Physical controls on the storage of methane in landfast sea ice

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Abstract

We report on methane (CH_4) dynamics in landfast sea ice, brine and under-ice seawater at Barrow in 2009. The CH_4 concentrations in under-ice water ranged between 25.9 and 116.4 nmol L^{-1}_{sw}, indicating a supersaturation of 700 to 3100 % relative to the atmosphere. In comparison, the CH_4 concentrations in sea ice, ranged between 3.4 and 17.2 nmol L^{-1}_{ice}, and the deduced CH_4 concentrations in brine, between 13.2 and 677.7 nmol L^{-1}_{brine}. We investigated on the processes explaining the difference in CH_4 concentrations between sea ice, brine and the under-ice water, and suggest that biological controls on the storage of CH_4 in ice was minor in comparison to the physical controls. Two physical processes regulated the storage of CH_4 in our landfast ice samples: bubble formation within the ice and sea ice permeability. Gas bubble formation from solubility changes had favoured the accumulation of CH_4 in the ice at the beginning of ice growth. CH_4 retention in sea ice was then twice as efficient as that of salt; this also explains the overall higher CH_4 concentrations in brine than in the under-ice water. As sea ice thickened, gas bubble formation became less efficient, CH_4 was then mainly trapped in the dissolved state. The increase of sea ice permeability during ice melt marked the end of CH_4 storage.

1 Introduction

Methane (CH_4) is a well-mixed greenhouse gas. Its concentration in the atmosphere is much lower than that of its oxidation product (CO_2) (1.9 ppm *versus* 397 ppm respectively) (http://www.esrl.noaa.gov/gmd/aggi/). However, since CH_4 global warming potential is 28 times higher than that of CO_2 over a 100-year frame, it accounts for 20 % of the global radiative forcing of the well-mixed greenhouse gases (Myhre et al., 2013).

Global ocean emission of CH_4 is estimated at 19 Tg per year (Kirschke et al., 2013), which is about 3 % of the global tropospheric CH_4 input. 75 % of that marine contribution is from coastal regions (Bange et al., 1994). CH_4 supersaturation relative to the atmosphere in estuaries (Borges and Abril, 2011; Upstill-Goddard et al., 2000) and coastal shelves (Kvenvolden et al., 1993; Savvichev et al., 2004; Shakhova et al., 2005; Shakhova et al., 2010) are indeed larger to that in the open ocean (Bates et al., 1996; Damm et al., 2010; Damm et al., 2008; Damm et al., 2007).

Methanogenesis in sub-marine sediments is thought to be the main process causing CH_4 efflux in the Arctic shelf regions. Nonetheless, other sources could also be significant: CH_4 seepage from coastal ice-complex deposits (Romanovskii et al., 2000) and from the deeper seabeds (Judd, 2004), and CH_4 dissociation in the shallow hydrates (Reagan and Moridis, 2008; Westbrook et al., 2009). Recently, aerobic CH_4 production in the water column related to DMSP degradation was reported in the central Arctic (Damm et al., 2010), tropical upwelling areas (Florez-Leiva et al., 2013) and tropical oligotrophic areas (Zindler et al., 2012). However, the significance of that process over the Arctic shelf still needs to be assessed.

Ongoing global warming is likely to affect the various sources of CH_4 cited above, with positive feedback on the climate. Indeed, increase in sea temperature should increase methanogenic activities, leading to a more efficient conversion of organic matter to CH_4 (Zeikus and Winfrey, 1976). In addition, the induced seawater stratification is likely to change the nutrients ratio, which favours aerobic CH_4 production (Karl et al., 2008). Moreover, warmer seawater is likely to weaken the coastal ice-complex (including sub-sea permafrost) (Lawrence et al., 2008) and to displace the gas hydrate stability zones (Reagan and Moridis, 2008), increasing gas seepage. Significant CH_4 escape has been recently detected via acoustic surveys along Spitsbergen continental margin (Westbrook et al., 2009), suggesting that

changes in the CH_4 storage system are ongoing. Since CH_4 has a high global warming potential, its release will enhance the global warming, which in turn will enhance methanogenic activities and gas seepages. This positive feedback contributed to rapid and significant climate warming in the past (O'Connor et al., 2010).

Understanding the current CH_4 budget is thus important to better simulate future climate scenarios. Many CH_4 measurements have been carried out in sediments and seawater throughout the coastal Arctic areas (Kvenvolden et al., 1993; Savvichev et al., 2004; Shakhova et al., 2005; Shakhova et al., 2010). These observations have led to speculations about potential CH_4 accumulation (Shakhova et al., 2010) and/or oxidation (Kitidis et al., 2010) under sea ice cover. Other studies further brought forward the role of sea ice in the exchange of CH_4 between seawater and the atmosphere (He et al., 2013; Kort et al., 2012). However, to the best of our knowledge, no study has yet discussed the physical controls on the storage of CH_4 in sea ice and its exchange at the atmosphere-ice-ocean interfaces. For instance, CH_4 mixing ratio up to 11 000 ppmV have been measured in sea ice bubbles (Shakhova et al., 2010), but the mechanisms leading to the incorporation of those gas bubbles within the ice have not been discussed. Similarly, He et al. (2013) suggested CH_4 consumption in the ice, based on their CH_4 fluxes above sea ice. However, they did not discuss the impact of sea ice permeability or ice melt on their results, while these parameters have been shown to affect other gas dynamics in sea ice (see e.g., Loose et al. (2009) for O_2 and SF_6, Geilfus et al. (2012) and Nomura et al. (2010) for CO_2 and Zhou et al. (2013) for Ar). Therefore, we felt it necessary to highlight the physical controls on CH_4 dynamics in sea ice, from ice growth to ice melt. We have done this by investigating the annual evolution of CH_4 concentrations ($[CH_4]$) in sea ice, in parallel with sea ice physical properties and $[CH_4]$ in seawater. To the best of our knowledge, we report here the first detailed time series of $[CH_4]$ in sea ice across seasons.

2 Material and methods

2.1 Study site and physical framework

Sea ice and under-ice seawater samples were collected during a field survey in the Chukchi Sea near Barrow (Alaska) (Fig. 1), from January through June 2009. The sampling was performed on level first-year landfast sea ice, within a square of 50 meters by 50 meters. The

north-eastern corner of the square was located at 71° 22.013' N, 156° 32.447' W. Seawater depth at the location was about 6.5 m (http://seaice.alaska.edu/gi/observatories/barrow_sealevel). Ice cores were extracted and kept in the laboratory at -35 °C in the dark to prevent brine drainage and to limit biological activity. Temperature recorders indicated that the samples were always kept below -20 °C during the transport. All of the analyses were completed within the following year. A complete physical framework of the present study is presented and discussed in Zhou et al. (2013). We have selected 6 sampling events to illustrate the evolution of [CH_4] at our location: one in the winter (BRW2; February 3), 4 in early spring (BRW4, BRW5, BRW6 and BRW7; corresponding to March 31, April 3, April 7 and April 10 respectively), and the final one in late spring (BRW10; June 5). The first 5 sampling events occurred during ice growth, the last one during ice decay.

2.2 CH_4 in seawater

[CH_4] in seawater were determined by gas chromatography (GC) with flame ionization detection (SRI 8610C GC-FID) (Skoog et al., 1997), after creating a 30 mL headspace with N_2 in 70 mL glass serum bottles, following the procedure described by Abril and Iversen (2002). After creating the N_2 headspace, samples were vigorously shaken for 20 min and were placed in a thermostatic bath overnight at -1.6 °C. The following day, the samples were shaken again for 20 min before starting the GC analysis. CH_4:CO_2:N_2 mixtures (Air Liquide, Belgium) of 1, 10 and 30 ppm CH_4 were used as standards. The concentrations were then computed using the CH_4 solubility coefficient given by Yamamoto et al. (1976). The accuracy of the measurements was 1 %.

We calculated the solubility of CH_4 in seawater that is in equilibrium with the atmosphere, following Wiesenburg and Guinasso (1979). The ratio between the measured [CH_4] in seawater and the calculated solubility in equilibrated seawater determines the supersaturation factor.

2.3 CH_4 in bulk ice and brine

We used the wet extraction method to extract CH_4 from sea ice, as described in Raynaud et al. (1982) for continental ice. Briefly, 80 g of ice sample were put in a small container, using a 5 cm vertical resolution. The ice sample was then melted in the container under vacuum (10^{-3}

torr), using a “bain-marie”. It was then slowly refrozen from the bottom, using an ethanol (96 %) bath that was cooled to -80 °C by addition of liquid N_2. After refreezing, the whole gas content (both dissolved and in the bubbles) was expelled to the headspace of the container. The expelled gas was then injected, through a 22 ml packed column (Mole Sieve 5 A 80/100; 5 m x 1/8”), into a gas chromatograph (Trace GC) equipped with a flame ionisation detector for [CH_4] measurement. The reproducibility of the measurement, based on triplicate analysis of 5 different standards, was 99.6%.

The method described here above gives [CH_4] in bulk ice. Providing that there is no CH_4 in the pure ice matrix (Weeks, 2010), and hence that the entire amount of CH_4 (dissolved or in gas bubbles) is found within the ice pores (i.e. brine channels), [CH_4] bulk ice divided by the brine volume fraction (Cox and Weeks, 1983) gives the deduced [CH_4] in brine.

Dissolved [CH_4] in brine was also measured on brine samples collected using the sackhole technique (e.g., Gleitz et al., 1995; Papadimitriou et al., 2007). Sackholes (partial core holes) were drilled at different depths, ranging from 20 to 130 cm. Brines, from adjacent brine channels and pockets, seeped into the sackholes and were collected after 10 to 60 min using a peristaltic pump (Cole Palmer, Masterflex® - Environmental Sampler). Each sackhole remained covered with a plastic lid to minimize mixing with the free-atmosphere. Brines were collected in 70 mL glass serum bottles, filled to overflowing, poisoned with 100 µL of saturated $HgCl_2$ and sealed with butyl stoppers and aluminium caps. The measured [CH_4] in brine is an integrated value of the CH_4 in brine from all the ice layers above the sampling depth. Therefore, the vertical resolution is lower than that of the [CH_4] in brine that is deduced from the [CH_4] in bulk ice. It is also noteworthy that the relative contribution of the various depth levels is unknown and dependent on the brine volume changes with depth. However, it is of interest to compare the measured [CH_4] in brine with the [CH_4] in brine that is deduced from the bulk ice values, as discussed later on.

For data interpretation, we calculated CH_4 solubility in brine and in ice (i.e., potential [CH_4] dissolved in brine and in bulk ice respectively). The solubility of CH_4 in brine was calculated using the temperature and salinity-dependent solubility of Wiesenburg and Guinasso (1979) as for seawater. This is allowed providing that the relationship of Wiesenburg and Guinasso (1979) is valid for the ranges of brine-temperature and -salinity. As for the conversion of [CH_4] in bulk ice into the deduced [CH_4] in brine, we simply multiplied the solubility of CH_4 in brine by the brine volume fraction to get the solubility of CH_4 in bulk ice. Brine salinity

and brine volume (used in the calculations) were derived from the relationship of Cox and Weeks (1983). The ratio between the observed [CH_4] in ice or brine to their respective calculated solubility determines the supersaturation factor.

In addition, we computed the standing stock of CH_4, i.e., the total amount of CH_4 within the ice cover. To do so, we integrated the concentrations of CH_4 in bulk ice vertically to obtain the CH_4 content per square meter of ice.

For further comparison with the literature, we also computed CH_4 mixing ratios. It is usually obtained by dividing the number of moles of CH_4 by the total gas content. However, since we did not measure the total gas content, we used instead the sum of measured atmospheric-dominant gases (O_2, N_2 and Ar, data not shown).

3 Results

3.1 CH_4 concentration in ice

[CH_4] in bulk ice ranged between 3.4 nmol L_{ice}^{-1} and 17.2 nmol L_{ice}^{-1}. Mean [CH_4] increased from BRW2 (6.4 nmol L_{ice}^{-1}) to BRW7 (7.8 nmol L_{ice}^{-1}) and decreased to 5.5 nmol L_{ice}^{-1} at BRW10. This evolution parallels that of the standing stocks of [CH_4] which increased from BRW2 (5070 to 5430 nmol m^{-2}) to BRW7 (9200 nmol m^{-2}), then decreased at BRW10 (7580 nmol m^{-2}) (Fig. 2). For data interpretation, sea ice thickness is also shown in Fig. 2. It appears that the mean [CH_4] and the standing stock increased as sea ice thickened from BRW2 to BRW7, but decreased at BRW10 despite the fact that sea ice was thicker there.

The individual profiles of [CH_4] in bulk ice (Fig. 3a) for each sampling event further highlight the contrasts between BRW10 and all the previous sampling events (BRW2 to BRW7): all the [CH_4] profiles in ice from BRW2 to BRW 7 can be divided into 3 main zones. The first one ranged from 0 to 25 cm, where a peak of [CH_4] was found at 15 to 25 cm. [CH_4] measurements made on a twin ice core of BRW2 (duplicate) show that spatial variability in the layer of 15 to 25 cm could reach 60 %. The second zone was found in the ice interior, and ranged from 25 cm to the upper limit of the permeable layers (shaded area), where [CH_4] were close to 5 nmol L_{ice}^{-1}. The third zone corresponds to the permeable layers where [CH_4] increased again toward the sea ice bottom, with values ranging between 5 to 10 nmol L_{ice}^{-1}. At BRW10, as the whole ice cover became permeable (shaded area at all depths), the whole

profile flattened: the peak of [CH_4] around 15 to 25 cm disappeared, the ice interior still has a baseline at 5 nmol L_{ice}^{-1} and the increase of [CH_4] at the bottom was less obvious than in the previous sampling events.

Beside the strong vertical variation, [CH_4] in bulk ice were always higher than the solubility values in surface seawater that would have been in equilibrium with the atmosphere (3.8 nmol L_{sw}^{-1}) and the theoretical solubility in ice at all depths (Fig. 3a – white dots). [CH_4] in bulk ice were in average 1.8 times higher than that in surface seawater and 75 times higher than the theoretical solubility in ice. The highest supersaturation factor reached 396 and was measured in BRW6, at 20 to 25 cm depth. Again, BRW10 differed from all the other sampling events, with lower supersaturation factor (mean supersaturation and standard deviation were 11+/-4 versus 86+/-68 for BRW2 to BRW7).

CH_4 mixing ratio (not shown) was also measured for BRW2, BRW4, BRW7 and BRW10. It ranged between 5.8 and 105.3 ppmV. The maximum mixing ratio was found in BRW4, at 15 to 20 cm depth; this is 3.6 times higher than the mean mixing ratio of 29 ppmV.

To summarize, BRW10 differed from all the other samplings events by its lower mean [CH_4] and its flatter [CH_4] profiles. Although all the ice samples were supersaturated relative to the ice and surface seawater, larger supersaturations were observed from BRW2 to BRW7 (less permeable ice cores) compared to BRW10 (entirely permeable ice core), especially at 15 to 25 cm depth where both [CH_4] and CH_4 mixing ratio were found to be the highest.

3.2 CH_4 concentration in brine

Deduced [CH_4] in brine (using [CH_4] in ice) ranged between 13.2 nmol L_{brine}^{-1} and 677.7 nmol L_{brine}^{-1}. These are thus much higher than the range of [CH_4] measured in brine sackholes (10.0 to 36.2 nmol L_{brine}^{-1}) (Fig. 3– triangles) and in seawater (25.9 and 116.4 nmol L_{sw}^{-1}).

The evolution of [CH_4] in brine across seasons was rather similar to that of [CH_4] in bulk ice, except in the bottom layers. Indeed, from BRW2 to BRW7, high [CH_4] in brine were also observed at 15 to 20-cm depth; but from that level, [CH_4] in brine decreased and reached the lowest values at the sea ice bottom, where it is similar to observed CH_4 values in seawater. There was thus no slight increase of [CH_4] in brine, as observed in the [CH_4] in bulk ice, at the sea ice bottom. The profile of [CH_4] in brine flattened at BRW10, with values ranging between 13.2 and 87.0 nmol L_{brine}^{-1}, which were less variable and much closer to both the solubility values in brine and the actual measured [CH_4] in brine than the ranges of values in

the previous sampling events (35.6 nmol L_{brine}^{-1} and 677.7 nmol L_{brine}^{-1}). The minimum of $[CH_4]$ in brine was calculated at 12.5 cm. Temperature data was missing at the very surface, so that we could not compute $[CH_4]$ in brine above 12.5 cm.

3.3 CH_4 concentration in seawater

Measured $[CH_4]$ in seawater ranged between 25.9 and 116.4 nmol L_{sw}^{-1} (Fig. 3c). This is 7 to 31 times higher than seawater in equilibrium with the atmosphere (3.8 nmol·L^{-1} for a salinity of 35 at 0°C) (Wiesenburg and Guinasso, 1979).

Measurements of $[CH_4]$ in seawater were homogenous in time from BRW2 to BRW7, with a mean value and standard deviation of 42.0 +/- 2.4 nmol L_{sw}^{-1} for BRW2 and 37.5 +/6 nmol L_{sw}^{-1} for BRW 4 to BRW7. They then increased at all depths, at BRW10 and reached a mean value and standard deviation of 77.4 +/- 27.8 nmol L_{sw}^{-1}.

4 Discussion

The present paper aims at understanding the physical controls on the $[CH_4]$ in sea ice. Discussing the physical controls only makes sense if the variations of $[CH_4]$ due to biological activity are negligible compared to those due to physical processes. Therefore, we will first assess the importance of biological activity on the variation of $[CH_4]$ (Sect. 4.1), before discussing the physical controls on the profiles of $[CH_4]$ in sea ice and brine (Sect. 4.2).

4.1 Impact of biological activity on $[CH_4]$

To assess the impact of biological activity on $[CH_4]$, we recalculated the standing stocks of BRW4 to BRW7 (Fig. 3), by considering every 5-cm ice sample in the 25 to 80 cm-depth layers. These choices are motivated by the following reasons: First, we suggest focusing on the standing stocks of the impermeable layers (i.e. layers that have a brine volume fraction below 5 % (Golden et al., 1998); layers above the shaded areas on Fig. 3a, b). These layers are considered as a closed system in terms of brine dynamics and are therefore suitable to assess biological transformation of CH_4. Second, we felt it appropriate to ignore the upper layer (0 to 25 cm), since spatial variability could be important in these layers (up to 60 % from 15 to 25 cm depth) as shown in Figure 3a – BRW2. Third, we only focused on the

sampling events that were collected at short time intervals (3 or 4 days), i.e., BRW4 to BRW7, rather than between BRW2 and BRW4 (56 days). This is mainly due to the similar physical properties of the ice cores collected at short-time-intervals (i.e., in terms of ice core length, ice temperature, ice salinity profiles).

Deduced CH_4 standing stocks in the 5-cm ice samples (in the 25 to 80-cm ice layers, from BRW4 to BRW7) varied between 198 and 375 nmol m^{-2}, with a mean and standard deviation of 271 +/- 41 nmol m^{-2}. We performed an ANOVA test on these standing stocks (n=44) and differences between the samplings were not significant enough to exclude the possibility of random sampling variability.

In addition, we plotted chlorophyll-a concentrations against [CH_4] in bulk ice, and phosphate concentrations against [CH_4] in bulk ice, to investigate on potential in situ production of CH_4 in both permeable and impermeable ice layers (see Appendix A). The rationale is that previous studies have shown strong correlation between these variables (Damm et al., 2008; Damm et al., 2010) where CH_4 production was found to occur. As there is no obvious correlation between the presented variables (see Appendix A), we surmise that the pathway of CH_4 production that was observed in Damm et al., 2008; 2010 may not have occurred in the present study.

Furthermore, the turnover time for CH_4 oxidation in the Arctic Ocean exceeds 1.5 years (Griffiths et al. 1982 and Valentine et al. 2001), which is much longer than the lifetime of first year landfast ice. If we assume that the turnover time is similar in landfast sea ice, then we do not expect to find major CH_4 oxidation in our ice samples.

Because CH_4 production is unlikely in sea ice and CH_4 oxidation may be slow, we conclude that biological transformation of CH_4 is negligible in comparison with the amount of CH_4 that was physically incorporated in the impermeable ice layers, which is consistent with the findings derived from the standing stocks. Therefore, the discussion below will mainly focus on the physical processes that regulate CH_4 concentrations in sea ice.

4.2 The mechanisms for CH_4 incorporation, enrichment and dilution in sea ice

4.2.1 Range of CH_4 in sea ice and seawater, comparison with the literature

Our [CH_4] in sea ice (3.4 - 17.2 nmol L_{ice}^{-1}) were slightly lower than those of Lorenson and Kvenvolden (1995) (15 nmol L_{ice}^{-1} to 40 nmol L_{ice}^{-1}) . The deduced mixing ratios (5.8 ppmV to 105.3 ppmV) were however much lower than the 11 000 ppmV of Shakhova et al. (2010). We attribute the observed differences to (1) [CH_4] in seawater and (2) ebullition processes (i.e., the seepage of CH_4 bubbles from the seafloor and their rising through the water column).

First, our [CH_4] in seawater (25.9 and 116.4 nmol L_{sw}^{-1}) are consistent with those reported in northern Alaska (10.7 nmol L_{sw}^{-1} to 111.8 nmol L_{sw}^{-1} (Kvenvolden et al., 1993)) and shallow shelf areas with CH_4 release from sediment and/or destabilized gas hydrate (2.1 nmol L_{sw}^{-1} to 154 nmolL_{sw}^{-1} (Shakhova et al., 2005)), but are much lower than the measurements reported by Shakhova et al. (2010) (1.8 to 2880 nmol L_{sw}^{-1}). The differences in [CH_4] in seawater lead to contrasting CH_4 supersaturations (700 % and 3100 % in the present study versus 100 % to 160 000% in Shakhova et al. (2010)). Assuming similar incorporation rates in both studies, lower CH_4 supersaturation in seawater leads to lower CH_4 incorporated into sea ice and hence lower CH_4 mixing ratio in sea ice.

Second, ebullition is a process associated with rapid bubble ascension, limiting gas equilibration with the surrounding water mass (Keller and Stallard, 1994). Therefore, in shallow locations, CH_4 bubbles released from the seafloor could reach the seawater surface (Keller and Stallard, 1994; McGinnis et al., 2006). We believe that ebullition could increase CH_4 at the sea ice-water interface and lead to larger CH_4 incorporation into sea ice than if the ebullition was absent. Ebullitions were clearly observed in the Siberian Arctic Shelf (Shakhova et al., 2010) and in that case, centimetre-size bubbles were found within the ice (Shakhova et al., 2010). Since we did not find any literature reporting ebullition processes at Barrow, and since our ice cores generally showed millimeter-size bubbles (Zhou et al., 2013), we believe that ebullition processes were much less important in our study than in Shakhova et al. (2010).

4.2.2 Mechanisms responsible for the evolution of the vertical profiles of [CH_4] in bulk ice and brine during ice growth

Although the CH_4 source was seawater, [CH_4] in bulk ice from BRW2 to BRW7 did not show a C-shape profile, as would salinity for growing sea ice (Petrich and Eicken, 2010). For instance, instead of a surface maximum for salt, we observed a sub-surface maximum for CH_4. As discussed below, we propose three abiotic mechanisms to explain the salient features of the [CH_4] vertical profiles in Barrow bulk ice: (1) gas escape during the initial ice growth phase in the surface layer (2) preferential gas accumulation in the sub-surface and (3) brine volume fraction effect for the bottom layer.

We assume that CH_4, similarly to CO_2, could escape from the ice to the atmosphere, at the beginning of the ice growth (Geilfus et al., 2013; Nomura et al., 2006) (Fig. 4). In addition, once sea ice is consolidated, changes in temperature and in the volume of brine pockets are likely to fracture the ice, causing the expulsion of brines (Notz and Worster, 2009) and air bubbles (Untersteiner, 1968) at the ice surface. These 2 processes could explain the decrease of [CH_4] in bulk ice at the very surface of sea ice (Fig. 3).

Preferential gas accumulation during ice growth has been described for argon (Ar) in Zhou et al. (2013): Temperature and salinity changes in brine at sea ice formation lead to a sharp decrease of CH_4 solubility that favours bubble nucleation in sea ice. Once formed, the bubbles migrate upward due to their buoyancy. They are blocked under the surface impermeable layer, leading to gas accumulation (Fig. 4). Such process is supported by 2 characteristics: the presence of bubbles and the occurrence of large supersaturation levels (compared to the rest of the ice core). The presence of bubbles was observed on thin sections by Zhou et al. (2013) and is also coherent with the large difference between the deduced CH_4 in brine (which includes both CH_4 in bubbles and CH_4 that is dissolved in brine) (Fig. 3b, squares) and the actual measurements of CH_4 in brine (only CH_4 that is dissolved in brine) (Fig. 3, triangles). Moreover, the largest CH_4 supersaturations relative to CH_4 solubility in ice were always found at 15 cm to 25 cm depth, which correspond to the ice depth were Zhou et al. (2013) have observed bubble accumulation and Ar supersaturation up to 2900 %. Therefore, the mechanism of preferential gas accumulation suggested for Ar may be relevant for CH_4 as well. Larger CH_4 supersaturation as compared to Ar supersaturation is likely due to the difference in CH_4 and Ar solubility; CH_4, which is less soluble than Ar, would be more affected by temperature and salinity changes. It is also noteworthy that this process of bubble

formation in sea ice led to large spatial variability as witnessed by the duplicate of BRW2, which showed up to 60% of CH_4 variation at 15 – 25 cm depth.

As the freezing front progresses, the temperature gradient in the permeable layer reduces; bubble nucleation from solubility decrease is less efficient. As a consequence, CH_4 accumulates less and [CH_4] in brine decreases towards the bottom. Such a decrease is however not observed for [CH_4] in bulk ice. We attribute this to the brine volume fraction effect: a larger brine volume may contain a larger amount of CH_4 molecules, which induces higher CH_4 concentrations in bulk ice. The fact that CH_4 in brine did not show the increase at the bottom of the ice supports this suggestion.

An alternative explanation to the preferential gas accumulation due to solubility changes would be that of a direct bubble incorporation after a sudden but intense release of CH_4 bubbles from the sediment to the ice bottom. CH_4 release from sediment is possible since our [CH_4] in seawater are consistent with that found in areas where CH_4 release from sediment and/or gas hydrate destabilization likely occur (see section 4.2.1). However, this process does not explain the slow decrease of [CH_4] in brine from 15 – 25 cm depth to the sea ice bottom (Fig. 3b), and we may also wonder why the ebullition only occurred once during the whole sampling period.

The contribution of in situ bubble formation in the retention of CH_4 in sea ice is assessed in Fig. 5. We calculated the ratio between CH_4 in ice and the CH_4 in seawater at BRW2 (44 nmol L^{-1}_{sw}), and the ratio between brine salinity and the salinity of seawater at BRW2 (32), at each ice depth, for all the sampling events. The CH_4 in seawater and the salinity of seawater of BRW2 were chosen as references for consistency with Zhou et al. (2013). Similar apparent fractionation means that CH_4 is retained (incorporated and transported) in sea ice in the same way to salt, while a difference in the apparent fractionation means a difference in their retention processes.

Four main observations can be made on Fig. 5. First, the apparent fractionation averaged 15 % but never reached 100 %. This is due to the rejection of impurities during sea ice formation (Weeks, 2010). Our study therefore suggests that sea ice rejects about 85 % of its impurities, but retains 15 % of them. This is in agreement with Petrich and Eicken (2010) suggesting that sea ice brine allows a retention of 10 to 40 % of seawater ions in the ice. Second, the highest apparent fractionation of CH_4 (up to 39 %) was observed at 15 to 25 cm-depth; in that layer, the retention of CH_4 could be higher than that of salt by a factor of 2. This supports the

previous suggestion about preferential gas accumulation: the presence of gas bubbles allows higher retention of CH_4 than salt. Third, the apparent fractionation of CH_4 was lower than that of salt at the surface of all the sampling events, except at BRW10. We believe that these are related to the large permeability of the ice during its formation and/or the formation of some cracks at the ice surface (during the cold period), which have allowed gas to escape from sea ice to the atmosphere, as explained earlier in this section. The lower [CH_4] in bulk ice at these sampling events (Fig. 3a) tends to support the conjecture of gas escape. Four, below the top layer of about 25 cm of ice, both CH_4 and salt enrichment values are similar, indicating that in these ice layers, CH_4 was mainly incorporated in the dissolved state, as salt was.

4.2.3 Sea ice permeability controls [CH_4] in bulk ice and brine during sea ice decay

At BRW10, both [CH_4] in bulk ice and deduced [CH_4] in brine decreased and became less variable than the previous samplings (BRW2 to BRW7). In addition, CH_4 standing stocks decreased by ca. 1600 nmol m^{-2} from BRW7 to BW10, and the deduced [CH_4] in brine became closer to the measured [CH_4] in brine. These measurements suggest an enhanced gas transport through the ice and that gas bubbles have escaped from sea ice to the atmosphere. Gas escape was allowed given that sea ice was permeable at all depths (Fig. 3a, b – shaded area). Concomitant Ar bubble escape was suggested in Zhou et al. (2013). However, in contrast to Ar that was then at saturation, CH_4 was still supersaturated compared to the solubility in brine. This could be related to a slow exchange between the atmosphere, brine and the supersaturated seawater through diffusion.

[CH_4] in brine at BRW10 (13.2 nmol L_{brine}^{-1} to 87.0 nmol L_{brine}^{-1}) ranged between [CH_4] at ice/water interface (116.4 nmol L_{sw}^{-1}) and the theoretical [CH_4] in surface seawater that is in equilibrium with the atmosphere (3.8 nmol L_{sw}^{-1}). Although [CH_4] in brine at the very surface (0 – 12.5 cm) could not be retrieved, we can hypothesize that the gradient of [CH_4] between the ice/seawater interface and the ice surface led to CH_4 diffusion from ice/seawater interface to the ice surface, and therefore maintained [CH_4] supersaturated in ice, after gas bubble escape. Since the source of [CH_4] was from supersaturated seawater, [CH_4] in brine was slightly higher at the sea ice bottom than at the top.

5 Conclusions and perspectives

We reported on [CH_4] evolution in landfast sea ice and in under-ice water from February through June 2009 at Barrow (Alaska). Our [CH_4] in sea ice and [CH_4] in seawater are consistent with records from the area with CH_4 release from sediment and gas hydrate destabilization (Kvenvolden et al., 1993; Lorenson and Kvenvolden, 1995; Shakhova et al., 2010).

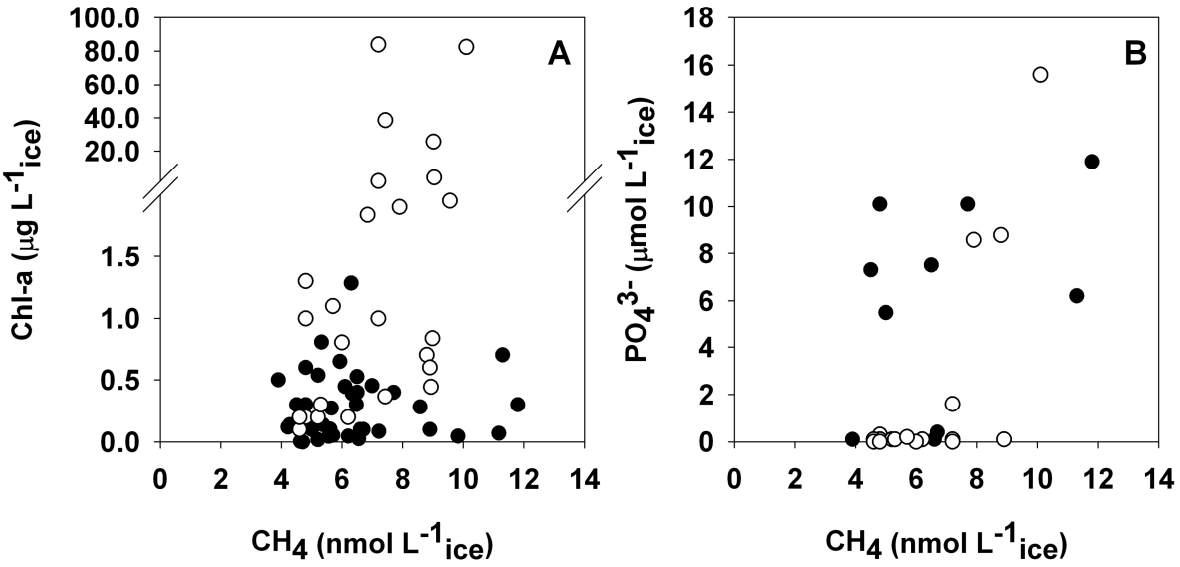
As summarized in Fig. 4, gas exchange likely took place during initial ice growth between sea ice and the atmosphere, and the formation of cracks could also lead to a decrease of CH_4 at the very surface of the ice. Then, when sea ice reached ca. 25 cm of ice thickness, strong solubility changes triggered gas bubble formation, which have favoured CH_4 accumulation in ice. CH_4 retention in the ice was twice as efficient as that of salt. However, as sea ice thickened, temperature and brine salinity gradient were no more sufficient to trigger bubble nucleation, and CH_4 was then trapped in the dissolved state, as salt did. The subsequent evolution of [CH_4] in sea ice layers mainly depended on physical processes, as chlorophyll-a and phosphate concentrations did not support in situ CH_4 production, and as CH_4 oxidation was likely insignificant. Abrupt changes in [CH_4] in sea ice occurred when sea ice became permeable; these were associated with the release of gas bubbles to the atmosphere. Therefore, the main role of our landfast sea ice in the exchange of CH_4 from seawater to the atmosphere was its control on the amount of CH_4 that it is able to store in its impermeable layers and the duration of such storage.

Although gas incorporation and sea ice permeability were two dominant factors driving CH_4 concentrations in sea ice in our study site, the magnitude of these processes may be different in other polar seas. Indeed, the contribution of the ebullition fluxes of CH_4 from sediment to the concentration of CH_4 in bulk ice, the transport of CH_4 through the ice, the significance of physical and biological controls on CH_4 dynamics rely on the nature of the sediment, the water depth, the physical parameters of the ice and biological activity within the ice, which may vary depending on the location.

In case of a higher mix of physical and biological controls on CH_4 concentrations in bulk ice, we would recommend to measure: (1) the carbon and hydrogen isotopes of CH_4 in sea ice, as isotopic fractionation is highly sensitive to biological processes, and (2) the same isotopes in the sources (e.g., organic matter). Indeed, previous studies have suggested that biogenic CH_4 within anoxic sediments may have carbon isotopic values as negative as -110 ‰ (Whiticar,

1999), in comparison to that formed by CH_4 oxidation (-10 to -24‰ (Damm et al., 2008; Schubert et al., 2011)), but few of them have considered that the measured isotopic values in the sediment or in seawater also depend on the isotopic composition of the sources.

Appendix A: Relationships between chlorophyll-a and [CH_4] and between phosphate and [CH_4] in sea ice



A1: Relationships between (A) chlorophyll-a (Chl-a) and methane (CH_4) concentrations, and (B) phosphate (PO_4^{3-}) and CH_4 concentrations, in sea ice. Open and closed circles indicate respectively permeable and impermeable ice layers (i.e., brine volume fraction above or below 5 %). Chl-a and PO_4^{3-} data are from Zhou et al. (2013): Chl-a data were available for all the sampling events that are presented here, while PO_4^{3-} were only available for BRW2, BRW7 and BRW10.

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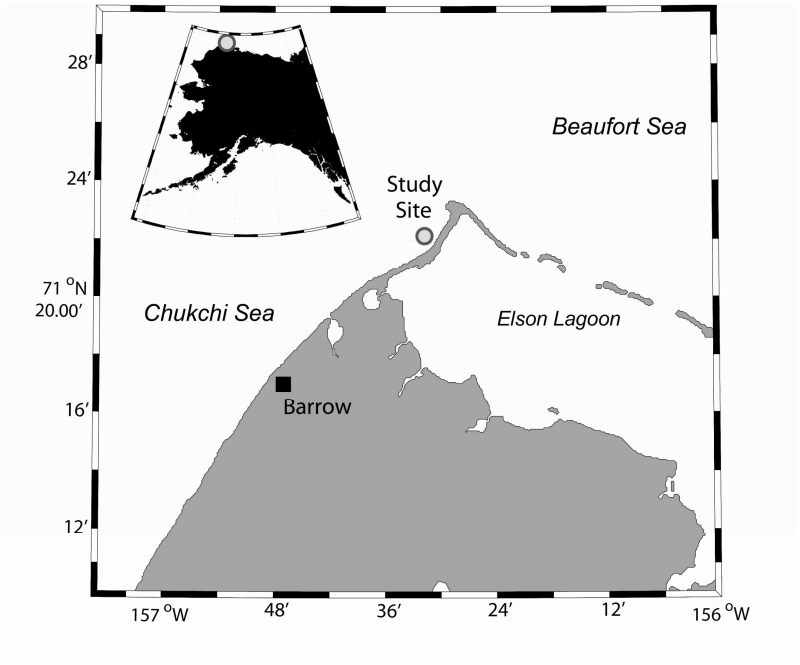

Figure 1. The study site. North of Barrow, Alaska, US.

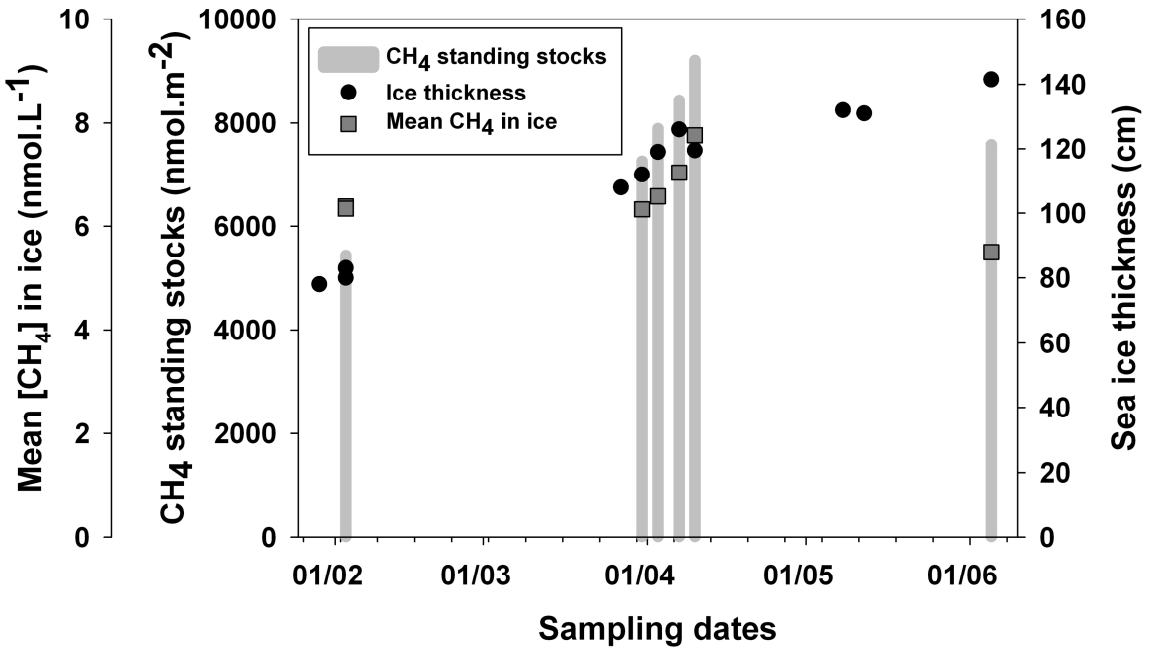

Figure 2. CH_4 standing stocks for selected samplings events (vertical bars, from left to right, BRW2, BRW4, BRW5, BRW6, BRW7 and BRW10) in parallel with mean [CH_4] in sea ice and sea ice thickness.

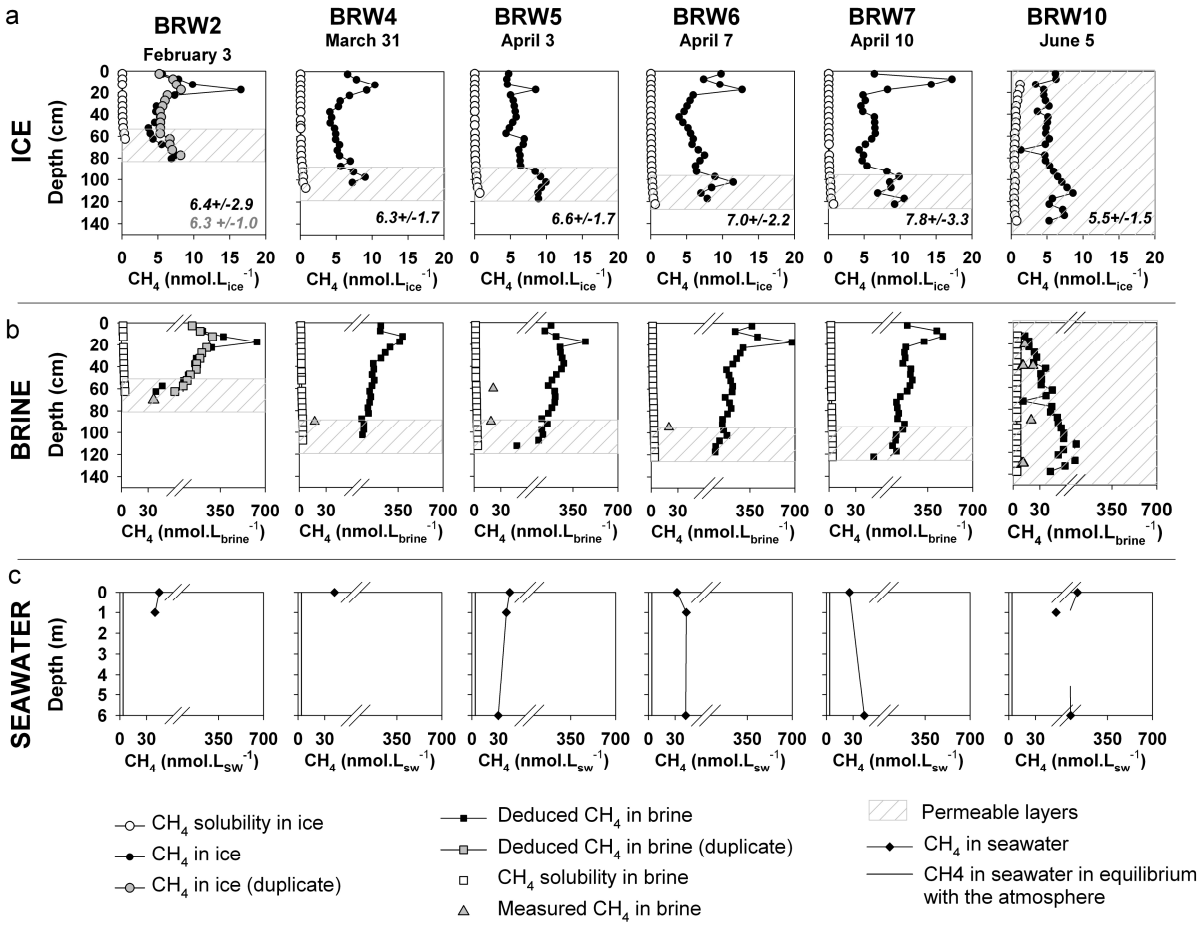

Figure 3. Evolution of CH_4 concentration in (a) bulk ice, (b) brine and (c) seawater (black dots, squares and diamonds respectively), compared to CH_4 solubility in ice, brine and seawater that is in equilibrium with the atmosphere (white dots, white squares and black straight lines respectively). Grey dots and grey squares are measurements made on duplicate samples of BRW2. Grey triangles in (b) are CH_4 measurements in brine sackholes. The break in the x axes of (b) and (c) is set at 60 nmol L. Dashed areas are permeable layers (i.e. layers with brine volume fraction above 5%)

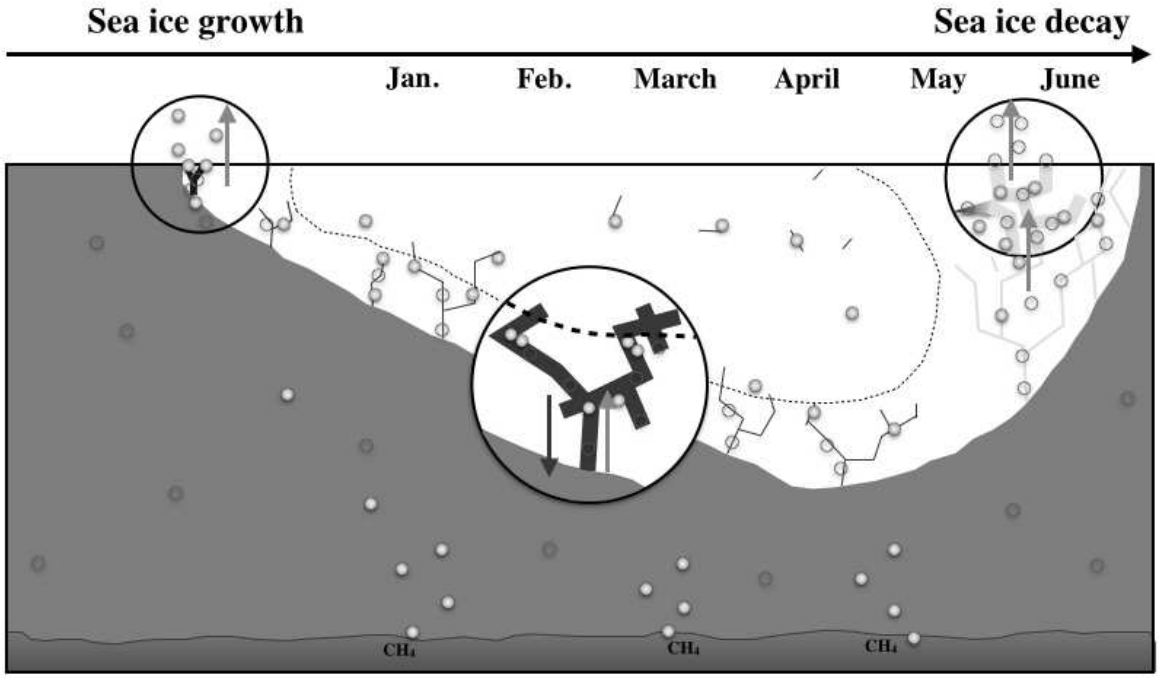

Figure 4. Schematic figure of CH_4 release and incorporation in sea ice. Sizes are intentionally disproportionate to better highlight processes. The area above the dotted line represents the impermeable layers. The small filled and empty circles represent CH_4 in gas bubbles and in dissolved state respectively. Upward grey arrows indicate the upward transport of gas bubbles due to their buoyancy, while downward blue arrows indicate the removal of dissolved gas through brine drainage. Large black circles zoom on particular processes described in the text (Sect. 4.2): gas exchanges at the beginning of ice growth, preferential gas accumulation under the impermeable layers and gas bubble escape during ice decay. Dark blue, light blue and cyan strokes in ice represent brine channels with high, moderate or low salinity respectively.

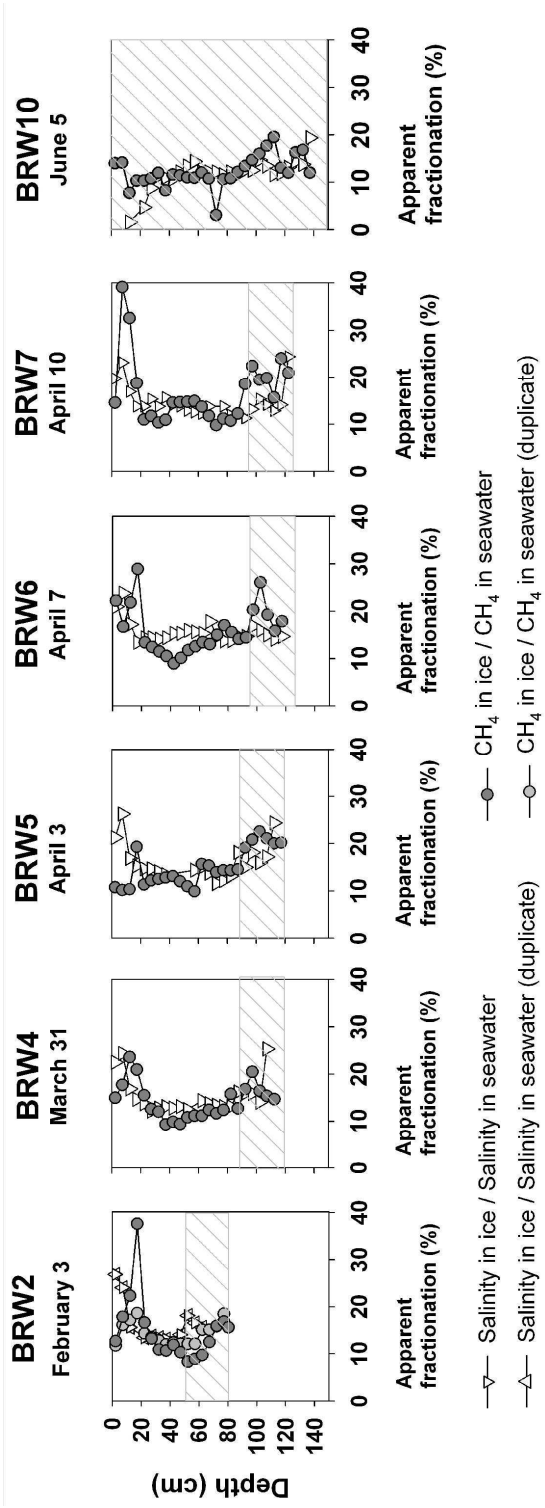

Figure 5. Comparison between the apparent fractionation of salinity in ice (the ratio between ice salinity and the seawater salinity (32)) and the apparent fractionation of CH_4 (the ratio between CH_4 in ice and CH_4 in seawater (44 nmol L^{-1}_{sw})). The seawater salinity and CH_4 in seawater that are chosen as references were the values obtained from BRW2. Dashed areas are permeable layers (i.e. layers with brine volume fraction above 5%).