Insights into oxygen transport and net community production in sea ice from oxygen, nitrogen and argon concentrations

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Abstract

We present the evolution of O$_2$ standing stocks, saturation levels and concentrations in landfast sea ice, collected in Barrow (Alaska), from February to June 2009. The comparison of the standing stocks and saturation levels of O$_2$ against those of N$_2$ and Ar suggests that the dynamic of O$_2$ in sea ice strongly depends on physical processes (gas incorporation and subsequent transport). We then discuss on the use of O$_2$/Ar and O$_2$/N$_2$ to correct for the physical contribution and to determine the biological contribution (NCP) to O$_2$ supersaturations. We conclude that O$_2$/Ar suits better than O$_2$/N$_2$, because O$_2$/N$_2$ is more sensitive due to the relative abundance of O$_2$, N$_2$ and Ar, and less biased when gas bubble formation and gas diffusion are maximized. We further estimate the NCP in the impermeable layers during ice growth and in the permeable layers during ice decay. Our results indicate that NCP contributed to a release of carbon to the atmosphere in the upper ice layers, but to an uptake of carbon at sea ice bottom. Overall, seawater (rather than the atmosphere) may be the main supplier of carbon for sea ice microorganisms.

1 Introduction

Sea ice is a porous material with a matrix of pure ice and brine inclusions (Weeks, 2010). The brine inclusions concentrate most of the impurities of the ice, and host micro-organisms that are able to survive to high salinities and low temperatures (Thomas and Dieckmann, 2002). Quantifying the net community production (NCP) – the balance between photosynthesis and respiration – of the microorganisms in sea ice is crucial, because the NCP affects the growth of higher trophic-level species (Arrigo et al., 2010; Brierley and Thomas, 2002; Michel et al., 1996) and the microbial net production of climate-active gases like CO$_2$ and DMS (Vancoppenolle et al., 2013).

Diverse experimental techniques exist for determining the NCP (see Arrigo et al. (2010) for further details); these are generally derived from seawater studies...
despite the heterogeneous structure of sea ice in comparison to seawater. A standard technique is to measure the accumulation of algal biomass and its temporal evolution via the measurements of chlorophyll a (chl a) or particulate organic carbon (POC). Another standard technique is to measure the maximum photosynthetic rate and the photosynthetic efficiency in laboratory. Then, assuming that these photosynthetic parameters still hold for field measurements, we can deduce the changes of biomass based on the concentration of chl a and the light intensity from the field. Both standard techniques have one major limitation: they require sea ice extraction and melting, which inevitably modify the growth environment of the microorganisms. Therefore, recent technical developments have privileged in-situ measurements of NCP that minimize the disturbance on sea ice.

The newly-developed techniques for NCP measurements include pulse amplitude modulated (PAM) fluorometry (Glud et al., 2002), O2 microelectrodes (McMinn and Ashworth, 1998), O2 micro-optodes (Mock et al., 2002) and O2 eddy correlation systems (Long et al., 2012). Although these techniques allow in situ measurements, the results may not directly represent the NCP, due to the heterogeneous structure of the ice and to sea ice physical properties (i.e., permeability and brine dynamics). For instance, the PAM fluorescence depends on the spatial distribution of the algal biomass and the optical properties of the ice (Glud et al., 2002). Another example is that the amount of O2 measured using microsensors depend on whether the sensors were set in brine, ice, gas bubbles or bacterial films (Mock et al., 2002) and whether the ice permeability allows the diffusion of O2 to the microsensors (Glud et al., 2002). Although the O2 eddy correlation system seems promising, because of its large footprint in comparison to the other techniques, it may be sensitive to the additional input of O2 from sea ice due to brine rejection and ice melt (Long et al., 2012). In that context, understanding the dynamic of O2 within the ice will better constrain the O2 fluxes at the ice–water interface, obtained with eddy correlation.

In the present study, we describe the dynamic of O2 in sea ice, based on a time-series of O2 concentrations within sea ice from ice growth to ice decay. The O2 mea-
measurements were obtained from ice crushing, which allow $O_2$ measurements (including
NCP estimate) in both permeable and impermeable sea ice layers (i.e., ice layer with
brine volume fraction above and below 5% respectively, Golden et al., 1998). This
extends our current knowledge on $O_2$ dynamic that was limited to the permeable ice
layers (e.g., associated with the use of microsensors and eddy correlation) to the im-
permeable ice layers.

We performed parallel measurements of nitrogen ($N_2$) and argon (Ar) to discuss on
the feasibility to decipher the contribution of both physical and biological processes
to $O_2$ variations using $O_2$/Ar and $O_2$/N$_2$. Some recent studies in seawater indeed
yielded NCP from the measurements of $O_2$/Ar (Cassar et al., 2009; Castro-Morales
et al., 2013; Hendricks et al., 2004; Reuer et al., 2007), while others have proven that
$O_2$/N$_2$ was sensitive to the biological activity in basal continental ice (e.g., Souchez
et al., 2006). These approaches consider Ar and N$_2$ as inert to biogeochemical pro-
cesses: hence, in abiotic conditions, $O_2$, Ar and N$_2$ would vary in the same way, and
$O_2$/Ar and $O_2$/N$_2$ should remain constant (or within an abiotic range depending on the
incorporation conditions); only NCP could draw $O_2$/Ar and $O_2$/N$_2$ beyond the abiotic
range.

2 Materials and methods

2.1 Sampling area and sampling events

Ice cores were collected during a survey that was carried out on landfast sea ice, off
Barrow (Fig. 1), from January through June 2009. The sampling area covered a surface
of 50 m by 50 m. The north-eastern corner of the square was located at 71°22.013′ N,
156°32.447′ W. The ice cores were extracted and then stored at −30°C in the dark, to
prevent brine drainage and to limit biological activity. All of the analyses were completed
within the following year. The physical framework has been presented and discussed
in Zhou et al. (2013). In brief, all of the ice cores had similar crystallographic structure, with a dominance of columnar ice that suggests low spatial variability.

In the present paper, 5 sampling events (out of 10) were selected to illustrate the evolution of chl $a$, O$_2$, O$_2$/Ar and O$_2$/N$_2$ at our location: one in the winter (BRW2 – 3 February), two in early spring (BRW4, BRW7 – corresponding to 31 March and 10 April respectively), one in mid spring (BRW8 – 8 May), and the last one in late spring (BRW10 – 5 June). The first 4 sampling events occurred during ice growth, the last one during ice decay. As mentioned in Zhou et al. (2013), BRW8 was affected by a full-depth convection event, leading to a drainage of the dissolved compounds in brine, and a partial replenishment of the dissolved compounds from seawater. This contrasted with the sampling events prior to BRW8, where convection only occurred in the permeable bottom ice layers. Finally, in BRW10, the increase of air temperature led to ice melt, full permeability and brine stratification.

2.2 Chlorophyll $a$ and phaeopigment

The ice samples were melted in the dark, in 0.2 µm filtered seawater (1 : 4 volume ratio) to avoid osmotic stress. We used 10 µm and 0.8 µm polycarbonate filters in a sequence in order to distinguish larger micro-algae species from the smaller ones. Extractions and calculations were made following the procedure of Arar and Collins (1997). The standing stocks of chlorophyll $a$ (chl $a$) were calculated by integrating the chl $a$ concentrations over the whole ice length. The percentage of phaeopigment was obtained by dividing the concentration of phaeopigment by the sum of both chl $a$ and phaeopigment concentrations. Phaeopigment results from chl $a$ degradation; High percentage of phaeopigment indicates strong grazing pressure (i.e. strong impact of the respiration on the NCP).

2049
2.3 O₂, Ar and N₂ concentration in ice and their respective solubility

We used the dry-crushing technique as developed for gas measurements in continental ice (Raynaud et al., 1982) to extract O₂, Ar and N₂ from the ice samples. This technique extracts both the gas bubbles in the ice and the gas in the dissolved state within liquid brine. Each ice core was cut every 5 cm, and about 60 g of sample was introduced into a vessel, with 7 stainless steel balls. The ice was crushed in the vessel, under vacuum (10⁻³ torr), as described in Stefels et al. (2012) at −25 °C. Subsequently, the vessel was kept at −50 °C in a cold ethanol bath, and was connected to the gas chromatograph equipped with a thermal conductivity detector for concentration analyses (Skoog et al., 1997). We used Alphagaz™ 2 He (Air Liquide – P0252) as carrier-gas and a 22 mL packed column (Mole Sieve 5A 80/100; 5 m × 1/8”). The reproducibility of the analyses, based on triplicate analysis of five different standards, was 99.3 % for O₂, 97.8 % for Ar and 99.9 % for N₂.

To determine the saturation levels of O₂, Ar and N₂ in ice and for further calculations (Sects. 2.4 and 2.5), we also determined the theoretical solubility of each gas in ice at saturation. The solubility was calculated using temperature and salinity in brine (following the relationship of Garcia and Gordon (1992) for O₂ and the relationship of Hamme and Emerson (2004) for N₂ and Ar) and the solubility was then weighted by the brine volume fraction in the ice. That weighting is necessary, as most of the impurities (including gases) are concentrated in the brine structure (and not in the pure ice matrix) (Weeks, 2010). It is noteworthy that the relationship of Hamme and Emerson (2004) was established for temperatures between 0 °C and 30 °C and for salinities between 0 and 34.5, and the relationship of Garcia and Gordon (1992) was established for temperatures between 0 and 40 °C and for salinities between 0 and 42. We thus assumed in our calculations of gas solubility that those relationships still hold for the range of temperature and salinity found in our brine samples.
Gas saturation levels is described following Craig and Hayward (1987) in seawater as

$$\Delta C_i = \frac{C_i}{C_{eq}} - 1.$$  \hspace{1cm} (1)

where $C_i$ is the measured concentration of the gas $i$ in bulk ice and $C_{eq}$ the solubility of gas $i$ in bulk ice at equilibrium with the atmosphere, calculated at in situ temperature, salinity and pressure as described above.

### 2.4 O$_2$/Ar and O$_2$/N$_2$

The use of O$_2$/Ar and O$_2$/N$_2$ is only valid if both Ar and N$_2$ are inert. Ar is a noble gas, i.e., inert and not affected by any biogeochemical processes. Denitrification was found to occur in sea ice (Rysgaard et al., 2008) and could affect N$_2$, but we assumed that N$_2$ is also inert to biogeochemical processes in the present study, because N$_2$ is correlated to Ar with a $r^2$ of 0.98 (Fig. 2). Hence, both N$_2$ and Ar can be used as tracers for physical processes.

O$_2$/Ar and O$_2$/N$_2$ ratios were calculated from the concentrations of O$_2$, Ar and N$_2$ in ice, and were compared with their respective ratios in seawater and the atmosphere. The relative solubility of O$_2$/Ar in seawater (at 0°C, with 32 of salinity) is 20.48 (Garcia and Gordon, 1992; Hamme and Emerson, 2004). However, even in abiotic conditions, the gas ratios in sea ice at initial incorporation may differ from that in seawater due to diffusion process at the ice/seawater interface (Killawee et al., 1998; Tison et al., 2002). We thus applied the relative diffusion coefficient of O$_2$ and Ar (1.2/0.8 = 1.5) (Broecker and Peng, 1982) to our relative solubility of O$_2$/Ar to obtain a value of O$_2$/Ar with maximized diffusion processes at the bottom of sea ice (13.65) as described below. Note that different diffusion coefficients exist in the literature (Table 1) for temperature close to 0°C or below, for seawater, water or ice; we chose to use the diffusion coefficients of Broecker and Peng (1982) because it is the most recent study that provides diffusion coefficients for O$_2$, Ar and N$_2$ near the freezing temperature. Salinity is not given in the text.
Broecker and Peng (1982), but one may expect at maximum a decrease of 4.9 % of the diffusion coefficient per increase of 35.5 of salinity (Jähne et al., 1987).

The initial values of $O_2/Ar$ could therefore range between 13.65 and 20.48, depending on the magnitude of gas diffusion at the ice/seawater interface. Further, as $O_2/Ar$ in the atmosphere is 22.5, gas input from the atmosphere (during frazil ice formation or when sea ice is permeable) and gas bubble formation in the permeable ice should pull the bulk ice $O_2/Ar$ towards 22.50. Therefore, if both dissolved and gaseous states exist in the ice, $O_2/Ar$ could range between 13.65 and 22.50, due to physical processes; that range is referred here after as the abiotic range of $O_2/Ar$.

We applied the same calculation to $O_2/N_2$. The relative solubility in seawater is 0.56 (Garcia and Gordon, 1992; Hamme and Emerson, 2004). Since the relative diffusion coefficient between $O_2$ and $N_2$ is 1.09 (Broecker and Peng, 1982), the relative solubility with maximized diffusion processes is 0.51. Given that the atmospheric ratio of $O_2/N_2$ is 0.27, the abiotic range of $O_2/N_2$ in ice is 0.27–0.51. $O_2/N_2$ that is above or below this abiotic range is attributed to an impact of biological activity (Souchez et al., 2006).

### 2.5 NCP-related $O_2$ deduced from $O_2/Ar$

We derived the NCP-related $O_2$ supersaturation, $\Delta(O_2/Ar)$, also referred to as biological $O_2$ supersaturation and NCP-related $O_2$ concentrations ($O_2$NCP), using Eqs. (2) and (3) respectively, as used in seawater studies (e.g., Castro-Morales et al., 2013):

$$\Delta(O_2/Ar) = \frac{[O_2]}{[Ar]} \frac{[O_2]_{eq}}{[Ar]_{eq}} - 1. \tag{2}$$

$$O_2$$NCP = $[O_2]_{eq} \Delta(O_2/Ar). \tag{3}$$

in which, $[O_2]_{eq}/[Ar]_{eq}$ is the solubility ratio in seawater at equilibrium in Castro-Morales et al. (2013), but the solubility ratio in ice at equilibrium in the present study (Sect. 2.4).

In a closed system, NCP then corresponds to the changes of $O_2$NCP between sampling events. Note that in seawater studies, because of the open system, additional
coefficients and equations are required to take into account the diffusion at air–sea interface, the changes in the mixed layer depth and the diffusion of $O_2$ across the base of the mixed layer (Castro-Morales et al., 2013).

3 Results

3.1 A general overview from the standing stocks

Fig. 3 shows the standing stocks of Ar, $O_2$ and $N_2$, in parallel with the ice thickness, for the different sampling events. $N_2$ reached the highest standing stocks among the three gases, followed by $O_2$ and then Ar. The three gas standing stocks evolved in the same way over the studied period, but not as the ice thickness: while sea ice continuously thickened from BRW2 (82 cm) to BRW10 (142 cm), the gas standing stocks increased from BRW2 to BRW8 but decreased at BRW10.

3.2 Gas saturation levels

The saturation levels of $N_2$, $O_2$ and Ar decreased with increasing brine volume fraction (Fig. 4). The highest supersaturation of $N_2$, $O_2$ and Ar (7030, 3180 and 2960 % respectively) corresponded to the lowest brine volume fraction (2.2 %), while the lowest undersaturations ($-33$, $-52$ and $-54$ % respectively) corresponded to the largest brine volume fraction (29.3 %). In addition, despite similar evolution in the standing stocks for all the gases, $N_2$ saturation levels contrasted with those of $O_2$ and Ar: $N_2$ reached higher supersaturation levels than $O_2$ and Ar, which have much similar saturation levels.

3.3 $O_2$ concentrations

In Fig. 5a, the dashed areas refer to the permeable ice (i.e., layers with brine volume fraction above 5 %, Golden et al., 1998). Hence, from BRW2 to BRW7, only the bottom...
layers of the ice were permeable while at BRW8 and BRW10, the whole ice core was permeable.

Figure 5a also shows the concentration of O$_2$ in bulk ice ([O$_2$], black dots) with the solubility of O$_2$ in ice (white dots). Mean [O$_2$] increased from BRW2 (67.4 µmolL$_{\text{ice}}^{-1}$) to BRW8 (122.4 µmolL$_{\text{ice}}^{-1}$) and decreased at BRW10 (93.4 µmolL$_{\text{ice}}^{-1}$). At BRW2 and BRW4, [O$_2$] generally exceeded the solubility of O$_2$ in the impermeable layers, but reached the solubility values in the permeable layers. The trends changed from BRW7 onwards: in BRW7 and BRW8, [O$_2$] was higher than the solubility at all depths, except in the 5 last centimeters of the ice core. In BRW10, [O$_2$] was close to the solubility of O$_2$ in the upper layers (from 12.5 to 72.5 cm), but exceeded the solubility of O$_2$ below these layers.

3.4 Chlorophyll a and phaeopigment concentrations

The concentrations of chl a [chl a] are reported in Zhou et al. (2013). Briefly, [chl a] varied largely with depth (Fig. 5b) and ranged from 0 to 83.9 µgL$_{\text{ice}}^{-1}$ for all the sampling events. The highest [chl a] were always in the ice bottom, except in BRW4. Above the bottom layer, the [chl a] was generally below 1 µgL$_{\text{ice}}^{-1}$. Drastic changes occurred in BRW8 when sea ice permeability increased sharply: [chl a] dropped at all depths, and particularly in the ice interior. [chl a] increased again at BRW10, showing a vertical profile and a standing stock similar to those of BRW7.

The percentage of phaeopigment also varied strongly with depth in BRW2, with over 60% of phaeopigments in the upper ice layers but less than 20% at the ice bottom. It varied between 20 and 40% in BRW4 and BRW7, and increased drastically in BRW8 (with phaeopigments reaching 100% in some layers). In BRW10, the percentage of phaeopigments varied between about 40 and 70%, with generally the higher values in the upper ice layers.
3.5 \( O_2/Ar \) and \( O_2/N_2 \)

\( O_2/Ar \) in ice ranged between 15.84 and 97.62 (Fig. 5c) and \( O_2/N_2 \) ranged between 0.27 and 1.47 (Fig. 5d). Both \( O_2/Ar \) and \( O_2/N_2 \) ratios are compared to their respective values in the atmosphere (22.5 and 0.27 – black and grey strait lines in Fig. 5c and d) and in seawater with maximized diffusion processes (13.65 and 0.51 – black and grey dashed lines in Fig. 5c and d).

\( O_2/Ar \) in ice at BRW2 was highly homogeneous at all depths, with a mean and standard deviation of 18.49±0.84. These ratios were found between the value of \( O_2/Ar \) in the atmosphere and that in seawater with maximized diffusion processes. Over the next sampling events, \( O_2/Ar \) in ice increased on average, exceeding the \( O_2/Ar \) in the atmosphere (the upper limit of \( O_2/Ar \) that can be explained by abiotic processes), and became more variable vertically (Fig. 5c). It is also noteworthy that from BRW4 onwards, the maximum \( O_2/Ar \) in each sampling event was found in the lower part of the ice, but never coincided with the maximum of [chl \( a \)], even at BRW10 where the whole profile of \( O_2/Ar \) clearly mimicked the one of [chl \( a \)].

The variations observed in \( O_2/N_2 \) in ice were less sensitive than those observed in \( O_2/Ar \) (Fig. 5c and d). \( O_2/N_2 \) only exceeded once the abiotic range of \( O_2/N_2 \) between BRW2 and BRW8, while \( O_2/Ar \) exceeded the abiotic range of \( O_2/Ar \) from BRW4 onwards. Similarities between \( O_2/Ar \) and \( O_2/N_2 \) were more obvious in BRW10: both ratios showed the atmospheric values at the ice surface, and they exceeded their respective abiotic range in the ice interior, with a maximum in the lower part of the ice that did not coincide with the maximum in [chl \( a \)].
4 Discussion

4.1 General dynamic of $O_2$ in comparison with $N_2$ and Ar

4.1.1 Standing stocks

To discuss the dynamics of $O_2$, we first compared the evolution of $O_2$ standing stocks against that of $N_2$ and Ar – two other dominant gases in sea ice that are considered to be only sensitive to physical processes in the present study (Sect. 2.4). The $O_2$ standing stocks that evolved in the same way as $N_2$ and Ar (Fig. 3) indicate that the physical controls on the $O_2$ standing stocks dominated over the biological ones.

Two main physical processes affect gas concentrations in ice: the incorporation during ice growth and the subsequent transport within the ice. Because of the incorporation of gases during ice growth, the gas standing stocks increased with increasing ice thickness, from BRW2 to BRW8. The decrease of gas standing stocks in BRW10, despite the fact that the ice in BRW10 was thicker than in BRW8, was then associated with subsequent transport. We attribute that subsequent transport to gas exchange through sea ice (including gas bubble escape), due to the increase of ice permeability, as discussed below.

The main evidence of gas bubble escape is the sharp decrease of gas supersaturation when the brine volume fraction exceeded 5% (Fig. 4), hence when impermeable layers became permeable (Golden et al., 1998). Indeed, $N_2$ supersaturation reached up to 7000% in the impermeable ice layers, while supersaturation of 2200% already corresponds to gas bubble formation (Killawee et al., 1998). This observation confirms previous findings about the presence of gas bubbles in the impermeable ice layers, based on [Ar] and ice thin sections (Zhou et al., 2013). Naturally, when the impermeable ice layers became permeable, with increasing brine volume fraction, gas exchanges may occur between sea ice and the atmosphere: supersaturated gas outgassed from brine to reach the saturation level (Zhou et al., 2013), which, in turns, lowered gas standing stocks, as observed in Fig. 3.
### 4.1.2 Saturation levels and concentrations

Obviously, permeable sea ice allows gas exchange, but gases are not necessarily at saturation in permeable layers. Indeed, Fig. 4 shows that gases remained supersaturated for brine volume fractions above 5% and reached 0% or became slightly negative only for brine volume fraction exceeding 25%. We will further discuss that relationship between O$_2$ saturation levels and the brine volume fraction, based on the vertical profiles of O$_2$ in ice (Fig. 5a).

The high O$_2$ supersaturations – also observed for Ar in (Zhou et al., 2013) – were associated with the upper ice layers (Fig. 5a) with brine volume fractions below 5% (Fig. 4). We attribute this to the large accumulation of gas and the low gas solubility in those layers. Because of the temperature gradient at the beginning of ice growth, gases were incorporated in brine with higher salinity than in seawater. As a consequence, the solubility of the gases decreased, leading to gas supersaturation, and potentially gas bubble formation. When this occurs, gases preferentially accumulate in sea ice in comparison to the dissolved compounds, because gas bubbles will move upwards due to their buoyancy while dissolved compounds are subject to gravity drainage (Zhou et al., 2013). Once the ice layers became impermeable, decreasing temperature and increasing brine salinity will further decrease gas solubility in the upper layer. Both the accumulation of gas and low gas solubility induced high O$_2$ supersaturations in the upper ice layers with low brine volume fractions.

In contrast to the high O$_2$ supersaturations, O$_2$ undersaturations, as for N$_2$ and Ar, were observed in BRW10 (Fig. 5a), in the upper layers where brine volume fractions exceeded 20% (Fig. 4). Because BRW10 was sampled during ice decay, gas bubbles have escaped from the brine due to the large brine volume fraction, and gas exchange through sea ice should allow O$_2$ to reach gas solubility, as for Ar (Zhou et al., 2013). Snow- and ice meltwater likely have added freshwater into brine and lowered the gas concentrations in comparison to the gas solubility. Previous analyses of water stable isotopes in brine nitrate concentrations in ice and ice texture (Zhou et al., 2013) support
the hypothesis of snow- and ice meltwater infiltration. The large $O_2$ concentrations observed in the topmost layer of BRW10 (Fig. 5a) was an exception to the general $O_2$ saturation and undersaturation trend, and was associated with the local development of superimposed ice layers (Zhou et al., 2013).

We qualify as moderate $O_2$ supersaturations those associated with ice layers where brine volume fractions exceeded 5% (Fig. 4). These permeable layers were either located in the ice bottom from BRW2 to BRW7 and throughout the ice cover in BRW8 and BRW10 (Fig. 5a). Gas solubility in these layers was higher than that in the impermeable layers, because of the higher ice temperature and lower brine salinity; the higher gas solubility lowered $O_2$ supersaturations, despite some local high $[O_2]$ in bulk ice (e.g., in the bottom of BRW 7 and BRW8), in comparison to the impermeable layers. Because gas exchange depends on the supersaturation levels, the observation reminds that the potential of air-ice gas exchange depends not only on the $[O_2]$ in ice, but also on the salinity and temperature-dependent solubility.

Finding moderate $O_2$ supersaturations in permeable layers may be counter-intuitive because permeable layers allow gas exchanges (diffusion and/or convection) that tend to remove the supersaturation. For instance, even if $O_2$ expulsion from growing sea ice leads to $O_2$ supersaturation in the ice bottom, as long as the $O_2$ remains in the dissolved state (Killawee et al., 1998), brine convection may replace the supersaturated $O_2$ with $O_2$ content from seawater – keeping therefore bulk $O_2$ close to the $O_2$ solubility (as observed in Fig. 5a – BRW2, BRW4, bottom third of the ice cover). Another evidence of gas exchange in permeable layer is the decrease of $O_2$ standing stocks and $O_2$ saturations in BRW10, associated with the increase of ice permeability, as demonstrated earlier. Therefore, we suggest that the moderate gas supersaturations in the permeable layers resulted from either a transition stage where gas exchange was ongoing (i.e., tending toward the saturation), and/or a net community production of $O_2$ (NCP) that overwhelmed the loss of $O_2$ through physical processes, as discussed here below.
A transition stage would characterize the impermeable ice layers that became permeable, like in the upper layers of BRW8. The initial supersaturated O$_2$ content tended toward saturation, as observed in some upper layers of BRW10. The duration needed for gas equilibrium depends on the efficiency of the gas transport through the brine network (Loose et al., 2010).

On the top of the physical transport of O$_2$ during the transition stage, NCP also contributed to O$_2$ supersaturation in permeable layers. The most obvious evidence of NCP contribution was from the bottom layers of BRW10. O$_2$ supersaturations due to physical processes were unlikely during ice decay: [Ar] was at saturation (or slightly undersaturated) over the whole ice length, indicating the absence of gas bubbles and the infiltration of snow- or ice meltwater (Zhou et al., 2013). The increase of [chl a] in the bottom layers of BRW10 (Fig. 5b – BRW10) then points to a NCP-related O$_2$ supersaturation. Note that despite the fact that the biological O$_2$ supersaturation (through NCP) dominated over the physical one, it did not prevent the decrease of O$_2$ standing stocks between BRW8 and BRW10 (Fig. 3). Further, the maximum of [chl a] (130–140 cm) mismatched with the maximum of [O$_2$] (125–130 cm), which is unexpected if the O$_2$ supersaturation was NCP-related. Because of the constant phaeopigment percentage in those bottom layers (i.e., potentially constant algal degradation), precluding difference in net community productivity (NCP/chl a ratio), we attribute the decrease of [O$_2$], from 125 cm to the interface, to the diffusion of the NCP-related O$_2$ from sea ice to seawater. Similar decrease of bulk O$_2$ concentrations in the 20 last cm of sea ice, in BRW7 and BRW8, may also depict the combined effect of NCP and O$_2$ transport.

4.2 O$_2$/Ar and O$_2$/N$_2$: sensitivity and ability to assess the biological contribution to O$_2$ dynamics

Because both NCP and physical processes (dilution, transport) affected the [O$_2$] in sea ice, we need to remove the physical contribution to determine the NCP-related O$_2$ in sea ice. Comparing the variation of O$_2$ against that of an inert gas (that is solely dependent on physical processes) allows to decipher the variation of O$_2$ related to NCP.
Recent studies have indeed used O$_2$/Ar to remove the physical contribution and to determine NCP in seawater (Cassar et al., 2009; Castro-Morales et al., 2013; Hendricks et al., 2004; Reuer et al., 2007), while O$_2$/N$_2$ was shown to be sensitive to the biological activity in basal continental ice (e.g., Souchez et al., 2006). In this section, we will discuss the behavior of both O$_2$/Ar and O$_2$/N$_2$ ratios, and discuss on the feasibility to use them for determining NCP in sea ice.

4.2.1 General trends of O$_2$/N$_2$ and O$_2$/Ar

The range of O$_2$/N$_2$ from BRW2 to BRW7 (0.27 and 0.41) remained within the abiotic range (0.27–0.51), hence the observed variations of O$_2$ against N$_2$ was not strong enough to preclude the possibility that these were solely associated with physical processes. Indeed, the observed range is consistent with those obtained from ice growth experiments in abiotic conditions (0.37–0.45) (Killawee et al., 1998), or with negligible bacteria activities (0.32–0.44) (Tison et al., 2002). In contrast, the increase of O$_2$/N$_2$ up to 1.47, i.e., beyond the abiotic range, in BRW10, indicates that the contribution of NCP to the [O$_2$] dominates over that of the physical processes. Therefore, the evolution of O$_2$/N$_2$ indicated a transition from a physical-dominated O$_2$ supersaturation (from BRW2 to BRW8) to a NCP-dominated O$_2$ supersaturation (in BRW10). This is in agreement with what we observed from gas standing stocks, gas saturation levels and brine volume fraction (Sect. 4.1).

From the best of our knowledge, O$_2$/Ar has never been measured in ice before; a comparison with the literature is therefore impossible. However, since O$_2$/Ar and O$_2$/N$_2$ evolve similarly toward higher values over the sampling events, sharp increase in O$_2$/Ar likely indicate, as O$_2$/N$_2$, the switch from physical-dominated to NCP-dominated O$_2$ supersaturation.
4.2.2 Comparison of the sensitivity of $O_2/N_2$ and $O_2/Ar$

The main difference between $O_2/Ar$ and $O_2/N_2$ (Fig. 5c and d) was their variability with depth: $O_2/Ar$ appeared more sensitive than $O_2/N_2$ to describe the NCP-related $O_2$ supersaturation, because it exceeded the abiotic range from BRW4 onwards (vs. BRW8 for $O_2/N_2$). That difference may result from (1) the relative abundance of $O_2$ compared to those of Ar and $N_2$, (2) the relative solubilities of the gases and (3) the relative diffusion rates of the gases. First, since $[O_2]$ is about 20 times higher than $[Ar]$, but about 3 times lower than $[N_2]$, adding the same amount of $O_2$ (due to NCP) will induce a higher increase in the $O_2/Ar$ ratio than in the $O_2/N_2$ ratio. Second, $N_2$ solubility in brine was clearly different to that of $O_2$ and Ar, as suggested by the larger supersaturation of $N_2$ in comparison to $O_2$ and Ar (Fig. 4). That difference in gas solubility impacts the fractionation between gases in brine and gas bubbles, which then affect differently the $O_2/Ar$ and $O_2/N_2$ ratios. Third, the diffusion coefficient in seawater of $O_2$, Ar, and $N_2$ are 1.2, 0.8 and 1.1 ($10^{-15}$ cm$^2$s$^{-1}$) respectively (Broecker and Peng, 1982). If diffusion occurs in the permeable bottom ice layers (Killawee et al., 1998), both $O_2/Ar$ and $O_2/N_2$ ratios will decrease: $O_2/Ar$ by a factor 1.5, but $O_2/N_2$ only by a factor 1.1.

We made a simple calculation to assess the impact of maximized gas bubble formation and diffusion on $O_2/Ar$ and $O_2/N_2$. Gas bubble formation will draw $O_2/Ar$ from 20.48 (solubility in seawater) to 22.5 (ratio in gas bubbles) (see materials and methods), resulting in an increase of $O_2/Ar$ by 9.9%. Gas diffusion privileges the loss of $O_2$ in comparison to Ar, with a ratio of 1.2/0.8 due to their respective diffusion coefficient (Broecker and Peng, 1982), resulting in a decrease of $O_2/Ar$ from 20.48 to 13.65, i.e., −33.3%. When we applied the same calculations to $O_2/N_2$, assuming $O_2/N_2$ ratios of 0.56 in seawater, 0.27 in gas bubbles and a relative coefficient of 1.1, we obtained a change of $O_2/N_2$ by −51.8% due to gas bubble formation and −8.9% due to diffusion. Therefore, maximizing both physical processes will decrease $O_2/Ar$ by 23.4%, but $O_2/N_2$ by 60.7%.
Table 2 summarizes the trends of changes that the $O_2$/Ar and $O_2$/N$_2$ ratios could experience due to NCP (photosynthesis and respiration) and maximized gas bubble formation and diffusion in the permeable layers. While biological processes impact both ratios in the same way, physical processes do not. Both gas bubble formation and diffusion decrease $O_2$/N$_2$, while gas bubble formation may compensate the impact of diffusion on $O_2$/Ar. Additional $O_2$ due to NCP needs to be important enough to overcome the decrease of $O_2$/Ar and $O_2$/N$_2$ due the physical processes, and that additional amount of $O_2$ is more important when using $O_2$/N$_2$ than $O_2$/Ar. This, in addition to the scale effect, indicates that $O_2$/Ar is more sensitive than $O_2$/N$_2$, and explains why $O_2$/Ar exceeded the abiotic range one month earlier (in BRW4) than $O_2$/N$_2$ (in BRW8) (Fig. 5c and d).

4.3  Feasibility of using $O_2$/Ar to estimate NCP in sea ice

4.3.1  The impermeable layers

The main issue that prevents deducing NCP from $O_2$ (Sect. 4.1) and $O_2$/Ar (Sect. 4.2) is the concomitant physical and biological impacts on both parameters in sea ice. This issue should not exist in the impermeable layers, because only NCP may have affected $O_2$ and $O_2$/Ar changes in these layers. Indeed, while the initial $O_2$ and $O_2$/Ar may have varied due to the variable physical conditions at incorporation and as long as the ice remained permeable, gas diffusion was unlikely after the bubble close-off, and solubility changes should not have affected the results, since the crushing technique extracts gases in both brine and gas bubbles. Therefore, to test the feasibility of using $O_2$/Ar to estimate NCP ice, we calculated the changes of standing stocks of $O_{2\text{NCP}}$ (derived from $O_2$/Ar as described in Eq. 3), from 0 to 50 cm depth (the thickness of the impermeable layers in BRW2, Fig. 5a) from BRW2 to BRW7, and compared it with the changes of standing stocks of $O_2$ from bulk ice [$O_2$] (Fig. 5a) in the same layers. We expect similar increase of both $O_2$ and $O_{2\text{NCP}}$ standing stocks between the sampling events.
Surprisingly, the NCP that was derived from O$_2$ standing stocks (NCP(O$_2$)) differed significantly from the NCP derived from O$_2$/Ar (NCP(O$_2$/Ar)) and varied much largely with depth (Table 3). We attribute this to the spatial variability of gases because extreme values of NCP(O$_2$) were observed at 20–40 cm depth, where bulk O$_2$ changed abruptly in BRW4 (Fig. 5a). It is unclear for us why [O$_2$] varied in this way in BRW4, but Ar showed the same trend (Zhou et al., 2013), precluding therefore drastic O$_2$ changes associated with NCP; the deduced NCP(O$_2$) was then likely an artifact of the spatial variability in BRW4. In that situation, the correction of O$_2$ using Ar, which was incorporated in the same conditions than O$_2$ (i.e., experiencing the same spatial variability) would correct the effect of spatial variability on NCP.

However, another cause of the differences between NCP(O$_2$) and NCP(O$_2$/Ar) may be the values of [O$_2$]$_{eq}$ prescribed in the calculation of NCP(O$_2$/Ar) (Eq. 3). In seawater studies, the NCP-related O$_2$ concentration is defined as [O$_2$]$_{eq}$Δ(O$_2$/Ar) (Eq. 3), where [O$_2$]$_{eq}$ is the temperature and salinity-dependent O$_2$ solubility in ice. In our impermeable sea ice layers, the initial O$_2$ concentration may be supersaturated, i.e., higher than the gas solubility calculated at in situ temperature and salinity following Garcia and Gordon (1992) ([O$_2$]$_{eq}$), because of the various processes described in Sect. 4.1.2. Indeed, Ar supersaturation approached 500 % for brine volume fraction of 5 % (the transition from permeable to impermeable layers) (Fig. 4) – in comparison to the 1 % of supersaturation reported in seawater studies (Hamme and Severinghaus, 2007), but 564 % in Antarctic lake ice (Hood et al., 1998) – indicating that the initial O$_2$ concentration, from which we can start to correct the physical processes using O$_2$/Ar, may be supersaturated as well: at least 500 % if we assumed similar solubility between O$_2$/Ar (Weiss, 1970), and even more if we take into account the O$_2$ production in the bottom ice layers.

Clearly, both O$_2$-based and O$_2$/Ar-based techniques to derive NCP in impermeable layers have their limitations. We multiplied the NCP(O$_2$/Ar) by 5 and by 30 to take into account the full range of O$_2$ supersaturation when the ice became impermeable (Fig. 4). Corrected NCP(O$_2$/Ar) then ranged between 5.0 and 81.4 (10$^{-3}$ mmolO$_2$ m$^{-2}$ d$^{-1}$) from BRW2 to BRW4, and between −333.6 and 356.4
(10^{-3} \text{ mmol} \text{O}_2 \text{ m}^{-2} \text{ d}^{-1}) \text{ from BRW4 to BRW7. These values are very modest compared to the NCP reported in springtime sea ice bottom in Greenland (Long et al., 2012) and in the Barents sea (McMinn and Hegseth, 2007) (\sim -1.45 and 3.1 \text{ mmol} \text{O}_2 \text{ m}^{-2} \text{ d}^{-1} respectively, assuming a O_2/C ratio of 1.43 following Glud et al., 2002), but one has to consider that surface ice layers are likely much less productive than the permeable sea ice bottom.}

The observed fluctuations of NCP(O_2/Ar) from BRW4 to BRW7 witness that heterotrophic and autotrophic processes may coexist in sea ice. This is not surprising because the presence of micro-niches allow both processes to coexist in sea ice (Rysgaard et al., 2008). The change from net autotrophic (BRW2-BRW4) to both autotrophic and heterotrophic system (BRW4-BRW7) is in agreement with the results of previous analyses suggesting increasing remineralisation (i.e., net heterotrophic processes) in BRW7 (Zhou et al., 2013).

4.3.2 The permeable layers

For the permeable layers, O_2 exchanges through sea ice were obvious (Sect. 4.1). As a consequence, changes in O_2 standing stocks do not allow retrieving NCP. O_2/Ar was clearly sensitive to NCP, but requires additional equations that describe gas bubble formation and gas diffusion to remove the physical imprints in O_2/Ar. As we could not assess the frequency or the impact of the convection on the variations of O_2 over the sampling period, we simplified the problem by considering only the case of BRW10 where convection was unlikely due to brine stratification (Sect. 2.1) (i.e., only diffusion and NCP took place). At that time, sea ice was completely permeable and physical O_2 supersaturation should be inexisten (Sect. 4.1), the technique of O_2/Ar should then be applicable as in seawater.

We described the variation of [O_2] at a depth z, over a period of time t (\frac{\partial [O_2]}{\partial t}), as a function of the net community production at the depth z (NCP_z) and the diffusion of O_2 between that depth (z) and the layers above (z-1) and below (z+1). The diffusion
itself depends on the concentration gradient, and DO$_2$ which is set as the molecular diffusion coefficient of O$_2$ in seawater at 0 °C, 1.2 x 10$^{-5}$ cm$^2$ s$^{-1}$ (Broecker and Peng, 1982). There is an error $\phi$ due to the impact of physical processes on O$_2$. This gives:

$$\frac{\partial [O_2]_z}{\partial t} = D_{O_2} \frac{\partial O_2}{\partial z^2} + \text{NCP}_z + \phi$$  \hspace{1cm} (4)

Assuming a steady state (i.e., all the new O$_2$ production due to NCP diffused away so that the profile of BRW10 (Fig. 5a) remained constant), and assuming that O$_2$/Ar corrects the changes of O$_2$ changes due to solubility changes as in seawater (Weiss, 1970), Eq. 4 can be approximate as

$$\text{NCP}_z = -D_{O_2} \frac{\partial^2 ([O_2]_{eq} \Delta(O_2/Ar))}{\partial z^2}$$  \hspace{1cm} (5)

could neither retrieve the NCP$_z$ in the last 5 cm of the ice bottom, as the calculation of NCP$_z$ of a layer depends on the adjacent layers, nor the NCP$_z$ in the superimposed ice at the top of the ice cover as temperature and salinity data were missing. It is also noteworthy that this calculation is sensitive to the diffusion coefficient, which is highly variable (Table 1): using the O$_2$ diffusion coefficient of Loose et al. (2010) instead of that of Broecker and Peng (1982) will triple the estimate of NCP. Discussing the causes of the variability in O$_2$ diffusion coefficient is beyond the scope of the present paper. Instead, we simply used the coefficients from Broecker and Peng (1982) to provide a conservative estimate of NCP.

Figure 6 shows the results of NCP$_z$, hence the deduced NCP at different depth assuming a steady state, where diffusion equals the NCP. NCP$_z$ varied vertically, but the sharp increase of NCP$_z$ at 125–130 cm clearly stood out, corresponding to an O$_2$ production of 51 mmolO$_2$ m$^{-2}$ d$^{-1}$, hence a C uptake of 435 mgC m$^{-2}$ d$^{-1}$. The smaller variations in the deduced NCP$_z$ may reflect the spatial heterogeneity of the system (Sect. 4.3.1) or a numerical effect, because the use of second derivatives implies strong
sensitivity to the gradient of concentrations. For example, the negative C uptake at 115–120 cm depth (Fig. 6) may be related to a sharp change of NCP (also noticeable in the profiles of O₂, Fig. 3a). Therefore, we suggest a conservative interpretation of the NCP based on the integration of NCP_z over some layers or over the whole ice length, which also facilitate the comparison with previous data. The integration gives as NCP −0.12, 23.52 and 23.51 mmolO₂ m⁻² d⁻¹ in the top 50 cm layer, bottom 20 cm and in the whole ice cover respectively.

The negative NCP in the top 50 cm layers indicates net heterotrophy, hence a C release of 1.0 mgCm⁻² d⁻¹ (assuming the photosynthetic quotient O₂/C of 1.43, Glud et al., 2002). The NCP in the bottom permeable layers (23.52 mmolO₂ m⁻² d⁻¹) contributed to a large part of the NCP over the whole ice length (23.51 mmolO₂ m⁻² d⁻¹), which is not surprising because chl a was mainly concentrated at the sea ice bottom. Comparison with the previous data in the literature is difficult because of the vertical resolution of the analyses. For instance, our equivalent C uptake in the bottom layer (197.3 mgCm⁻² d⁻¹) is much larger than the 84.2 mgCm⁻² d⁻¹ observed in Barrow landfast sea ice bottom (Lee et al., 2008) the 27 May 2003, but considering that we integrated the O₂ production over 20 cm of ice layer vs. the 3-bottommost-cm ice layer in Lee et al. (2008), we may expect higher deduced NCP. Therefore, we will only highlight that we are confident about our estimate of NCP, as it is within the range of primary production in the springtime bottom sea ice of the Canadian Arctic Archipelago (21–463 mgCm⁻² d⁻¹) (Smith et al., 1988) and Baffin Bay (26–317 mgCm⁻² d⁻¹) (Nozais et al., 2001).

The deduced C uptake over the whole ice length (197.3 mgCm⁻² d⁻¹) was 10 times higher than the maximum C uptake of 12 mgCm⁻² d⁻¹ from the atmosphere (Nomura et al., 2010). Given to the variation of C uptake with depth (C release in the upper layers and C uptake in the bottom layer), we believe that the under-ice water was the main source of C supply for sea ice.
5 Conclusion and perspectives

We presented the evolution of O$_2$ standing stocks, saturation levels and concentrations in landfast sea ice, collected in Barrow (Alaska) from February to June 2009. The comparison of the standing stocks and saturations levels of O$_2$ with those of N$_2$ and Ar reveals that the dynamic of O$_2$ in sea ice was highly sensitive to physical processes. Ice growth and gas bubble formation had favored the incorporation of O$_2$ in sea ice, and low brine volume fraction (i.e., low permeability) maintained high supersaturation of O$_2$ in sea ice. Increasing ice permeability during ice melt led to gas exchange through sea ice, which lowered the O$_2$ standing stocks, despite significant net biological O$_2$ production (NCP). Because of gas exchange through sea ice (i.e., with seawater and the atmosphere), understanding the variations of O$_2$ and NCP with depth in sea ice is highly complementary to the eddy-correlation technique that measures NCP at the ice–water interface; it should highlight the proportion of O$_2$ transferred from sea ice to seawater and the proportion that is transferred from sea ice to the atmosphere (respectively measured and neglected in the eddy-correlation technique).

O$_2$ exchange through sea ice depends not only on ice permeability (i.e., brine volume fraction), but also on O$_2$ solubility. While increasing temperature increases ice permeability, which allows gas exchanges, it also increases O$_2$ solubility (through decreasing brine salinity). As a consequence, although high O$_2$ supersaturations were found in impermeable layers, the potential for gas exchanges decreased as sea ice became permeable. That relationship between saturation levels and brine volume fraction also implies that gas exchange may be intense in winter (low ice temperature) on mechanically-weakened sea ice covers. Further analyses in ice ridging areas should confirm that conjecture.

Because O$_2$ was mainly sensitive to physical processes, we tested the use of O$_2$/Ar and O$_2$/N$_2$ to correct for the physical contribution and to determine the net biological contribution to O$_2$ variations (i.e., NCP). O$_2$/Ar suited better than O$_2$/N$_2$ for NCP determination, because the relative abundance of O$_2$, N$_2$ and Ar induced higher sensitivity in
O$_2$/Ar, and the combined effect of maximized gas bubble formation and gas diffusion induced less bias in O$_2$/Ar. Further, O$_2$/Ar showed the ability to correct for the impact of spatial variability on the determination of NCP based on O$_2$ solely, as both O$_2$ and Ar were incorporated in the same physical conditions (i.e., subject to the same spatial variability).

We estimated conservative NCP in the impermeable layers of sea ice. These are the first estimates derived from O$_2$ measurements in sea ice, because the technique of crushing allows measurements in the impermeable layers. However, the estimates were only conservative, because of uncertainties related to O$_2$ concentrations (and potential supersaturation) at bubble close-off. Further work that deals with gas solubility for temperature and salinity in brine may solve this issue and provide more accurate NCP estimate in the impermeable layers.

We also derived NCP using the O$_2$/Ar technique for the permeable layers (BRW10). The results suggest heterotrophic conditions in the upper ice layers, but autotrophic conditions at sea ice bottom – which contributed to most of the total NCP of the whole ice cover. Because O$_2$ and C are tightly-related in photosynthetic and respiration processes, the vertical profile of NCP indicates C release to the atmosphere in the upper layers, but C uptake in the bottom ice layers, where seawater was likely the main source of C supply.

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References


Table 1: Diffusion coefficients of O$_2$, Ar and N$_2$ found in the literature for different medium (water, seawater and sea ice) for temperature at or below 0°C. Salinity is given when available. The diffusion coefficients in use in the present study are those of Broecker and Peng (1982).

<table>
<thead>
<tr>
<th>Medium</th>
<th>Temperature °C</th>
<th>Salinity</th>
<th>O$_2$ $10^{-5}$ cm$^2$ s$^{-1}$</th>
<th>Ar $10^{-5}$ cm$^2$ s$^{-1}$</th>
<th>N$_2$ $10^{-5}$ cm$^2$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Broecker and Peng (1974)</td>
<td>Water</td>
<td>0</td>
<td>1.17</td>
<td>0.88</td>
<td>0.95</td>
</tr>
<tr>
<td>Broecker and Peng (1982)</td>
<td>Seawater</td>
<td>0</td>
<td>1.2</td>
<td>0.8</td>
<td>1.1</td>
</tr>
<tr>
<td>Loose et al. (2010)</td>
<td>Ice</td>
<td>−12 to −4</td>
<td>3.78–6.58</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
Table 2. Synthesis on the trends of changes of $O_2$/Ar and $O_2/N_2$ at the ice–water interface. An upward arrow indicates that the process increases the ratio, while a downward arrow indicates that the process decreases the ratio. The percentages in brackets indicate the maximal changes of the ratio associated with the physical processes (see Sect. 4.2.2 for details).

<table>
<thead>
<tr>
<th></th>
<th>$O_2$/Ar</th>
<th>$O_2/N_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photosynthesis</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>Respiration</td>
<td>↓</td>
<td>↓</td>
</tr>
<tr>
<td>Gas bubble formation</td>
<td>↑ (+9.9%)</td>
<td>↓ (−51.8%)</td>
</tr>
<tr>
<td>Diffusion</td>
<td>↓ (−33.3%)</td>
<td>↓ (−8.9%)</td>
</tr>
</tbody>
</table>
Table 3. NCP in the impermeable ice layers (0–50 cm depth) from BRW2 to BRW4 and from BRW4 to BRW7, in mmol O$_2$ m$^{-2}$ d$^{-1}$. The columns entitled “O$_2$/meth.” refer to the NCP derived from the standing stocks of [O$_2$] in bulk ice, while the columns entitled “O$_2$/Ar” refer to the NCP derived using the O$_2$/Ar (see Eqs. 2 and 3).

<table>
<thead>
<tr>
<th>Ice depth (cm)</th>
<th>BRW2-BRW4 O$_2$/meth.</th>
<th>BRW2-BRW4 O$_2$/Ar meth.</th>
<th>BRW4-BRW7 O$_2$/meth.</th>
<th>BRW4-BRW7 O$_2$/Ar meth.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–10</td>
<td>−6.9</td>
<td>1.0</td>
<td>−124.1</td>
<td>11.9</td>
</tr>
<tr>
<td>10–20</td>
<td>−1.0</td>
<td>1.1</td>
<td>−378.8</td>
<td>−3.8</td>
</tr>
<tr>
<td>20–30</td>
<td>−76.9</td>
<td>1.4</td>
<td>488.7</td>
<td>3.4</td>
</tr>
<tr>
<td>30–40</td>
<td>106.9</td>
<td>2.1</td>
<td>−661.1</td>
<td>−11.1</td>
</tr>
<tr>
<td>40–50</td>
<td>33.2</td>
<td>2.7</td>
<td>−387.2</td>
<td>−11.0</td>
</tr>
</tbody>
</table>
Fig. 1. The study site, North of Barrow (Alaska, USA).
Fig. 2. Concentrations of $N_2$ in ice plotted against the concentrations of Ar in ice. The equation and $r^2$ are calculated assuming a linear regression between both gas concentrations.
Fig. 3. Evolution of the standings stocks of $N_2$, $O_2$ and Ar (squares, circles and triangles respectively) compared to the evolution of sea ice thickness (vertical grey bars). The break in gas standing stocks is set at 50 mmol m$^{-2}$. 

2078
Fig. 4. Saturation levels ($\Delta C_i$ in Eq. (1), in percentage) of $N_2$, $O_2$ and $Ar$ (squares, circles and triangles respectively) compared to the brine volume fraction.
Fig. 5. (a) O$_2$ concentration in bulk ice (black dots) compared to its solubility in ice (white dots), the dashed areas refer to permeable ice layers (i.e. with a brine volume fraction above 5%); (b) Chl $a$ concentrations (horizontal bars) with a break at 2 $\mu$g L$^{-1}$ ice compared to the percentage of phaeopigments (diamonds); (c) O$_2$/Ar in ice (upside triangles) with a break at 25, compared to the same ratios in seawater (straight black line) and in the atmosphere (dashed black line); (d) O$_2$/N$_2$ in ice (downside triangles) compared the same ratios in seawater (straight grey line) and in the atmosphere (dashed grey line).
Fig. 6. NCP in BRW10 assuming equilibrium between the diffusion and NCP (see Sect. 4.3). The results were converted into C uptake, assuming a photosynthetic quotient $O_2/C$ of 1.43 (Glud et al., 2002).