Nutrient distributions associated with snow and sediment-laden layers in sea ice of the southern Sea of Okhotsk

Daiki Nomura[a, b, c, d]*, Jun Nishioka[a], Mats A. Granskog[e], Andreas Krell[f], Sumito Matoba[a] Takenobu Toyota[a], Hiroshi Hattori[g] and Kunio Shirasawa[a]

Daiki Nomura (e-mail: nomura.daiki@nipr.ac.jp)
phone: +81-42-512-0746
fax: +81-42-528-3492

Jun Nishioka (e-mail: nishioka@lowtem.hokudai.ac.jp)
phone: +81-11-706-7655

Mats A. Granskog (e-mail: mats.granskog@npolar.no)
phone: +47-77-75-05-58

Andreas Krell (e-mail: Andreas.Krell@awi.de)
phone: +49-471-4831-1812

Sumito Matoba (e-mail: matoba@pop.lowtem.hokudai.ac.jp)
phone: +81-11-706-5485

Takenobu Toyota (e-mail: toyota@lowtem.hokudai.ac.jp)
phone: +81-11-706-7431

Hiroshi Hattori (e-mail: hattori@tspirit.tokai-u.jp)
phone: +81-11-571-5111

Kunio Shirasawa (e-mail: kunio@pop.lowtem.hokudai.ac.jp)
phone: +81-11-706-5425

a. Institute of Low Temperature Science, Hokkaido University, Kita-19, Nishi-8, Kita-ku, Sapporo, Hokkaido, 060-0819, Japan.

b. Japan Society for the Promotion of Science, 6 Ichiban-cho, Chiyoda, Tokyo 102-8471, Japan.

c. National Institute of Polar Research, 10-3 Midori-cho, Tachikawa-shi, Tokyo 190-8501, Japan.

d. Graduate School of Environmental Science and Faculty of Environmental Earth Science, Hokkaido University, Kita-10, Nishi-5, Kita-ku, Sapporo 060-0810, Japan.

e. Norwegian Polar Institute, The Polar Environmental Centre, Tromsø, NO-9296, Norway.

f. Alfred-Wegener-Institute for Polar and Marine Research, Am Handelshafen 12, D-27570 Bremerhaven, Germany.

g. Tokai University, Minamisawa, Minamiku Sapporo, Hokkaido 005-8601, Japan.

*Corresponding author (Daiki Nomura)
Daiki Nomura: Present address: National Institute of Polar Research, 10-3 Midori-cho, Tachikawa-shi, Tokyo 190-8501, Japan.

Abstract

Samples of first-year sea ice, snow and under-ice water were collected in the southern Sea of Okhotsk in mid-February 2007 and 2008 to elucidate the processes controlling nutrient concentrations in sea ice. Temperature, salinity, oxygen isotopic ratio ($\delta^{18}O$) and inorganic nutrient concentrations (NO_3, NH_4, NO_2, PO_4 and SiO_2) were measured. Sea ice was categorized into four types; snow-ice, frazil ice, columnar ice and a mixture of granular and columnar ice, based on $\delta^{18}O$ composition and ice texture. Frazil ice dominated the total ice thickness (52.8%), and columnar ice was sandwiched between frazil ice layers, indicating dynamic ice-growth processes such as rafting and ridging. Furthermore, the ice was banded by layers of particulate materials (sediment layers), which were frequently encountered during cruises. High NO_3 and NH_4 concentrations were found in snow and snow-ice implying that these were supplied from the atmosphere with snowfall and incorporated into the sea ice through snow-ice formation. In the sediment-laden layers, which were categorized as frazil ice, NO_2, PO_4 and SiO_2 concentrations were highest of all the ice types and considerably enriched compared to parent seawater, suggesting the remineralization of the particulate organic matter. On the other hand, NO_3 concentrations in sediment layers were low (depleted), leading to extremely low N (NO_3+NH_4+NO_2) : P ratios in sediment layers, from 0.2 to 0.8, with respect to that of under-ice water or Redfield ratio. These results suggest that in part of sediment-laden layers fixed-nitrogen was removed partially as molecular nitrogen (N_2) from the sea ice environment by anaerobic nitrate reduction processes (denitrification) by denitrifying bacteria while adding phosphate from associated remineralization of organic phosphorus. The effect of melting of snow and sea ice is dilution for salinity, NO_3 and SiO_2, no change in NO_2 and PO_4, and a minor enrichment for NH_4 in the mixed layer in spring and early summer. This suggests that snow/ice meltwater with different nutrient ratios than in under-ice water/Redfield ratio is supplied to under-ice water during melt season in April/May in southern Sea of Okhotsk. However, the impact of sediment-laden sea ice can not be assessed at this point.

Keywords: Sea ice; snow; nutrient; remineralization; sediment; Sea of Okhotsk

1. Introduction

Sea ice contains, besides pure ice, substantial amounts of gases, liquids, particulate and dissolved materials (Weeks and Ackley, 1982; Granskog and Kaartokallio, 2004; Eicken et al., 2005; Masqué et al., 2007). These materials are incorporated mainly by the following processes: the incorporation from parent water during ice formation (e.g. Weeks and Ackley, 1982), the exchange with seawater via brine channels, especially in the presence of organisms that can take up dissolved materials and render them as part of particulate matter (e.g. Thomas and Papadimitriou, 2003; Nomura et al., 2009) and atmospheric supply with precipitation, that can be incorporated into the ice cover (e.g. Granskog et al., 2003a; Granskog and Kaartokallio, 2004). Sea ice can move over long distances, and become a "transporter" for incorporated material (Masqué et al., 2007). During ice melt, this material is released to under-ice water. This suggests that sea ice has a potential role to contribute to the geochemical cycling in polar marine waters (Pfirman et al., 1997; Masqué et al., 2007). There are evidence that ice formation processes and dynamics of the ice cover support extensive ice rafting of sediments in Sea of Okhotsk (Lisitzin, 2003), although observations of sediment-laden sea ice are rare (Granskog, 1999), but there is indirect evidence that sea ice would carry material in southern Sea of Okhtosk (Hiwatari et al., 2008).

The extensive brine channel system in sea ice provides a habitat for organisms such as ice algae, which are the dominant inhabitants within the brine pockets and channels (e.g. Arrigo, 2003; Lizotte, 2003). During photosynthesis by ice algae, dissolved nutrient concentrations in sea ice decrease due to algal uptake, although nutrients are supplied and sometimes replenished from under-ice water at the bottom of sea ice (Thomas and Papadimitriou, 2003; Nomura et al., 2009), nutrient depletion has been observed even relatively close to the ice-water interface in Antarctic fast ice (McMinn et al., 1999). In the Baltic Sea and the White Sea, atmospheric deposition of nutrients into sea ice has been shown to be an important source of nutrients to the potentially nutrient depleted sea ice cover (Kaartokallio, 2001; Granskog et al., 2003a; Krell et al., 2003).

Sea ice also contains substantial amounts of heterotrophic organisms and bacteria (e.g. Gradinger et al., 1992). The oxidative remineralization of organic matter by these organisms leads to a release of nutrients (Thomas et al., 1995). Therefore, an increase of nutrient concentrations in sea ice relative to their concentrations in surface water is often correlated with decreasing oxygen concentrations (e.g. Rysgaard and Glud, 2004). There have been a few reports suggesting that denitrification in sea ice is due to oxygen demand imposed by aerobic metabolism in a closed (diffusion-limited) system leading to anaerobic conditions (Kaartokallio, 2001; Rysgaard and Glud, 2004; Rysgaard et al., 2008). More information of denitrification in sea ice is evidently needed in order to enable a better understanding of nutrient cycling in sea ice and nutrient budgets during sea ice melt.

Sea ice field observations in the southern Sea of Okhotsk, have mainly been conducted with a focus on understanding the physical characteristics of sea ice (Toyota et al., 2004; Toyota et al., 2007). The amount of particulate impurities in sea ice have been reported by Granskog (1999), but studies on the biogeochemistry, for example, dissolved inorganic nutrient concentrations in sea ice have not been reported from the southern Sea of Okhotsk. Since sea ice is mainly produced in the northern part of the Sea of Okhotsk and advected to the southern part, where it melts (Kimura and Wakatsuchi, 2004), therefore sea ice is, besides for fluxes of heat and freshwater, also potentially important for supply of any material transported with the ice.

The objective of this paper is to present, for the first time, nutrient concentrations in sea ice and snow in southern Sea of Okhotsk, and to discuss the mechanisms controlling nutrient distribution in sea ice in this region. The results obtained in this study would shed light towards understanding the role of sea ice in biogeochemical cycling in the southern Sea of Okhotsk, where large volumes of sea ice are advected from the north and melt.

2. Methods

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

Field observations were carried out during cruises on Japan Coast Guard icebreaker P/V Soya in the southern Sea of Okhotsk on 12 and 13 February 2007, and from 11 to 13 February 2008 (Fig. 1, Table 1). Six first-year sea ice samples were collected at five locations. Sea ice, snow on sea ice and under-ice water samples were collected from a steel basket suspended by the ship's crane through a hole in the basket floor at each station.

Sea ice samples were collected using an ice corer with an inner diameter of 9 cm (Mark II coring system, KOVACS Enterprises, Inc., USA). Immediately after sea ice was collected, ice temperatures were measured by inserting a needle-type temperature sensor (Testo 110 NTC, Brandt Instruments, Inc., USA) in holes drilled into the core. The ice cores were thereafter placed in a polyethylene bag and kept horizontally in a freezer (at -15℃) during the cruise.

Under-ice water samples were collected through the ice core holes using a 500 ml Teflon water sampler (GL Science Inc., Japan) at depths of 2-3 m below the surface of sea ice. Those water samples were collected approximately 15 min after drilling of ice cores to avoid disturbance caused by drilling. Under-ice water was sub-sampled, for salinity and oxygen isotopic ratio ($\delta^{18}O$) measurements into a 10 ml glass vial and into a 10 ml polyethylene screw cap vial for measuring inorganic nutrient concentrations. Nutrient samples were immediately put into a freezer (-15℃) and stored during the cruise. Salinity and $\delta^{18}O$ samples were kept at room temperature (+15℃).

Snow samples, integrated over the whole snow depth, were collected using a clean polycarbonate shovel into polyethylene zip-lock bags and then kept in the freezer (-15℃) during the cruise. Snow temperatures were measured using a needle-type temperature sensor (Testo 110 NTC, Brandt Instruments, Inc., USA) every 2-4 cm above the snow-sea ice interface.

The frozen samples were transferred to a cold room (-16℃) at an onshore laboratory immediately after the cruise.

2. 2. Sample analysis

In the cold room (-16℃) at Hokkaido University, ice cores were split lengthwise into two halves with an electric band saw, and photographs of the ice sections were taken in transmitted light. One half was used for thin section analysis to examine the ice texture, while the other half was used for measurement of ice salinity, $\delta^{18}O$ and nutrient concentrations. For thin section analysis, ice sections of 0.7 cm thickness were attached on glass plates and sliced off to 0.1 cm thickness with a microtome (Model SM2400, Leica Microsystems, Germany). Then, photographs of ice crystallographic structures were taken by illuminating the thin sections between crossed polarizers. For measurement of ice salinity, $\delta^{18}O$ and nutrient concentrations, the other half was cut to a 4.5 cm x 2.5 cm rectangular cross section and then sliced into 3.0-10.0 cm thick sections. To avoid contamination during sampling and handling processes, 0.3 cm of the outside of the ice sections were removed with a clean stainless steel plane. The remaining was thereafter put into polyethylene zip-lock bags for melting. These samples were melted shortly before analysis at room temperature, as were the snow samples.

Salinity of the melted snow and sea ice, and under-ice water were measured using a salt analyzer (SAT-210; Toa Electronics Ltd., Japan). A standard deviation for salinity calculated from 15 sub-samples taken from a reference water sample (S = 10.00) was 0.03 (Nomura et al., 2006). Nutrient concentrations (NO_3, NH_4, NO_2, PO_4, and SiO_2) were determined by an auto-analyzer system (Quattro; Bran+Luebbe, Germany) according to the joint global ocean flux study (JGOFS) spectrophotometric method (JGOFS, 1994). A standard deviation for nutrient concentrations calculated from 10 sub-samples taken from a reference water sample with 50.02 μmol l^{-1} for NO_3, 9.99 μmol l^{-1} NH_4, 2.51 μmol l^{-1} NO_2, 5.00 μmol l^{-1} PO_4, and 356.05 μmol l^{-1} SiO_2 was 0.53 μmol l^{-1} for NO_3, 0.18 μmol l^{-1} for NH_4, 0.03 μmol l^{-1} for NO_2, 0.07 μmol l^{-1} for PO_4, and 0.58 μmol l^{-1} for SiO_2, respectively. $\delta^{18}O$ was determined with a mass spectrometer (DELTA plus; Finnigan MAT, USA). $\delta^{18}O$ in per mil (‰) was defined as the deviation of $H_2{}^{18}O/H_2{}^{16}O$ ratio of the measured sample to that of the standard mean ocean water (SMOW). The precision of $\delta^{18}O$ analysis from duplicate determinations is ±0.02‰ (Toyota et al., 2007).

3. Results and discussion

3. 1. Physical properties of snow, sea ice and under-ice water

We collected six first-year sea ice cores (Table 1). The thickness ranged from 29.8 cm to 84.0 cm. Snow depth over sea ice ranged from 2.5 cm to 9.0 cm. Vertical profiles of temperature, salinity and $\delta^{18}O$ in snow, sea ice and under-ice water are shown in Figure 2. Snow temperatures varied corresponding with air temperature (Table 1). Sea ice temperatures were low at the upper part of the sea ice as compared to that of the bottom (Fig. 2a) because air temperatures were lower than in under-ice water (Table 1). Snow $\delta^{18}O$ ranged from -15.6‰ to -2.5‰, and these values were low compared to that in sea ice and under-ice water (Fig. 2c). Although sea ice temperatures distributed linearly through the sea ice (Fig. 2a), sea ice salinity and $\delta^{18}O$ variations were significant (Figs. 2b and c).

In order to examine ice growth processes, the ice cores were classified based on the thin section analysis into: granular ice, columnar ice and mixture of granular and columnar ice (g/c) (Eicken and Lange, 1989). The granular ice can be further divided into frazil ice and snow-ice (or superimposed ice) based on the $\delta^{18}O$ value (e.g. Granskog et al., 2003b; Toyota et al., 2004, Toyota et al., 2007). The criterion for snow-ice in the southern Sea of Okhotsk is given by the granular ice with negative $\delta^{18}O$ value (i.e. $\delta^{18}O < 0‰$) (see Toyota et al., 2004). However, when the layer of snow-ice is thinner than a unit ice segment (3-10 cm), $\delta^{18}O$ can be slightly positive. In this case, the boundary of snow-ice and snow-ice thickness was determined from vertical texture (Toyota et al., 2007). The fraction of each ice type for individual core was calculated by dividing the thickness of each ice type by the total ice thickness (Table 2).

Vertical thin sections indicate that granular ice was prominent in the ice cores (e.g, Fig. 3). The results indicate that frazil ice dominated the total ice thickness (52.8%) and that snow-ice contributed almost 10% (Table 2). These values agree well with results obtained previously in southern Sea of Okhotsk (Toyota et al., 2007). An additional highlight of Figure 3 is that columnar ice was sandwiched between frazil ice and mixture of granular and columnar ice (g/c). These results further support observations that dynamic ice-growth processes, such as rafting and ridging, are important for ice thickening in Sea of Okhotsk (cf. Toyota et al., 2007).

Sediment layers with a dark color were found at depths of 27-32 cm, 35-40 cm, and 45-55 cm below the ice surface at station A2 (Fig. 3a), and at a depth of 7-8 cm below the ice surface at station A1 (not shown). We consider that these sediment layers were attributed to the incorporation of suspended materials, such as sediments, ice algae and/or detritus from under-ice water during ice formation (cf. Masqué et al., 2007) and possibly by subsequent local microbial growth in sea ice, especially of photosynthetic algae. Sediment layers were found in layers of frazil ice (Fig. 3), therefore, it is difficult to consider that the material of the sediment layers to be supplied from atmospheric dust or snowfall, but rather incorporation of material in suspension (or seafloor) (e.g. Barnes et al., 1982). The possible origins of these sediment layers will be discussed in more detail below.

3.2. 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, and the nutrient concentrations for each ice type and snow are shown in Table 3. High NO_3 and NH_4 concentrations were found in snow compared to that of sea ice and under-ice water (Table 3). NO_3 concentration in snow was high, up to 49.2 $\mu mol\ l^{-1}$ at St. E, which was approximately 4 times higher than that of under-ice water (Fig 4a). NH_4 concentration in snow was also high, up to 16.9 $\mu mol\ l^{-1}$, which is 34 times higher than that of the under-ice water at St. E and the NH_4 concentration in sea ice was high compared to that of under-ice water at all stations (Fig. 4b). These might be caused by the geographical location of the study area, off the east coast of the Asian continent, since particulate pollutants contain high NO_3 and NH_4 concentrations (Ooki and Uematsu, 2005), brought along with snowfall deposit over sea ice in the Sea of Okhotsk. Same order of NO_3 (about 9-24 $\mu mol\ l^{-1}$) and NH_4 (about 3-18 $\mu mol\ l^{-1}$) concentrations in snow cover were measured on the Japan Sea side of Hokkaido (Aga et al., 2001). Therefore, our results suggest that NO_3 and NH_4 were supplied from the atmosphere with snowfall and incorporated into the sea ice with snow-ice formation. NO_3 concentrations in sea ice at St. C-E collected in 2008 were high compared to St. A1, A2 and B collected in 2007. This difference might be attributed to the area of the origin of sea ice, since for example, near the east coast of Sakhalin the NO_3 concentration in seawater is high (Nakatsuka et al., 2004).

NO_2, PO_4 and SiO_2 concentrations in snow and sea ice indicate different trends than those of NO_3 and NH_4 (Table 3 and Figs. 4c-e). Although NO_2, PO_4 and SiO_2 concentrations in snow were low compared to that of under-ice water (Figs. 4c-e and Table 3), extremely high NO_2, PO_4 and SiO_2 concentrations in sea ice were found at a depth of 8 cm below the ice surface at St. A1 and at a depth of 30-55 cm below the ice surface at St. A2. These concentrations were higher than in under-ice water, except for SiO_2 (Figs. 4c-e). Only one SiO_2 sample exceeded the values measured in under-ice water (Fig. 4e). The portions of extremely high NO_2, PO_4 and SiO_2 concentrations corresponded with sediment layers (see Fig. 3 and Figs. 4c-e), indicating a relationship between the sediment layers and elevated NO_2, PO_4 and SiO_2 in the ice.

In Baltic Sea accumulation of snow on sea ice was an important source of nitrogen, and could play an important role in biological productivity during ice melt when surface deposited nutrients were transported through the ice (Granskog et al., 2003a; Granskog and Kaartokallio, 2004). Therefore, in the southern Sea of Okhotsk, due to high NO_3 and NH_4 concentrations in snow in comparison to sea ice and under-ice water (see Table 3), the input of snow-melt water to sea ice and snow-ice formation become potentially an important nutrient source for sea ice and under-ice organisms (cf. Granskog et al., 2003a).

In order to estimate the potential effect of snow and sea ice melt on the water column, changes in salinity and nutrient concentrations in the water column (the mixed layer) before and after ice melt were evaluated (Table 4). Since sea ice is mainly produced in the northern part of Sea of Okhotsk and advected to the southern part by winds and ocean currents (Kimura and Wakatsuchi, 2004), much of the sea ice actually melts in the southern parts of Sea of Okhotsk. Therefore, the potential effect of melting snow and sea ice on the water column might be higher than deduced from the area of sea ice in the southern parts of Sea of Okhotsk. The southward sea ice transport off Sakhalin in the west central Okhotsk Sea from January to April was estimated to be 310-730 km^3 based on the combination of the ice thickness measured by the IPS (Ice Profiling Sonar) and ice-velocity data measured by ADCP (Acoustic Doppler Current Profiler) at moorings (Fukamachi et al., 2009). We assume that sea ice was covered with snow with a mean depth and density of 4.8 cm and 157.0 kg m^{-3}, respectively, melts in the southern Sea of Okhotsk (area estimated at about 15 x 10^4 km^2), and added to the surface mixed layer in the southern Sea of Okhotsk (20 m deep in July (Ohshima et al., 2005)). We used the mean salinity and nutrient concentrations of snow, sea ice, and under-ice water listed in Table 3. The results suggest that the potential effect of melting of sea ice in the water column results in dilution for salinity, NO_3 and SiO_2, no change in NO_2 and PO_4, and an increase up to factor of two for NH_4 (Table 4). Estimates of the particulate loading from sea ice are hard to give, as observations of sediment-laden sea ice are virtually non-existent, although there is contemporary evidence that lithogenic and detritus fluxes are large under melting sea ice in the southern Sea of Okhotsk (Hiwatari et al., 2008).

3.3. Remineralization and reduction processes in sea ice

Salinity and nutrient concentrations for each ice category were plotted and compared with the theoretical dilution line (e.g. Clarke and Ackley, 1982; Meese, 1989; Thomas et al., 1995; Giannelli et al., 2001) (Figs. 5a-e). Most plots of salinity-NO_3 (>86.8 % of the samples), -PO_4 (>76.5% of the samples) and -SiO_2 (>83.5% of the samples) in sea ice were below the theoretical dilution line (Figs. 5a, d and f). In salinity-NO_3, some plots (13.1 % of the samples) are way above the dilution line (Fig. 5a). These data were obtained from ice type of frazil and columnar ice collected at St. C-E in 2008, where NO_3 concentrations in sea ice were high compared to that at St. A1, A2 and B collected in 2007 (Fig. 4a). All plots of salinity-NO_2 and -NH_4 concentrations were above the dilution line (Figs. 5b and c). In salinity-PO_4 and -SiO_2 plots, sediment layers are way above the dilution line (Figs. 5d and f), suggesting that enrichment of PO_4 and SiO_2 in respect to salinity occurred. Low/depleted NO_3 concentrations in sediment layers correspond to excess NO_2, PO_4 and SiO_2 concentrations (Figs. 5a, and c-f). With respect to the N (NO_3+NO_2+NH_4) : P ratio of under-ice water of 10.2 and the Redfield ratio of 16.0, extremely low N:P ratios from 0.2 to 2.8 were observed in the sediment layers.

Here, we will examine the mechanisms controlling nutrient distribution in sea ice. In the part of frazil ice, columnar ice and g/c, the distributions of the NO_3, PO_4 and SiO_2 (Figs. 5a, d and f) indicate that the depletion of the nutrient occurred by biological uptake by ice algae (Thomas et al., 1995). On the other hand, some input or accumulation of NO_2 and NH_4 occurred in sea ice (Figs. 5b and c). For the nitrogen species, organic nitrogen compounds are transformed to NH_4 by ammonification by bacteria. Such high NH_4 values in sea ice have been measured in Arctic sea ice (about 0.8-3.5 μmol l^{-1}) caused by the regeneration of nitrogen compounds in sea ice (Dieckmann et al., 1991). The resulting NH_4 is then oxidized to NO_2 by ammonium oxidation and NO_3 by nitrite oxidation. Therefore, our results suggest that the combined reaction (biological uptake and remineralization) took place.

Sediment layers probably contained a high portion of particulate organic matter because sea ice incorporates suspended materials, such as sediments, algae and/or detritus during ice formation (Weeks and Ackley 1982, Granskog, 1999; Granskog and Kaartokallio, 2004; Eicken et al., 2005; Masqué et al., 2007). Granskog (1999) reported that the amount of total particulate matter (TPM) in Okhotsk sea ice was 2.7-51.6 mg l^{-1}, and TPM consisted mainly of organic matter, 75% on average. The enrichments of NO_2 and NH_4 observed in the Okhotsk sea ice sediment layer (Figs. 5b and c) suggest the remineralization of the organic matter by aerobic respiration. However, the extremely low N (NO_3+NO_2+NH_4) : P ratio in sediment layers as compared to that of Redfield ratio or under-ice water suggested that in part of sediment-laden layers fixed-nitrogen was removed partially as molecular nitrogen (N_2) from the sea ice environment by anaerobic nitrate reduction processes (denitrification). When oxygen is depleted, NO_3 replaces oxygen as the oxidant to mineralize organic matter, and denitrification occurs by denitrifying bacteria while adding phosphate by remineralization of organic phosphorus (Kaartokallio, 2001; Rysgaard and Glud, 2004; Rysgaard et al., 2008). Denitrification generally proceeds through some combination of the following intermediate forms:

$$NO_3 \rightarrow NO_2 \rightarrow NO + N_2O \rightarrow N_2\,(g).$$

Another anaerobic process that removes fixed nitrogen from water is the anaerobic ammonium oxidation (anammox) process, in which bacteria combine ammonium and nitrite to form N_2 in anoxic conditions (e.g. Rysgaard et al., 2008). Because both NH_4 and NO_2 concentrations remained high in the sediment layers (Figs. 5b and c), anammox process might have a minor effect. We surmise that the enrichment of SiO_2 in sediment layers, is a result of biogenic-opal (diatom) dissolution, as a result of undersaturation of the aqueous phase with respect to this mineral phase.

In southern Sea of Okhotsk we frequently observed sediment layers in sea ice, which broke at the ship's bow and then turned into side-up positions alongside the hull, not only during 2007 and 2008 but also during 2006 and 2009 Soya cruises (T. Toyota, unpubl.). Although we only sampled sediment-laden sea ice at limited locations, it occurs frequently. This compares to sediment-laden sea ice transported from Siberian shelf seas in the Arctic Ocean (e.g. Nürnberg et al., 1994; Eicken et al., 2005). And fluxes of sediment and detritus under sea ice, suggest that this is also an important phenomena in the Sea of Okhotsk (Hiwatari et al., 2008). Therefore, in order to understand the biogeochemical cycling in the southern Sea of Okhotsk, further investigations are highly desirable to on the one hand describe the extent and magnitude of sediment layers in sea ice which would also aid to better quantify the impact during ice melt and on the other hand to examine their influence on nutrient dynamics in sea ice.

4. Conclusions

We examined the nutrient distribution of sea ice in the southern Sea of Okhotsk in relation to environmental variables. High NO_3 and NH_4 concentrations were found in snow deposited over sea ice and in snow-ice layers, suggesting that NO_3 and NH_4 were supplied from the atmosphere with snowfall and incorporated into the sea ice by snow-ice formation. Similar tendencies have also been reported from other sub-arctic seas (Granskog et al., 2003a; Granskog and Kaartokallio, 2004). On the other hand, NO_2, PO_4 and SiO_2 concentrations were highest while NO_3 concentration was low/depletion at the dark sediment layers. The extremely low N (NO_3+NO_2+NH_4) : P ratio observed in the Okhotsk sea ice sediment layers as compared to that of Redfield ratio indicated the N_2 production that removes fixed nitrogen from the sediment layer occurred.

The effect of melting of snow and sea ice in the mixed layer is a dilution for salinity, NO_3 and SiO_2, no change in NO_2 and PO_4, and a minor enrichment for NH_4. This suggests that the ice-meltwater with a different nutrient ratio (e.g. N:P ratio) than under-ice water/Redfield ratio is supplied to under-ice water during the ice melting season typically occurring in April/May in the Sea of Okhotsk although the effect is minor. On the other hand, the effect of the particulate loading released from sea ice can not be easily evaluated, although there is evidence for significant release of particulate material from melting sea ice in the region (Hiwatari et al., 2008). Evidently there is a further need to investigate the exact role of sediment-laden sea ice, on the one hand on sea ice biogeochemistry, and on the other hand on the biogeochemical cycling in Sea of Okhtosk as a whole. Particulate transport in sea ice might be an important mechanism for contaminant and material transport, as observed in the Arctic (e.g. Pfirman et al., 1997).

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Fig. 1 Location of sampling stations in the southern Sea of Okhotsk (see Table 1). The dashed and solid lines indicate the ice edge on 13 February 2007 and 12 February 2008, respectively. Solid markers denote stations in 2007, open markers in 2008.

Fig. 2 Vertical profiles of (a) temperature, (b) salinity and (c) $\delta^{18}O$ in snow, sea ice and under-ice water. The areas of gray and black indicate snow and under-ice water, respectively. The solid white circles and the error bars indicate the mean and standard deviation for each property of under-ice water. Insert in (c) shows the $\delta^{18}O$ in snow.

Fig. 3 Pictures of (a) an ice core half in transmitted light, (b) a thin section in polarized light from station A2. Diagrams of (c) to (h) indicate the bar diagram of ice type for each station.

Fig. 4 Vertical profiles of (a) NO_3, (b) NH_4, (c) NO_2, (d) PO_4 and (e) SiO_2 concentrations in snow, sea ice and under-ice water for each sample. The areas of the gray and black indicate the snow and under-ice water, respectively. The solid white circles and the error bars indicate the mean and standard deviation in under-ice water. The solid blue and light blue bars indicate the portion of the sediment layers for St. A1 and A2, respectively. Inset in (a) indicates the NO_3 concentration in snow.

Fig. 5 Salinity versus (a) NO_3, (b) NH_4, (c) NO_2, (d) PO_4 and (e) SiO_2 concentrations in sea ice for frazil ice (open triangles), sediment layers (solid triangles), columnar ice (open circles) and g/c (open squares). The solid and dashed lines indicate the dilution line predicted from the mean and extreme values in under-ice water, respectively.

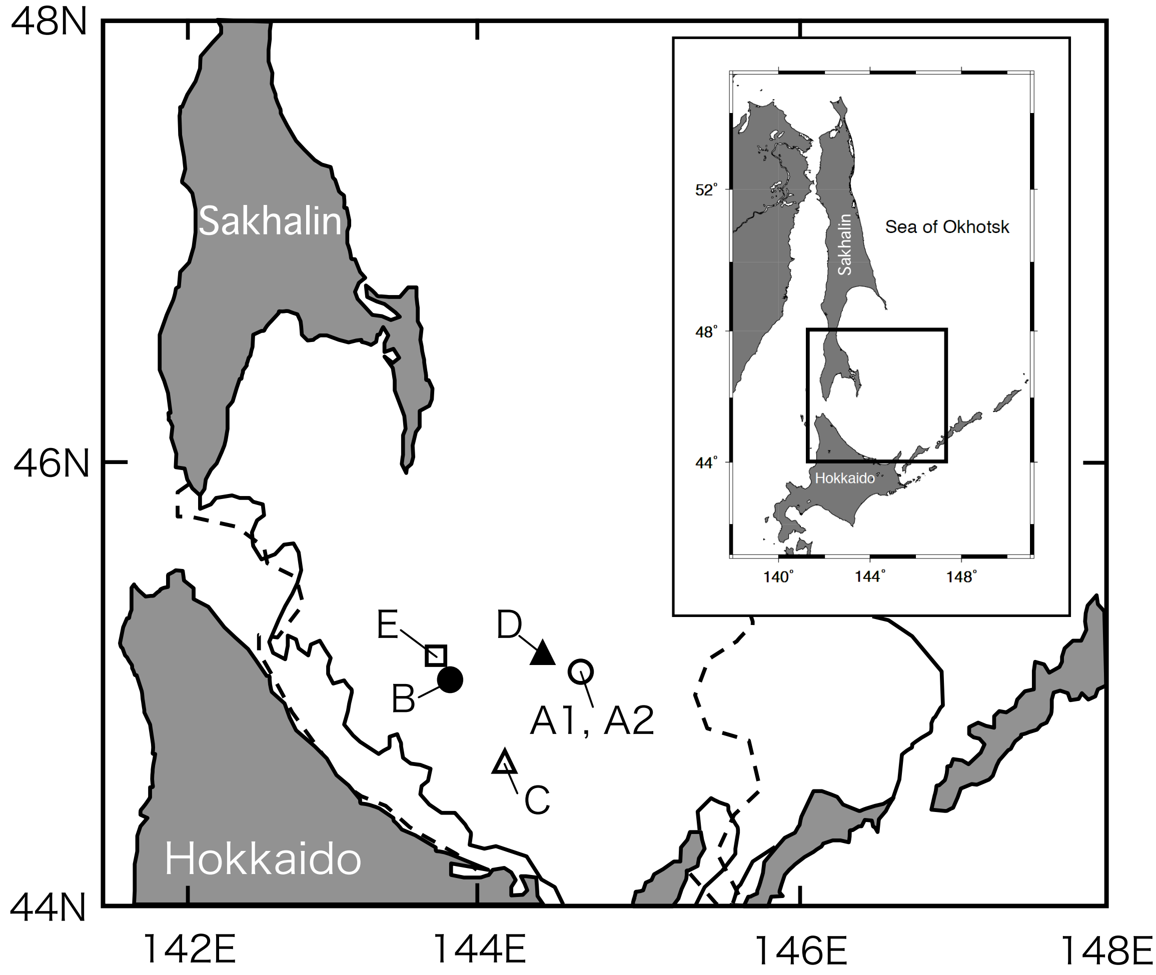


Fig. 1 Nomura et al.

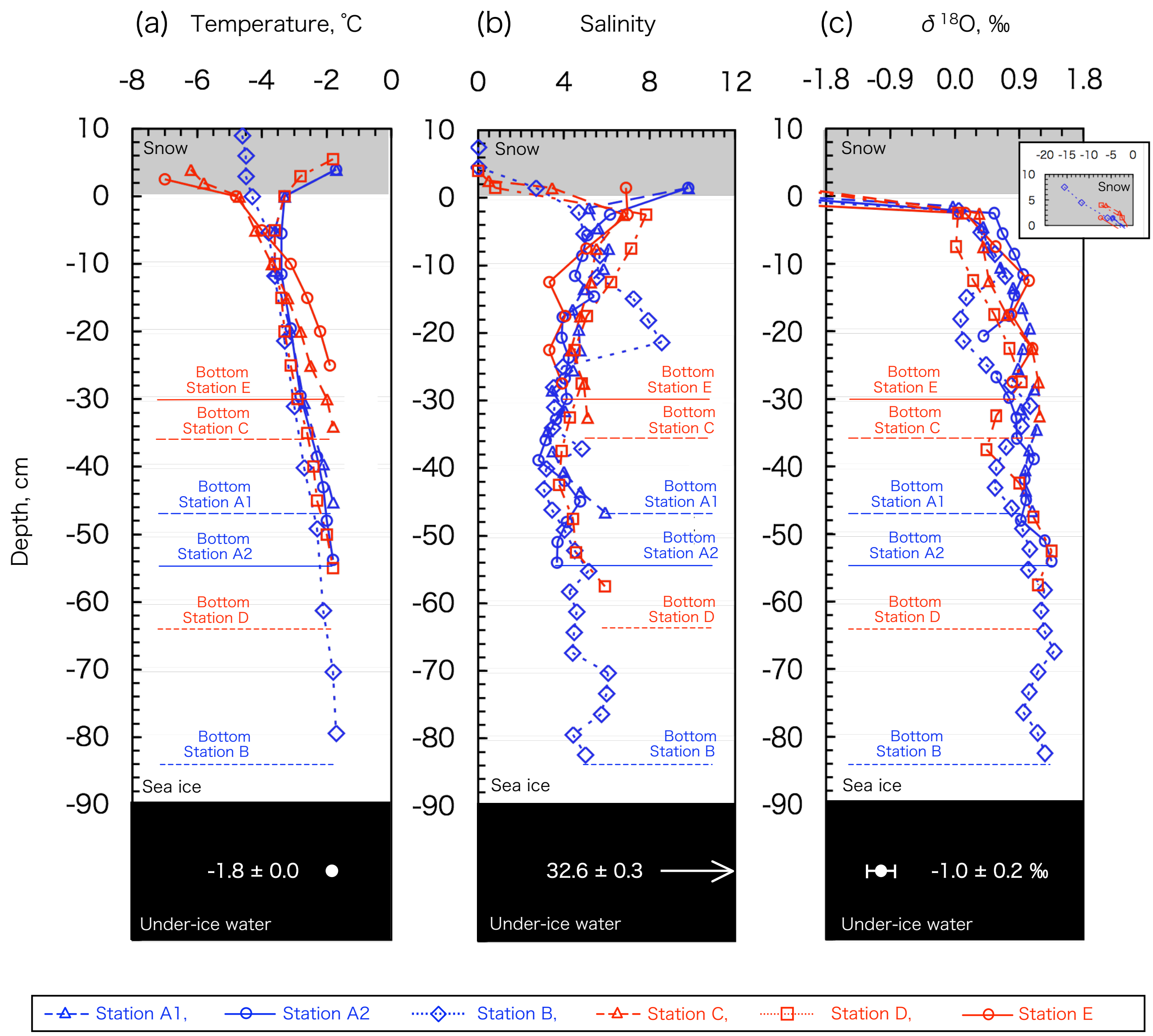
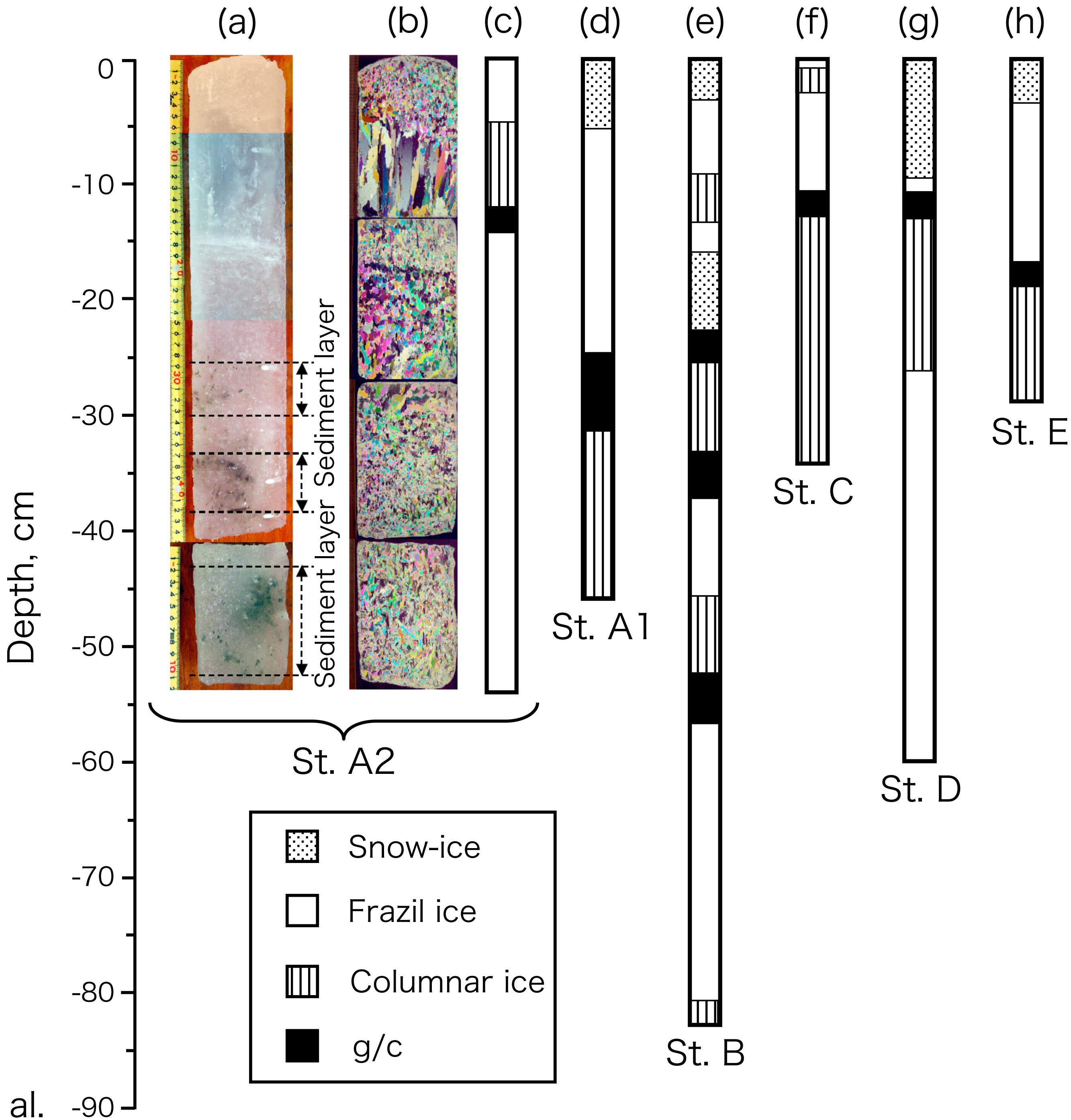


Fig. 2 Nomura et al



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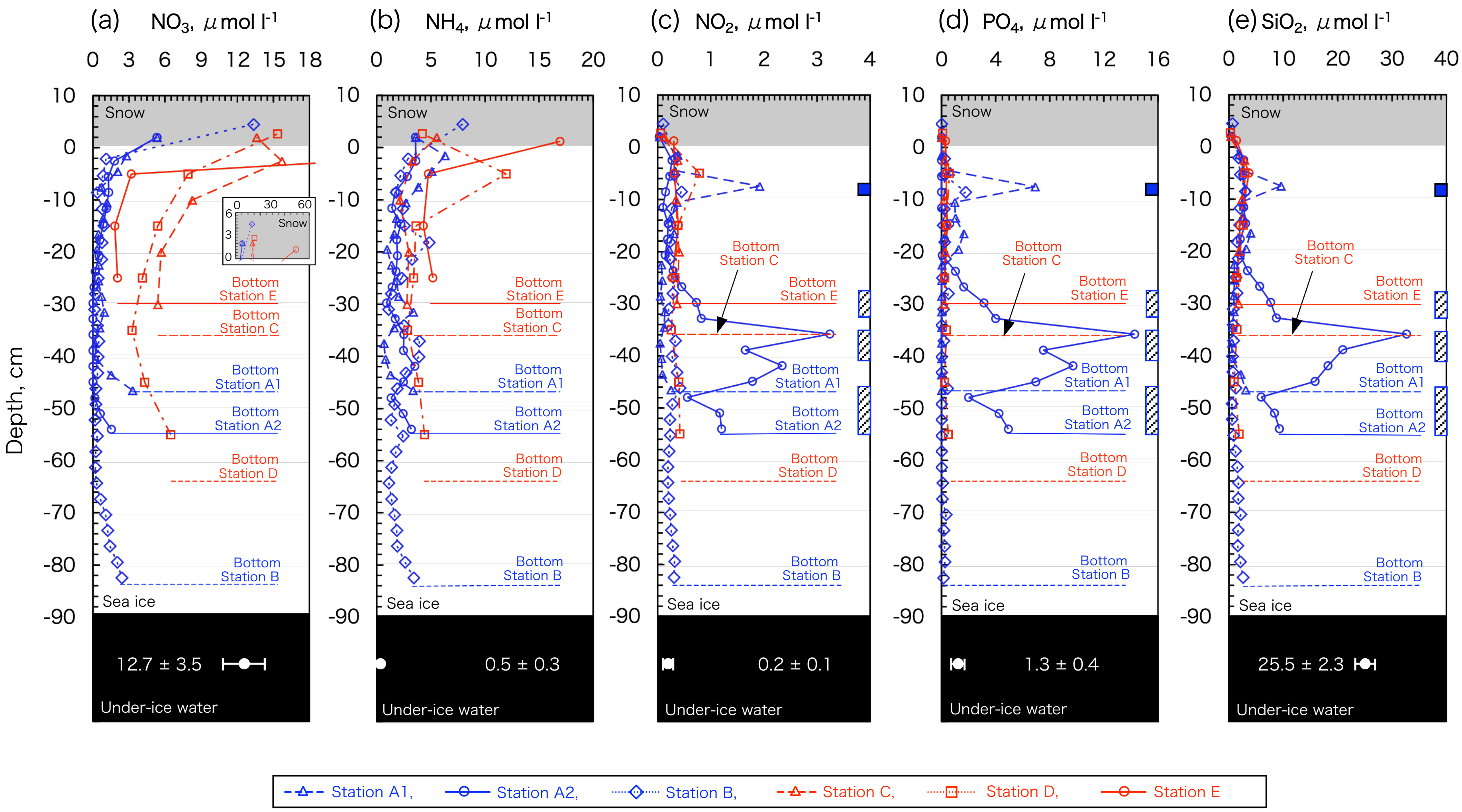

Fig. 4 Nomura et al.

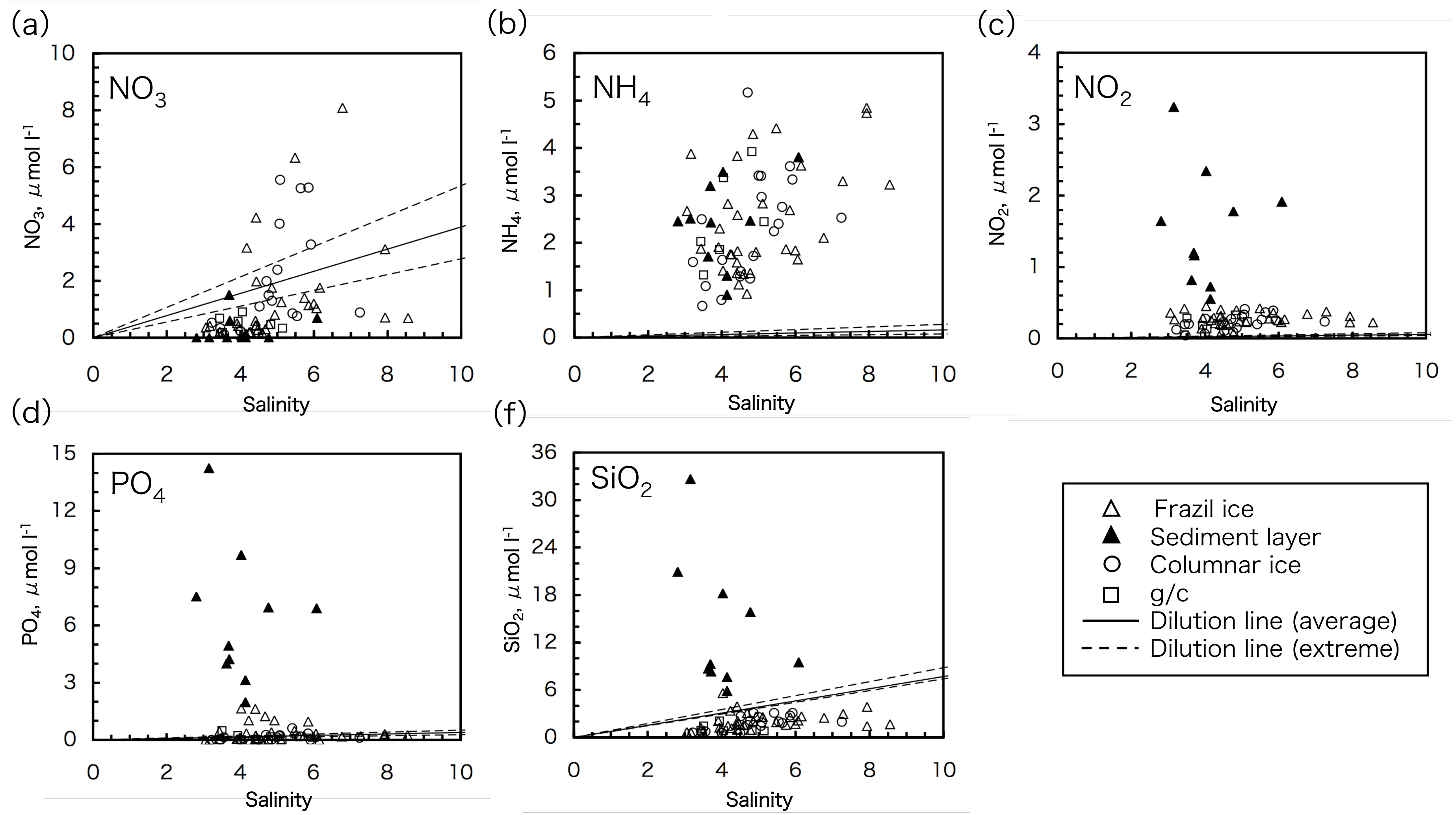

Fig. 5 Nomura et al.

Table 1. Sampling date, station, location, air temperature, snow depth and ice thickness.

Date	Station	Location	Air temperature (°C)	Snow depth (cm)	Ice thickness (cm)
12 February 2007	A1	45º03'10"N, 144º34'45"E	–3.1	4.0	47.0
12 February 2007	A2	45º03'10"N, 144º34'45"E	–3.1	4.0	55.0
13 February 2007	B	45º01'23"N, 143º47'14"E	–5.5	9.0	84.0
11 February 2008	C	44º35'31"N, 144º02'37"E	–7.1	4.0	35.0
12 February 2008	D	45º09'28"N, 144º20'01"E	–0.2	5.5	60.4
13 February 2008	E	45º07'22"N, 143º34'53"E	–8.2	2.5	29.8

Table 1 Nomura et al.

Table 2. Fraction of ice type for ice samples collected at each station.

Ice type	Fraction (%)						
	St.A1	St.A2	St.B	St.C	St.D	St.E	Mean[b]
Snow-ice	12.5	0.0	11.1	0.0	18.5	12.8	9.7
Frazil ice	43.8	77.8	51.9	29.1	55.0	47.3	52.8
Columnar ice	31.3	16.7	25.9	65.7	24.5	34.6	30.1
g/c[a]	12.5	5.6	11.1	5.1	2.0	5.4	7.3

[a]"g/c" indicates the mixture of granular and columnar ice.

[b]"Mean" was calculated by dividing the total thickness of each ice type by the total ice thickness.

Table 2 Nomura et al.

Table 3. Mean nutrient concentrations (μmol l^{-1}) and salinity with standard deviation for snow, ice category (snow-ice, frazil ice, columnar ice and g/c), mean (sea ice) and sediment layers for ice samples and under-ice water.

	Number of samples	Salinity	NO_3	NH_4	NO_2	PO_4	SiO_2
Snow	6	3.7 (±4.8)	17.0 (±16.3)	7.0 (±5.2)	0.1 (±0.1)	0.1 (±0.1)	0.6 (±0.4)
Snow-ice	6	5.6 (±0.9)	2.5 (±2.8)	5.0 (±3.8)	0.4 (±0.2)	0.6 (±0.6)	2.4 (±0.5)
Frazil ice	43	4.8 (±1.4)	1.5 (±2.8)	2.5 (±1.1)	0.6 (±0.7)	1.8 (±3.1)	4.8 (±6.4)
Columnar ice	20	4.8 (±1.0)	1.8 (±1.9)	2.3 (±1.2)	0.2 (±0.1)	0.1 (±0.2)	1.7 (±1.0)
g/c[a]	6	4.8 (±0.7)	0.5 (±0.3)	2.5 (±1.0)	0.2 (±0.1)	0.1 (±0.2)	1.2 (±0.5)
Mean (sea ice)	75	4.8 (±1.2)	1.6 (±2.5)	2.6 (±1.6)	0.4 (±0.5)	1.1 (±2.5)	3.5 (±5.1)
Sediment layers[b]	10	4.0 (±0.9)	0.3 (±0.5)	2.4 (±0.9)	1.5 (±0.8)	6.4 (±3.6)	13.7 (±8.3)
Under-ice water	5	32.6 (±0.3)	12.7 (±3.5)	0.5 (±0.3)	0.2 (±0.1)	1.3 (±0.4)	25.5 (±2.3)

[a]"g/c" indicates the mixture of granular and columnar ice.

[b]"The location of "sediment layers" in the cores was based on the examination of an ice core half in transmitted light (e.g., Fig. 3).

Table 3 Nomura et al.

Table 4. Changes of the salinity and nutrient concentrations (μmol l^{-1}) in the water column before and after ice melt in the southern Sea of Okhotsk.

	Salinity	NO_3	NH_4	NO_2	PO_4	SiO_2
Before ice melt[a]	32.6	12.7	0.5	0.2	1.3	25.5
After ice melt	27.2-30.0	10.5-11.7	0.7-0.9	0.2	1.2-1.3	21.2-23.4

[a]We used the mean values obtained during our observations (see Table 3).

Table 4 Nomura et al.