−213	−177	
1–31	2.5	−174	−167	
1–22	10.2			
1–6	2.8			−162*
		−217		
1967			−215	−161
12–30	4.8			
12–26	10.2	−217		
12–20	3.8			
12–12	9.4	−199	−196	−182
12–9	1.5	−194	−186§	−173
12–1	13.2	−229	−165	−168
11–25	12.4	−106		
11–21	17.8	−163	−161	−158
11–10	1.3			
11–2	15.7		−159	−158
			−168†	−160†
Total	215.6			−161‡

* Surface 10 mm.

† Moist lower layer.

‡ Ice layer.

§ Includes some snow of 12–1–67.

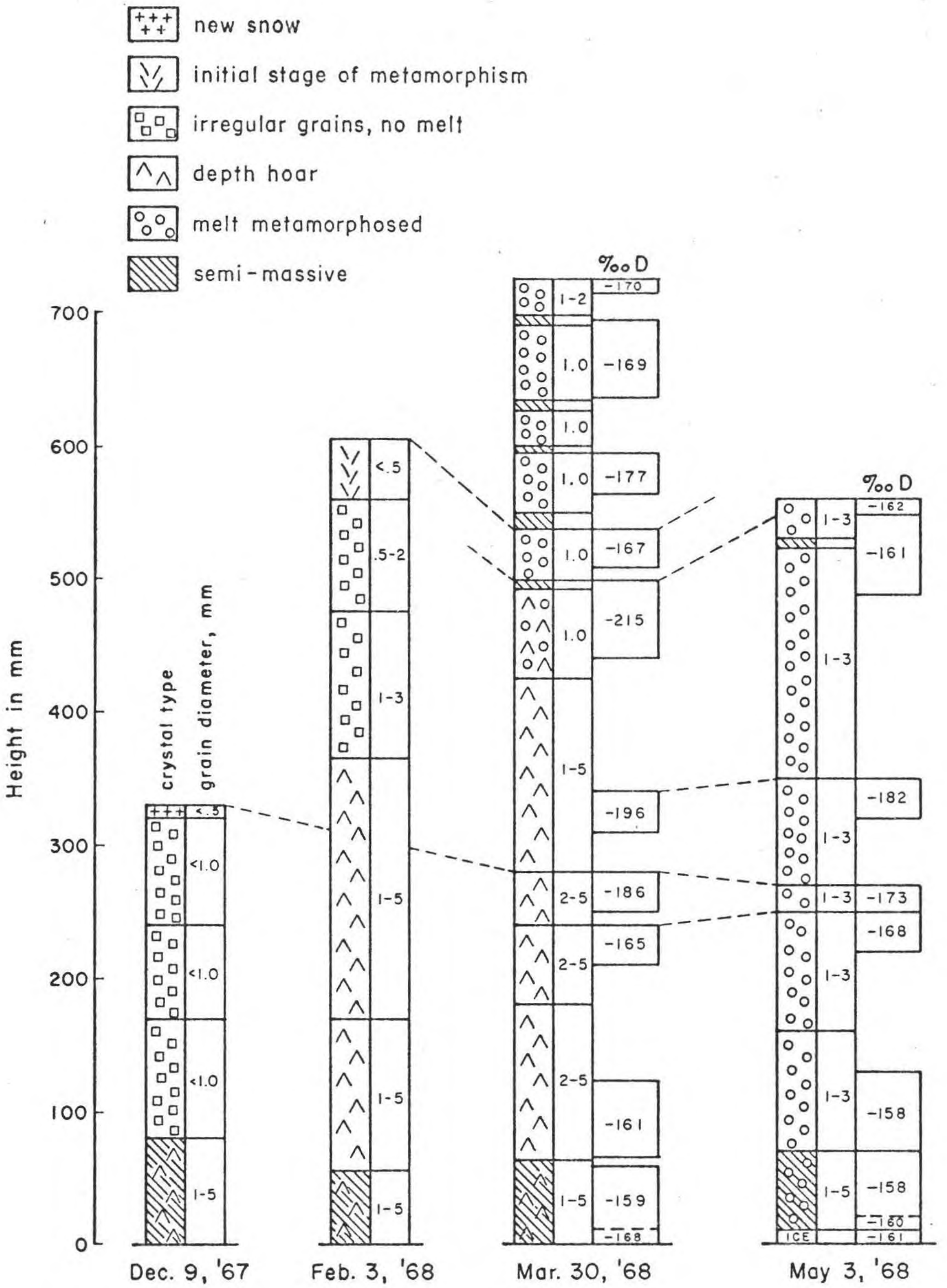


Fig. 4. Selected snow profiles from the Pingree Park sample area. The boxes containing the deuterium values represent the locations of the samples. The dashed lines show the locations of the threads used as profile markers.

snow profiles shown in figure 4. All precipitation events during the study period were snow. The deuterium values on the same line, from left to right, trace the new snow to the equivalent layers in the March 30 and May 3 profiles. Also included in table 1 are deuterium values for the surface 10 mm of snow, the layer of moist snow occurring at the bottom of the snowpack, and the layer of ice (May 3 only) that had formed at the soil-snow interface.

Approximately one third of the precipitation was not sampled for deuterium. Table 2 gives a weighted average for the deuterium content of the precipitation actually sampled. The samples taken from the snowpack profiles were also weighted by the water equivalent of the sample concerned and an average deuterium content for the entire profile calculated.

Figure 4 gives the descriptions of selected snowpack profiles. The locations of the samples taken from the March 30 and May 3 profiles are shown by the bars enclosing the deuterium values of the respective samples. Depth hoar densities ranging from 0.200 to 0.230 had developed by mid-February. The March 30 profile was taken just after the pack had turned isothermal and the density of the depth hoar ranged from 0.236 to 0.270. By May 3, melt metamorphism had increased these densities to the range of 0.304 to 0.404. Detailed temperature and density profiles are given on pages 81 and 82 of the appendix.

Table 2. Weighted averages for the deuterium content of the snow.

Type	Date	‰ D Weighted Average	% Precipitation Not sampled
New snow actually sampled	11-2-67 to 3-30-68	-185	34%
Entire profile	3-30-68	-180	
New snow actually sampled	11-2-67 to 5-3-68	-174	29%
Entire profile	5-3-68	-164	

DISCUSSION

Interpretation of the data presented in tables 1 and 2 and in figure 4 suggests three conclusions for this study:

1. There is a large variation in the deuterium content of different snow storms even though the samples are taken at one location.
2. There is a marked homogenization of the deuterium content of snow by the processes of snowpack metamorphism.
3. Melt water percolation appears to be the major process causing this homogenization.

The storms sampled have a very wide range of deuterium content, from -229‰ to -106‰ D relative to SMOW. Ambach et al. (1968) mention the source of the vapor, the temperature of condensation, and evaporation while falling as among the factors affecting the isotope content of precipitation. The isotopic exchange between falling precipitation and the atmospheric vapor may be significant for rain drops (Friedman et al., 1963) but it is doubtful if it has much effect on snow crystals.

Because of the inland position of the sampling area, the approach path of the storm and what happened to the air mass before it reached Colorado are important. Most storms originated in the northwest, but especially in the spring it is possible for vapor originating in the Gulf of Mexico to act as a source of snow for the eastern slope of the Rocky Mountains. Brown (1970) found that in Canada the deuterium content of the precipitation was dependent upon the origin of the air mass. Air masses from the north and west had a low deuterium content, while those from the south and east had a higher deuterium content.

The temperature of condensation of a given sample of snow is difficult to determine. Because of a lack of better data, the mean temperature of the first day of the snowstorm was plotted against the deuterium content of the snow (figure 5). The least squares equation of the line through the data points is D = 3.9 (°C) - 168. Brown (1970) obtained an equation of D = 10.5 (°C) - 140 for the variation of the deuterium content of annual precipitation with temperature in Canada.

The homogenization of the deuterium content in the snowpack profile could result from both vapor and liquid transfers during the various stages of metamorphism. Arnason (1970), Dincer et al. (1970), and Moser and Stichler (1970) presented papers at the March 1970 symposium of the International Atomic Energy Agency in Vienna. These authors agree that melt water percolation may be a major cause of the homogenization of the isotopic content of snow. The papers of Dincer et al. (1970) and Moser and Stichler (1970) included profile samples similar to those made in this study.

Arnason (1969a) indicates an isotopic exchange occurs between the ice and the water and this may be an important factor in the homogenization of snow. Dincer et al. (1970) believe that during the first part of the melt period the upper layers of snow and rain percolate through the snowpack

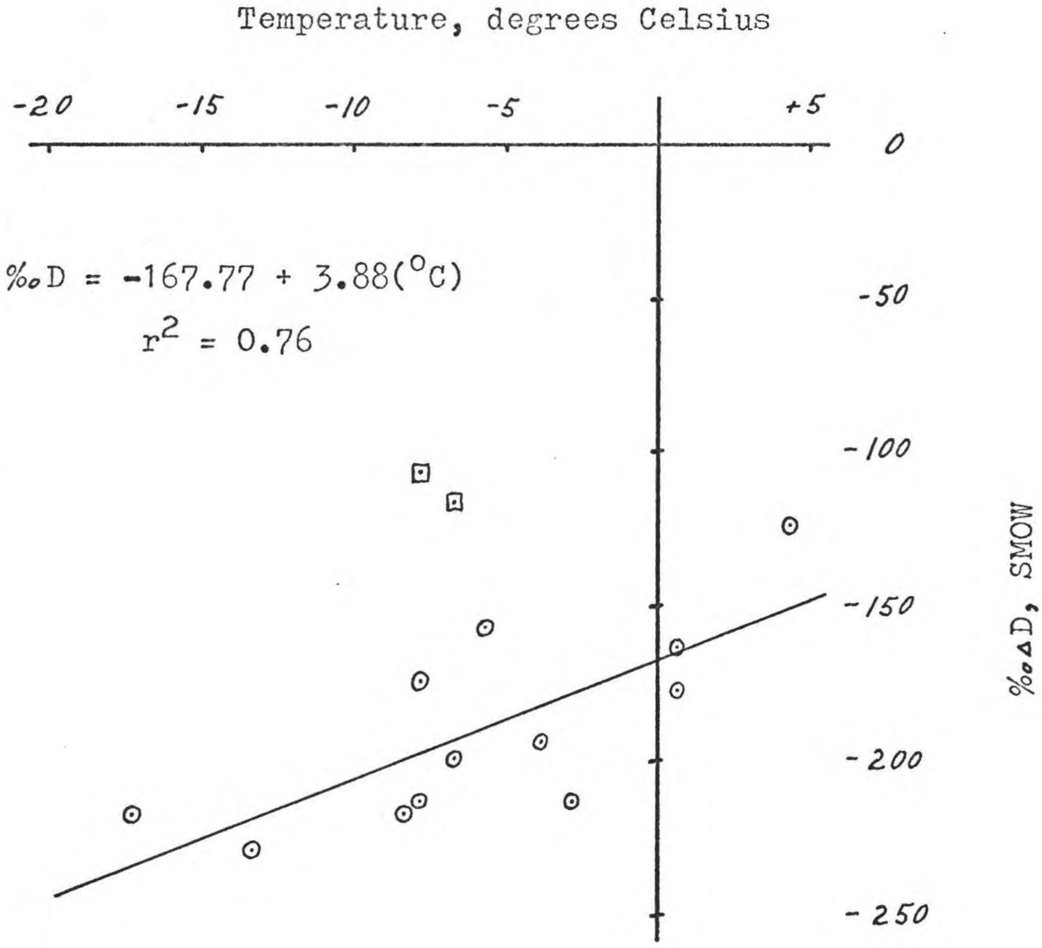


Figure 5. The mean air temperature on the first day of the snowstorm plotted against the HDO content of the snow that fell during the entire storm. The two points enclosed by squares were not used in the calculation of the regression line.

without losing isotopic identity, especially if the thermal quality (a measurement of how dry the snow is) is near 100%.

Water percolating through a snowpack would form a thin film flowing over the snow crystals. This would provide a large area of contact along the ice-water interface. Also the rate of flow would be quite slow. The rate of diffusion of HDO in water or ice is very small, so there would be little isotopic exchange by diffusion. But, there would be a continuous freezing and melting process going on at a small scale, an equilibrium reaction between the ice and the liquid film. Both Arnason (1969a) and Friedman et al. (1964) have shown that isotopic fractionation will take place under such circumstances.

It is not possible to determine the exact role of vapor transport in the homogenization of the snowpack studied. Some melt water percolation had occurred before the March 30 profile samples were taken. Strong temperature gradients existed in the shallow snow cover as evidenced by the pronounced depth hoar formation. Information obtained later in a laboratory experiment indicates that vapor transport during depth hoar formation can cause isotopic fractionation and may contribute to snowpack homogenization.

A graphic presentation of the data (figure 6) suggests that the center part of the March 30 profile (from 250 mm to 500 mm) had not yet been affected by the homogenization processes. This implies the possibility of vapor transport

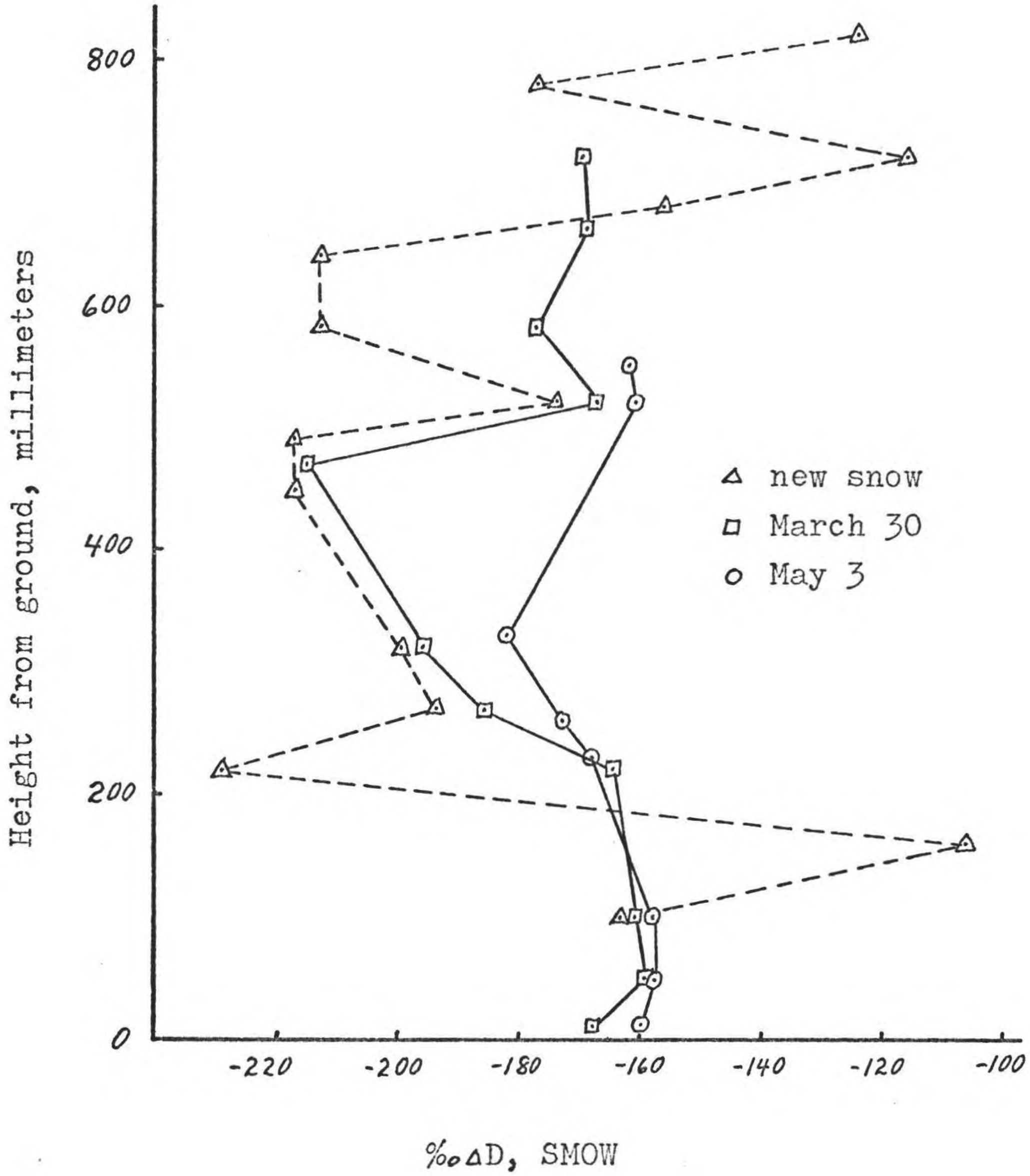


Figure 6. The deuterium content of the new snow and the snowpack profiles showing the effect of isotopic homogenization. The deuterium values for the new snow have been plotted at the height of the equivalent layer of snow in the March 30 profile.

causing the homogenization of the lower part of the snowpack prior to the melt period.

Dincer et al. (1970) noted the partial homogenization of a high altitude snowpack which occurred without any signs of melt water percolation. Perhaps an indication of homogenization by vapor transport. Temperature profiles are not given so it is not know if the gradients necessary for vapor transport were present.

There appears to be an increase in deuterium content with time within the profile. Considering the amount of precipitation not sampled, this difference may not be meaningful. There are some logical reasons for an increase in deuterium. Enrichment caused by fractional evaporation from the surface of the melting snow (Dansgaard, 1961) and preferential condensation of HDO from the atmosphere onto the cold surface of the snow are possibilities. The fractionation of percolating melt water would enrich the remaining snow.

Another factor which could modify the HDO content of the snowpack would be the movement of soil moisture, by vapor transport, into the lower layers of the snowpack. The relatively small changes in the HDO content of the lower layers of snow suggest that this was not an important factor in this study even though there was 84 mm of rain in September and October, before the beginning of snowpack formation.

CHAPTER IV

DEPTH HOAR FORMATION

The literature previously mentioned contains some information on the role of melt metamorphism in the homogenization of the isotope content of a snowpack. Nothing has been reported about the role of constructive metamorphism, depth hoar formation, in the homogenization process.

Results presented in the previous chapter indicated that the deuterium content of the snowpack was homogenized by the end of the melt period. Melt water percolation was believed to be the primary cause. But there was evidence to suggest the vapor transport occurring during depth hoar formation had caused the homogenization of the lower part of the snowpack prior to the melt period.

Depth hoar, a fragile network of crystals of the type shown in figure 7, is common in the shallow snowpacks of the Rocky Mountains. It was decided that a further study of the deuterium variations associated with this form of snow should be made.

The only mention of depth hoar noted in the literature on isotopes is by Epstein et al. (1965). They noted that depth hoar had a higher H_2O^{18} content than the rest of the snow cover.

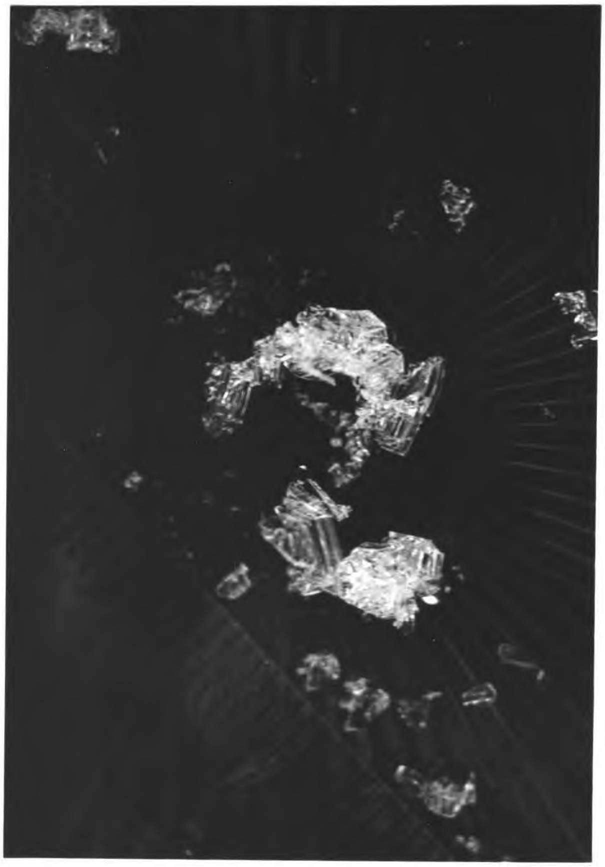
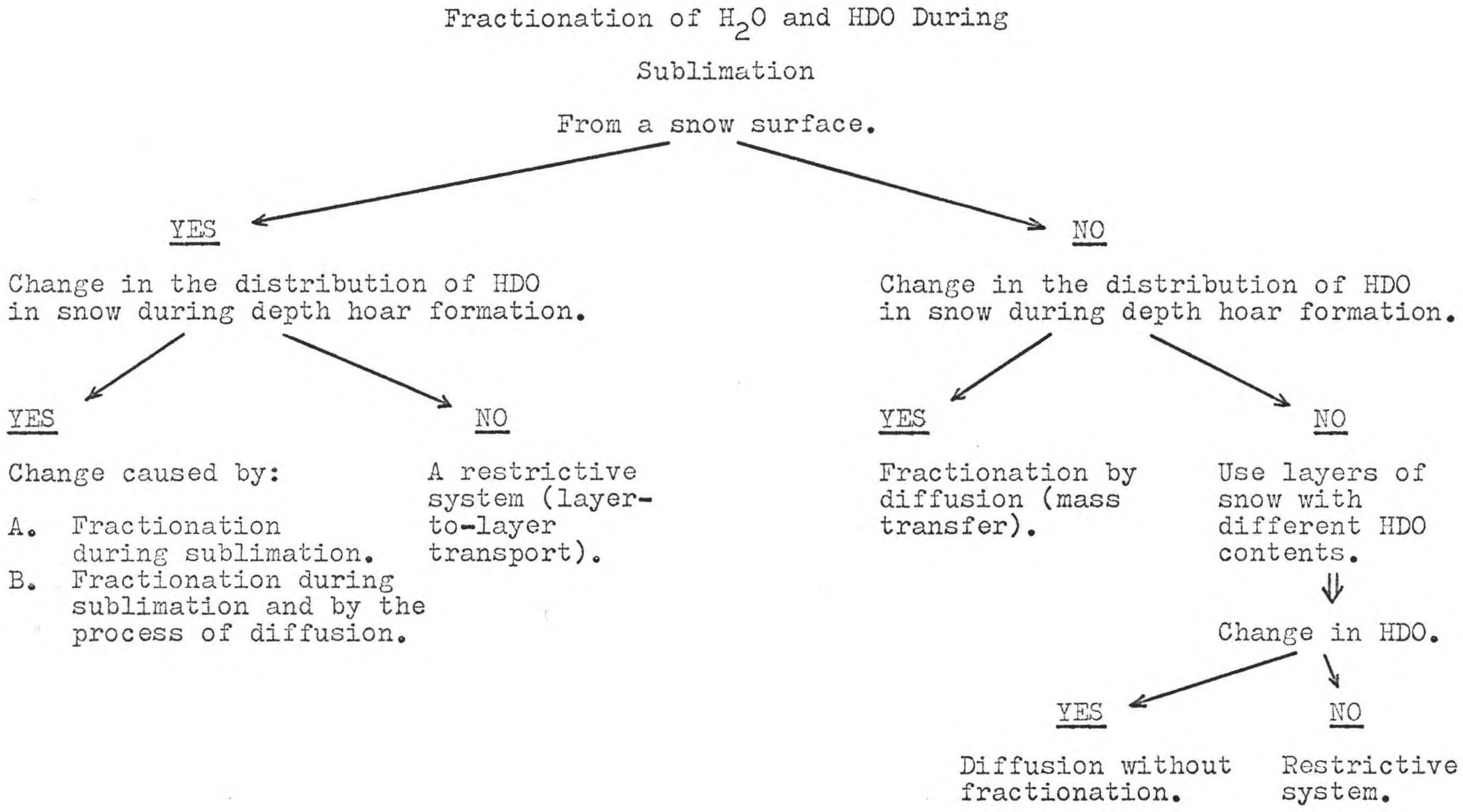


Figure 7. Depth hoar crystals that developed naturally in the Pingree Park snowpack. The ruler is graduated in millimeters.

Figure 8. Flow chart for depth hoar formation.



Sommerfeld (1969) describes depth hoar formation as a temperature-gradient metamorphism in which water vapor is transported from the warmer to the colder layers by sublimation and deposition. Yosida et al. (1955) state that the movement of the vapor tends to be restricted by the snow crystals and that there is a hand-to-hand movement of the vapor from the top of one crystal to the bottom of the crystal above it. This allows a large mass translation without any individual water molecule having to move more than a few millimeters.

Vapor and liquid water movement through snow is complicated. Unlike the flow of a fluid through sand, where the sand particles remain constant and the fluid moves around them, there can be an exchange of molecules between the snow and the fluid flowing through it.

The many possible alternatives for changes in the deuterium content of snow during depth hoar formation are shown by the flow chart (figure 8). As indicated by the first heading on the chart it had not been proven if there is a fractionation of H_2O and HDO during sublimation from a snow surface.

PROCEDURE

Snow of a known deuterium content was placed under a temperature gradient. After half of the snow had undergone constructive metamorphism, a vertical series of samples was taken and the samples analyzed for their deuterium content.

Figure 9. The styrofoam container at the end of the second depth hoar experiment. The false front has been removed and a series of samples taken. The wires going into the snow are thermistor leads.

A large, family-style freezer was used to house a styrofoam container for the snow. The freezer could maintain a temperature of $-26.0^{\circ} \pm 1.0^{\circ}$ C. The styrofoam container (figure 9) was made of two-inch thick foam plastic gluded to a one-quarter inch thick plywood base. The top of the container was left open to the inside of the freezer and the front panel was designed so it could be removed with a minimum of disturbance to the snow.

The container of snow rested on a heat source, a plywood and styrofoam box containing a heating element controlled by a voltage regulator (figure 10). The heating element was an eight-foot length of heat tape, as is commonly used to keep water pipes from freezing, fastened in the bottom of the box in a circular pattern. A sheet of aluminum was suspended approximately ten millimeters above the heating element to distribute the heat evenly and reduce the chance of hot or cold spots occurring in the lower part of the snow.

Thermistors placed at various levels in the snow and the freezer were used to monitor the temperature gradient. The temperature at the bottom of the snow could usually be controlled to within $\pm 0.2^{\circ}$ C, though fluctuations in the line voltage caused some problems at night and on weekends.

Calculations using the formula of Giddings and LaChapelle (1962) suggested a time duration of four weeks would produce sufficient depth hoar formation (appendix, page 83). At the end of this time the false front of the

Figure 10. The empty styrofoam container showing the construction of the container and the heat source it was placed upon.

styrofoam container was removed, the first fifty millimeters of snow disposed of to eliminate border effects, and samples taken for isotopic analysis.

The samples were taken by inserting a sharpened piece of three-eighths inch copper tubing horizontally into the snow. After the samples for isotopic analysis had been removed, a parallel series of samples were taken so the snow crystals from each location could be photographed.

The densities and net weights of the snow were obtained differently each time. For the first experiment, each 50 mm layer of snow was weighed to the nearest gram. This procedure was abandoned because when the upper layers of snow were added the lower layers were disturbed and layer-by-layer density values lost any meaning. During the second experiment the entire container of snow was suspended in a cradle and weighed with a spring balance. This technique was refined for the third experiment, during which the container and heat source were allowed to rest on a platform balance for the duration of the experiment.

RESULTS

The results of the isotopic analyses are shown graphically in figures 11-13. Note that the standard the deuterium analyses are referred to is different for the second set of samples. Temperature profiles are given in figure 14. Details about the density, crystal structure,

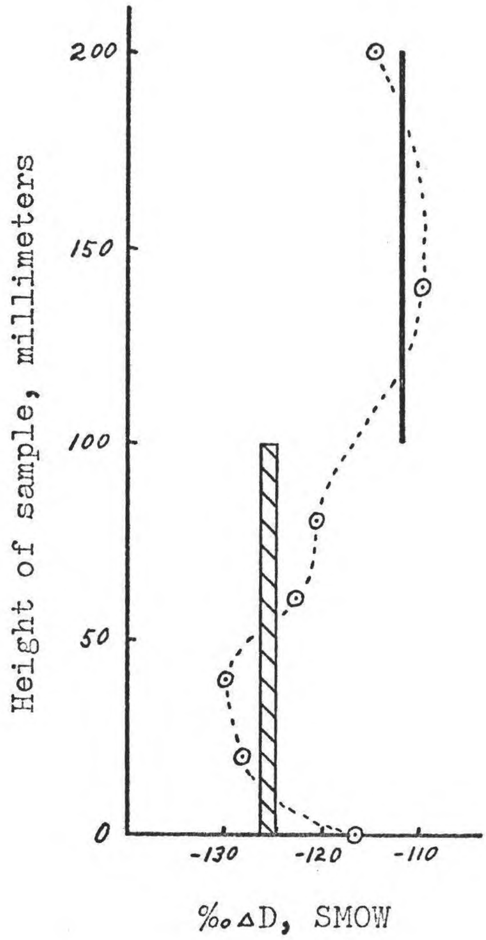


Figure 11. Isotope profile for the first depth hoar experiment. Two layers of snow of slightly different isotope content (vertical bars) were used. The deuterium measurements are relative to SMOW.

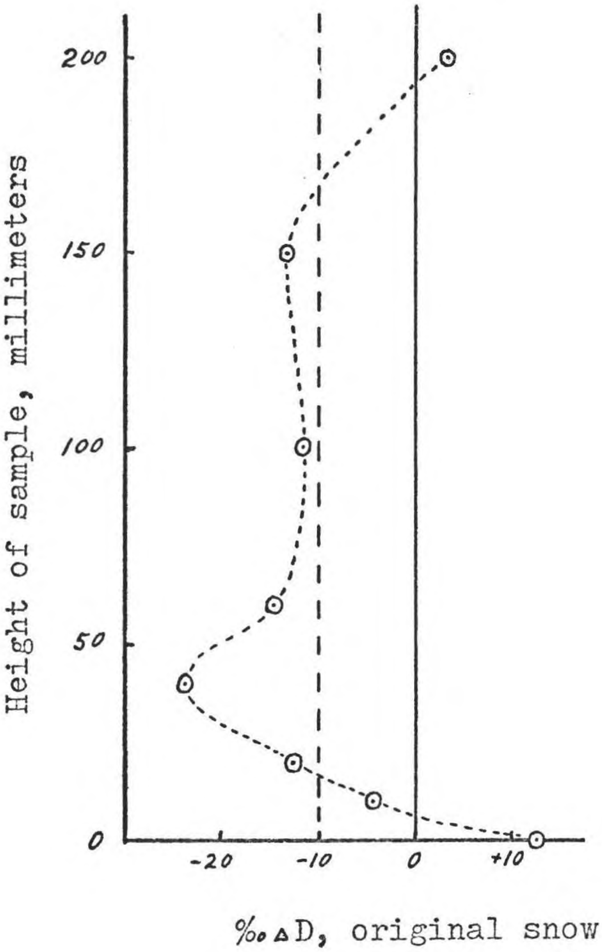


Figure 12. Isotope profile for the second depth hoar experiment. The deuterium measurements are relative to a sample of the original snow (zero line). Two samples of the original snow gave HDO measurements within 1.5‰ of each other. A third sample of the original snow, which was analyzed at a later date, gave a measurement of -19.0‰. Apparently the isotope content of the snow was not uniform. A ΔD value of -10.0‰ (dashed line) appears to be representative of the entire mass of snow.

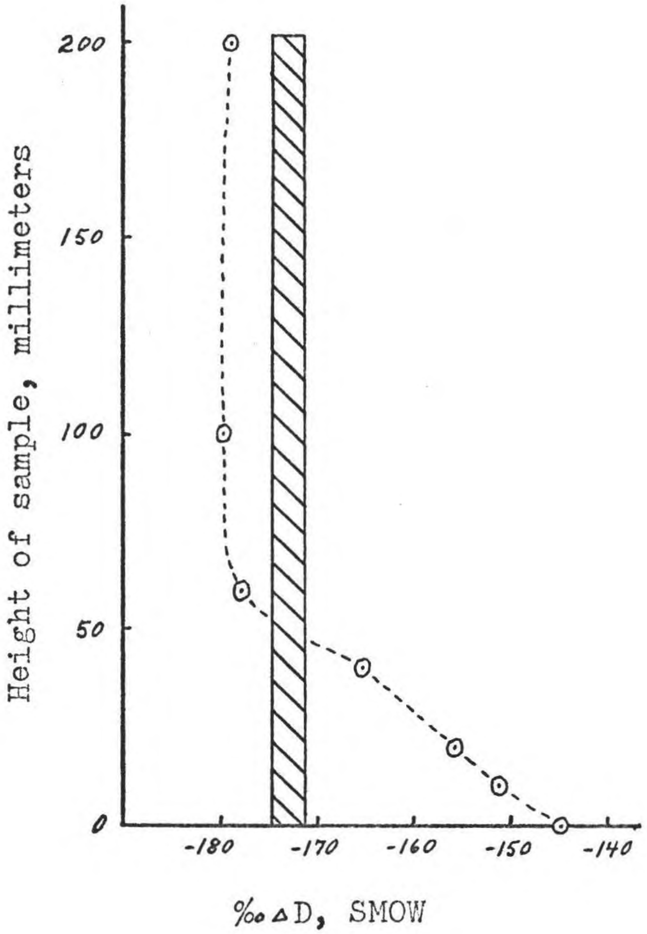


Figure 13. Isotope profile of the third depth hoar experiment. The vertical bar represents the spread of the HDO content of the original snow. The deuterium measurements are relative to SMOW.

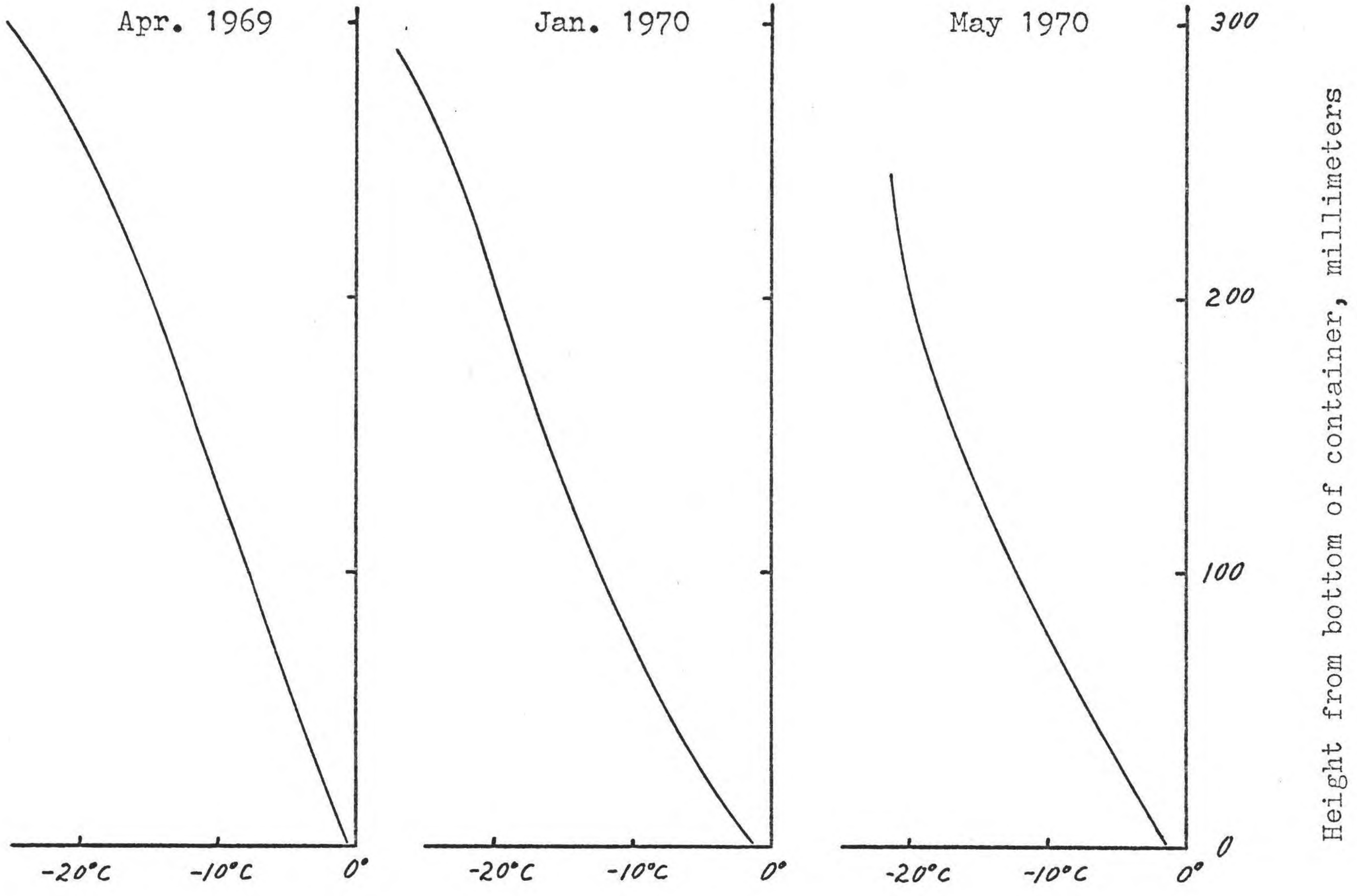


Figure 14. Temperature profiles for depth hoar experiments.

and deuterium values of the snow are provided on pages 88 to 100 of the appendix.

Fractionation between H_2O and HDO occurred during the process of sublimation. There was also a loss of mass from the styrofoam container. The third experiment shows a loss of 276 g of snow. Frost collected from the side of the freezer was 9‰ lighter than the snow in the container.

Figure 15 indicates that there was a total sublimation of the lower 30-50 mm of snow in experiment three. A close look at figure 9 shows similar gaps near the bottom of the snow at the end of experiment two. This phenomenon was not noticed at the conclusion of experiment one.

DISCUSSION

Some terms should be defined to prevent confusion. SUBLIMATION, to pass directly from the solid to the vapor state or to pass directly from the vapor to the solid state. FRACTIONATION BY DIFFUSION, fractionation while the different types of water molecules move through air. FRACTIONATION DURING DIFFUSION, fractionation from the preferential sublimation of the heavier molecules onto and the lighter molecules from the matrix of snow crystals during the diffusion of the vapor through the snow.

The data presented suggests four conclusions from this study:

1. Fractionation and vapor transport occurring during depth hoar formation could contribute to the homogenization of deuterium in the snowpack.

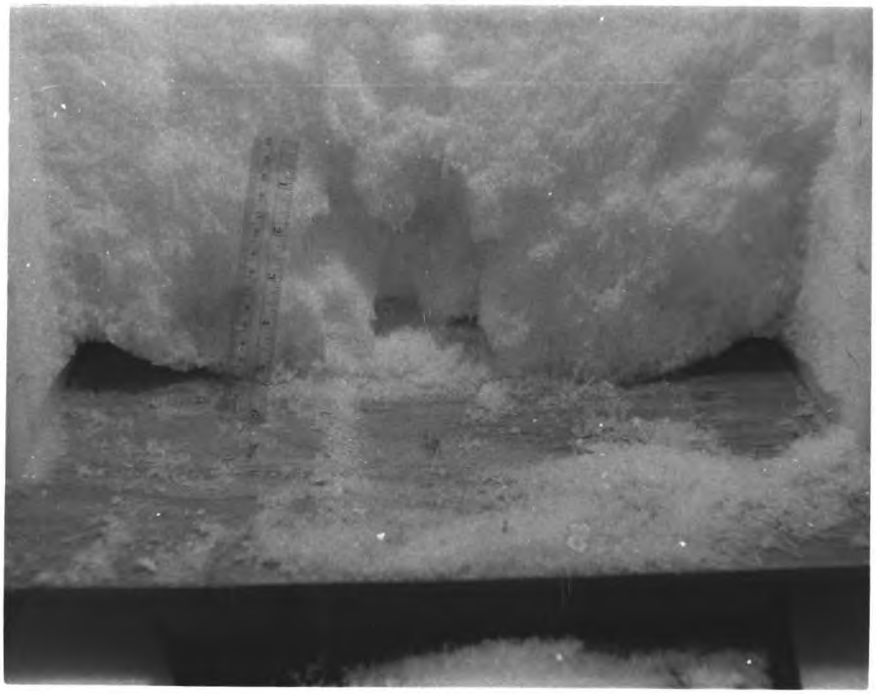


Figure 15. The gaps under the snow at the end of the third depth hoar experiment. The snow near the sides of the container was prevented from settling because of a bonding between the snow and the styrofoam.

2. Fractionation by sublimation is the basic process causing the isotopic fractionation occurring during depth hoar formation.
3. When depth hoar formation occurs over a dry substrate there is a total loss of mass from the lower part of the snowpack.
4. The continuous diffusion of material was more important as a mechanism of depth hoar formation than the crystal-to-crystal transfer of mass.

The redistribution of the deuterium content of the snow during depth hoar formation could be due to fractionation by sublimation or fractionation by diffusion. Ehhalt et al. (1964) found a slight difference in the diffusion constants of H_2O and HDO, but calculations indicate that for the relatively long time interval of the depth hoar experiments fractionation by the diffusion of the water vapor through air would be negligible (appendix, page 79). A short experiment was run (see next chapter) which indicated that fractionation would occur during sublimation from a snow surface.

The deuterium profiles show a concentration of HDO in the lower part of the snow. There appears to be a relationship between the height of the point of transition from increased to decreased HDO content and the density of the snow. This suggests the more dense the matrix of snow the quicker the deposition of the material occurs.

The total sublimation of the lower 20-50 mm of snow in experiments two and three provided a source of vapor which was light at first (preferential sublimation of H_2O) and quite heavy toward the end (the HDO had been concentrated in the last portion of the snow). There is probably a point where the concentration of HDO counteracts the fractionation factor and an equilibrium rate of sublimation between H_2O and HDO is approached.

The lack of depth hoar in the lower part of experiment one is puzzling. The higher temperatures in the lower part of the snow would indicate a greater potential for vapor transport, but the lower layer of snow was rather dense because of compaction when the upper layers of snow were added. Apparently the theory of Yosida et al. (1955), that density would not be a limiting factor in depth hoar formation because sublimation from the area around the developing depth hoar crystal provides a small cavity for the crystal to grow in, was not valid in this experiment.

CHAPTER V

FRACTIONATION OF DEUTERIUM DURING SUBLIMATION

The flow chart used to guide the depth hoar experiments indicates a need to determine if H_2O and HDO are fractionated during the sublimation of snow.

Ragotzkie and Friedman (1965) and Ambach et al. (1968) discuss sublimation as a layer-by-layer removal of material from the surface of ice. This total removal of each layer of ice would mean fractionation could not occur during sublimation.

Nakaya and Matsumoto (1954) showed the existence of a quasi-liquid layer on the surface of ice, within which individual molecules and groups of molecules can move around. Cross (1969b) published several photographs of ice taken with a scanning electron microscope. The surface of polycrystaline ice has a very fibrous texture.

The combination of a quasi-liquid surface layer with the large surface area per unit volume presented by a fibrous texture may provide the necessary molecular exchange required for isotopic fractionation. A brief experiment was designed to measure any fractionation occurring during sublimation from a snow surface.

PROCEDURE

A plexiglass container was filled with snow and placed in the freezer. A hole was cut in another piece of plexiglass and a metal can fitted snugly into this hole. The second piece of plexiglass was placed on the container of snow so the bottom of the can was 10 mm from the surface of the snow and solid CO_2 placed in the can (see figure 16). A thermistor was placed in the snow to monitor its temperature.

The experimental setup was checked every few hours and additional solid CO_2 added when necessary. When the frost crystals had grown 4-5 mm outwards from the can, the frost was scraped into a 5 ml widemouth glass bottle. Immediately afterwards, the surface 3-4 mm of snow was removed and placed in another bottle. The samples were analyzed for deuterium as described previously.

RESULTS

Fractionation between H_2O and HDO did occur during sublimation from snow. The data on the experiment is given in table 3.

DISCUSSION

This experiment was preliminary in nature and should be repeated, but it indicates a substantial fractionation during sublimation from a snow surface.

Moser and Stichler (1970) mention that the ageing of snow in a freezer at -5° C caused fractionation with $\alpha =$

Figure 16. The plexiglass container used in the sublimation experiment. A foam rubber gasket sealed the area of contact between the cover and the cylinderical container. Dry ice was placed in can which is inserted part way through the cover.

Table 3. Data on the sublimation of snow.

Description of the snow: 0.5-1.0 mm lumps, same snow as used for the third depth hoar experiment except that it had undergone equi-temperature metamorphism for 35 days at -26° C.

Density of snow: 0.269 g/cm^3

Temperature of snow: -10° C

Temperature of depositional surface: -78° C

Time duration: 31 hours

Deuterium content, per mil relative to the standard used for the third depth hoar experiment:

surface of snow:	+3.4 +1.8	ave. = +2.6
frost deposited:	-94.4 -93.8	ave. = -94.1
snow:*	-2.8	-2.8
std. #3:**	-4.4 -3.6	ave. = -4.0

Fractionation factor:

$$\alpha = \frac{HDO/H_2O \text{ of source}}{HDO/H_2O \text{ of deposition}}$$

$$\alpha = 1.11$$

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* a sample of the snow that had been stored in the freezer for use in this study, this value should fit within the range of values given for the original snow for the third depth hoar experiment.

** see std. #3 under the data for the third depth hoar experiment on page 100 of the appendix.

1.10 to 1.11 for a snow-vapor system. The fractionation factor is the same as was determined in this study, but they give no details about their sampling technique.

During this study approximately 3000 g of snow with a deuterium content of -171.2‰ to -174.5‰ ΔD, SMOW was stored in a polyethylene sack in the freezer at -26° C. After 35 days a sample of the snow from near the plastic-snow interface was removed and analyzed for its deuterium content. This fell within the 3.3‰ variation of the original snow.

CHAPTER VI

VARIATION OF DEUTERIUM WITH ALTITUDE

A variation of the isotopic content of precipitation with elevation is commonly mentioned in the literature. It was decided that this should be investigated in the Rocky Mountains as a knowledge of altitudinal and related areal variations in the deuterium content of snow would be important in snow hydrology studies.

PROCEDURE

Samples were taken along U.S. 6, a major road going west from Denver, Colorado, and crossing the Continental Divide. U.S. Geological Survey topographic maps were used to determine the elevations of the sample points. The samples were stored in glass bottles and analyzed as described previously.

RESULTS

Figure 17 shows a plot of the deuterium content along with a plot of the elevation of the sample points. There is no obvious relation between the deuterium content of the snow and the elevation of the sample point.

Table 4 gives a description of the snow found at each sample site as well as the time and location of each sample.

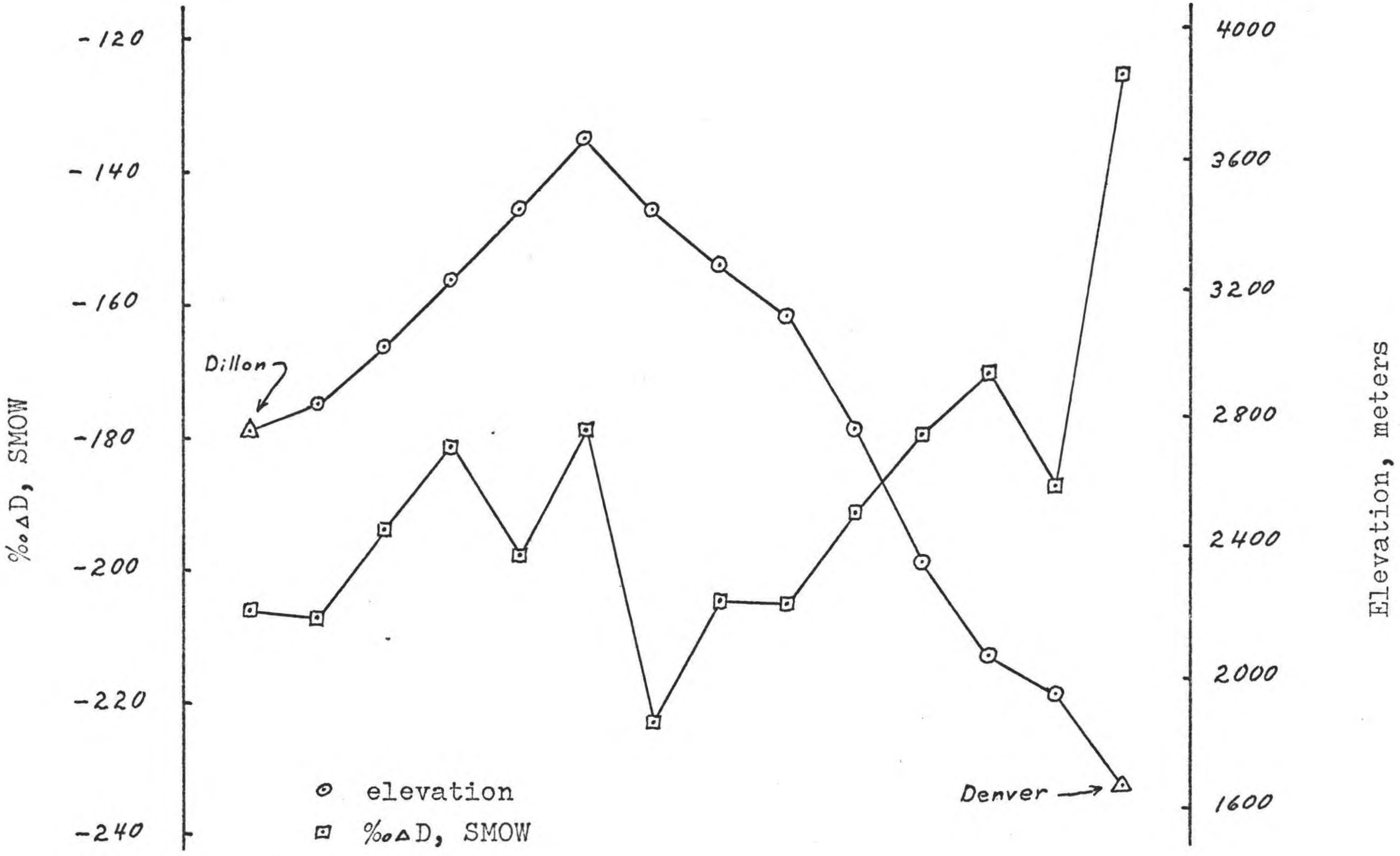

Figure 17. The HDO content of snow samples taken on a transect over Loveland Pass, Colorado during the snowstorm of April 3, 1968.

Table 4. Data about the snow samples taken on a transect over the Continental Divide on April 3, 1968.

‰ ΔD SMOW	Time, MST	Elevation, Meters	Location	Comments
-125	8:25 am	1,670	Federal Center	Spatial dendrites -3° C
-191	9:30 am	2,760	Silver Plume	From cornice -- may be wind blown -- not snowing
-205	9:50 am	3,240	Loveland Basin	Not snowing -- 24 mm new snow -- no wind -- a little destructive metamorphism
-223	10:00 am	3,420	Loveland Pass	0.5-1.0 mm spatial dendrites with a little destructive metamorphism; no wind; sunny; 100 mm snow
-179	10:15 am	3,640	Loveland Pass	Spatial dendrites; 0.5-1.0 mm -13° C; small drifts by restroom
-198	10:25 am	3,430	2.1 km above Arapahoe Basin	0.5-1.0 mm spatial dendrites; 100 mm snow
-181	10:35 am	3,210	1.3 km west of Arapahoe Basin	0.5-1.0 mm spatial dendrites with some destructive metamorphism; 125 mm snow
-194	10:50 am	3,000	At spring west of Arapahoe Basin	As above; 50 mm snow; -7° C

Table 4, continued.

‰ △ D SMOW	Time, MST	Elevation, Meters	Location	Comments
-207	11:00 am	2,820	At Montezuma Highway	As above; 25 mm snow
-206	11:20 am	2,720	Lake level Dillon Reservoir	Drifting snow off lake
-205	12:05 pm	3,080	East of Loveland Pass at campground	Spatial dendrites, some metamorphism; 75 mm snow
-180	4:55 pm	2,340	U.S. 40, Genesee Park	Slight snow fall of 0.5-1.0 mm spatial dendrites; on ground, 0.5-1.0 mm spatial dendrites, also needles and plates of 1-2 mm; 25 mm snow; -7° C
-170	5:05 pm	2,060	U.S. 40	Medium snowing; 1-2 mm plates and stellors, 0.5-1.0 mm spatial dendrites; -6° C; 75 mm snow
-187	5:15 pm	1,940	U.S. 40 and Colo. 26	As above; light snowing; -5° C; 40 mm snow

DISCUSSION

This study indicates a complex relation, dependent upon air mass movements, between the deuterium content of snow and elevation.

On the eastern slope of the Rocky Mountains it is difficult to determine if an air mass from the Gulf of Mexico is acting as a source of vapor for a snow storm. It is believed that air masses originating over the gulf sometimes move up some valleys to elevations as high as 3000 m. Thus snow in the valley may be from an isotopically heavy source while snow at higher elevations may be from an air mass which has traveled over several mountain ranges since originating in the northern Pacific.

For the storm studied, the high deuterium content (-125‰) of the snow at the Denver Federal Center suggests the presence of a Gulf of Mexico air mass along the eastern edge of the mountains. The weather map (figure 18) shows a low pressure area centered on eastern Colorado.

A recent study by Ambach et al. (1968) indicated a lack of any altitudinal effect on the deuterium content of snow. On the contrary, Moser and Stichler (1970) noted a decrease of 4‰ ± 2‰ ΔD, SMOW per 100 m rise in elevation for snow.

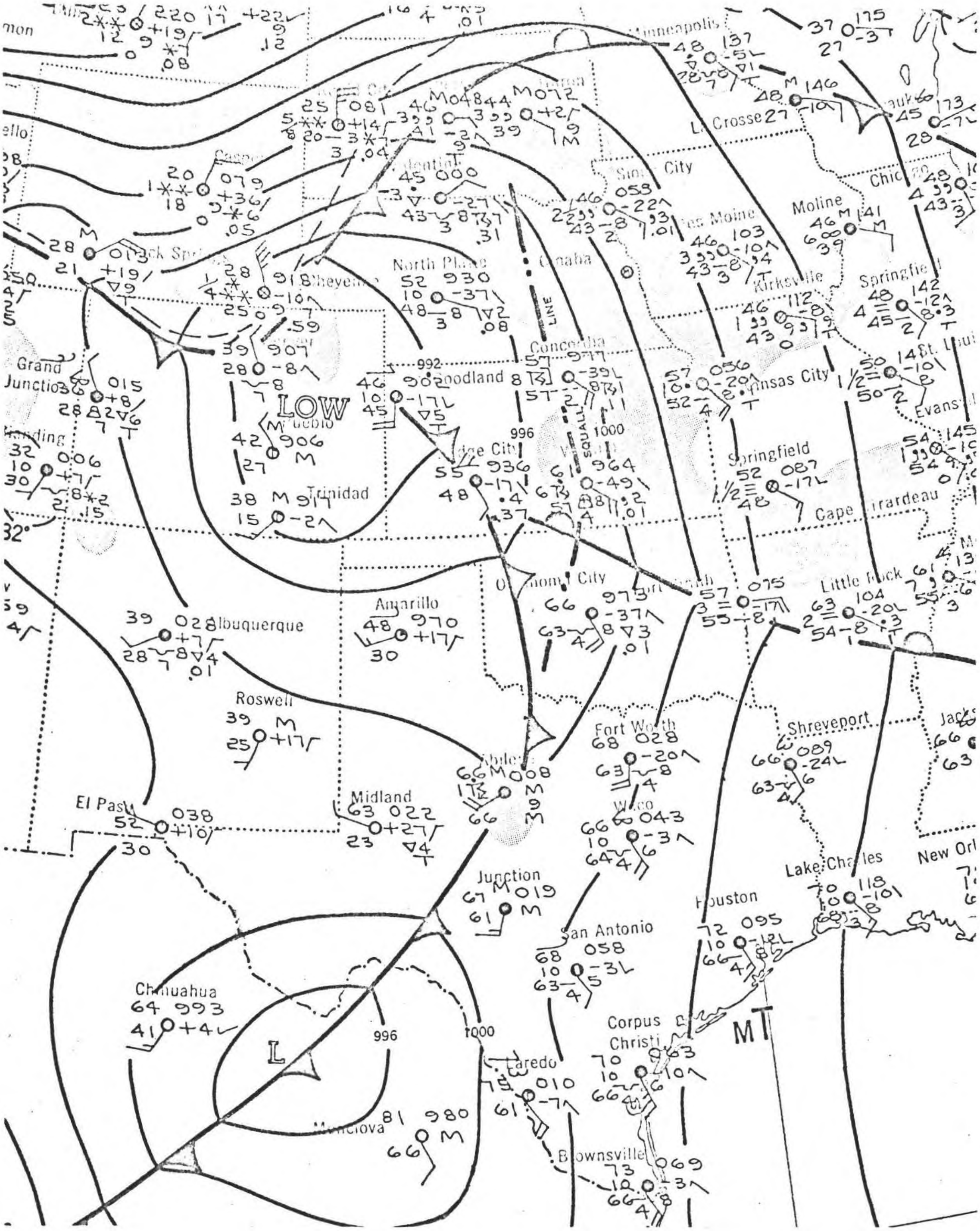

Figure 18. U.S. Weather Bureau surface weather map for April 3, 1968. The wind direction arrows indicate a flow of air from the Gulf of Mexico north through Kansas, turning to the west in Nebraska, and then south along the mountains in Colorado.

CHAPTER VII

SUMMARY

The results of this study indicate that deuterium may be a useful tracer in snow hydrology studies. Several conclusions may be derived from the data gathered.

There is a great variability in the original deuterium content of snow. This variability is shown by the differences between individual storms (-229‰ to -106‰) at a given location. The metamorphism of the snowpack reduced this variation to a spread of -182‰ to -158‰. This homogenization of the snowpack greatly reduces the original isotopic variability of the snow and is due mainly to the percolation of melt water.

Vapor transport during depth hoar formation may cause some homogenization in the lower part of the snowpack before melt occurs. It was shown that isotopic fractionation and mass transfer did occur over measurable distances during depth hoar formation. The isotopic fractionation results from a fractional sublimation occurring during the movement of water vapor through the snow matrix.

The spatial variability of the deuterium content of snow was shown by the variation of -223‰ to -125‰ within one day's snow from a complex storm system. The samples were taken on a transect over the Continental Divide in the

Rocky Mountains of Colorado which covered an east-west distance of 78 km and a vertical change to 1970 m. No clear relationship existed between the altitude of the sample point and the deuterium content of the snow.

CHAPTER VIII

RECOMMENDATIONS FOR FUTURE WORK

Several types of field and laboratory studies are needed to further our knowledge about the use of deuterium in hydrologic studies. The most basic recommendation is that some of these studies be cooperative projects with the meteorologists and physical chemists. The following suggestions are not given any order of priority. Each has a special value to certain people.

1. Obtain areal and altitudinal variations in the deuterium content of a mountain snowpack by using the cores from snow tubes to give a vertically integrated sample of the snowpack. This study should be coordinated with samples of the streamflow from the basin.

2. Find out how the melt water behaves when it enters the soil. Can the snowmelt contribution be separated from previous rainfall moisture? How fast does the melt water front move? How far can it be traced?

3. Determine what atmospheric conditions cause changes in the deuterium content of the precipitation. This is a difficult question. Whenever deuterium samples of individual storms are taken, a meteorologist should be working with the project.

4. Repeat the sublimation experiment under more carefully controlled conditions.

5. Develop a working vapor transport - mass balance model of a mountain snowpack undergoing constructive metamorphism.

6. Determine the magnitude of the soil moisture contribution to a snowpack undergoing constructive metamorphism.

7. Investigate easier or cheaper methods of analysis for HDO, possibilities might be neutron activation (Baranov et al., 1959) or Raman spectral analysis.

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APPENDIX

Page

THE OCCURRENCE OF THE ISOTOPES OF HYDROGEN AND OXYGEN

	Lorius (1963)*	Rankama (1963)**	Handbook of Chemistry & Physics (1968)**
H^1	99.9839%	99.9844%	99.985%
H^2	0.0161%	0.0156%	0.015%
H^3	(half-life of 12.26 yr.)		
O^{16}	99.76%	99.7590%	99.759%
O^{17}	0.04%	0.0374%	0.037%
O^{18}	0.20%	0.2039%	0.204%

(several oxygen isotopes with half-lives of under three minutes)

THE OCCURRENCE OF SELECTED FORMS OF WATER

	Hutchinson (1957)
H_2O	99.745%
H_2O^{18}	0.198%
HDO	0.015%
D_2O	0.000002%

* Believed to refer to the distribution of isotopes in ocean water.

** Believed to be a weighted average for the entire earth.

DEFINITION OF SMOW

Standard Mean Ocean Water (SMOW) is the standard that all samples are defined relative to. The notation; ‰ Δ D, SMOW; is often used. This shows the per millage that the HDO content of the sample deviates from the HDO content of SMOW.

$$‰\ \Delta\ \mathrm{D,\ SMOW} = \left[\frac{\left(\mathrm{D\ sample}/\mathrm{H\ sample}\right) - \left(\mathrm{D\ SMOW}/\mathrm{H\ SMOW}\right)}{\left(\mathrm{D\ SMOW}/\mathrm{H\ SMOW}\right)}\right]\left[1000\right]$$

SMOW is defined relative to a set of samples furnished by the National Bureau of Standards. Craig (1961b) describes the proper procedure for presenting the results of HDO determinations. He also describes the HDO content of SMOW as follows:

SMOW = 158 ± 2 parts per million atomic (ppma) HDO
the D/H ratio of SMOW = 1/6328

Other authors have considered SMOW to contain from 157 ppm to 161 ppm HDO.

Russian literature often describes samples as being so many γ different than the standard. Rankama (1963) describes the procedure.

γ = 0.000927 mole percent HDO. It is a measure of the ppm difference between the sample and the standard.

```
CLARK JUDY   VAPOR PRESSURES
 TEMP     HHO          HDO-M     HDO-K        AVE        HDO-V   F IN VAP    DEP BY

 -30.0    .2859        .2380     .2386       .2383       .2372   .000125    .166479

 -29.0    .3171        .2646     .2651       .2649       .2636   .000125    .164770

 -28.0    .3514        .2939     .2943       .2941       .2928   .000126    .163064

 -27.0    .3891        .3261     .3265       .3263       .3249   .000126    .161361

 -26.0    .4305        .3616     .3619       .3617       .3602   .000126    .159662

 -25.0    .4758        .4006     .4008       .4007       .3990   .000126    .157965

 -24.0    .5256        .4434     .4435       .4435       .4416   .000127    .156272

 -23.0    .5800        .4904     .4904       .4904       .4884   .000127    .154582

 -22.0    .6396        .5419     .5418       .5419       .5397   .000127    .152896

 -21.0    .7048        .5984     .5981       .5982       .5958   .000127    .151213

 -20.0    .7760        .6602     .6597       .6600       .6573   .000128    .149533

 -19.0    .8538        .7279     .7272       .7275       .7246   .000128    .147857

 -18.0    .9386        .8019     .8009       .8014       .7981   .000128    .146184

 -17.0   1.0311        .8827     .8814       .8821       .8785   .000128    .144515

 -16.0   1.1318        .9710     .9693       .9701       .9661   .000129    .142850

 -15.0   1.2415       1.0673    1.0652      1.0662      1.0617   .000129    .141188

 -14.0   1.3608       1.1722    1.1697      1.1710      1.1660   .000129    .139530

 -13.0   1.4905       1.2866    1.2835      1.2851      1.2795   .000129    .137875

 -12.0   1.6315       1.4111    1.4074      1.4093      1.4030   .000130    .136225

 -11.0   1.7845       1.5465    1.5422      1.5444      1.5374   .000130    .134579

 -10.0   1.9505       1.6938    1.6888      1.6913      1.6834   .000130    .132936

  -9.0   2.1306       1.8538    1.8479      1.8509      1.8420   .000130    .131298

  -8.0   2.3256       2.0275    2.0207      2.0241      2.0142   .000131    .129664

  -7.0   2.5369       2.2160    2.2082      2.2121      2.2009   .000131    .128033

  -6.0   2.7655       2.4204    2.4115      2.4160      2.4034   .000131    .126408

  -5.0   3.0128       2.6419    2.6318      2.6368      2.6227   .000131    .124786

  -4.0   3.2800       2.8818    2.8703      2.8761      2.8601   .000132    .123170

  -3.0   3.5687       3.1415    3.1284      3.1349      3.1170   .000132    .121557

  -2.0   3.8803       3.4224    3.4075      3.4149      3.3949   .000132    .119949

  -1.0   4.2166       3.7260    3.7093      3.7176      3.6949   .000132    .118346

   0.    4.5791       4.0540    4.0352      4.0446      4.0191   .000132    .116749
```

FRACTIONATION FACTORS

The theoretical separation occurring between HDO and H_2O when water evaporates or sublimes is often given as a fractionation factor, α.

$$\alpha = \frac{(\text{D/H ratio of liquid})}{(\text{D/H ratio of vapor})}$$

Values of α from several sources are listed below.

	α, liquid/vapor		α, solid/vapor			
°C	A	B	A	B	C	D
-30	1.157		1.183	1.198		1.200
-25	1.147		1.173	1.185	1.187	1.187
-20	1.138	1.143	1.162	1.173	1.174	1.176
-15	1.128	1.133	1.152	1.162	1.161	1.164
-10	1.120	1.124	1.142	1.151	1.148	1.153
- 5	1.112	1.115	1.132	1.141	1.137	1.143
0	1.105	1.106	1.122	1.132	1.128	1.132
10	1.091					
20	1.078					
30	1.068					

A. Lorius (1963)
B. Merlivat and Nief (1967)
C. Matsuo et al. (1964)
D. From previous page, the value of HHO/AVE

CRITICAL DATA

The units are degrees Celsius or calories/mole.

	H_2O	HDO	D_2O
Melting Point	0.00	2.32[2]	3.85[2] 3.82[11]
Heat-melting	1436[1]		1515[1]
Boiling point	100.00[3]	100.76[3]	101.55[3] 101.42[10]
Heat-vaporization	9719[3]	9849[3] 9847[4]	9927±20[1]
Heat-sublimation	12,170[1]	12,401[8]	12,631±20[1] 12,584±72[1]
Heat-formation[9], liquid phase		+15.5[5] -28[6]	
gas phase		+34[7]	

1 Kirshenbaum (1951)
2 Van Hook (1968), theoretical
3 Riesenfeld and Chang (1936)
4 Wahl and Urey (1935)
5 Skripov (1962), experimental
6 Skripov (1962), theoretical
7 Skripov (1959), theoretical
8 Calculated from a plot of log P vs 1/T
9 For the reaction $H_2O + D_2O \rightleftharpoons 2\ HDO$
10 Lewis and MacDonald (1933)
11 Long and Kemp (1936)

EQUILIBRIUM REACTION

If some D_2O is put into H_2O, a reaction takes place and most of the D_2O is converted to HDO.

$$H_2O + D_2O \rightleftharpoons 2\ HDO$$

The mole fraction of each component is given by the equation:

$$K = \frac{(HDO)^2}{(H_2O)\ \ (D_2O)}$$

The K values mentioned in the literature fall in the following ranges:

0° C K = 3.76 to 4.15

25° C K = 3.26 to 4.0

These values were determined by several scientists and are referenced in Kiss et al. (1966) and Skripov (1959).

Using K = 4.0 and the HDO content of water as 0.000158 mole fraction, the calculated D_2O content of water is:

$$4.0 = \frac{(0.000158)^2}{(0.999842)\ (D_2O)}$$

$$D_2O = 0.00000000624$$

Therefore Standard Mean Ocean Water would contain:

0.00000000624 mole fraction D_2O

0.000000624 mole % D_2O

0.00624 ppma D_2O

DIFFUSION COEFFICIENTS

The following diffusion coefficients are for an equation of the type: $R = -D\ (dc/dx)$

The units are cm^2/sec.

H_2O in air at 273° K. . . . . D = 0.220 (1)

at 8° C. . . . . D = 0.239 (6)

H_2O, self-diffusion at 17.5° C. . D = 1.77×10^{-5} (2)

HDO in water at 10° C . . . . . . D = 1.57×10^{-5} (2)

at 18° C . . . . . . D = 2.06×10^{-5} (2)

at 1° C . . . . . . D = 1.128×10^{-5} (4)

at 25° C . . . . . . D = 2.261×10^{-5} (4)

HDO in ice at -2° C . . . . D = 1.0×10^{-10} (3)

HTO in ice at -2° C . . . . D = 3.2×10^{-11} (5)

These diffusion coefficients are assumed to be correct for sea level conditions. International Critical Tables gives the following equation for correcting the diffusion coefficient of water in air to other pressures and temperatures.

$$D = (D_{273})\ (T/273^{\circ})^{1.75}\ (760\ \text{mm}/P)$$

H_2O in air at 623 mm Hg and 273° K: D = 0.268 cm^2/sec

623 mm Hg and 263° K: D = 0.251 cm^2/sec

1 International Critical Tables (1928)
2 Wang et al. (1953)
3 Kuhn and Turkauf (1958)
4 Longsworth (1954)
5 Ramseier (1967)
6 Handbook of Chemistry and Physics (1968)

Ehhalt et al. (1964) give the ratio of the diffusion coefficients of HDO and H_2O in air:

$$D_{H_2O} / D_{HDO} = 1.015 \text{ at } 20^{\circ} \text{ C}$$

The use of this ratio would give a diffusion coefficient for HDO in air, at 623 mm Hg and 263° C of:

$$D_{HDO} = 0.247 \text{ cm}^2/\text{sec}$$

The diffusion equation, $R = -D\,(dc/dx)$, previously mentioned is Fick's First Law and deals with rates of diffusion. Fick's Second Law yields an equation which can be integrated and used to provide an estimate of the concentration of a material some distances from its source.

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

$$\ln C = -\frac{x^2}{4Dt} + \ln \frac{C_o}{(\pi Dt)^{\frac{1}{2}}}$$

C = concentration of material at distance x

C_o = concentration of material at the source

x = distance in centimeters

t = time in seconds

D = diffusion constant in cm^2/sec

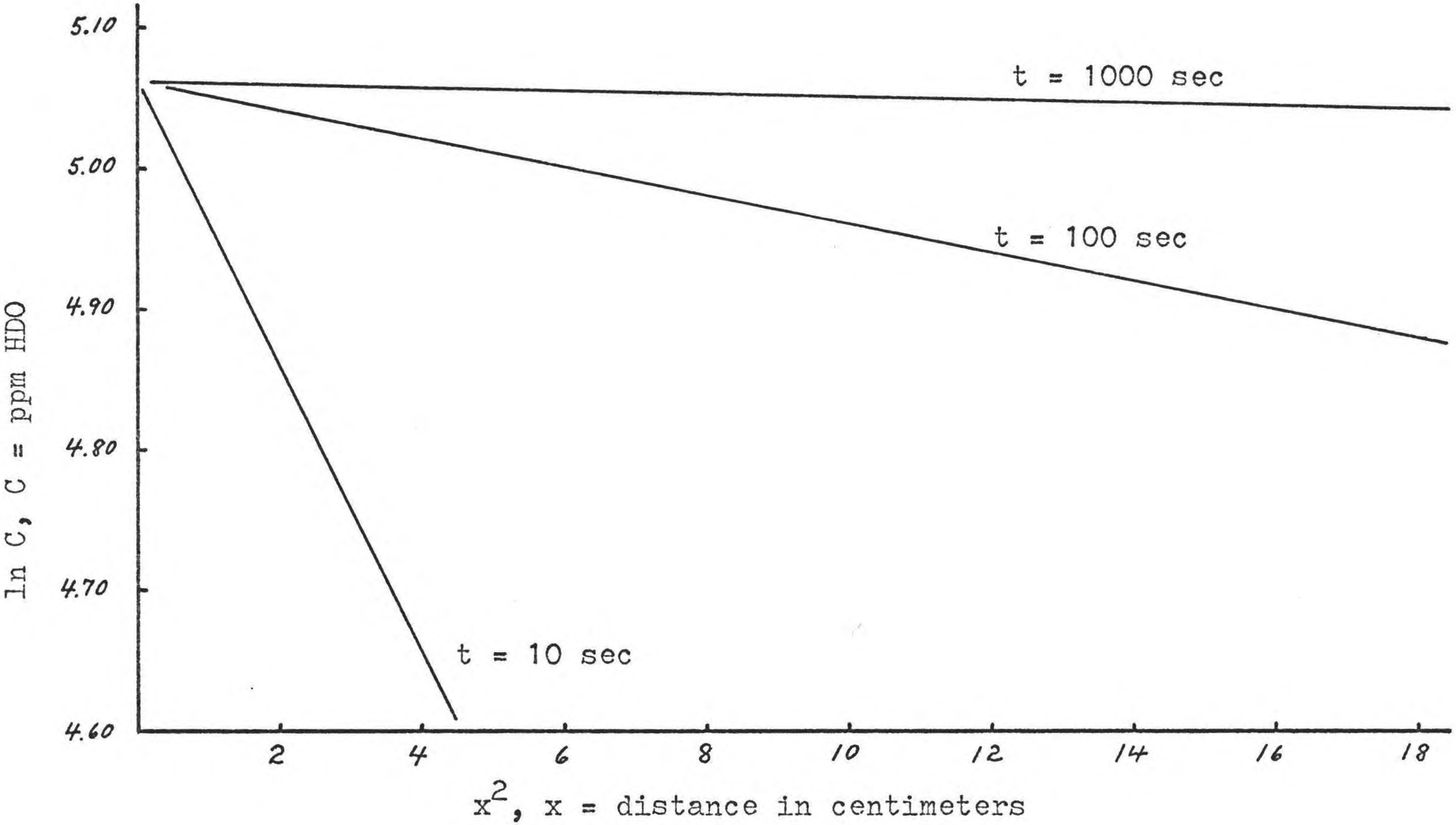
Two conditions were implied when the equation for Fick's Second Law was integrated: that at $t = 0$, $C = 0$ except at $x = 0$, and that C is infinite. As the boundary condition of an infinite concentration cannot be fulfilled, the equation is invalid at the extremes. As used by Ramseier (1967) the boundary conditions are not critical as he was working with very small diffusion coefficients (on the order of 10^{-10}). When diffusion coefficients of 0.1 to 1.0 are used along with a time period of 100,000 seconds, the first term of the equation drops out.

The rate of diffusion of HDO can be illustrated if a graph of concentration versus distance is plotted. The integrated diffusion equation resembles the equation for a straight line, $y = mx + b$, with:

$y = \ln C$ $\quad x = x^2$ $\quad m = 1/4Dt$ $\quad b = \ln C_o$

Or, $\ln C = (1/4Dt)(x^2) + \ln C_o$

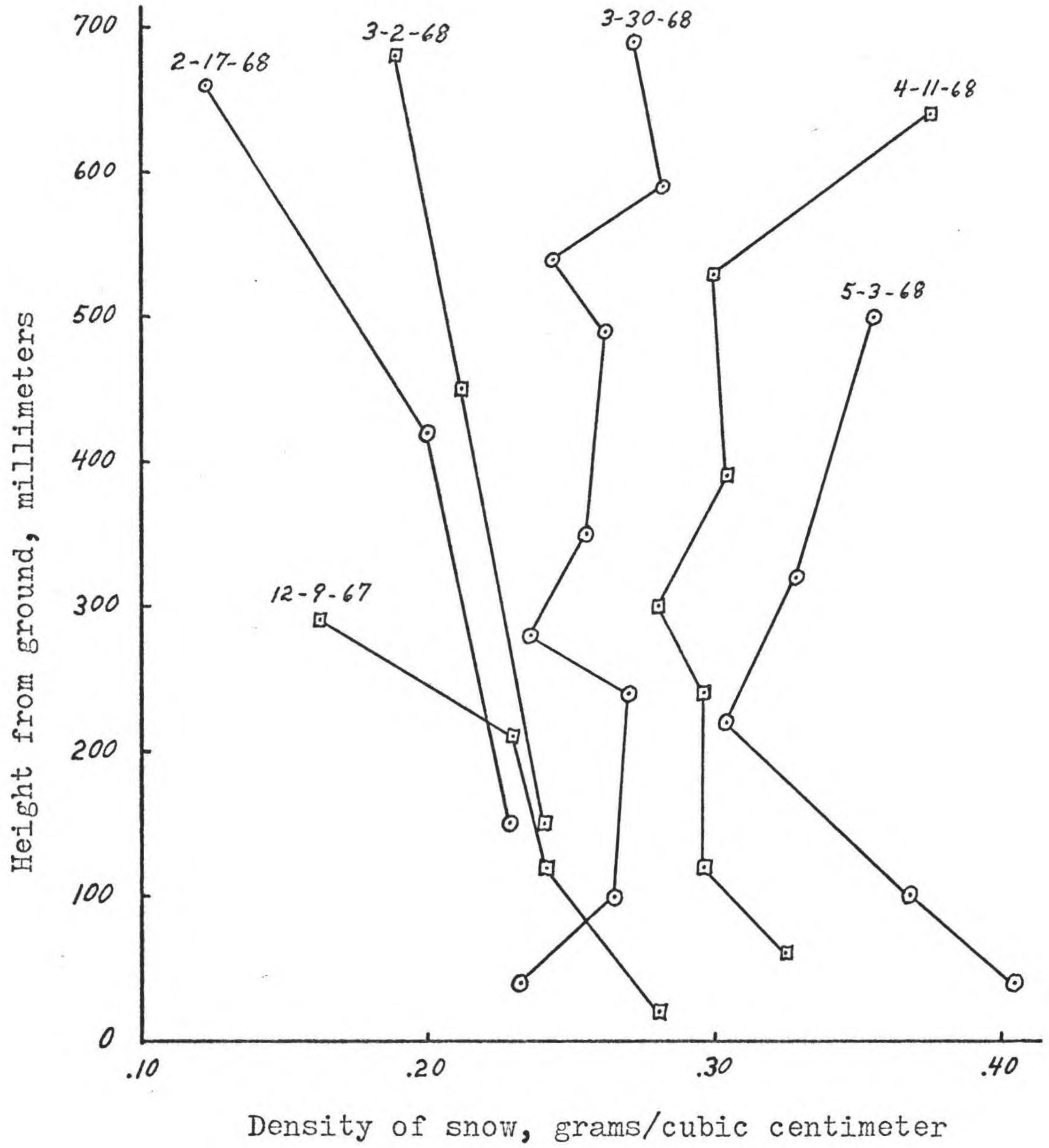
The plot of this equation on the next page for the diffusion of HDO vapor in air shows that for the periods of time involved in the depth hoar experiment, the concentration of HDO at one to five centimeters from the source is virtually the same as at the source. Therefore, any measurable fractionation between HDO and H_2O would appear to be due to the differences in vapor pressures, not because of differences in the rate of movement of the molecules through the air between the snow crystals.



A plot of ln C versus x^2 for the diffusion of HDO in air at -10° C. It is based on Ramseier (1967) and shows the lack of fractionation for time durations greater than 1000 seconds.

Snowpack temperatures, in degrees Celsius, taken at the Pingree Park sample site during the winter of 1967-1968.

Height from ground, mm	Date of Measurement							
	12/1	12/9	1/19	2/3	2/17	3/2	3/15	3/30
surface	-8.3	-6.7	---	-4.0	-4.5	+0.6	-1.6	---
700						-1.1	0.0	0.0
600					-4.0	-4.5	0.0	0.0
500			-3.9	-3.8	-3.2	-2.8	0.0	0.0
400			-6.7	-3.0	-2.5	-1.7	+0.2	0.0
300	-7.8	-8.9	-4.5	-2.2	-1.8	-0.8	+0.2	0.0
200	-4.5	-5.6	-2.8	-1.0	-0.7	-0.3	+0.2	0.0
100	-2.8	-2.8	-0.6	-0.8	-0.5	0.0	0.0	0.0
0	-1.7	-1.1	0.0	-0.3	0.0	0.0	0.0	0.0



Selected snowpack density profiles from the Pingree Park sample area.

RATE OF DEPTH HOAR FORMATION

Giddings and LaChapelle (1962) present a formula for the computation of the formation rate of depth hoar.

$$t = \frac{37\ d\ p}{P\ (\Delta T/\Delta Z)} \left(1 + \frac{T_c^{3/2}}{21.5}\right)\left(\frac{\rho}{.28}\right)$$

t = time of formation, days

p = local atmospheric pressure

P = atmospheric pressure at sea level

$\Delta T/\Delta z$ = temperature gradient, $^{\circ}C/cm.$

T_c = negative of snowpack temperature, $^{\circ}C$

d = thickness of layer (average crystal size), cm.

ρ = density of the developed depth hoar layer

The authors use a diffusion coefficient of 0.22 $cm^2/sec.$ at 0° C and 760 mm Hg. The term $(1 + T_c^{3/2}/21.5)$ accounts for the variation of vapor pressure with temperature. The term $(\rho/0.28)$ has been added as a correction for the density of the snow as the authors assumed a density of 0.28 g/cm^3.

If an atmospheric pressure of 623 mm Hg. is assumed for Fort Collins, Colorado, the formula becomes:

$$t = (30.34)\ (d)\ (\Delta z/\Delta T)\ (\rho)\ (1 + T_c^{3/2}/21.5)$$

Data from the experiments was used to obtain the calculated time at which the initial snow grains would have been completely replaced by depth-hoar crystals deposited from water vapor.

Experiment 1: $\rho = 0.30$ $T = -15.5^{\circ}C$ $\Delta T/\Delta Z = 0.7^{\circ}C/cm$

$d = 0.2$ cm

$t = (30.34)\ (0.2)\ (1.429)\ (0.30)\ (1 + 2.702) = 33.68$ days

actual duration = 33 days

Experiment 2: $\rho = 0.24$ $T = -14.1^{\circ}C$ $\Delta T/\Delta Z = 0.8^{\circ}C/cm$

$d = 0.4$ cm

$t = (30.34)\ (0.4)\ (1.25)\ (0.24)\ (1 + 2.463) = 45.02$ days

actual duration = 28 days

Experiment 3: $\rho = 0.19$ $T = -14.2^{\circ}C$ $\Delta T/\Delta Z = 0.95^{\circ}C/cm$

$d = 0.4$ cm

$t = (30.34)\ (0.4)\ (1.053)\ (0.19)\ (1 + 2.489) = 30.27$ days

actual duration = 31 days

HDO VERSUS H_2O AS A VAPOR SOURCE FOR DEPTH HOAR FORMATION

The Giddings and LaChapelle (1962) formula can be used to show the different rate at which depth hoar will form if HDO is used as a source of vapor instead of H_2O. First the formula is set up to show its basic components. Then the diffusion coefficient, heat of sublimation, and vapor pressure for HDO are substituted in place of the values for H_2O. If the formula is solved for ρd instead of t, for both HDO and H_2O, the differences in the amounts of mass transported can be determined.

$$t = \frac{\rho d}{J} = \frac{\text{amount of mass transported}}{\text{rate of transport}}$$

$$J = \left(\frac{D\ e_s\ L}{R^2\ T^3}\right)\left(\frac{p}{P}\right)\ \frac{dT}{dZ}$$

If: $T = 273^{\circ}$ $\quad P = 760$ mm $\quad p = 623$ mm

$$J = \left(\frac{D\ e_s\ L}{R^2}\right)\ (4.03 \times 10^{-8})\ \ \frac{dT}{dZ}$$

$t = \rho d/J$ or $\rho d = t\,J$ = the total mass flux over a period of time

$$\rho d = (t)\,(8.64 \times 10^{4}\ \text{sec/day})\ \frac{D\,e_s\,L}{R^2}\ \frac{\Delta T}{\Delta Z}\ \ (4.03 \times 10^{-8})$$

$$\rho d = (t)\left(\frac{D\,e_s\,L}{R^2}\right)\left(\frac{\Delta T}{\Delta Z}\right)\ \ (3.482 \times 10^{-3})$$

Substituting the values for HDO into the last equation.

$t = 30$ days

$\Delta T/\Delta Z = 0.95^{\circ}/\text{cm}$

$R = 4.38 \times 10^{6}$ ergs/g-$^{\circ}$K

$D = 0.264\ \text{cm}^2/\text{sec}$

$e_s = 5.40 \times 10^{3}\ \text{dynes/cm}^2$

$L = 2.732 \times 10^{10}$ ergs/g

$$\rho d = (30)\left(\frac{(0.264)(5.40 \times 10^{3})(2.732 \times 10^{10})}{1.918 \times 10^{13}}\right)(0.95)(3.482 \times 10^{-3})$$

$$\rho d = 0.2015\ \text{g/cm}^2$$

Substituting the values for H_2O.

$t = 30$ days
$\Delta T/\Delta Z = 0.95^{\circ}/cm$
$R = 4.62 \times 10^{6}$ ergs/g-°K
$D = 0.268\ cm^2/sec$
$e_s = 6.11 \times 10$ dynes/cm^2
$L = 2.732 \times 10^{10}$ ergs/g

$$\rho d = (30)\left(\frac{(0.268)(6.11 \times 10^{3})(2.732 \times 10^{10})}{2.134 \times 10^{12}}\right)(0.95)(3.482 \times 10^{-3})$$

$\rho d = 0.2155\ g/cm^2$

Changing to moles of material transported.

$$\frac{0.2015}{19} = 0.010606 \text{ moles HDO/cm}^2$$

$$\frac{0.2155}{18} = 0.011972 \text{ moles H}_2\text{O/cm}^2$$

Ratio of H_2O to HDO transported.

$$\frac{0.011972}{0.010606} = 1.129$$

Depth Hoar Experiment #1

Initial snow: 0.4 - 0.8 mm diameter angular crystals, more like very small pieces of ice than lumps of snow

Initial density: 0.318 g/cm^3

Final density: 0.334 g/cm^3

Time under temperature gradient: 33 days

Total mass of the snow:

initial	12,990 g
final	12,490 g
loss	500 g

Comments:

The density of the entire mass of snow was assumed to be the same as the density of the lower 250 mm of snow.

Visual description of final crystal type for the first depth hoar experiment.

270 - 300 mm: 0.4 - 1.0 mm slightly rounded, angular crystals

220 - 270 mm: 1.0 mm angular crystals with some depth hoar features

100 - 220 mm: approximately 50% depth hoar of 1 - 2 mm
many 0.5-1.0 mm angular crystals

40 - 100 mm: approximately 25% depth hoar
many 0.5 - 1.0 mm angular crystals
all crystals fused together

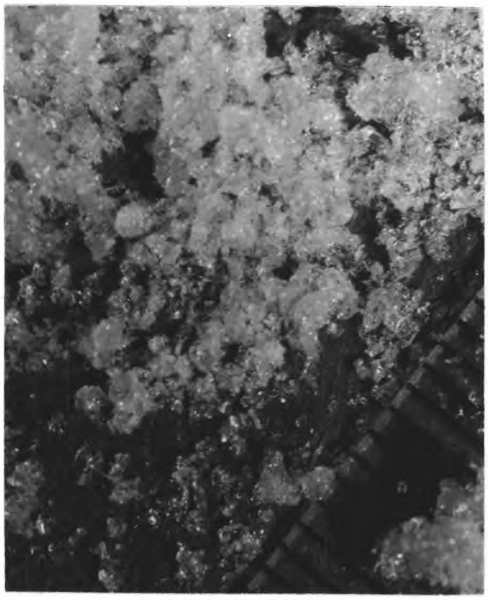
0 - 40 mm: 0.4 - 1.0 mm rounded crystals, 10% with depth hoar characteristics
all crystals fused together

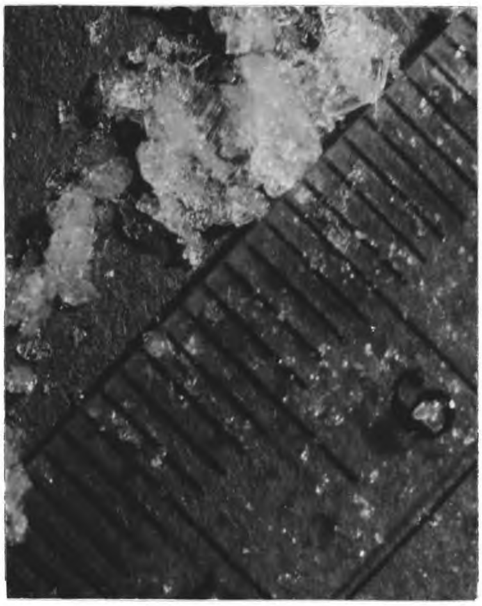
Comments:

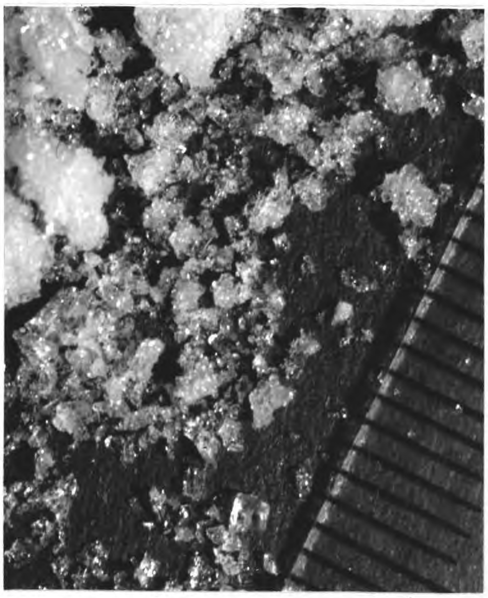
The 40 - 100 mm area contained 10% large (4 mm) plates.

The most depth hoar was in the area around 120 mm, where 80% of the snow was in noticeable plates. Few classic cup-like crystals were present anywhere in the snow.

Photographs were taken at 0, 80, 140, and 200 mm.







The deuterium analysis of the samples from the first depth hoar experiment. The results are given as the per mil deviation relative to SMOW.

Samples of the original snow.

Height	Individual runs	Average
150-200 mm	-110.9 -112.2	-111.5
100-150 mm	-111.3 -111.5	-111.4
50-100 mm	-126.4 -126.4	-126.4
0-50 mm	-124.3 -124.1	-124.2

Samples taken after depth hoar formation.

Height	Individual runs	Average
200 mm	-114.9 -114.4	-114.6
140 mm	-109.5 -110.0	-109.7
80 mm	-120.7 -120.0	-120.3
60 mm	-122.5 -122.9	-122.7
40 mm	-130.3 -129.4	-129.8
20 mm	-127.9 -128.4	-128.1
0 mm	-116.1 -116.9	-116.5

Depth Hoar Experiment #2

Initial snow: 0.5 - 0.9 mm diameter lumps without any noticable crystaline structure, approximately 1½ days since it fell as fresh snow

Initial density: 0.213 g/cm^3

Final density: 0.24 g/cm^3

Time under temperature gradient: 28 days

Total mass of the snow:

initial	8727 g
final	8387 g
loss	340 g

Comments:

The values given for the final density and final mass of the snow are of questionable accuracy.

Visual description of final crystal type for the second depth hoar experiment.

175 - 290 mm: 0.5 - 1.0 mm soft lumps

125 - 175 mm: transition zone,
rounded depth hoar of 1 - 4 mm

85 - 125 mm: 90% depth hoar of 2 - 5 mm

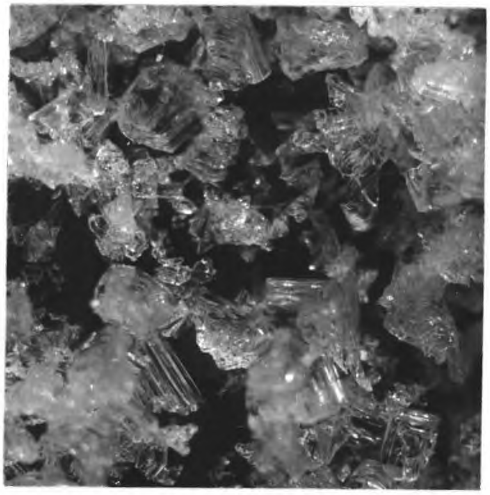
5 - 85 mm: 70% depth hoar of 3 - 8 mm
crystals noticeable fused together

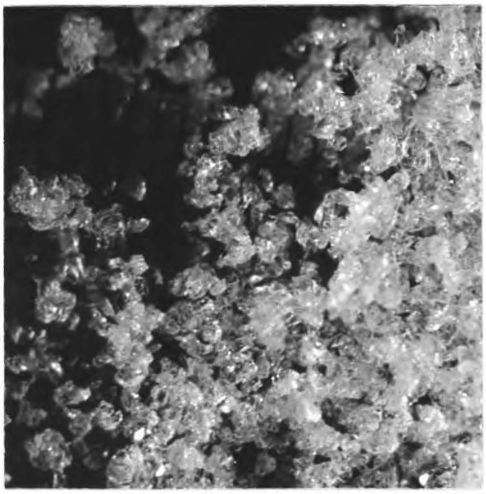
0 - 5 mm: 70% depth hoar of 3 - 8 mm
crystal structure rather fragile

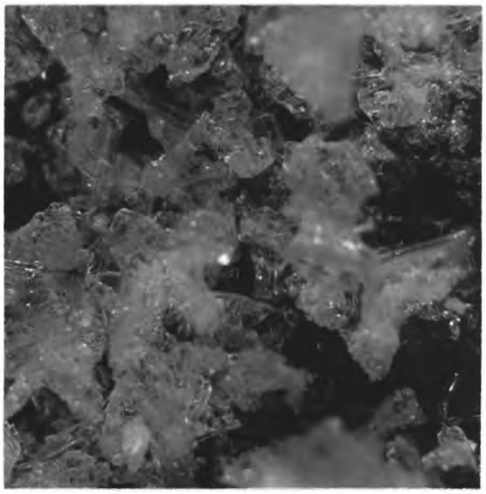
Comments:

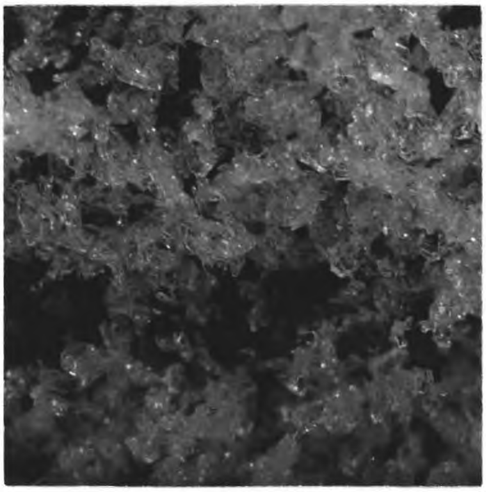
Photographs were taken at 0, 20, 40, 60, 80, 100, 120, 150, and 200 mm.

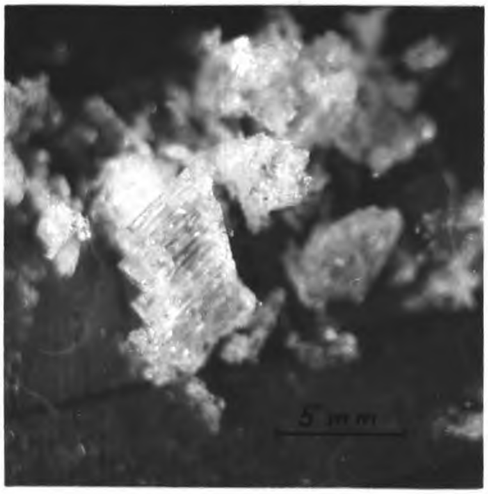
Evidence of total sublimation of the lower 20 - 30 mm of original snow.

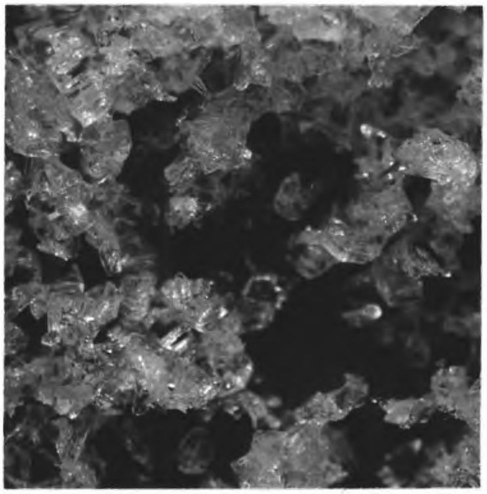









5 mm



The deuterium analysis of the samples from the second depth hoar experiment. The results are given as the per mil deviation relative to a sample of the original snow.

Samples taken after depth hoar formation.

Height	Individual runs	Average
200 mm	+3.6	+3.6
150 mm	-13.0	-13.0
100 mm	-8.6 -14.2*	-11.4
60 mm	-14.6	-14.6
40 mm	-23.8 -23.9*	-23.8
20 mm	-12.9 -12.1*	-12.5
10 mm	+0.5 -9.4*	-4.4
0 mm	+12.6	+12.6

Two samples of the original snow gave HDO measurements within 1.5‰ of each other. A third sample of the original snow, which had been kept in a polyethylene sack in the freezer for the duration of the experiment was analyzed and found to be -19‰ relative to the above standard.

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* sample was taken 25 to 30 mm to the left of the first sample in the set

Depth Hoar Experiment #3

Initial snow: 0.5 - 1.5 mm diameter feathery lumps, apparently dendritic stellars which had undergone some destructive metamorphism

Initial density: 0.141 g/cm^3

Final density: 0.197 g/cm^3

Time under temperature gradient: 31 days

Total mass of the snow:

initial	9966 g
final	9690 g
loss	276 g

Comments:

The surface of the snow had settled slightly by the thirteenth day of the experiment.

Weight measurements were made with a balance sensitive to 0.01 pound (4.5 g).

Visual description of final crystal type for the third depth hoar experiment.

160 - 245 mm: 0.5 - 1.0 mm soft lumps

120 - 160 mm: transition zone
rounded depth hoar of 1.0 mm

75 - 120 mm: 1 - 4 mm classic depth hoar

35 - 75 mm: 3 - 5 mm depth hoar
many stick-like or needle-like crystals

0 - 35 mm: 2 - 4 mm depth hoar with many "fuzzy" crystals
crystals slightly fused together

Comments:

Photographs were taken at 0, 20, 40, 60, 80, 100, 120, 160, 200, and 245 mm but were not in focus.

Evidence of total sublimation of the lower 20 - 40 mm of the original snow.

The 0 - 4 mm layer of final snow had a glazed appearance.

The deuterium analysis of the samples from the third depth hoar experiment. The results are given as the per mil deviation relative to an integrated sample of the entire mass of remaining snow and as the per mil deviation relative to SMOW.

Height	Individual runs	Average	SMOW
200 mm	-7.6 -7.6	-7.6	-178.9
100 mm	-8.6 -8.4	-8.5	-179.6
60 mm	-6.2 -6.2	-6.2	-177.7
40 mm	+8.4 +9.7	+9.0	-165.2
20 mm	+20.7 +20.5	+20.6	-155.6
10 mm	+26.6 +25.5	+26.0	-151.1
0 mm	+34.1 +33.7	+33.9	-144.7
frost*	-12.5	-12.5	-183.0
std. #1**			-174.5
std. #2**			-171.2
std. #3**	-3.9	-3.9***	-173.2
std. #4**			-172.0

* frost scraped from the side of the freezer at the end of the experiment

** random samples of the original snow

*** an indication of the difference between the original snow and the integrated snow sample taken at the end of the experiment