FLUCTUATION OF δ^{18} O OF SURFACE SNOW WITH SURFACE HOAR AND DEPTH HOAR FORMATION UNDER RADIATIVE COOLING

Akihiro HACHIKUBO¹, Hideaki MOTOYAMA², Keisuke SUZUKI³ and Eizi AKITAYA¹

¹Institute of Low Temperature Science, Hokkaido University, Kita-ku, Sapporo 060 ²National Institute of Polar Research, 9-10, Kaga 1-chome, Itabashi-ku, Tokyo 173 ³Department of Environmental Sciences, Faculty of Science, Shinshu University, 1-1, Asahi 3-chome, Matsumoto 390

Abstract: δ^{18} O and major ions of the snow surface layer were measured during hoarfrost formation. In the nighttime, δ^{18} O decreased when surface hoar and depth hoar crystals formed above and beneath the snow surface, respectively, while δ^{18} O increased due to evaporation in the daytime. These results suggested that H₂¹⁶O was enriched by condensation of the hoar crystals, whereas H₂¹⁸O was concentrated on the snow surface by the evaporation of light H₂O to the atmosphere. Concentrations of major ions were observed to change as well according to condensation and evaporation of water vapor. δ^{18} O of hoar crystals condensed on March 5 to 6 was estimated to be approximately 5‰ lower than that of the original surface layer.

1. Introduction

In ice core studies, the record of chemical substances has been of interest for the investigation of the past environment. Since oxygen isotopic ratios of deposited snow primarily depend on the condensation temperature of water vapor, we can estimate the variation of temperature with past time. On the other hand, AGETA (1993) concluded from analyses of deposited snow layers and drifting snow at Mizuho Station in Antarctica that sublimation was important to discuss the isotope profiles in the deposited snow. Sublimation and condensation at the surface or depth hoar formation beneath the surface may change the oxygen isotopic ratio there. In this study, we report how the $\delta^{18}O$ contents of the snow surface layer changes under sublimation in the daytime and under the condensation of surface hoar and depth hoar at night.

2. Observation Site and Methods

Observations were carried out from March 3 to 6, 1996 at the avalanche research station of Institute of Low Temperature Science in the Teshio Experimental Forest of Hokkaido University located in Toikanbetsu, northern Hokkaido, Japan (Fig. 1). The site (45°N, 142°E) is close to the Japan Sea (about 20 km in distance), and the predominant wind direction is southwest. There are no sources of air pollution around the site.

Snow samples for chemical analyses were collected over two different thicknesses



Fig. 1. Location map of the observational site.

(several millimeters and tens of millimeters) near the surface before and after surface hoar formation (Fig. 2). They were stored in clean polyethylene bottles and kept frozen. The oxygen isotopic ratio was determined with a mass spectrometer (Finnigan MAT: delta S) on CO₂ equilibrated with melt water from snow samples. Major soluble species (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, NO₃⁻, SO₄²⁻) were also determined with an ion chromatograph (Dionex-2020i/SP).

The meteorological elements, air temperature, humidity, wind speed and snow surface temperature, were measured every one minute and averaged for 30 min. The surface temperature was obtained with a copper-constantan thermocouple in the nighttime, and with an infrared radiation thermometer (HORIBA IT-340W) in the daytime. HACHIKUBO and AKITAYA (1997) described other instrumentation in detail. The latent heat flux *lE*,



Fig. 2. Sampling method of surface layer: including surface hoar crystals.

which corresponds to the vapor condensation rate or evaporation rate, was estimated with a bulk transfer method (STULL, 1988),

$$lE = \rho C_e U_z (q_z - q_s), \tag{1}$$

where *l* is the latent heat, *E* the condensation rate of water vapor, ρ the air density, C_e the bulk transfer coefficient of water vapor, *U* the wind speed, and *q* the specific humidity calculated from the relative humidity and temperature. The subscripts *z* and *s* indicate the height of 1 m and the snow surface, respectively. The value 2.9×10^{-3} obtained from field observations (HACHIKUBO *et al.*, 1995) was used as C_e .

In addition, from March 5 to 6 the vapor condensation was measured with the two weighting-type evaporimeters made of vinyl chloride. These devices were first developed



Fig. 3. Schematic view of vapor transport around the two weighting-type evaporimeters.

by SHIRAIWA et al. (1996) and were 250 mm in length, 250 mm in width and 40 mm in depth. They were set in a pit in the snow surface filled with snow and weighed with an electric balance before and after surface hoar formation. Although one of the devices, of which the bottom was stainless steel mesh, could pass water vapor, the other, of which the bottom was made of vinyl chloride, was observed to form hoarfrost under the bottom (Fig. 3). It was scraped off carefully with a plastic card before the measurement. Accordingly, we could obtain not only the surface hoar condensation from the latter device but also the amount of vapor transfer at 40 mm depth from the weight difference between the two devices.

3. Observation Results and Discussion

3.1. Meteorological conditions from March 3 to 6

It was clear during this period and the snow surface was cooled by outgoing radiation in the nighttime. Surface hoar crystals formed in the two nights, March 3 to 4 and 5 to 6, and their sizes reached 1 mm and 3 mm, respectively. The depth hoar crystals were also formed beneath the snow surface due to the large temperature gradient. Figure 4 shows the snow structure near the surface on March 6. A surface layer about 30 mm thick was composed of large grains of depth hoar crystals.

Figure 5a-d shows the time variations of the air temperature T_a , the surface tempera-

 δ^{18} O Fluctuations of Surface Snow Due to Hoar Formation

depth (mm) grain shape grain size (mm) density (kg/m³)

chow curface	\vee \vee	0.5 - 2	
	$\wedge \wedge$	0.5 - 2	190
30	0 \	1 - 4	
40		0 - 1	250
60		0 - 0.5	420
90		0 - 0.5	440
120		0 - 0.5	400
150			

●: compacted snow ○: granular snow

 \Box : solid- type depth hoar \land : depth hoar \lor : surface hoar





Fig. 5. The time variations of meteorological elements from March 3 to 6, 1996. (a) The air temperature at 1 m height and the snow surface temperature. (b) The relative humidity at 1 m height. (c) The wind speed at 1 m height. (d) The calculated latent heat flux, and positive values show the incoming heat flux to the snow surface.

ture T_s , the relative humidity, the wind speed and the calculated latent heat flux at the snow surface. In the nighttime except for March 4 to 5, the temperature difference between T_a and T_s reached 10°C and the relative humidity was more than 80% under breezy winds. These conditions were suitable for surface hoar growth (HACHIKUBO and AKITAYA, 1997), as the latent heat flux indicated the vapor condensation in Fig. 5d. In contrast, both the relative humidity and the temperature difference between T_a and T_s decreased in the daytime, and amount of evaporation was estimated to be large.

3.2. Changes of $\delta^{i*}O$ and the concentrations of major ions

Figure 6 shows time variations of the δ^{18} O contents of the surface layer. Snow sampling was done in the morning and the evening (3/3 0900, 3/3 1900, 3/4 0900, 3/5 1800, 3/6 0800), although there were no data from the night of March 4 to 5 and we did not obtain a sample of two to three millimeter thickness at 0900 on March 3. In this graph, δ^{18} O decreased about 1–2‰ when the surface hoar and the depth hoar crystals formed in the nighttime. The decrease of δ^{18} O of the two to three millimeter thick sample. On the other hand, δ^{18} O increased in the daytime from 0900 to 1900 on March 3, and was relatively high at 1800 on March 5. From these results, we can say that δ^{18} O of the surface layer decreased with hoar condensation, and increased with evaporation from the surface hoar and depth hoar crystals, whereas H₂¹⁶O was enriched by condensation of surface hoar and depth hoar crystals, whereas H₂¹⁸O was concentrated on the snow surface due to the evaporation of light H₂O to the atmosphere.

The changes of electric conductivity and pH are shown in Fig. 7. The changes of electric conductivity were similar to that of δ^{18} O, whereas pH decreased during the



Fig. 6. Time variations of the $\delta^{*8}O$ contents of the surface layer from March 3 to 6, 1996. Dotted lines mean that there were no data from the night on March 4 to the morning on 5 and we did not obtain a two to three millimeter thick sample at 0900 on March 3.



observation period. Figure 8 shows concentrations of major ions. Except for Ca^{2+} and NO_3^{-} , the major ion concentration decreased in the nighttime, and increased in the daytime. Moreover, the concentrations of the two to three millimeter thick sample fluctuated larger than that of a ten millimeter thick sample except for NH_4^+ , Ca^{2+} and NO_3^{-} . These tendencies can be understood in that the condensation of surface hoar and depth hoar crystals, which were composed of pure ice, decreased the concentrations of impurities near the snow surface, while evaporation increased them. These processes were more effective in a thin surface layer.

As stated above, there were a few exceptions: the fluctuations of NH_4^+ , Ca^{2+} and NO_3^- . Several reasons can be considered: dry deposition onto the snow surface, chemical reactions and insufficient data; only one sample (about 100 g) was obtained at one position.

3.3. Estimation of $\delta^{18}O$ of hoar crystals formed on March 5-6

The measurements using the evaporimeters showed that the surface hoar condensation and the amount of vapor transfer at 40 mm depth from 1800 on March 5 to 0800 on March 6 were 0.118 kg m⁻² and 0.050 kg m⁻², respectively. The amount of vapor condensation from the air calculated with eq. (1) was 0.123 kg m⁻², which agrees fairly well with the value obtained with the evaporimeters.

We shall focus on the weight change of the surface layer (10 mm in thickness), the density of which was 190 kg m⁻³ at 1230 on March 6 (Fig. 4). Table 1 shows the ratio of the concentrations of major ions at 0800 on March 6 to those at 1800 on March 5. Since these values were $91.7 \pm 1.2\%$ with the exception of NH₄⁺, K⁺ and Ca²⁺, it may safely be assumed that the impurities were diluted with hoar crystals at this rate. It is likely that the excess of Ca²⁺ was due to dry deposition, but NH₄⁺ and K⁺ require further consideration. The total hoar condensation x kg m⁻² is expressed with this ratio and the density of the



Fig. 8. Time variations of concentrations of major ions.

Table 1. The ratio (%) of the concentrations of major ions at 0800 on March 6 to those at 1800 on March 5. The sample was the surface layer (10 mm in thickness).

Na ⁺	NH4+	K+	Mg ²⁺	Ca ²⁺	Cl-	NO ₃ -	SO ₄ ²⁻
90.5	62.5	77.8	92.5	156	92.1	92.9	90.9

	3/5 1800	3/6 0800
Original snow	1.732 kg m ⁻²	1.732 kg m ⁻²
Surface hoar	_	0.118 kg m ⁻²
Depth hoar	_	0.050 kg m^{-2}
Total	1.732 kg m^{-2}	1.900 kg m ⁻²
O ⁴⁸ O	-9.9‰	- 10.3 ‰

Table 2. The changes of mass components of surface layer (10 mm in thickness) and $\delta^{18}O$.

surface layer,

 $\{190(\text{kg m}^{-3}) \times 0.01(\text{m}) - x(\text{kg m}^{-2})\} / \{190(\text{kg m}^{-3}) \times 0.01(\text{m})\} = 0.917 \pm 0.012.$ (2)

x is calculated as 0.158 ± 0.023 kg m⁻². It also corresponded to 0.168 kg m⁻², which was the sum of surface hoar and depth hoar condensation, obtained with evaporimeters supposing that the amount of vapor transfer at 10 mm depth was nearly equal to the one at 40 mm depth.

The changes of mass components and δ^{18} O before and after the hoar formations are written as Table 2. If we assume that only the hoar crystal formation caused the change of δ^{18} O, we can calculate δ^{18} O of hoar crystals y condensed on March 5 to 6 as follows,

$$-9.9(\%) \times 1.732(\text{kg m}^{-2}) + y(\%) \times 0.168(\text{kg m}^{-2}) = -10.3(\%) \times 1.900(\text{kg m}^{-2}), \quad (3)$$

y is -14.4%, which was about 5‰ lower than the one of the original surface layer. Depth hoar crystals are relatively light because they are made of light water vapor which evaporate from the lower part of deposited snow at the rate of a specific fractionation factor. However, δ^{18} O of surface hoar crystals depends on the origin of water vapor in the air. Since samples of only surface hoar crystals formed on March 5-6 were not collected, δ^{18} O of them were unknown. It remains an unsettled question how surface hoar crystals change the δ^{18} O of surface snow.

4. Concluding Remarks

 δ^{18} O and major ions of the snow surface layer were measured before and after hoarfrost formations in the field. δ^{18} O decreased when the surface hoar and depth hoar crystals formed in the nighttime, whereas it increased due to the evaporation of snow surface in the daytime. The concentrations of major ions fluctuated as well according to the condensation and evaporation of water vapor. From the fluctuation of these concentrations, δ^{18} O of total hoar crystals condensed on March 5 to 6 was estimated to be about 5‰ lower than that of the original surface layer. These results indicate that δ^{18} O of deposited snow near the surface where condensation and evaporation often occur may change easily because of isotopic mass fractionation.

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