Isotopic mass balance measurements of spray ice

Toshihiro Ozeki¹, Kyohei Yamane¹, Satoru Adachi², Shigeru Aoki³

¹ Sapporo Campus, Hokkaido University of Education, ² Snow and Ice Research Center, NIED,

³ Institute of Low Temperature Science, Hokkaido University

ozeki.toshihiro@s.hokkyodai.ac.jp

Abstract: Spray ice is frozen ice formed from sea or lake spray water in cold regions and accreted on ships, offshore structures, and trees in lakeside, developing into a massive ice form. Freezing spray is the main cause of spray icing; however, sprav ice accretion often occurs under intense snowfall. We investigated the contribution of snow to spray icing. We collected samples of spray ice, snow, and water on the west coast of Hokkaido Island and in Lake Inawashiro and Lake Towada of Main Island, Japan. The structural characteristics of the spray ice were analyzed using conventional thin-section and NMR imaging. The observed layer structure in the samples depends on the growth history of the spray ice. Additionally, the spray ice was composed of two ice types with different crystal structures: granular ice with uniform, rounded smaller grains and columnar ice. The differences in ice composition may be influenced by snow accretion. The snow mass fraction of the spray ice samples was calculated from the isotopic mass balance. The oxygen isotopic composition of the melted samples was analyzed using a standard mass spectrometer. The oxygen isotopic composition values of spray ice were higher than that of the sea or lake water supply. This difference suggests that isotope fractionation has occurred during the wet growth of spray ice. We verified the isotope fractionation during the wet growth of artificial spray ice produced in cold room experiments. The snow mass fraction of spray ice responds to icing events and the oxygen isotopic composition values of granular ice layers tend to be lower than the other layers, suggesting the contribution of snow accumulation. High snow fractions in the samples demonstrate that snow contributed significantly to the growth of spray ice.

Keywords: spray icing, snow accumulation, isotopic mass balance, $\delta^{18}O$

INTRODUCTION

Spray ice is ice formed from the spray of sea or lake water in cold regions that accumulates on ships, offshore structures, or trees at the waterside, and develops into a massive ice form. Coast of Hokkaido Island on the Sea of Japan is characterized by extreme sea-water spray icing. Marine disasters caused by ice accretion occur frequently, however, even today, deicing continues to be a manual operation that usually involves the use of a hammer. On the other hand, "spray ice" is an interesting ice phenomenon in natural lakes, also observed around Lake Inawashiro and Lake Towada, Japan. It is a popular motif for photographs, and a tourist attraction.

Several recent studies have investigated the feature of seawater spray ice. [1] developed a theoretical model of salt entrapment in sea-water spray ice; a thin liquid-water film on the icing surface runs off from the surface and consequently traps liquid in the spray ice matrix. [2] studied the microstructural features of spray ice on ships and demonstrated the presence of a channelized network of brine. [3] measured the threedimensional microstructure of sea-water spray ice using the Nuclear Magnetic Resonance (NMR) imaging technique, and confirmed the presence of such a channelized network of brine in natural sea-water spray ice samples. Numerous researchers estimated sea-water spray icing. A ship-icing prediction algorithm [4] is used operationally by the National Oceanic and Atmospheric Administration office (NOAA). The factor used to estimate the severity of potential spray icing is derived from a simplified heat balance of the icing surface. [5] investigated the growth rate of sea-water spray icing using telephotographs recorded in intervals and found that the growth rate of the cross sectional area of the spray icing increases monotonically with the product of air temperature and wind speed (i.e., the heat loss by convective heat flux). In addition, [6] reviewed computer simulations of marine ice accretion and discussed the US Coast Guard's Cutter Midgett model and a three-dimensional timedependent vessel-icing model.

Freezing spray is the main cause of spray icing; however, spray ice accretion often occurs during intense snowfall. It is important, therefore, to estimate the contribution of snow to the growth rate of spray icing. [7] investigated the characteristics of lake-water spray ice. The structural characteristics of the ice were analyzed using thin sections of the samples, while the snow mass fraction of the ice samples was calculated from the isotopic mass balance. They suggested that the high snow fraction in the samples indicates a significant contribution of snow.

In this study, the contribution of snow to spray icing is investigated using field observations and laboratory experiments.

I. OBSERVATIONAL SITES AND ICE SAMPLES

We collected samples of spray ice, snow, and water on the west coast of Hokkaido Island and in Lake Inawashiro and Lake Towada of Main Island, Japan (Figure 1).



Figure 1: Locations of observational sites. Hamamasu harbor in Hokkaido Island, Lake Inawashiro and Lake Towada of Main Island, Japan.



Figure 2: Schematic view of Hamamasu Harbor.



Figure 3: Dummy light beacons on breakwater at Hamamasu Harbor. Stormy weather often generated not only heavy spray jets but intense snowfall.



Figure 4: Massive ice forms on trees. upper: Lake Inawashiro, lower: Lake Towada.

A. West coast of Hokkaido Island

The observations of sea-water spray ice were conducted at the Hamamasu Harbor, located at the west coast of Hokkaido. Figure 2 shows the location of the observational site. Two dummy light beacons were set up at the northern breakwater extending from the north to the south: one consisted of fiberreinforced plastics (FRP) and the other one consisted of steel coated with acrylic silicon resin. The height of both dummy light beacons was approximately 4 m. The breakwater line was chosen perpendicularly to the primary wind direction during the winter season. High waves caused by north-westerly wind often generated a heavy spray jet at the dummy light beacons. The spray icing grew under heavy sea-water spray and during low temperatures [5]. Additionally, stormy weather often generated not only heavy spray jets, but also intense snowfall (Figure 3).

B. Spray icing on trees beside lake

Lake Inawashiro and Lake Towada are located on the main island of Japan (Figure 1). Lake Inawashiro, situated at 514 m a.s.l., has an area of approximately 100 km2 and an average depth of 50 m. Lake Towada, situated at 400 m a.s.l., has an area of approximately 60 km2 and an average depth of 70 m. Because of the depth of both lakes, almost the entire water surface is ice free, even in the middle of winter, when spray ice is usually formed along the shore. The exception is a narrow area at the northeast shore of the lakes that is covered with very thin ice.

Spray ice accumulates on trees at the lakeside, and often develops into a massive ice form (Figure 4). The samples of spray ice were collected on the east side of the lakes.

II. METHODS

The contribution of snow to spray ice formation is important to consider when estimating the growth rate of spray ice. In this study, we focused on the isotopic mass balance in sea-water, snow, and spray ice. Generally, the concentration of the heavy stable isotope ¹⁸O varies with phase changes, and depends on the temperature of the phase changes [8]. The oxygen isotopic composition δ^{18} O can be calculated using the following equation:

$$\delta^{18} O = \frac{R - R_{SMOW}}{R_{SMOW}} \times 1000 \, [\%]$$
(1)

where *R* is the isotopic ratio $H_2^{18}O / H_2^{16}O$ in the sample and *R*_{SMOW} is the isotopic ratio in Standard Mean Ocean Water.

The snow mass fraction of the spray ice samples is calculated from the isotopic mass balance. [9] [10] used an isotopic mass balance to estimate the contribution or fraction of snow in sea ice, where the snow ice consists of a mixture of snow and sea-water. The stable oxygen isotopic composition δ^{18} O in an ice segment (δi) can be estimated using the δ^{18} O values of sea-water (δw) and of snow (δs) in the following equation:

$$\delta i = (1 - f_s) \times (\delta w + f) + f_s \times \delta s \tag{2},$$

where f_s is the snow mass fraction in the ice segment and f is an effective fractionation coefficient associated with the freezing of sea-water. For the effective fractionation coefficient f, a value of 3.0 ‰ [11] or 2.9 ‰ [12] is used. Both values are empirical values for ice grown relatively slowly from pure water.



Figure 5: cross section of a sea spray ice sample.

III. OBSERVATIONAL RESULTS

The structural characteristics of the spray ice are analyzed using conventional thin-section and NMR imaging. Figure 5 shows the layered structure of a sea-water spray ice sample in cross section. The observed layering in the samples depends on the growth history of the spray ice. Additionally, the spray ice is composed of two ice types with different crystal structures: a granular layer with uniform, rounded smaller grains and an ice layer with columnar ice. The differences in the ice composition may be caused by snow. The granular structure is similar to rounded polycrystals in a seasonal snow layer on the ground. On the other side, the columnar ice layer is similar to ice layers in icicles [2] [13], although the ice layer included brine. NMR imaging indicates that these layers have brine drainage channels. NMR imaging of a lake-water spray ice indicates the absence of a channelized network within the columnar grains. The crystal shape is similar to that of sea-water spray ice, but its structure differs from the structure of sea-water spray ice due to the presence of brine.

The oxygen isotopic composition of the melted samples is analyzed using a standard mass spectrometer. Table 1 and Table 2 show the results of the average δ^{18} O values for the ice, snow, and water samples. In event 1, an average δ^{18} O value of -10.80 ‰ was calculated for the snow samples, while the average δ^{18} O value of the sea-water samples is -0.11 ‰. We could not obtain δ^{18} O values for the snow and sea-water samples of event 2, here we assume the same average values as for the samples of event 1. It is remarkable that almost all oxygen isotopic composition values of spray ice are higher than the values of the sea- or lakewater supply.

IV. LABORATORY EXPERIMENT

A. Equipment and Method

The oxygen isotopic composition values of spray ice were higher than that of the sea or lake water supply. This difference

Table 1 : Observed δ 18O values of sea spray ice samples
together with snow and sea-water samples. The values of
some spray ice samples are shown divided into two ice
types i e granular grains and ice laver

<u>, , , , , , , , , , , , , , , , , , , </u>	0	2
Sample	Ice type	$\delta^{18}O$
		(‰)
Event 1		
1A-1	Average	1.38
1A-2	Average	0.83
1A-3	Ice	1.09
1A-4	Granular	1.16
1B-1	Ice/Granular	0.42
1B-2	Ice	-0.24
1B-3	Granular	-0.09
1C-1	Ice/Granular	1.15
1C-2	Ice	1.13
1C-3	Granular	1.22
1D	Average	0.26
Event 2		
2A	Ice/Granular	-0.55
2B	Granular	-0.75
2C	Granular	-3.53
Snow		-10.80
Sea water		-0.11

Table 2: Observed δ^{18} O values of spray ice samples in lake together with snow and lake-water samples.

Sample	Ice type	$\delta^{18}O$
		(‰)
Lake Inawashiro		
Spray ice	Average	-8.2
Snow		-9.6
Lake water		-9.6
Lake Towada		
Spray ice	Average	-6.8
Snow		-12.5
Lake water		-8.1

suggests that isotope fractionation has occurred during the wet growth of the spray ice. It is conceivable that the fractionation coefficient of sea ice, i.e. f = 3.0, is over-estimated. Since this value decreases with an increment in the growth rate as suggested in sea ice study of [14], f of spray ice might be lower than these values.

To verify the *f* value, we investigated the isotope fractionation during the wet growth of spray ice through laboratory experiments. The experimental apparatus was set in a cold room at Hokkaido University of Education (Sapporo). The textile, Sky Clear Coat (SCC), was set on a cylinder (height: 2 m; diameter: 0.3 m). SCC (Taiyo Kogyo Corp., Tokyo, Japan) comprises polyester cloth and polyvinyl chloride coated with a T_iO₂ film; it exhibits hydrophilic behavior with a water contact angle of less than 30° owing to the photoinduced effect on the T_iO₂ surface [15]. A schematic view of the apparatus is shown in Figure 6. The air temperature in the cold room was maintained at approximately -20 °C. Small water droplets with a diameter of approximately 0.3-0.5 mm were supplied by a fan-shaped spray nozzle; they were sprayed on the cylindrical test specimen. The distance of the specimen from the spray nozzle was 1.1 m.

B. Experimental Results of Isotope Fractionation

Under the aforementioned conditions, wet growth of ice occurred on the windward side of the specimen. Spray water formed a thin fluid film flowing on SCC, which has a hydrophilic surface. Part of the water froze into spongy ice as it flowed down the textile surface. The surface gradually began to be covered by sheet-like ice. The duration of spray supply was 30 min. The maximum thickness of ice was 10 mm.

We carried out the experiments 6 times. Oxygen isotopic composition of the melted samples was analyzed using a standard mass spectrometer. From the results, the average δ^{18} O value of the spray ice was calculated as -10.52 ‰ with a standard deviation of 0.24. The average δ^{18} O value of the water supply was -11.92 ‰. The difference between the spray ice and the water was 1.41.

To decrease the growth rate of icing, the room temperature was raised to -10 °C, and an additional four experiments were conducted. The result of the average δ^{18} O value of the spray ice is -10.20 ‰ with a standard deviation of 0.18. The average δ^{18} O value of the water supply was -11.96 ‰. The difference between the spray ice and the water is, therefore, 1.76. As a result, the fractionation coefficient of -10 °C experiments is higher than the fractionation coefficient of the -20 °C experiments. This tendency agrees with the sea ice study [14].

Air temperature, wind speed, and growth rate of the spray ice fluctuates from hour to hour in nature, therefore the effective fractionation coefficient is not settled. In this study, we assumed an effective fractionation coefficient *f* of 1.5 for the calculation of the snow mass fraction. Lake Inawashiro was excluded from the calculation because the δ^{18} O value of snow was close to the value of lake-water.



Figure 6: Apparatus for laboratory experiment.



Figure 7: Snow Mass Fraction of Spray Ice.

V. DISCUSSION OT THE RESULTS

Figure 7 indicates the snow mass fraction of the spray ice samples in Table 1 and Table 2. The snow mass fraction of spray ice corresponds to icing events and ice samples. The snow mass fraction of spray ice responds to icing events and the oxygen isotopic composition values of granular ice layers tend to be lower than in other ice layers, suggesting the contribution of snow accumulation. High snow fractions in the samples demonstrate that snow contributed significantly to the growth of spray ice.

The values of granular ice layers tend to be higher than in other layers, suggesting the contribution of snow accumulation. High snow fractions in the samples demonstrate that snow contributed significantly to the growth of spray ice.

[7] investigated the structural characteristics of the spray ice in detail using the samples from Lake Inawashiro. They suggested that the ice structure consists of two different types of ice, a uniform orbicular granular type and a columnar type with large elongated grains. The characteristic granular structure is similar to snow ice in sea ice. They further suggested that the granular segment is composed of a mixture of snow and water spray tossed up on the beach, produced by penetration of water into the snow layer, which froze within such a structure.

VI. CONCLUSIONS

The contribution of snow to spray icing was investigated through field observations and laboratory experiments. The samples of sea-water spray ice and lake-water spray ice were analyzed using a conventional thin-section, NMR imaging and oxygen isotopic composition.

The observed layer structure in the samples depends on the growth history of the spray ice. Additionally, the spray ice consists of two ice types with different crystal structures: granular ice with uniform, rounded smaller grains and columnar ice. The differences in ice composition may be influenced by snow accretion.

The oxygen isotopic composition of the melted samples was analyzed using a standard mass spectrometer. The oxygen isotopic composition values of spray ice are higher than the values of the sea or lake water supply. This difference suggests that isotope fractionation has occurred during the wet growth of spray ice. We verified the isotope fractionation during the wet growth of artificial spray ice produced in cold room experiments.

The oxygen isotopic composition of the artificial spray ice indicates that the δ^{18} O values of the spray ice is higher than the value of the water supply. The difference between the values of spray ice and of water depends on the air temperature. The result suggests that the fractionation decreases with an increment in the growth rate of spray ice. We suggest an effective fractionation coefficient of 1.5 for the spray ice event.

The snow mass fraction of the spray ice samples is calculated from the isotopic mass balance. The snow mass fraction of spray ice responds to icing events and ice samples. The values of granular ice layers tend to be higher than for the other layers, suggesting the contribution of snow accumulation.

ACKNOWLEDGMENT

We wish to express our gratitude to Prof. H. Yamaguchi of University of Tokyo, and Dr. T. Kawamura of Hokkaido University for their useful discussion about spray icing. We would like to thank to Dr. S. Matoba and Ms. M. Kitagawa of Hokkaido University for their support of isotope ratio measurements. We are grateful to 1st Regional Coast Guard Headquarters for their support in the field observation. The field observation was supported by JSPS KAKENHI Grant Number 22310110. The laboratory experiment was supported by the research program of the Green Network of Excellence, MEXT, Japan.

REFERENCES

- L. Makkonen, "Salinity and growth rate of ice formed by sea spray", Cold Regions Sci. Technol., 14, pp. 163-171, 1987.
- [2] C. C. Ryerson and A. J. Gow, "Crystalline structure and physical properties of ship superstructure spray ice", Phil. Trans. Roy. Soc. Lond., A358, pp. 2847-2871, 2000.
- [3] T. Ozeki, K. Kose, T. Haishi, S. Nakatsubo and Y. Matsuda, "Network images of drainage channels in sea spray icing by MR microscopy", Mag. Res. Imag., 23, pp. 333-335, 2005.
- [4] J. E. Overland, "Prediction of Vessel Ising for Near-Freezing Sea Temperature", Weather and Forcasting, 5, pp. 62-77, 1990.
- [5] T. Ozeki, Y. Tamate, S. Adachi, K. Izumiyama and T. Tazawa, "Field observation of sea spray icing on lighthouses and ice adhesion test of superhydrophilic pliable sheet for deicing", Proc. 13th Int. Workshop Atmos. Icing Structures, 2009, 4 pp.
- [6] E. P. Lozowski, K. Szilder and L. Makkonen, "Computer simulation of marine ice accretion", Phil. Trans. Roy. Soc. Lond., A358, pp. 2811-2845, 2000.
- [7] T. Kawamura, T. Ozeki, H. Wakabayashi, M. Koarai, "Unique lake ice phenomena observed in Lake Inawashiro, Japan: Spray ice and ice balls", J. Glaciol., 55, pp. 939-942 (2009).

- [8] W. Dansgaard, S. J. Johnsen, H. B. Clausen and N. Gundestrup, "Stable Isotope Glaciology", Meddelelser om Gronland, 197, pp 1-53, 1973.
- [9] M. A. Lange, P. Schlosser, S. F. Ackley, P. Wadhams and G. S. Dieckmann, "180 Concentrations in sea ice of the Weddell Sea, Antarctica", J. Glaciol., 36(124), pp. 315-323, 1990.
- [10] M. O. Jeffries, A. P. Worby, K. Morris and W. F. Weeks, "Seasonal variations in the properties and structural an isotopic composition of sea ice and snow cover in the Bellingshausen and Amundsen Seas, Antarctica", J. Glaciol., 43(143), pp. 138-151, 1997.
- [11] J. R. O'Neil, "Hydrogen and oxygen isotope fractionation between ice and water", J. Phys. Chem., 72, pp. 3683-3684, 1968.
- [12] M. Lehmann and U. Siegenthaler, "Equilibrium oxygen- and hydrogen-isotope fractionation between ice and water", J. Glaciol., 37(125), pp. 23-26, 1991.
- [13] T. Tabata and N. Ono, "On the crystallographic study of several kinds of ices", Low Temperature Science, A20, pp.199-213, 1962. (in Japanese with English résumé)
- [14] H. Eicken, "Factors determining microstructure, salinity and stableisotope composition of Antarctic sea ice: Deriving modes and rates of ice growth in the Weddell Sea", AGU Antarctic Research Series, 74, pp. 89-122, 1998.
- [15] T. Ozeki, R. Yamamoto, K. Izumiyama and T. Sakamoto, "Ice Adhesion Tests on Pliable Polymer Sheets for Protection against Sea Spray Icing", J. Adhesion Sci. Tech., 26, pp. 651-663, 2012.