

Scientific Note

The reduction of chloride ion concentration in basal ice near Hamna Icefall, East Antarctica

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Abstract: The present paper mainly discusses chloride ions (Cl^-) in debris-laden basal ice near Hamna Icefall, Queen Maud Land, East Antarctica. The basal ice consists of alternating layers of bubble-free and bubbly ice of the order of mm to cm in thickness. Detailed analyses of Cl^- and stable isotopes ($\delta^{18}\text{O}$ and δD) on the alternating layers were performed. The Cl^- concentrations in the bubble-free ice layers and in the bubbly ice layers whose isotopic fluctuations decrease from neighboring bubble-free ice layers are reduced compared to those in the bubbly ice layers having quasi-neutral values on the isotopic profile. The reduction of Cl^- concentration in frozen ice compared to that in pre-freezing water was also observed from an experiment on ion fractionation by freezing. These results suggest that the bubble-free ice layers and the bubbly ice layers whose isotopic fluctuation is decreased from that in neighboring bubble-free ice layers were formed by melt-refreezing processes. The reduction of Cl^- concentration in the basal ice is considered to be an indicator to distinguish whether the basal ice has experienced melt-refreezing or not.

1. Introduction

In order to make clear the flow dynamics of ice sheets and glaciers, it is necessary to elucidate the nature of the basal part of the ice sheets and glaciers; especially, the hydrological condition under the ice sheets and glaciers. Analysis of debris-laden basal ice of the ice sheets and glaciers is one of the most promising techniques to elucidate the hydrological condition at the inaccessible inland bases of ice sheets and glaciers (Knight, 1999). In general, stable isotopes in the basal ice are widely used to distinguish whether the origin of the basal ice is non-melted glacier ice or melt-refrozen ice (Souchez and Jouzel, 1984; Souchez and De Groot, 1985). Hubbard *et al.* (2000) suggested that a reduction of chloride ion (Cl^-) concentration in basal ice at Glacier de Tsanfleuron is caused by a melt-refreezing process. This result means that not only the stable isotopes but also the reduction of Cl^- concentration in basal ice can be an indicator to distinguish whether the basal ice has experienced melt-refreezing or not.

The present paper discusses Cl^- in basal ice near Hamna Icefall, Queen Maud Land, East Antarctica (hereafter we call it the Hamna basal ice). Iizuka *et al.* (2001) discussed formation processes of the Hamna basal ice, using stratigraphic features and co-isotopes of the basal ice. A summary of the study is given below.

1) The Hamna basal ice about 6.8 m thick exhibits two peculiar stratigraphic features. One is the upper part of the basal ice (5.5 m in thickness), which consists of alternating layers of bubble-free and bubbly ice on the order of mm to cm in thickness. The other is the lower part of the basal ice (1.3 m in thickness), which consists predominantly of bubble-free ice.

2) The Hamna basal ice and ice sheet ice above the basal ice originated from precipitation in the inland regions of the Sôya drainage of the ice sheet.

3) It has been suggested that the bubble-free ice layers and the bubbly ice layers whose isotopic fluctuation is decreased from that in neighboring bubble-free ice in the upper part of the basal ice were formed by a regelation process in an open system (Souchez and Jouzel, 1984; Souchez and De Groot, 1985), and the bubbly ice layers having quasi-neutral values on the isotopic profile were not affected by melt-refreezing.

2. Study site and analytical procedures

A basal ice sampling site was selected at the left bank near Hamna Icefall located at 30 km south of Syowa Station, Sôya Coast, Queen Maud Land ($69^{\circ}20'S$, $39^{\circ}45'E$). Further details of the study site are reported by Iizuka *et al.* (2001).

Laboratory analyses of the Hamna basal ice and the ice sheet ice above the basal ice were conducted. Specific analyses include stratigraphy of bubbles, chloride ions (Cl^{-}) and stable isotopes ($\delta^{18}O$ and δD). Two kinds of laboratory analyses, which have different measurement intervals for Cl^{-} , $\delta^{18}O$ and δD , were conducted. The first was a general analysis of the entire basal ice layer. Analyses for Cl^{-} , $\delta^{18}O$ and δD were performed continuously every 100 mm in thickness. The second was a detailed analysis focusing on particular stratigraphic sections. A characteristic part about 150 mm in length was used for detailed analyses of Cl^{-} , $\delta^{18}O$ and δD , which were done every 2 mm in thickness.

Stable isotope analyses were carried out with a mass spectrometer (PRISM). Analytical procedures for stable isotopes are described in Iizuka *et al.* (2001). Errors are estimated to be less than $\pm 0.1\%$ for $\delta^{18}O$ and $\pm 1.4\%$ for δD (1 sigma error). Analysis for Cl^{-} was performed after the samples were filtered (pore size $0.45\mu m$). Cl^{-} was measured by ion chromatography with the same method used by Igarashi *et al.* (1998). Errors are estimated to be less than 5%.

3. Results

In the first column from the left margin of Fig. 1, an entire stratigraphy of bubbly ice and bubble-free ice layers observed on the Hamna basal ice is shown. The figure also shows concentrations of Cl^{-} , $\delta^{18}O$ and δD in the basal ice and the ice sheet ice. The vertical axis of this figure represents a height measured upward from the boundary between the basal ice and the bed. Hereafter, we take the height in this way. Results for stratigraphic features and $\delta^{18}O$ in ice have been reported by Iizuka *et al.* (2001), and the result for Cl^{-} in ice has been reported by Iizuka *et al.* (2000). Table 1 shows the average concentrations of Cl^{-} . The concentration of Cl^{-} in the ice sheet ice is $2.78\mu mol/l$ on average; the concentration of Cl^{-} in the basal ice is $1.15\mu mol/l$ on average.

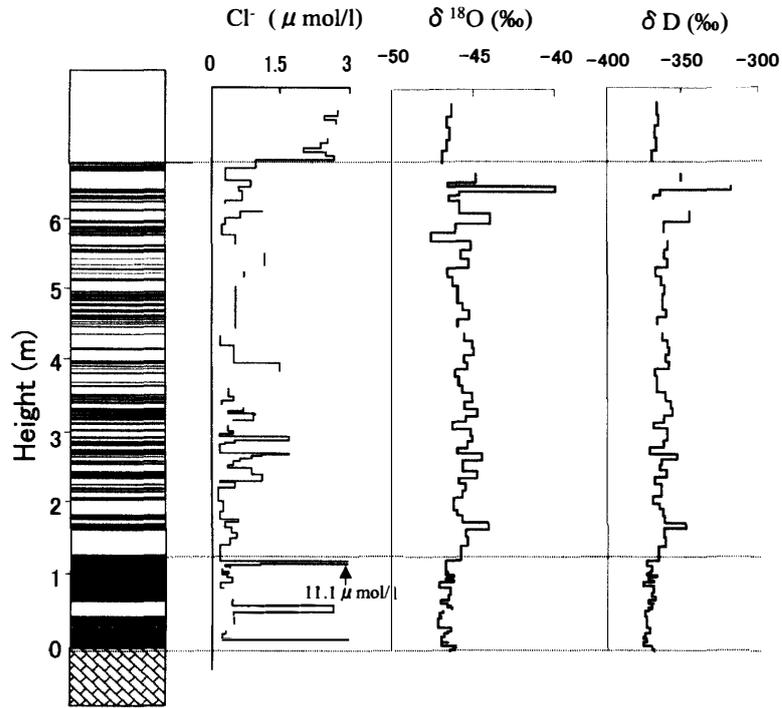


Fig. 1. Vertical profiles of the entire stratigraphy of bubbly ice and bubble-free ice observed on the Hamna basal ice, together with Cl^- ($\mu\text{mol/l}$), $\delta^{18}\text{O}$ (‰) and δD (‰) in ice. Bubbly ice is represented by open spaces and bubble-free ice by black spaces. Dotted lines show interfaces between the ice sheet ice and the basal ice (6.8 m in height), the upper part and the lower part of the basal ice (1.3 m in height), and the basal ice and the base of the ice sheet (0 m in height).

Table 1. Average concentrations and standard deviations of Cl^- ($\mu\text{mol/l}$).

The ice sheet ice	The basal ice	
	1.15 ± 2.07 (N = 165)	
	The bubble-free ice	The bubbly ice
2.78 ± 0.89 (N = 24)		1.92 ± 0.75 (N = 43)
	1.54 ± 0.86 (N = 24)	A
		B
		1.38 ± 0.29 (N = 17)
		2.38 ± 0.70 (N = 26)

Notes: A=the bubbly ice layers whose isotopic fluctuation is decreased from that in neighboring bubble-free ice in Fig. 2; B=the bubbly ice layers having quasi-neutral values on the isotopic profile in Fig. 2.

Figure 2 shows vertical profiles of Cl^- , $\delta^{18}\text{O}$ and δD at about 1.5 m in height. The isotopic profiles are closely related to the alternating layers of bubble-free and bubbly ice, the same as the results at about 1.7 m and 5.8 m in heights reported by Iizuka *et al.* (2001). In each alternating layer, almost all the δ values of the bubble-free ice layers are heavier than those of the neighboring bubbly ice layers. The average differences defined by the maxima in the bubble-free ice layers and minima in the neighboring

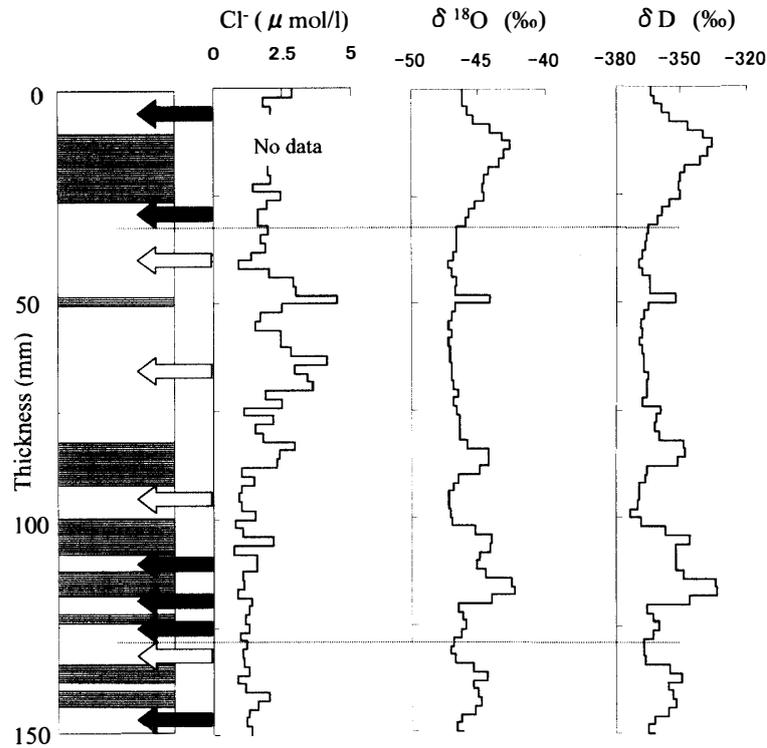


Fig. 2. Vertical profiles of stratigraphy of bubbles, Cl^- ($\mu\text{mol/l}$), $\delta^{18}\text{O}$ (‰) and δD (‰) at about 1.5 m in height in the upper part of the basal ice. Dotted and open squares show bubble-free ice and bubbly ice layers, respectively. The vertical axis represents the thickness (mm). Each value was measured through about a 2 mm thickness. Thick black arrows show the bubbly ice layers whose isotopic fluctuation is decreased from that in neighboring bubble-free ice. Thick white arrows show the bubbly ice layers having quasi-neutral values in the isotopic profile. Dotted lines are boundary lines between thick black and white arrows in a bubbly ice layer.

bubbly ice layers are 2.5 ± 1.3 (standard deviation) and $17 \pm 10\text{‰}$ for $\delta^{18}\text{O}$ and δD , respectively. The freezing slope of $\delta^{18}\text{O}$ vs. δD of all the samples in Fig. 2 is 7.2. These results suggest that the bubble-free ice layers shown in Fig. 2 (at about 1.5 m in height) were formed by melt-refreezing processes in an open system, such as the results at about 1.7 m and 5.8 m in heights reported by Iizuka *et al.* (2001). The open system is defined by the existence of input and/or runoff water during freezing. The average concentrations of Cl^- in the bubble-free ice layers, in the bubbly ice layers whose isotopic fluctuation is decreasing from neighboring bubble-free ice layers and in the bubbly ice layers having quasi-neutral values on the isotopic profile are 1.54, 1.38 and $2.38 \mu\text{mol/l}$, respectively. The average concentrations are statistically distinguishable between the former two and the latter one (Table 1).

4. Experiment

In order to make clear the mechanism of ion fractionation caused by the freezing process, we performed an experiment as follows: 1) about 500 g of the Hamna basal ice was melted, 2) the ion concentration in the melted sample was analyzed by ion

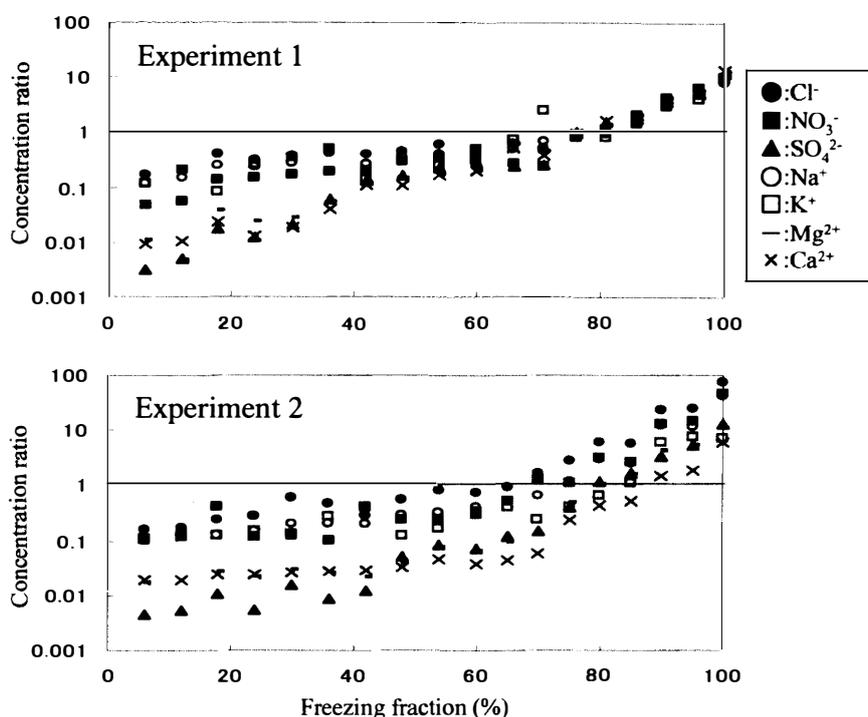


Fig. 3. The experimental result of ion fractionation by freezing. The vertical axis represents the concentration ratio of refrozen ice to melted water before refreezing. The horizontal axis represents the freezing fraction (%). We define the freezing fractions before and after freezing to be 0 and 100 (%), respectively. The experiment was performed twice.

chromatography by the same method as used by Igarashi *et al.* (1998), 3) a melted sample in a cylindrical tube (about 500 mm in length) was refrozen from one end of the tube to the other end by cold air at -20°C , 4) a refrozen sample was cut into about ten pieces of ice vertically to the freezing direction, 5) ion concentrations of the ice pieces were analyzed by ion chromatography.

Figure 3 shows the result of the experiment. In all of the analyzed ion species, ion concentrations of the ice pieces increase from ice pieces frozen in the early stage to ice pieces frozen in the last stage, such as reported by Malo and Baker (1968). Ion concentrations of ice pieces frozen in the early stage are lower than that of the melted sample before refreezing. Three types of ion fractionation are observed among the ion species. For Na^+ , Cl^- , K^+ and NO_3^- , ion concentrations of ice pieces frozen in the early stage (up to 50% for freezing fraction) are within 0.06 to 0.6 times that of the melted sample. For Ca^{2+} and Mg^{2+} , ion concentrations of ice pieces frozen in the early stage are within 0.01 to 0.1 times that of the melted sample. For SO_4^{2-} , ion concentrations of ice pieces frozen in the early stage are within 0.003 to 0.06 times that of the melted sample.

5. Discussion

Iizuka *et al.* (2000) suggested that almost all of the Cl^- in the Hamna basal ice originated from a supraglacial source, because Cl^- is not considered to originate from

the chemical erosion of rock minerals. Iizuka *et al.* (2001) showed that the basal ice and the ice sheet ice have almost the same origin, that is, precipitation in inland regions of the ice sheet. Therefore, it is considered that concentrations of Cl^- in the basal ice and the ice sheet ice should be at the same level. Actually, reduction of Cl^- concentration in the basal ice was observed (Table 1).

We showed experimentally that when water freezes, fractionation of ions occurs between initial water and refrozen ice. Namely, ice frozen in the early stage contains a low concentration of ions compared with the initial meltwater. From the experimental result, the reduction of Cl^- concentration in the Hamna basal ice is considered to be caused by the melt-refreezing process at the inland base of the ice sheet.

Strictly speaking, the reduction of Cl^- concentration was observed only in bubble-free ice layers ($1.54 \mu\text{mol/L}$ on average) and in bubbly ice layers whose isotopic fluctuation is decreased from that in neighboring bubble-free ice ($1.38 \mu\text{mol/L}$ on average). Because the average concentration of Cl^- in the bubbly ice layers having quasi-neutral values in the isotopic profile ($2.38 \mu\text{mol/L}$) is similar to that of the ice sheet ice ($2.78 \mu\text{mol/L}$), the bubbly ice layers having quasi-neutral values in the isotopic profile are considered to be not affected by melt-refreezing. The Cl^- concentrations in the bubble-free ice layers and in the bubbly ice layers whose isotopic fluctuation is decreased from that in neighboring bubble-free ice are considered to be reduced about 0.55 to 0.65 ($1.38/2.38$ to $1.54/2.38$) times compare to that in the non-melted layers. In the experimental result, the Cl^- concentrations in the ice refrozen in the early stage are also reduced about 0.6 times compared to that in the initial water (Fig. 3). The experimental result supports that refrozen ice having 0.6 times of the Cl^- concentration compared to that in the initial water can be formed by the melt-refreezing process.

These results suggest that the bubble-free ice layers and the bubbly ice layers whose isotopic fluctuation is decreased from that in neighboring bubble-free ice were formed by the melt-refreezing process, and suggest that the bubbly ice layers having quasi-neutral values in the isotopic profile were not affected by melt-freezing. This interpretation derived from the Cl^- concentration agrees with that derived from isotopic results reported by Iizuka *et al.* (2001) and from the Cl^- concentration observed by Hubbard *et al.* (2000). From these results and considerations, the reduction of Cl^- concentration in the Hamna basal ice is considered to be an indicator to distinguish whether the basal ice has experienced melt-refreezing or not.

6. Conclusion

We have discussed Cl^- in the Hamna basal ice. The Cl^- concentrations in the bubble-free ice layers ($1.54 \mu\text{mol/l}$ on the average) and in the bubbly ice layers whose isotopic fluctuation is decreased from that in neighboring bubble-free ice layers ($1.38 \mu\text{mol/l}$ on the average) are considered to be reduced by the melt-refreezing process. This consideration is supported by isotopic results reported by Iizuka *et al.* (2001) and by the experimental result for ion fractionation by freezing. The reduction of the Cl^- concentration in the Hamna basal ice is considered to be an indicator to distinguish whether the basal ice has experienced melting or not.

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