

Nutrient status of snow cover and sea ice in the southern Sea of Okhotsk

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Abstract

Samples of sea ice and snow cover on sea ice were collected with the icebreaker P/V *Soya* in early February 2007 in the southern Sea of Okhotsk in order to evaluate the amount of nutrients in the sea ice and snow. The concentration of nitrate + nitrite, phosphate and silicic acid in the samples was measured in conjunction with such physical parameters as temperature, salinity, oxygen isotopic ratio and ice texture. Sea ice was categorized into three types: snow-ice, granular ice and columnar ice, based on the oxygen isotopic ratio and ice texture. A higher nitrate + nitrite concentration up to 13.5 $\mu\text{mol L}^{-1}$ was found in the snow and snow-ice, implying the deposition from the atmosphere, occurring as snowfall. Phosphate and silicic acid concentrations up to 14.3 $\mu\text{mol L}^{-1}$ and 32.7 $\mu\text{mol L}^{-1}$, respectively, were highest in granular ice. These results indicate the incorporation of organisms and/or sediment from under-ice water and subsequent remineralization reactions in sea ice.

Introduction

In the Sea of Okhotsk, spring brooms were observed from satellite images after the ice melting season (e.g., <http://www.eorc.jaxa.jp/imgdata/topics/2004/tp040108.html>). Despite the indications that sea ice melting has been considered to play a role in the chemical budget and cycling in the Sea of Okhotsk, there is a distinct paucity of information on this aspect of sea ice.

During the ice formation process, sea ice contains a lot of particulate and dissolved materials (Masqué *et al.*, 2007). These materials are incorporated through atmospheric deposition (Granskog *et al.*, 2003; Granskog *et al.*, 2004) and suspension freezing in under-ice water (Masqué *et al.*, 2007). Therefore, sea ice acts as an effective transporter for particulate and dissolved materials. During the ice melting season, these materials are released and supplied to the under-ice water.

In this study, in order to examine the nutrient profiles in snow and sea ice, and mechanisms controlling the distribution of nutrients in snow and sea ice, samples of snow and sea ice were collected with the icebreaker P/V *Soya* during early February 2007 in the southern Sea of Okhotsk.

Materials and Methods

Sampling of snow, sea ice, and under-ice water

Field observations were carried out during the icebreaker P/V *Soya*'s cruise in the southern Sea of Okhotsk on February 12 and 13, 2007 (Fig. 1). Two different ice stations (A and B) were selected. Samples of sea ice cores, brine in sea ice and under-ice water were collected at each station. By using a basket suspended from the ship's crane, we could get access above the sea ice (Toyota *et al.*, 2007). Sea ice cores were collected with an ice core sampler of 9 cm diameter through a hole on the basket floor. Immediately after the ice core was collected, ice thickness and temperature of the ice core were measured by scale and by inserting a needle-like thermometer sensor into a drilled hole of the core, respectively. Thereafter, the ice cores were kept in a polythene bag in a deep freezer at -15°C during the cruise period, and transferred to the cold room at -16°C at the Institute of Low Temperature Science (ILTS) immediately after the cruise.

The under-ice water sample was collected through an ice core hole with a 500 mL Teflon water sampler (GL Science Inc., Japan) at depths of 1 m below the surface of sea ice. The sample was divided into a

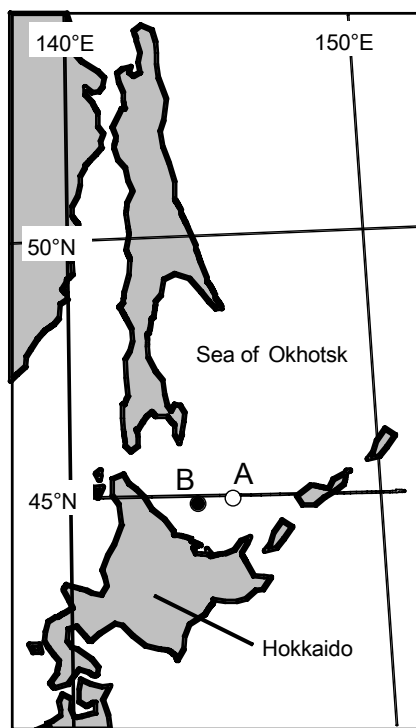


Fig. 1 Location map of Stn. A and B in the southern Sea of Okhotsk. Open circle indicates Stn. A (45°N 03'09.8", 144°E 34'44.5"). Solid circle indicates Stn. B (45°N 01'23.0", E143°E 47'14.0").

10 mL glass vial as a sub-sample for measuring salinity and oxygen isotopic ratio ($\delta^{18}\text{O}$) and into a 10 mL polyethylene screw vial for measuring nutrients. Samples for nutrients were kept in the same manner as that for the sea ice core samples.

The snow sample deposited over sea ice was collected through the side of the basket directly into pre-cleaned polyethylene zip-lock bags. The depth and temperature of the snow were measured by scale and by inserting a needle-like thermometer sensor, respectively.

Sample analysis

In the cold room of the ILTS, the sea ice core was divided into two pieces longitudinally. One side of the ice core was used for the measurement of salinity, $\delta^{18}\text{O}$ and nutrients. The other was used for the analysis of physical properties.

The sea ice sample was cut to 4.5 cm \times 2.5 cm in plane size by a band saw and then sliced into 3-cm thick sections to measure ice salinity, $\delta^{18}\text{O}$ and nutrients. In addition, the sea ice section was divided

into two pieces longitudinally. One side of the section was kept in a Teflon container and then melted to measure salinity and $\delta^{18}\text{O}$. In order to avoid contamination, the other piece was trimmed with a knife previously washed by acid, and then put into pre-cleaned polyethylene bags and melted to measure nutrients.

Pictures of the sea ice section divided into two pieces were taken. Then, we analyzed the physical properties of sea ice using thin and thick sections in order to clarify the ice formation history. Details of this analysis were described by Granskog *et al.* (2004). In this study, sea ice was categorized into three types: snow-ice, granular ice and columnar ice, based on the oxygen isotopic ratio and ice texture.

Salinity of the under-ice water, melted snow and sea ice were measured using a salt analyzer (SAT-210, Toa Electronics Ltd., Japan). A standard deviation calculated from the 15 sub-samples taken from a single sample bottle gave a salinity of 0.03. Nutrients (Dissolved Inorganic Nitrogen: DIN-N, $\text{Si}(\text{OH})_4$ -Si and PO_4 -P) were determined by an auto-analyzing system (AACS II, Bran+Luebbe, Germany) according to the JGOFS spectrophotometric method (JGOFS, 1994). DIN-N refers to the sum of the concentration of NO_3 -N, NO_2 -N and NH_4 -N. $\delta^{18}\text{O}$ was determined with a mass spectrometer (DELTA plus, Finnigan MAT, USA). The $\delta^{18}\text{O}$ in per mil was defined as the deviation of $\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$ ratio of the measured sample to that of the international standard water (SMOW). The precision of $\delta^{18}\text{O}$ analysis from duplicate determinations was within $\pm 0.02\text{‰}$ (Toyota *et al.*, 2007).

Results and Discussion

Characteristics of snow, sea ice and under-ice water

Two ice cores with an ice thickness of 47 cm (Core 1) and 55 cm (Core 2) were collected at Stn. A on February 12, 2007. One ice core with an ice thickness of 84 cm (Core 3) was collected at Stn. B on February 13, 2007. Snow depth was 4 cm at Stn. A and 9 cm at Stn. B.

Vertical profiles of temperature, salinity and $\delta^{18}\text{O}$ in snow and sea ice are shown in Figure 2. Temperatures at the upper part of the sea ice were lower than that at the bottom of the sea ice. At the bottom of the sea ice, temperatures corresponded to the freezing point of -1.8°C . Snow temperature was

dependent on the atmospheric temperature of -3.1°C on February 12, 2007 and -5.5°C on February 13, 2007. Although the ice temperature increased linearly with increasing ice depth, the shape of the profile for ice salinity and $\delta^{18}\text{O}$ were irregular through the ice cores. These results suggest that the dynamic processes were dominated by ice growth in the southern Sea of Okhotsk (Toyota *et al.*, 2007).

Figure 3 shows the vertical profiles of the ice section, thick and thin section for Core 2. As seen in Figure 3(a), dirt layers were found at a depth of -30 cm, from -35 to -40 cm and from -40 to -50 cm. Because $\delta^{18}\text{O}$ was greater than 0‰ through the ice core for Core 2 (Fig. 2), sea ice was made from the seawater. Therefore, dirt layers were attributed to the incorporation of dissolved or particulate materials from under-ice water. Dirt layers were also observed at a depth of -10 cm in Core 1.

Based on the results obtained from the ice texture and $\delta^{18}\text{O}$ (Figs. 2(c) and 3), sea ice was categorized into three types: snow-ice, granular ice and columnar ice (Table 1). The average data shown in Table 1 indicate that granular ice was dominant in the total ice thickness. These relationships agreed well with the results obtained previously in same area (Toyota *et al.*, 2004).

Nutrient concentrations in snow, sea ice and under-ice water

Vertical profiles of nutrient concentrations in snow, sea ice and under-ice water are shown in Figure 4. A higher nitrate + nitrite concentration was found in the upper part of the sea ice and snow, while phosphate and silicic acid concentrations were low. Although phosphate and silicic acid concentrations were very small in Cores 1 and 3, extremely high concentrations were observed in Core 2, where the dirt layers were found. This suggests that high phosphate and silicic acid concentrations were due to the incorporation of the materials from under-ice water.

Table 2 shows the nutrient concentrations for snow and each ice type. High nitrate + nitrite concentrations were found in the snow and snow-ice, implying the deposition was from the atmosphere, occurring as snowfall. In the Baltic Sea, high dissolved inorganic nitrogen (DIN) concentrations in snow and snow-ice were observed (Granskog *et al.*, 2003). DIN deposited from the atmosphere with snowfall can accumulate on sea ice, and can also become incorporated into the ice due to snow-ice formation. Because our study area is located off the east coast of Asia, it is possible that polluted snow

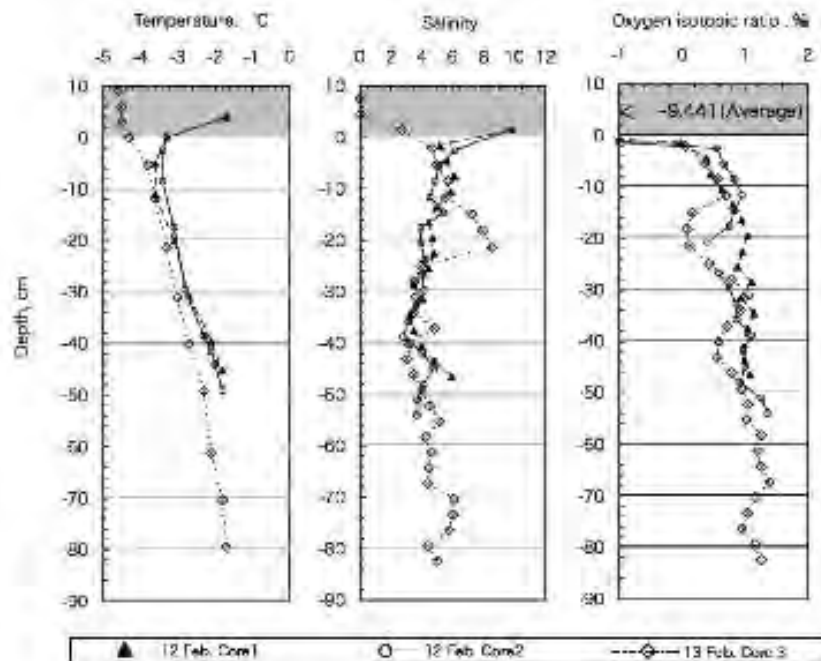


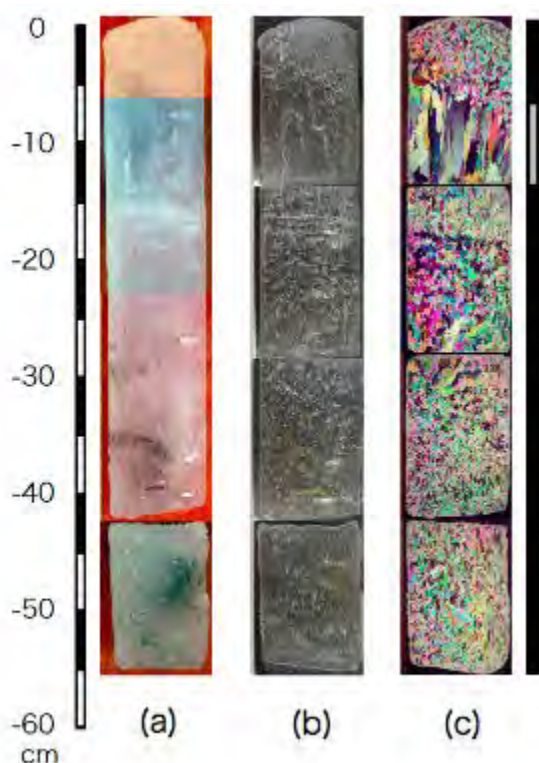
Fig. 2 Vertical profiles of temperature, salinity and $\delta^{18}\text{O}$ in sea ice and snow. Shaded areas indicate the part of the snow deposited over sea ice.

Table 1 Statistics of ice types and layer thicknesses.

Sample type	Core 1, Feb. 12, 2007		Core 2, Feb. 12, 2007		Core 3, Feb. 13, 2007		Average	
	Thickness (cm)	Fraction (%)	Thickness (cm)	Fraction (%)	Thickness (cm)	Fraction (%)	Thickness (cm)	Fraction (%)
Snow	4.0	7.8	4.0	6.8	9.0	9.7	17.0	8.4
Snow-ice	6.0	11.8	0.0	0.0	10.0	10.8	16.0	7.9
Granular	22.0	43.1	47.5	80.5	54.5	58.6	124.0	61.1
Columnar	19.0	37.3	7.5	12.7	19.5	21.0	46.0	22.7
Total	51.0	100.0	59.0	100.0	93.0	100.0	203.0	100.0

Table 2 Average nutrient concentration ($\mu\text{mol L}^{-1}$) for snow and each ice type (average \pm standard deviation (number of samples)).

Sample type	Average		
	$\text{NO}_2 + \text{NO}_3$	Si	P
Snow	8.05 ± 4.68 (3)	0.47 ± 0.12 (3)	0.0 ± 0.0 (3)
Snow-ice	1.77 ± 0.96 (5)	2.25 ± 0.52 (5)	0.57 ± 0.71 (5)
Granular	1.04 ± 0.62 (40)	4.87 ± 6.61 (40)	1.86 ± 3.19 (40)
Columnar	1.10 ± 0.90 (16)	1.62 ± 1.06 (16)	0.07 ± 0.16 (16)

**Fig. 3** Vertical profiles of (a) a picture of the section, (b) thick and (c) thin sections for Core 2. The black and gray bars indicate granular ice and columnar ice, respectively.

(high nitrate + nitrite concentration) was deposited over the sea ice. Therefore, in the Sea of Okhotsk, the atmospheric supply of DIN plays an important role in biological productivity within the sea ice and under-ice water, as in the Baltic Sea.

Phosphate and silicic acid concentrations were highest in granular ice, up to $14.3 \mu\text{mol L}^{-1}$ and $32.7 \mu\text{mol L}^{-1}$, respectively. This probably results from the selective incorporation of phosphate and silicic acid from seawater to sea ice. During granular ice formation, suspended and planktonic organisms were scavenged by frazil ice crystals (Lisitzin, 2002). In shallow areas, sediments are incorporated into sea ice when sea ice rests on the seafloor. In addition, the aerobic remineralization and denitrification occurred in sea ice (Thomas *et al.*, 1995; Rysgaard and Glud, 2004). Therefore, nitrate + nitrite concentrations were low in granular ice. On the other hand, phosphate and silicic acid concentrations were high in granular ice.

Conclusions

In order to examine the nutrient profiles in snow and sea ice, and mechanisms controlling the distribution of nutrients in snow and sea ice, samples of snow and sea ice were collected with the icebreaker P/V

Soya in early February of 2007 in the southern Sea of Okhotsk. A higher nitrate + nitrite concentration up to $13.5 \mu\text{mol L}^{-1}$ was found in the snow and snow-ice, implying the deposition was from the atmosphere, occurring as snowfall. Phosphate and silicic acid concentrations were highest in granular ice up to $14.3 \mu\text{mol L}^{-1}$ and $32.7 \mu\text{mol L}^{-1}$, respectively. This probably results from the incorporation of organisms and/or sediment from under-ice water and subsequent remineralization reactions in sea ice.

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