The quantitative evaluation of sublimation and the estimation of original hydrogen and oxygen isotope ratios of a firn core at East Queen Maud Land, Antarctica

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Abstract

The quantitative evaluation of sublimation during firnification and the estimation of original hydrogen and oxygen isotope ratios of deposited snow were attempted by a simultaneous measurement of δD and $\delta^{18}O$ values in a firn core having well-developed depth hoar collected at East Queen Maud Land, Antarctica. The d-parameter of the core ranged from 11 to 18 and showed good positive correlation with the depth hoar level suggesting that the increase in the d-parameter from 10 was caused by post-depostional firnification in which sublimation plays an important role. Based on the d-parameters, the firn was estimated to have lost 30−35 % of deposited snow during firnification and to be enriched in deuterium and oxygen-18 by about 50 and 6 ‰, respectively, relative to the deposited snow.

1. Introduction

A stable isotope is a very popular tool for the study of the nature and behavior of snow and ice in polar regions. Since the 1960s, the dating of the ice cores, sedimentation rate and paleoclimates have been investigated by measuring the oxygen or hydrogen isotope ratios of snow and ice (*e.g.*, Epstein *et al.*, 1965 ; Dansgaard *et al.*, 1969). In some inland areas within Antarctica, however, the annual amount of sublimation is almost equal to the annual precipitation (*e.g.*, Satow and Watanabe, 1985). In such areas, post depositional metamorphism may alter the original isotope ratio of deposited snow. Indeed, Watanabe *et al.* (1988) measured oxygen isotope profiles of 10 m long cores collected at the Mizuho plateau, Antarctica, and observed larger $\delta^{18}O$ values which coincide with highly developed depth hoar. The oxygen isotope fractionation factor between vapor and ice, $(^{18}O/^{16}O)_{ice}/(^{18}O/^{16}O)_{vapor}$, is larger than one (Matsuo and Matsubaya, 1969). Therefore, the $\delta^{18}O$ of sublimating vapor from ice is always lower than that of ice. Thus the enrichment of ^{18}O accompanying the highly developed depth hoar observed in a dry snow

zone is obviously due to sublimation.

In most isotope studies of firn and ice, a single isotope ratio (mostly oxygen) has been measured and a simultaneous measurement of both δD and $\delta^{18}O$ values is scarcely performed (*e.g.*, Epstein *et al.*, 1965). Because, in most cases, the hydrogen isotope profile in a firn core shows a pattern very similar to that of oxygen and the simultaneous measurement is not needed. As stated above, a single isotope measurement can provide qualitative information concerning postdepositional increase in isotope ratios mainly due to sublimation. However, quantitative information such as the extent of sublimation and extent of the increase in isotope ratios cannot be obtained from single isotope profiles. We performed coincident oxygen and hydrogen isotope measurements of a firn core from East Queen Maud Land, Antarctica, and attempted to provide a quantitative evaluation of the sublimation and isotopic alteration after deposition.

2. Methods

The firn core, 1.26 m long and 7 cm in diameter, was collected at the γ-1 station (71°59'07"S, 42°24'05"

E ; 2252 m a.s.l.) in East Queen Maud Land, Antarctica, on October 28, 1984 (Fujii *et al.*, 1985). The γ-1 station is about 150 km southwest of the Mizuho Station. This core was packed in aluminum foil and a polyethylene bag and was transported to the laboratory. The collected core was cut lengthwise and the stratigraphy such as grain size and depth hoar level (DHL) (Watanabe, 1978) of the firn was observed. After observation, one of the split cores was cut into 2 cm slices and its density was measured. It was then melted to measure the hydrogen and oxygen isotope ratios. Another split core was cut into 5 cm slices for tritium measurement.

For the D/H measurement, water was converted to hydrogen by uranium at 750 °C and its hydrogen isotope ratio was measured using a mass spectrometer, Micromass 602E (Bigeleisen *et al.*, 1952). To measure the oxygen isotope ratio, water was isotopically equilibrated with carbon dioxide at 25 °C. After equilibration, carbon dioxide was recovered and its $^{18}O/^{16}O$ ratio was measured (Yoshida and Mizutani, 1986). Hydrogen and oxygen isotope ratios are expressed by δ values in permill

units relative to SMOW denoted by the following equation.

$$\delta(\text{‰}) = [(R_{sample} - R_{SMOW})/R_{SMOW}] \times 1000$$
$$R : (D/H) \text{ or } (^{18}O/^{16}O)$$

The precision of the δD and $\delta^{18}O$ values is ± 1 and ± 0.1 ‰ respectively.

For the tritium measurement, a distilled sample water (40 ml) was mixed with a liquid scintillator, Insta Gel (60ml). Its tritium concentration was then measured by a liquid scintillation counter, Aloka LB-1. The tritium concentration is expressed in Tritium Unit, TU (1 TU=1T/10^{18}H). The precision of the tritium concentration is better than ± 5 TU (1 sigma error).

3. Results and Discussion

The vertical profiles of DHL, grain size, tritium concentration, oxygen and hydrogen isotope ratios in a firn core are shown in Fig. 1. In the upper part of the core shallower than 26 cm, the grain size is very small (0.7 mm) and the depth hoar is not developed
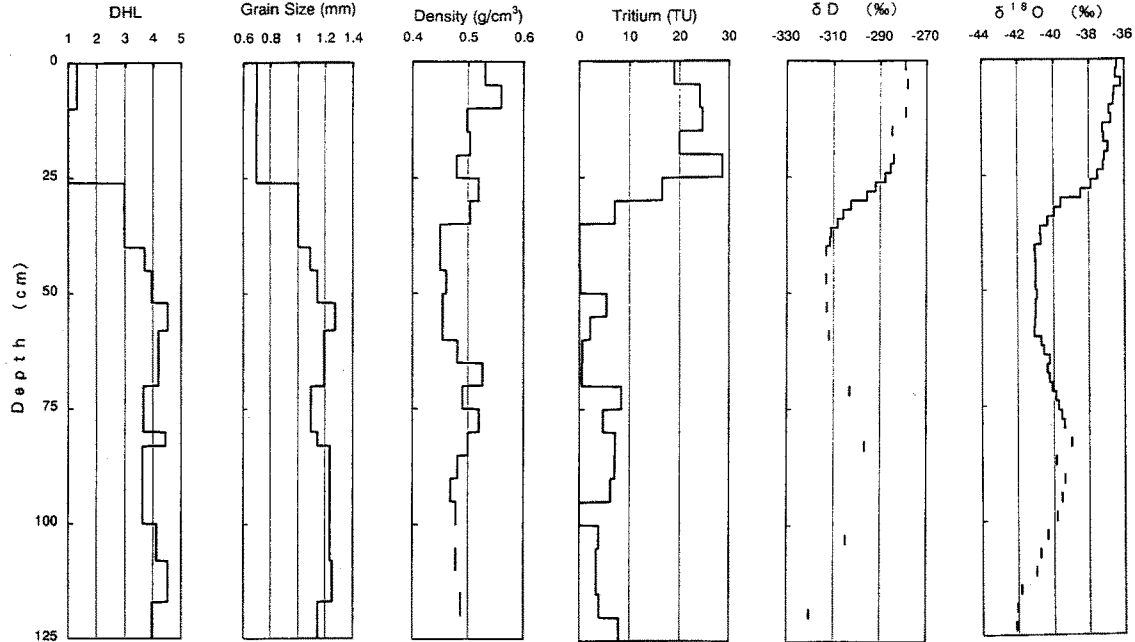

Fig. 1 Vertical profiles of DHL, grain size, density, tritium concentration, oxygen and hydrogen isotope ratios in a firn core at the γ-1 station. Tritium concentration is as of October 1984.

(DHL=1−1.2). The tritium concentration in the upper part of the core is 18−24 TU. This tritium concentration is almost the same as the tritium concentration (9.1−38.3 TU, av. 19.7 TU) of monthly snow collected at the Mizuho Station, 150 km northeast of γ-1, in 1984 (Satake et al., 1986). These facts suggest that the upper part of the firn core shallower than 26 cm is very recent snow. On the contrary, in the lower part of the core, the grain size is large (1−1.3mm) and the depth hoar is well crystallized (DHL= 3−4.5). Further, the tritium concentrations in the core lower than 30 cm are in the range of 0−8 TU. These tritium concentrations are significantly lower than those in the monthly snow at the Mizuho Station. These tritium concentrations lower than 8 TU strongly suggest that the lower part of the firn core is snow deposited before the 2nd half of the 1950s when the tritium concentration in precipitation steeply increased due to thermonuclear tests. Fujii and Masuda (1985) measured the vertical profile of Pb-210 activity at the γ-1 station to 10m depth. Based on this result, they estimated the firn at 0.45−1.01 m depth to have been deposited 56±18 years previously. The deposition age estimated from the tritium concentration obtained in this work shows good agreement with that from Pb-210. Thus it is safely concluded that the absence of sedimentation for a fairly long period of more than 40 years exists between the upper layer shallower than 25 cm and the lower layer.

Oxygen isotope ratios in this core range from −42.1 to −36.4 ‰. It is almost constant (within −37±1 ‰) in the upper part shallower than 26 cm and then decreases to −42.1 ‰ in the lower part below 26 cm with a small peak of −39.0 ‰ (82−84 cm). The hydrogen isotope ratio is −320 to −279 ‰ and shows a similar profile. These hydrogen and oxygen isotope ratios are within the variation of δD (−352 to −254 ‰) and $\delta^{18}O$ (−45.0 to −33.7 ‰) of monthly snow at the Mizuho Station (Satake et al., 1986). Judging from these isotope ratios, the postdepositional deuterium or ^{18}O enrichment in the γ-1 core cannot be detected.

The d-parameter, $d = \delta D - 8\ \delta^{18}O$, is a good indicator for tracing the water cycle including the vapor phase (Dansgaard, 1964). It is well-known that most of the meteoric waters in the world concentrate along a line, $\delta D = 8\ \delta^{18}O + 10$, and have a d-parameter of 10 (Craig, 1961). In Antarctica, however, it is reported that the d-parameter in surface snow having a δD value of −350 to −150 ‰ ranges from 0 to 10 (av. 5),

and it steeply increases with decreasing δD value (Dahe et al., 1994). As shown in Fig. 2, the d-parameter of the γ-1 core ranges from 11 to 18. In a surface layer shallower than 26 cm, it is 11−13 except for the firn at 10−12 cm depth. In the lower layer, the d-parameter steeply increases from 11 to 15 with increasing depth to 54 cm. It is then almost constant (16−18) at depth lower than 60 cm. The d-parameter in the lower layer is systematically higher than that of the surface layer. Judging from the relationship between the d-parameter and the δD value in the Antarctic surface snow stated above (Dahe et al., 1994), the high d-parameter such as 18 observed in the lower layer ($\delta D = -320$ to -295) cannot be regarded as that of the original snow. The d-parameter of monthly snow at the Mizuho station, 150 km northeast of γ-1 station, in 1984 was observed to be 7−13 except for October ($d=16$) without seasonal variation and the averaged annual d-parameter was 10 (Satake et al., 1986). Thus we can regard the d-parameter of snow at the γ-1 station to be about 10.

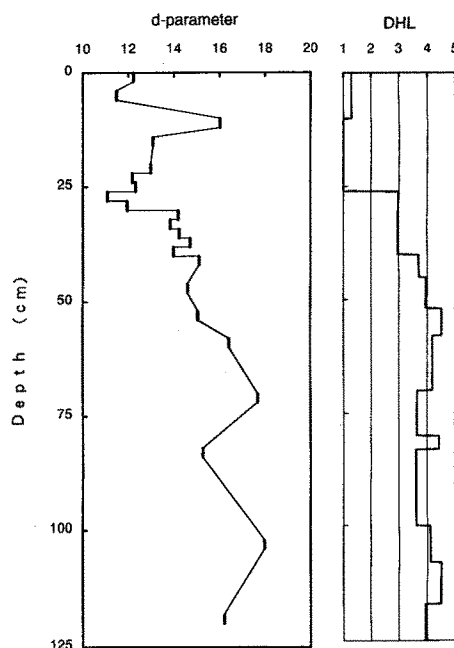In Fig. 2, the vertical profile of the depth hoar level (DHL) is also shown. From Fig. 2, it can be

Fig. 2 Vertical profile of d-parameter observed at the γ-1 station. The vertical profile of DHL is also shown.

clearly observed that the vertical profile of the depth hoar level reveals a good correlation with that of the d-parameter. This strongly suggests that the d-parameter of the firn in the lower layer was originally about 10 and it increased to 18 during firnification after deposition. The ten-meter snow temperature at the γ-1 station was observed to be about -40 °C (-37.7 °C), and this temperature can be regarded as an annual mean temperature (Fujii et al., 1985). Unfortunately, both the hydrogen and oxygen fractionation factors between ice and water vapor were not measured at -40 °C but in the temperature range from 0 to -20 °C (Matsuo et. al., 1964 ; Matsuo and Matsubaya, 1969). Both the hydrogen and oxygen isotope fractionation factors observed in this temperature range show a very linear relationship to the temperature. By extrapolating the oxygen and hydrogen fractionation factors to -40 °C, we obtain 0.815 as the hydrogen fractionation factor, $(D/H)_{vapor}/(D/H)_{ice}$, and 0.9851 as the oxygen fractionation factor, $(^{18}O/^{16}O)_{vapor}/(^{18}O/^{16}O)_{ice}$, at -40 °C. Using these fractionation factors and the following Railigh's equation,

$$\ln(R/R_0)=(\alpha-1)\ln(1-f)$$

    R : $(^{18}O/^{16}O)$ or (D/H) ratio of firn
    R_0 : $(^{18}O/^{16}O)$ or (D/H) ratio of deposited snow
    α : $(^{18}O/^{16}O)$ or (D/H) fractionation factor
    f : fraction of vaporized snow during firnification

we can calculate the δD and $\delta^{18}O$ values and the d-parameter of residual snow (firn), when the vapor sublimates from deposited snow during firnificarion.

We assume the δD and $\delta^{18}O$ values of precipitated snow to be -310 and -40 ‰, respectively, and the d-parameter to be 10. When 10 % of the snow is sublimated under isotopic equilibrium conditions, hydrogen and oxygen isotope ratios of firn (residual snow) are then calculated to be -296 and -38.5 ‰, respectively, and the d-parameter increases from 10 to 12. Similarly, the d-parameter of firn is calculated to be 14, 16 and 20, respectively, when 20, 30 and 40 % of the snow is vaporized.

The increase in the d-parameter according to the increase in DHL observed in the γ-1 core is probably due to the sublimation of vapor during the absence of sedimentation for a fairly long period of more than 40 years which was discussed previously. Thus we can estimate that the firn lower than 60cm with a d-parameter of $16-18$ lost $30-35$ % of the deposited snow during firnification and became enriched with D

and ^{18}O of about 50 and 6 ‰, respectively, relative to the original deposited snow. The original hydrogen and oxygen isotope ratios in the firn lower than 60 cm are then estimated to be -370 to -350 ‰ and -48 to -46 ‰, respectively. These isotope ratios are almost same to the minimum δD and $\delta^{18}O$ values in the monthly snow at the Mizuho station. This suggest that the original snow in the firn lower than 60 cm deposited in winter season. On the contrary, the firn shallower than 26 cm has the hydrogen and oxygen isotope ratios slightly higher than the maximum isotope ratios in the monthly snow at the Mizuho station, suggesting that the snow in the upper layer shallower than 26 cm deposited in summer. This may be the reason why the D/H and $^{18}O/^{16}O$ ratios in the lower layer are lower than those in the upper layer, in spite of the large enrichment with the deuterium and ^{18}O in the lower layer due to the sublimation.

As described previously, oxygen isotope analysis has been done in most isotopic studies of firn and ice. One of the reasons for this may be that carbon dioxide for oxygen isotope analysis of water can be easily prepared by isotope exchange between carbon dioxide and water. This method is suitable for automatization, and a commercial system for automated oxygen isotope analysis of water samples has been available since the early 1980s. In the conventional sample preparation method for D/H measurement, water is reduced to hydrogen with uranium or zinc (Bigeleisen et al., 1952 ; Coleman et al., 1982). This method is complicated and time-consuming compared with that for oxygen. Recently, a new hydrogen preparation method for D/H analysis has been developed using hydrogen isotope exchange between water and hydrogen with a platinum catalyst (Ohsumi and Fujino, 1986). Using this technique, the hydrogen isotope analysis of water samples can be easily automated with an apparatus for oxygen isotope analysis of water samples (Horita et al., 1989 ; Ohba and Hirabayasi, 1996).

The d-parameter of firn is a good indicator for determining the extent of sublimation after deposition and for restoring the original oxygen and hydrogen isotope ratios. Hydrogen isotope ratios as well as oxygen should be measured for precise investigation especially for cores from inland regions where there is little annual accumulation and the sublimation effects on oxygen and hydrogen isotope ratios are not negligible.

Acknowledgments

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