

Sea ice CO₂ dynamics across seasons: impact of processes at the interfaces

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Key Points:

- First long-term monitoring of both pCO₂ and CO₂ fluxes at sea ice interfaces in McMurdo Sound (Antarctica) from late winter to summer
- Large biomass build-up is strikingly associated with transient heterotrophy and nitrate plus nitrite accumulation
- New conceptual approach involving biofilm formation can explain observed inconsistencies: accumulation of nitrate plus nitrite and CaCO₃

Abstract

Winter to summer CO₂ dynamics within landfast sea ice in McMurdo Sound (Antarctica) were investigated using bulk ice pCO₂ measurements, air-snow-ice CO₂ fluxes, dissolved inorganic carbon (DIC), total alkalinity (TA) and ikaite saturation state. Our results suggest depth-dependent biotic and abiotic controls that led us to discriminate the ice column in three layers. At the surface, winter pCO₂ supersaturation drove CO₂ release to the atmosphere while spring-summer pCO₂ undersaturation led to CO₂ uptake most of the time. CO₂ fluxes showed a diel pattern superimposed upon this seasonal pattern which was potentially assigned to either ice skin freeze-thaw cycles or diel changes in net community production. In the ice interior, the pCO₂ decrease across the season was driven by physical processes, mainly independent of the autotrophic and heterotrophic phases. Bottom sea ice was characterized by a massive biomass build-up counterintuitively associated with transient heterotrophic activity and nitrate plus nitrite accumulation. This inconsistency is likely related to the formation of a biofilm. This biofilm hosts both autotrophic and heterotrophic activities at the bottom of the ice during spring and may promote calcium carbonate precipitation.

Plain Language Summary

Sea ice participates actively in the regional cycling of CO₂ both as a source and a sink at different times of the year depending on ice physics, ice chemistry and ice trophic status (autotrophic vs heterotrophic). We identified the key processes driving the CO₂ dynamics in each sea ice layer (surface, interior and bottom) from McMurdo Sound (Antarctica) from late winter to summer. At the surface, CO₂ release from the ice to the atmosphere occurred in late winter while CO₂ uptake occurred in summer. Superimposed upon this seasonal pattern, we observed a diurnal pattern with both release and uptake occurring over 24 h period. This diurnal pattern can be related to physical processes (nocturnal freeze-up and diurnal melting) or biotic processes (autotrophy or heterotrophy). In the ice interior, a succession of autotrophic and heterotrophic phases took place. At the sea ice bottom, a particular assemblage of microbial cells and organic matter, called biofilm, enabled the accumulation of biomass and nitrate plus nitrite simultaneously leading to both autotrophic and heterotrophic activities. In addition, this biofilm is suggested to promote calcium carbonate precipitation.

1 Introduction

Over the global oceans, polar oceans act as a major sink for atmospheric CO₂ (Gruber et al., 2019; Takahashi et al., 2002), with air-sea fluxes estimated at -199 Tg C yr⁻¹ (Rysgaard et al., 2011). At high latitudes, the CO₂ cycle is strongly affected by the presence of sea ice. More than just an interface affecting gas transfers, sea ice is also one of the most extensive and dynamic ecosystems, that consumes and produces CO₂. Over the last decade, studies highlighted the complex role of sea ice in CO₂ exchanges and reported CO₂ fluxes over sea ice ranging from -5.4 μmol m⁻² d⁻¹ to +9.9 μmol m⁻² d⁻¹, with a negative value indicating CO₂ uptake and a positive value indicates CO₂ release from ice to air (Table S1). Fluxes have been documented mainly in spring and summer (Brown et al., 2015; Delille et al., 2014; Geilfus et al., 2012a, 2013, 2014, 2015; Nomura et al., 2010a, 2013). No studies have examined the winter CO₂ exchanges above sea ice in Antarctica – a prerequisite to budget air-ice CO₂ fluxes over the whole year.

The partial pressure of CO₂ (pCO₂) within sea ice is a highly relevant parameter to understand the carbonate system. Factors affecting the sea ice pCO₂ include biotic (e.g. primary

66 production and respiration (Delille et al., 2007)) and abiotic (e.g. CO₂ transport and exchanges,
67 freezing, melting, calcium carbonate precipitation and dissolution (Rysgaard et al., 2007))
68 processes. The strong seasonality of these biotic and abiotic processes in brine inclusions,
69 coupled with the thermodynamically driven evolution of brine inclusions volume, salinity, and
70 connectivity lead to strong temporal variability in the sea ice CO₂ dynamics (Geilfus et al.,
71 2012a; Papadimitriou et al., 2012).

72 The gradient of pCO₂ between the ice and the atmosphere is driving CO₂ exchanges,
73 controlling both the fluxes direction and magnitude. Ice-atmosphere CO₂ exchanges are
74 moreover strongly affected by the conditions at the interface, including ice type (superimposed
75 ice, snow ice, granular ice), presence or absence of snow cover and the ice and snow chemical
76 and physical properties. Snow salinity, wetness, density, grain sizes among others are likely to
77 affect the magnitude and direction of CO₂ fluxes (Delille et al., 2014; Nomura et al., 2010a,
78 2018). The presence of brine within the snowpack is induced by four processes: flooding, brine
79 wicking, frost flowers formation and aerosols deposition (Domine et al., 2004; Massom et al.,
80 2001). Brine-wetted snow is a multiphase reactor hosting specific physical and chemical
81 processes that may influence CO₂ fluxes: uptake and migration of trace gas, diffusion, and
82 sources and sinks processes (Bartels-Rausch et al., 2014). While the impact of fresh snow cover
83 on gas fluxes has been documented for terrestrial environments (Brooks et al., 2005; Takagi et
84 al., 2005), the role of the snow on sea ice is still overlooked.

85 As a biome, sea ice provides a dynamic habitat for diverse communities of
86 microorganisms including algae, bacteria, heterotrophic protists, fungi as well as viruses
87 (Deming, 2010; Horner et al., 1992; Luhtanen et al., 2018; Poulin et al., 2011; Thomas &
88 Dieckmann, 2010). In landfast sea ice, i.e. immobile sea ice anchored either to coasts or
89 continental ice formations or grounded over shoals (Meiners et al., 2018), communities are
90 mainly concentrated either at the bottom of the ice or within a loose and unconsolidated layer of
91 ice crystals, known as platelet underneath the columnar ice (Arrigo et al., 1995). Platelet ice is
92 formed in supercooled waters observed around Antarctic ice shelves (Jeffries et al., 1993;
93 Leonard et al., 2006). Bacterial and algal production affect the CO₂ dynamics by releasing or
94 consuming CO₂, impacting concentrations of dissolved inorganic carbon (DIC) and total
95 alkalinity (TA) - key parameters that drive the ocean-sea ice-atmosphere CO₂ fluxes. In oxic
96 conditions, apart from the calcification, the contribution of microbial processes to DIC changes
97 is best described by the net community production (NCP). NCP corresponds to the balance
98 between photosynthesis and respiration of all organisms and determines the net trophic status of
99 the ice (autotrophic vs heterotrophic). Positive NCP (autotrophic) leads to a consumption of DIC
100 and a production of O₂, whose stoichiometry is tightened to photosynthetic and respiratory
101 reactions (i.e., photosynthetic quotient) (Anderson, 1995; Glud et al., 2002). Some studies
102 documented the net community production across the Arctic using standard measurement
103 methods such as incubation of melted ice cores (Campbell et al., 2017; Søgaard et al., 2010) and
104 highlighted succession of distinct heterotrophic and autotrophic phases. However, the processes
105 and conditions in which heterotrophy or autotrophy dominates remain unclear.

106 Considering the lack of long-term and diurnal surveys of sea ice CO₂ dynamics and the
107 need to integrate the full development of a microalgae bloom, we present results from a year-round
108 survey of landfast sea ice carbon dynamics in Cape Evans, McMurdo Sound (Antarctica). We
109 report O₂ and pCO₂ profiles within bulk sea ice as well as seasonal and diel patterns of CO₂ fluxes
110 at the air-snow-ice interface. The potential for calcium carbonate precipitation is also investigated.

We further examine chlorophyll *a* (chl-*a*) abundance, particulate organic carbon (POC), nitrate plus nitrite concentrations, and DIC changes over the bloom. We also compare these parameters with estimates of NCP and related ice trophic status.

2 Materials and Methods

2.1 Study site and sampling scheme

Year Round survey of Ocean-Sea Ice-Atmosphere Exchanges (YROSIAE) was a temporal survey at one single ice location at Cape Evans (77°38'S, 166°23'E), on the eastern side of McMurdo Sound, Antarctica (Figure 1). Sampling was supported by Scott Base facilities and carried out in two phases, from November to December 2011 and from September to December 2012. The sampling area is characterized by the annual occurrence of smooth, thick first-year landfast ice. Ice retreat began in early February 2011 in Cape Evans and the area remained ice-free until the beginning of April 2012, approximatively 5 months before the second sampling phase (19 September 2012). Ice cores, snow and seawater samples were collected during twelve ice stations. For the sake of consistency with other reports of YROSIAE results (Carnat et al., 2014, 2018), each station number, referenced hereafter as YRS#, corresponds to a dedicated sampling date as indicated in Figure 2 and in Table 1. Each time the site was visited, a new sampling square area of 10 m² was delimited next to the sampling site of the previous station in order to minimize the bias from spatial heterogeneity. The snow cover was first sampled using plastic scoops and LDPE bottles, then the ice coring started. Ice cores were collected using an electropolished stainless-steel ice corer (14 cm ID). Immediately after drilling, cores were sealed in polyethylene bags and stored in a box containing -30°C frozen bags. Attention was paid to prevent brine drainage by keeping ice cores horizontally. Seawater sampling through core holes was performed at three different depths (0, 1 and 30 m) using a peristaltic pump (Cole Palmer, MasterflexVR - Environmental sampler) with Tygon® tubing.

Outside the sampling site, one soil CO₂ flux system (LI-COR LI8100A) was deployed with two long term deployment automatic chambers (LI-COR 8100-104). Chambers for CO₂ fluxes measurements were deployed over the snow and ice surfaces and were continuously running until they were blocked by the snowdrift. Every four to seven days, maintenance and repositioning of the chambers on an unaltered surface were performed. From September to December 2012, an *Ice-T* ice mass balance buoy developed at LOCEAN (UPMC, Paris) provided continuous measurements of air temperature and ice temperature at different depths. The experimental setting and sampling scheme are also detailed in Carnat et al. (2014).

2.2 Measured parameters

2.2.1 Physical parameters

In situ ice temperature was measured on ice cores immediately after sampling with a vertical resolution of 5 cm using a calibrated probe TESTO® 720 (precision $\pm 0.1^\circ\text{C}$, accuracy $\pm 0.2^\circ\text{C}$). Bulk ice salinity measurements were performed using the same 5 cm vertical resolution as for temperature measurements using a Thermo Scientific Orion® 3 Star conductivity meter (accuracy of 0.1‰). The conductivity meter was calibrated at the beginning and at the end of the survey with standard solutions. The conversion from conductivity to salinity is performed via a built-in temperature-dependent conversion program (UNESCO, 1966). Further details about physical measurements are provided in Carnat et al. (2013, 2014).

2.2.2 Air-snow-ice CO₂ fluxes

CO₂ fluxes were measured using a LI-COR® LI-8100A soil CO₂ flux system. During the survey, two chambers were used and installed on the snow or on the ice after removing the initial snow cover. The chambers consist of a metal cylinder, with a diameter of 20 cm and a height of 9.7 cm, closed at the top by a mobile cap to vent the chamber and maintain an ambient pressure inside. A rubber seal surrounds the cylinder and ensures an airtight connection at the chamber-ice interface. For measurements over snow, a stainless-steel seal was mounted at the base of the chamber and pushed down to the ice to enclose snow and prevent lateral diffusion of air in the snowpack.

The chambers (LI-COR® 8100-104) were temporarily closed above the snow or ice interface and were connected using a LI-COR® LI-8150 Multiplexer to an infrared gas analyzer a LI-COR® LI-8100A recording the pCO₂ during a designated time interval (30 min). The flux was determined by measuring the change of pCO₂ within the chamber. Flux calculations were performed routinely using the LI-COR® SoilFluxPro software, with volumes adjusted to include collar offsets (i.e. rim height above the surface) and applying water vapor corrections for dilution and band broadening. The fluxes were determined by the slope of the linear or exponential regression of pCO₂ over time, depending on the best fit. All fluxes were visually checked to discard measurements biased by contamination or poor sealing of the chamber. The detection limit was $\pm 0.004 \mu\text{mol m}^{-2} \text{s}^{-1}$. Fluxes below the detection limit were considered as null. The uncertainty of the flux computation due to the standard error of the regression slope was $\pm 8 \%$.

2.2.3 Thin sections of ice

Thin sections of thickness ranging from 600 μm to 700 μm were obtained using a Leica SM2400 microtome. These thin sections were then examined on a light table equipped with cross-polarized sheets (Langway, 1958). The textural types were visually identified based on the size, shape, and orientation of the ice crystals and compared to descriptions found in the literature (Eicken & Lange, 1991; Tison et al., 2013).

2.2.4 Biomass and nutrients

One core per station was dedicated to chl-*a*, nutrients and POC analyses. For chl-*a* analyses, ice sections of 10 cm were cut with a band saw, in the cold lab (at -25°C) on the day of extraction and subsequently melted at 4°C in the dark, in pre-filtered seawater. Melted ice was filtered using 10 μm then 0.8 μm Nuclepore® polycarbonate membranes. Filters were stored frozen in cryovials until measurements at the home laboratory. Extraction was performed in 10 mL acetone at 4°C for 16 h. Chl-*a* concentrations were determined using a Turner Design TD700 fluorometer.

Particulate organic carbon (POC) and nutrient analyses were performed at a 10 cm depth resolution for the bottom of the core, and at 30 cm resolution for the rest of the core. Samples were melted at room temperature in the dark and then filtered on 0.7 μm precombusted (5 h at 450 °C) GF/F filters (Whatman®). The filtrate was collected and stored in 60 ml acid-washed, pre-rinsed HDPE bottles. Both filters and filtrate were stored at -25°C. For POC analysis, filters were acid fumed (HCl) to remove carbonates and packed in silver cups fitting the autosampler. POC concentrations were determined using an Elemental analyzer (Eurovector®) coupled with an isotope ratio mass spectrometer (Delta V, Thermo®).

Nitrate+nitrite ($[\text{NO}_3^-] + [\text{NO}_2^-]$), nitrite ($[\text{NO}_2^-]$) and phosphate ($[\text{PO}_4^{3-}]$) concentrations from filtered water samples were measured spectroscopically using a colorimetric method and a QuAatro39 auto-analyzer (Seal Analytical Inc., Mequon, WI, USA).

The change over time of the nitrate plus nitrite concentrations was obtained from the following equation:

$$\Delta [\text{NO}_3^-] + \Delta [\text{NO}_2^-] = \frac{[\text{NO}_3^-](t_{n+1}) + [\text{NO}_2^-](t_{n+1}) - [\text{NO}_3^-](t_n) - [\text{NO}_2^-](t_n)}{\Delta t} \quad (\mu\text{mol L}^{-1} \text{d}^{-1}) \quad (1)$$

Δt denotes the elapsed time between two stations, t_n and t_{n+1} correspond to one station n and the next station ($n+1$), respectively. The change over time of the POC concentrations was computed in the same way.

2.2.5 Total alkalinity and pH

Ice cores were cut into 10 cm sections in a cold room (at -25°C). Each section was placed in a gas-tight Supelco® Tedlar® bag equipped with a push/pull lock valve. The bag was sealed with a clip, and the air was removed using a vacuum pump through the valve. The bagged sea ice samples were then melted at room temperature for less than 24h. Attention was paid to mix the bags regularly in order to keep the meltwater at melting temperature and to treat meltwater as soon as possible after complete melting to avoid warming of the meltwater and subsequent carbonate dissolution as suggested by Dieckmann et al. (2008). Meltwater was shaken to resuspend the crystals and aliquots were collected for pH, bulk alkalinity (TAb) and filtered alkalinity (TAf) analyses. pH was measured using a Metrohm® combined electrode calibrated on the total hydrogen ion scale using TRIS (2-amino-2hydroxymethyl-1.3-propanediol) and AMP (2-aminopyridine) buffers prepared at salinities of 5, 35 and 75 according to the formulations proposed by DOE (1994). The pH measurements were carried out at low temperature (typically below $+4^\circ\text{C}$). The accuracy of pH measurements was ± 0.01 pH units. Samples for TAf were filtered on $0.2 \mu\text{m}$ polycarbonate filters. Filtration was carried out at 4°C in order to avoid any dissolution of calcium carbonate. TA was measured by open-cell titration with HCl 0.1 M on 50 ml of sea ice melt samples, following Gran (1952) endpoint determination. Titration was stopped for 10 minutes at pH 4.2 to ensure the dissolution of any CaCO_3 crystals, prior to perform the measurements between pH of 4.2 and 3 required for the Gran function. The accuracy of TA measurements was $\pm 4 \mu\text{mol kg}^{-1}$. Data were quality checked with certified reference material from Andrew Dickson (Scripps Institution of Oceanography, University of California, San Diego).

2.2.6 O_2 and Ar concentrations

The dry-crushing technique, developed for gas measurements in continental ice (Raynaud et al., 1982), was used to extract O_2 and Ar from the ice samples. This technique allows the extraction of both gas bubbles and gas dissolved in liquid brines. The ice core was cut into 5 cm sections, and each ice cube of about 60 g was placed into a vessel, with seven stainless steel balls. The latter was crushed in the vessel as described in Stefels et al. (2012), at a temperature of -25°C and under a vacuum of 10^{-3} torr. The vessel was then kept at -50°C in a cold ethanol bath and connected to the gas chromatograph equipped with a thermal conductivity detector for concentration analyses. We used He (Air Liquide® – Alphagaz 2) as the carrier gas and a 22 ml packed column (Mole Sieve 5A 80/100; $5 \text{ m} \times 1/8 \text{ in.}$). The repeatability of the analyses (i.e., the precision of the gas chromatograph) was 0.7% for O_2 and 2.3% for Ar (Zhou et al., 2014).

2.2.7 Bulk ice pCO₂ measurements

Bulk ice pCO₂ was measured using the method developed by Verbeke (2005) and Geilfus et al. (2012b) and adapted by Crabeck et al. (2014). The general principle of the method is to equilibrate sea ice samples with a N₂/CO₂ gas mixture of known concentration (standard gas) as close as possible to the in situ temperature (i.e. the temperature of the ice upon ice collection). Once the ice sample is equilibrated, the gas phase is injected into a gas chromatograph (Varian 3300) to measure the CO₂ concentration (Geilfus et al., 2012b).

The ice core was first cut with a vertical resolution of 5 cm. Ice sections were then precisely cut into 4 x 4 x 4.5 cm cubes to tightly fit the equilibration container. Attention was paid to maximize the sea ice volume, to minimize the headspace volume and to keep it equivalent for each sample. Standard gas was injected at atmospheric pressure into the headspace of the container containing the ice sample. Tests were carried out with standard gas at 150 ppm, 300 ppm and 500 ppm. While the three standards gave consistent results below 200 ppm, as expected the 150 ppm standard provided underestimated measurements above 200 ppm. Standards at 300 ppm and 500 ppm provided consistent results below 350 ppm and above 500 ppm, overestimated values in between were observed with the standard at 500 ppm. As a consequence, we used a standard gas of 300 ppm for all samples. The container, kept at -50°C during the standard injection, was then placed in a thermostatic bath to bring the ice sample to the in situ temperature. After 20 h, the sample was assumed to be in equilibrium with the standard gas (Crabeck et al., 2014; Geilfus et al., 2012b). The headspace was then injected in the gas chromatograph to measure the CO₂ concentration. Shortly afterward, the sample temperature was measured using a calibrated probe (TESTO® 720). The method is expected to be valid if the ice is permeable at the in situ conditions. Standard gas concentration should be as close as possible from the expected concentration of the sample in order to achieve sufficient accuracy (Verbeke, 2005).

The precision of the measurements was estimated based on 28 injections of standard gas 300 ppmv (injection pressure ranged between 10 and 99 Torr). We obtained a mean relative error of 2.1%, a standard deviation of 9.8 ppm and a variation coefficient of 3.3%

2.3 Computed parameters

2.3.1 Brine volume and Rayleigh number

The brine volume fraction (BrV), a proxy of sea ice permeability, was computed from ice temperature and salinity following the equations of Cox and Weeks (1983) for ice temperature < -2°C and Leppäranta and Manninen (Leppäranta & Manninen, 1988) for ice temperature ≥ -2°C. We considered that the ice was permeable for a brine volume fraction exceeding 5% (Golden et al., 1998). The Rayleigh number (Ra) was used as a proxy of the intensity of brine convection (Notz & Worster, 2008) which is driven by the density difference between high-salinity brine in sea ice and the seawater underneath (Vancoppenolle et al., 2013). Theoretically, convection can occur in an ice layer when Ra exceeds a critical value of 10 (Notz & Worster, 2008) or 8 (Zhou et al., 2013) according to experimental studies. The critical value could also be considered as low as 4 (Carnat et al., 2013; Vancoppenolle et al., 2013) although this critical value is still quite debated and also sensitive to the potential delay between occurrence and observation.

2.3.2 DIC

Dissolved inorganic carbon (DIC) was computed from TAF and pH (presented in Figure S1), according to CO₂ acidity constants of Goyet and Poisson (1989) as suggested by Brown et al. (2014) for measurement in brines at sub-zero temperatures, and other constants proposed by DOE (1994). We used TAF for DIC computation in order to avoid bias from the potential dissolution of particulate inorganic carbon (e.g. ikaite formed in sea ice).

DIC and TAF were normalized to a salinity of 6, the mean bulk ice salinity, in order to remove the salinity-related changes (i.e. brine rejection, concentration, and dilution). The normalized DIC and TAF are referenced hereafter as DIC₆ and TAF₆, respectively.

2.3.3 NCP from DIC

Net community production based on inorganic carbon deficits (NCP_{DIC}), was computed from changes in observed DIC, TAF, nitrate plus nitrite, and phosphates according to:

$$NCP_{DIC} = -\frac{\Delta DIC}{\Delta t} + 0.5 \frac{\Delta TAF + \Delta NO_3^- + \Delta NO_2^- + \Delta PO_4^{3-}}{\Delta t} \quad (2)$$

where Δt denotes elapsed time between two stations (Delille et al., 2005). The second term of the equation (2) corresponds to the difference in carbonate alkalinity due to the formation or dissolution of calcium carbonate. ΔDIC is the difference between DIC_{tn+1} and DIC_{tn} normalized to the S_{tn+1}, t_n and t_{n+1} corresponding to the station n and the next station (n+1). ΔTAF , ΔNO_3^- + ΔNO_2^- and ΔPO_4^{3-} were computed in the same way. We assumed that no physical process has affected the bulk impurity content of the ice from one station to the next one, and that all these changes are therefore due to biological processes. NCP_{DIC} is given in mg C m⁻² d⁻¹.

2.3.4 NCP from O₂/Ar ratios

Oxygen concentrations in sea ice depend on both biological activity and physical processes. We used argon measurements to remove the influence of physical impact on O₂ concentrations. Argon has indeed no biological sources or sinks but it is affected by physical processes in the same way as oxygen concentrations. O₂ concentrations associated to in situ biological activity ([O₂]_{bio}) were obtained from O₂/Ar ratios and their deviation from saturation as described for seawater by Reuer et al. (2007) and adapted for sea ice by Zhou et al. (2014).

O₂/Ar ratios observed in ice were compared with atmospheric and seawater ratios to determine the abiotic range of O₂/Ar values. Within the abiotic range of O₂/Ar values, it is not possible to discriminate biological processes from physicochemical processes, since changes of O₂/Ar ratio can be ascribed to biological processes but also to the input of atmospheric air or underlying seawater. The atmospheric O₂/Ar ratio is 22.5 based on O₂ and Ar mixing ratios in the atmosphere (NOAA, 1976). Any gas input from the atmosphere or gas bubble formation would push the bulk ice O₂/Ar ratio towards 22.5. At the seawater interface, considering conditions of -1.8°C and a salinity of 34, the O₂/Ar ratio is 20.5 (Garcia & Gordon, 1992; Hamme & Emerson, 2004). Given these ratios, the abiotic range of O₂/Ar in sea ice is determined to lie between 20.5 and 22.5. Out of this range, O₂/Ar values were attributed to the impact of biological activity only and have been considered for computation of net community production.

In order to do so, we first calculated the theoretical brine solubility of each gas using temperature, the salinity of the brine calculated from ice temperature (Cox & Weeks, 1986) and the relationships from Garcia and Gordon (1992) for O₂ and Hamme and Emerson (2004) for Ar.

Brine solubility multiplied by the brine volume fraction gives the gas solubility in bulk ice (hereafter referred as $[O_2]_{eq}$ and $[Ar]_{eq}$).

The O_2/Ar deviation from saturation was calculated as follows:

$$\Delta(O_2/Ar) = \frac{[O_2]/[Ar]}{[O_2]_{eq}/[Ar]_{eq}} - 1 \quad (3)$$

$[O_2]$ and $[Ar]$ are the sea ice concentrations measured at a vertical resolution of 5 cm and interpolated using the IDL program (Harris Geospatial). O_2 and Ar supersaturation are commonly observed in sea ice (Zhou et al., 2014), indicating that equilibrium concentrations can differ from their solubilities due to physical processes. In order to deal with potential biases while using O_2 and Ar solubilities for $[O_2]_{eq}$ and $[Ar]_{eq}$, we modified the calculations from Zhou et al. (2014) as follows:

$$[O_2]_{phy} = [O_2]_{eq} ([Ar]/[Ar]_{eq}) \quad (4)$$

The O_2 concentration associated with in situ biological activity is then defined using the following equation:

$$[O_2]_{bio} = [O_2]_{phy} \Delta(O_2/Ar) (\mu mol L^{-1}) \quad (5)$$

The daily O_2 production is given in $\mu mol L^{-1} d^{-1}$. We considered the ice thickness, a O_2/C ratio of 1.43 (Glud et al., 2002) and the molar mass of C in order to derive the C uptake equivalent ($mg C m^{-2} d^{-1}$).

The propagation of uncertainties on $[O_2]_{bio}$ was estimated using a Monte Carlo approach. We neglected the error on gas diffusion assuming equivalent diffusivities for O_2 and Ar in sea ice as in Crabeck et al. (2014). Each parameter was given a distribution to represent its uncertainty sampled over 10^5 iterations. Normal or uniform distributions between the mean \pm error of measurements were used. Measured parameters (T, S, O_2 , Ar) were given normal distribution with the mean population and an error of 0.2 for T, 0.1 for S, 0.7% for O_2 and 2.2% for Ar. The error on $[O_2]_{eq}/[Ar]_{eq}$ ratio is prone to larger uncertainties and was therefore given a uniform distribution of 9.9% either side of calculated value to account for gas bubble formation in sea ice (Zhou et al., 2014). The obtained maximum uncertainty of $[O_2]_{bio}$ was 19.6%.

Net community production (NCP) is determined from the change over time of oxygen concentrations associated to in situ biological activity ($[O_2]_{bio}$), as follows:

$$NCP = \frac{[O_2]_{bio}(t_{n+1}) - [O_2]_{bio}(t_n)}{\Delta t} (\mu mol L^{-1} d^{-1}) \quad (6)$$

Δt denotes elapsed time between two stations, t_n and t_{n+1} correspond to the station n and the next station (n+1), respectively.

2.3.5 Assessment of calcium carbonate content

Two different indicators were used to assess $CaCO_3$ precipitation: the overall calcium carbonate content ($[CaCO_3]$) and the saturation state of ikaite (Ω_{ika}).

The overall calcium carbonate content was estimated from the difference between total alkalinity of a nonfiltered sample, denoted as bulk alkalinity (TAB) and total alkalinity of the filtered sample, denoted as filtered alkalinity (TAf) (Geilfus et al., 2013). $CaCO_3$ concentration was estimated according to:

$$[\text{CaCO}_3] = \frac{1}{2}(TAb - T Af) \quad (7)$$

Calcium carbonate precipitation (dissolution) can take place if the saturation state of ikaite in brine $\Omega_{\text{ika}} > 1$ ($\Omega_{\text{ika}} < 1$). The saturation state of ikaite Ω_{ika} in brine depends on the concentrations of calcium and carbonate in brine and their solubility product described as a function of temperature $T(\text{K})$ by Papadimitriou et al. (2013):

$$pK_{sp,ikaite} = -15489.09608 + 623443.70216 T^{-1} + 2355.14596 \ln T \quad (8)$$

While this solubility product has been established for temperatures above -8°C , we used it below this threshold and assumed it constant. We acknowledge that we neglected some physical processes such as concentration and dilution. This approach thus presents some limitations. We estimated the salinity of brines using a third-order fit from Assur (1958) and Notz (2005). We also computed TA_{brines} and DIC_{brines} by considering their linear dependence to salinity in order to obtain CO_3^{2-} brine concentrations from CO2SYS program for the carbonate system (Lewis et al., 1998). More details can be found in Moreau et al. (2015).

3 Data, or a descriptive heading about data

3.1 Sea ice and snow properties

Main sampling took place from late winter (September 2012), when daylight was still short and the air temperature was low (down to -32°C), to late spring (November 2012). Three stations were also carried out in December 2011 with an air temperature above 0°C and high solar irradiance (Figure 3). The mean sea ice thickness ranged between 145 cm and 171.4 cm (Figure 2). The ice texture was homogenous between stations. From top to bottom, we observed a thin layer of granular ice followed by a mixture of granular and columnar ice, a thick layer of columnar ice, columnar ice with isolated platelets and a bottom layer of columnar and platelet ice (Figure 2). The snow cover ranged from 0 to 4 cm thick, with salinities ranging from 7.4 to 24.5.

The bulk ice temperature ranged from -19.8°C to -0.8°C and showed a strong vertical gradient (Figure 4a). The lowest ice temperature appeared in the upper layer in winter while the temperature in bottom ice was close to the freezing point (i.e. -1.8°C). At the end of the spring (stations YRS1 to YRS3), the ice displayed a nearly isothermal profile. As the ice temperature increased in spring, the ice became fully permeable from station YRS10 (Figure 4c), when the brine volume fraction exceeded 5%, the threshold for fluid transport (Golden et al., 1998).

The vertical distribution of salinity showed little changes from YRS4 to YRS10 after which surface salinity decreased (Figure 4b). Homogenous salinity profiles were observed in late spring 2012 (stations YRS11 and YRS12) and 2011 (stations YRS1-3). The average bulk salinity for the whole data set was 6. The Rayleigh (Ra) number started to increase at station YRS7 and reached a maximal value of 17 at station YRS11, exceeding the critical convection threshold of 10 (Notz & Worster, 2008). Ra values indicated a convective event in station YRS11 (Figure 4d). However, apart from this specific event, Ra values did not indicate any other obvious convection event, consistently with the salinity distribution.

3.2 Ice carbon content

3.2.1 A “three-layers” model based on DIC₆

DIC₆ ranged from 194 to 563 $\mu\text{mol kg}^{-1}$ (Figure 5b) and exhibited strong vertical gradients within the ice column. These gradients were used to discriminate the ice column in three layers: surface, interior, and bottom. The layer between 20% and 83% of the ice thickness is considered as the interior layer and corresponds to relatively constant (standard deviation below 69 $\mu\text{mol kg}^{-1}$) and highest DIC₆ values (except in late spring from stations YRS1 to YRS3). The surface and bottom layers account for 20% and 17% of the total ice column, respectively (Figure 6b).

DIC₆ increased at all depths from stations YRS4 to YRS6 and then rapidly decreased between stations YRS6 and YRS7. From station YRS7 onwards, DIC₆ values in the surface and bottom layers significantly deviate compared to the mean value observed in the ice interior. Surface DIC₆ oscillated with both increasing and decreasing periods while bottom DIC₆ remained low ($<352 \mu\text{mol kg}^{-1}$ except for station YRS11) and below seawater values (mean DIC_{SW} normalized to salinity 6: $378.8 \pm 17.3 \mu\text{mol kg}^{-1}$ at 0 m depth), although slightly increasing at the end of the study (YRS 11-12).

Changes in DIC₆ are mainly due to biogeochemical processes such as CO₂ consumption or production, precipitation, and dissolution of calcium carbonate and exchanges of CO_{2(g)}.

3.2.2 Calcium carbonate precipitation

TAF₆ increased gradually at the bottom of the ice from late winter (station YRS7) to late spring (station YRS12) reaching values up to 550 $\mu\text{mol kg}^{-1}$ (Figure 5a). The calcium carbonate content followed the same trend as TAF₆ at the bottom of the ice suggesting localized CaCO₃ precipitation. We estimated that up to 350 $\mu\text{mol kg}^{-1}$ CaCO₃ precipitated in late spring (Figure 5c). Accordingly, high Ω_{ika} values were mainly observed at the bottom of the ice from stations YRS7 to YRS12 (Figure 5d). At the sea ice surface, no significant CaCO₃ precipitation occurred at the sea ice surface except potentially at stations YRS11 and YRS12.

3.3 Biomass and nitrate concentrations

Most of the ice algal biomass (66 to 99.9%) was concentrated in the bottom 10 cm of the ice (Table S2) with values reaching over 2400 $\mu\text{g L}^{-1}$ in spring (Figure 6a). Under-ice seawater concentrations remained low ($<0.41 \mu\text{g L}^{-1}$) from stations YRS4 to YRS12. The onset of the spring ice-algal bloom was initiated at YRS6 and Chl-*a* was accumulating until station YRS10.

POC accumulated in parallel with the increasing algal biomass in the bottom ice. POC concentrations increased by 1100 $\mu\text{mol L}^{-1}$ between stations YRS8 and YRS10 (in 12 days) to reach maximum value around 2600 $\mu\text{mol L}^{-1}$ in station YRS10 (Figure 6b). Bulk concentrations of nitrate plus nitrite ranged from 0.1 $\mu\text{mol L}^{-1}$ to 97.1 $\mu\text{mol L}^{-1}$ (Figure S2). Changes over time of nitrate plus nitrite concentrations and POC concentrations, calculated using Eq. (1) are shown in the Figure 7a,b. Positive values indicate an increase between the two stations considered while negative values indicate a decrease. Both nitrate plus nitrite and POC concentrations were higher in absolute value at the bottom of the ice than in the ice interior and at the surface.

Concentrations increased between each station until YRS10 before collapsing at station YRS11.

3.4 Oxygen concentrations

The O_2 and O_{2bio} concentrations ranged from 14 to 272 $\mu\text{mol L}^{-1}$ and -13 to 206 $\mu\text{mol L}^{-1}$, respectively (Figure 8a, b). The maximum concentrations of O_2 and O_{2bio} were encountered in the bottom sea ice where maximum values of Chl-*a* were observed. An increase in oxygen concentrations was observed from YRS4 to YRS8 during the exponential phase of the bloom and a decrease occurred afterward. Our data highlighted a major biogenic contribution to the molecular oxygen pool: O_{2bio} concentrations accounted for 60 to 80% of the O_2 pool at the bottom (Figure 8c).

3.5 NCP

Figure 7 presents the variables used as tracers of production during this study, which have been computed consistently (i.e. same depths and time steps). Tracers of production are changes in nitrate plus nitrite (in $\mu\text{mol L}^{-1} \text{d}^{-1}$, Figure 7a), POC (in $\mu\text{mol L}^{-1} \text{d}^{-1}$, Figure 7b), NCP derived from O_2/Ar ratios ($\text{NCP}_{O_2:\text{Ar}}$ in $\mu\text{mol L}^{-1} \text{d}^{-1}$, Figure 7c) and NCP derived from DIC (NCP_{DIC} in $\text{mg C m}^{-2} \text{d}^{-1}$, Figure 7e). These assessments are given for each layer (surface, interior, bottom) with the exception of NCP_{DIC} given only for the interior ice. While $\text{NCP}_{O_2:\text{Ar}}$ accounts for gas exchanges thanks to the use of Ar concentrations to trace physical processes, NCP_{DIC} is sensitive to CO_2 fluxes at the interfaces - surface and bottom layers -, preventing robust estimates in these layers. In order to allow comparison with the literature, we also provided integrated $\text{NCP}_{O_2:\text{Ar}}$ ($\text{mg C m}^{-2} \text{d}^{-1}$) for the entire ice column (Figure 7d).

Bottom $\text{NCP}_{O_2:\text{Ar}}$ ranged between -4.3 to 3.8 $\mu\text{mol L}^{-1} \text{d}^{-1}$. Positive NCP indicates an oxygen production (equivalent to an inorganic carbon uptake) while negative NCP corresponds to oxygen consumption (equivalent to inorganic carbon production). We compared our measurements with available data of net community production in Arctic sea ice (Table 2). Our measurements fall within the estimates carried out either by O_2/Ar assessment or oxygen incubation. Our values are at the lower end of previous estimates of NCP for bottom Antarctic sea ice from McMinn et al. (2012) derived from in situ oxygen fluxes across the downwards boundary layer estimated with an oxygen micro-electrode.

$\text{NCP}_{O_2:\text{Ar}}$ was higher in absolute value in the bottom sea ice compared to the upper layers (Figure 7c). At the bottom, NCP was positive at the end of the winter indicating a net autotrophy (stations YRS4-8), then heterotrophy dominated during spring (YRS8-11) before it turned back to autotrophy at the end of the spring (YRS11-12). In the ice interior, the same pattern was observed, although with a lower amplitude. Autotrophy dominated the sea ice surface except from stations YRS4 to YRS6.

We compared $\text{NCP}_{O_2:\text{Ar}}$ with NCP_{DIC} for the interior ice. NCP_{DIC} showed similar trends and the same order of magnitude as $\text{NCP}_{O_2:\text{Ar}}$ for stations YRS8-10 and YRS11-12. A discrepancy in terms of magnitude appeared for stations YRS6-8.

3.6 $p\text{CO}_2$

The sea ice $p\text{CO}_2$ ranged from 2 ppm to 810 ppm during the survey (Figure 9). The strongest $p\text{CO}_2$ gradient throughout the ice column was observed at YRS6, where the $p\text{CO}_2$ increased from 120 ppm at the bottom to 810 ppm at the top of the ice core. The general conditions in late winter revealed a $p\text{CO}_2$ under-saturation relative to the atmosphere at the bottom of the ice with $p\text{CO}_2$ increasing to the top of the ice where over-saturation conditions prevailed.

The upper 10 cm of sea ice became undersaturated at station YRS9 with surface $p\text{CO}_2$ as low as 230 ppm. From station YRS10, the $p\text{CO}_2$ decreased throughout the ice column with particularly low $p\text{CO}_2$ at the surface (< 45 ppm) for stations YRS11 and YRS12. The YRS3 profile obtained the previous year at a similar stage of the ice melting season showed a similar trend (Figure S3). The entire ice column was under-saturated in late spring.

Bottom $p\text{CO}_2$ remained particularly low during the entire study period (below 210 ppm or even below 40 ppm for stations YRS11, 12 and 3).

The $p\text{CO}_2$ values observed in this study fall within the same range of previous sea ice measurements in the Southern Ocean (Delille et al., 2014; Geilfus et al., 2014) despite the fact that the measurement methods differ (bulk vs brines). All the studies reported in Table 3 showed recurrent low $p\text{CO}_2$ values observed in the ice and brines.

3.7 Air-snow-ice CO_2 fluxes

The CO_2 fluxes measured over bare sea ice and snow ranged from $-2.51 \text{ mmol m}^{-2} \text{ d}^{-1}$ to $1.81 \text{ mmol m}^{-2} \text{ d}^{-1}$, and from $-9.76 \text{ mmol m}^{-2} \text{ d}^{-1}$ to $6.22 \text{ mmol m}^{-2} \text{ d}^{-1}$, respectively. In late winter and early spring (September-October), fluxes at the snow-air interface generally exceeded fluxes over bare ice (Figure 10). In late spring (end of November), both negative and positive fluxes occurred over 24h periods (Figure 11).

Data were slightly higher than values previously reported in Antarctica at the same season and using the chamber technique, although falling within the same order of magnitude (Table S1). Available data showed that both negative and positive fluxes are observed during spring in polar regions.

4 Results, or a descriptive heading about the results

4.1 The bottom: biofilm implication

4.1.1 The high TAF – high Ω_{ika} conundrum

The most striking feature of TAF_6 is the increase in the bottom layers at the end of the spring 2012 (Figure 5a). The dissolution of CaCO_3 crystals (e.g., ikaite) would have increased the TAF_6 . However, this increase in TAF_6 co-occurred with CaCO_3 precipitation supported by high Ω_{ika} and high estimated CaCO_3 content at the bottom of the ice (Figure 5c,d). We find the origin of this particulate inorganic carbon to be puzzling since inorganic CaCO_3 precipitation or any biogenic calcification (i.e. colonization by planktic foraminifera) would decrease TAF_6 in a closed system, which is opposite to our observations. This implies that excess TAF_6 must have a different origin.

This accumulation of TAF_6 mimics the increase of nutrients at the bottom of the ice during the survey (Figure S2) that has been ascribed to the development of a biofilm (Roukaerts, 2018). Ice-associated biofilms have been suggested in several studies (Boetius et al., 2015; Deming, 2010; Meiners et al., 2003, 2008). Extracellular polysaccharide substances (EPS) secreted by bacteria and algae in sea ice (Krembs & Engel, 2001; Meiners et al., 2003, 2008; Riedel et al., 2006, 2007) are forming a gelatinous network (Decho, 2000; Decho & Gutierrez, 2017; Stewart & Franklin, 2008) and are therefore the backbone of the biofilm. Roukaerts (2018) showed that the development of a biofilm could drive the accumulation of nutrients at the bottom of the ice. In the same way, nutrient trapping was suggested as one of the functions of EPS aggregates and associated biofilm by Franklin and Stewart (2008). Biofilm microenvironments host intense

remineralization of organic matter and allow accumulation of nutrients due to the relatively slow diffusion of dissolved compounds between the static biofilm and flowing brine (Stewart, 2003; Stewart & Franklin, 2008). We surmise that the increase in TAF_6 is partly due to the same process or accumulation of dissolved compounds in the biofilm. Besides promoting the storage of CaCO_3 , the presence of the biofilm might also trigger its precipitation. EPS functional groups, mainly negatively charged, can bind to substantial amounts of free Ca^{2+} or other metals (Braissant et al., 2007). This calcium-binding property may initially inhibit CaCO_3 precipitation, but subsequent sequential EPS degradation can create nucleation sites and foster CaCO_3 precipitation (Braissant et al., 2009). The authors developed a conceptual model of microbially mediated CaCO_3 precipitation in the EPS matrix (Figure 12). In the first two steps, the calcium binds to various EPS chemical functional groups (i.e. carboxyl, phosphate, amine, and sulfate esters). This EPS-Ca binding form a complex with a low-molecular-weight (LMW) organic carbon compound. Upon microbial enzymatic activity, the LMW organic carbon compounds are released and oxidized to bicarbonate, which in turn increases the alkalinity inside the biofilm. Enzymatic activity in sea ice is supported by the presence of cold-active extracellular enzymes able to drive enzymatic hydrolysis or breakdown (Deming, 2007; Helmke & Weyland, 1995; Huston et al., 2000). Finally, the remaining free EPS-Ca sites allow for CaCO_3 precipitation within the EPS matrix. CaCO_3 precipitation can thus occur in parallel with an increase of alkalinity within the biofilm at the bottom of sea ice, as nitrate plus nitrite concentrations increase in parallel with organic carbon production.

4.1.2 NCP as an indicator of trophic status

The contribution of O_2_{bio} to the oxygen pool in sea ice increases steadily with depth. Besides the impact of physical processes (e.g., solubility changes, brine concentration or dilution, vertical transport), biological processes account for up to 80% of the overall oxygen content of the sea ice. The maximal contribution is observed at the bottom of the ice, where the largest biomass concentrations are observed. Sea ice in McMurdo Sound is indeed considered as very productive, with an extremely high build-up of chl-*a* (Arrigo et al., 1995). Basal concentrations of chl *a* reached up to $2443 \mu\text{g L}^{-1}$ and $2342 \mu\text{g L}^{-1}$ (station YRS 9 and YRS10, Figure 6a) and particulate organic carbon up to $2600 \mu\text{mol L}^{-1}$. This massive build-up of biomass associated with O_2 accumulation indicates autotrophy. According to the O_2/Ar ratio, autotrophy indeed dominated the bottom sea ice but a transient heterotrophic period was observed between stations YRS8 and YRS11 (Figure 7c,d). Heterotrophy associated with biomass build-up has been reported earlier in the Arctic (Campbell et al., 2017; Rysgaard et al., 2008; Rysgaard & Glud, 2004). To the best of our knowledge, this is the first report of a large biomass build-up associated with a transient heterotrophic period in Antarctic sea ice. The best explanation for such a striking feature at the bottom of the ice is the rapid remineralization of the organic matter (Fripiat et al., 2014, 2017) entrapped within the biofilm (Roukaerts, 2018).

4.2 The interior of the sea ice cover

4.2.1 NCP

A significant imprint of biological processes on the oxygen pool can also be observed in the ice interior (Figure 8c). $\text{NCP}_{\text{O}_2:\text{Ar}}$ in the ice interior exhibited the same temporal trend as in the bottom ice with dominant autotrophy (Figure 7c,d). NCP values in the interior ice were lower than in the bottom ice, in agreement with biomass concentrations, except for stations YRS11 to

YRS12. This higher NCP in the interior at stations YRS11 to YRS12 could be due to upward diffusion of biogenic oxygen enabled with the opening of the brine network (Zhou et al., 2013).

NCP_{DIC} in interior ice showed the same trophic dynamics (autotrophy vs. heterotrophy) as NCP_{O₂:Ar} except for stations YRS4-6 and YRS10-11. From stations YRS11 to YRS12, values agree within 3.4 mg C m⁻² d⁻¹. The largest difference from stations YRS6 to YRS8 is 32 mgC m⁻² d⁻¹. Overall, with the exception of stations YRS6 to YRS8, this suggests that biological activity was the main driver of DIC₆ temporal changes in the ice interior.

4.2.2 pCO₂ gradient

Three temporal stages in pCO₂ dynamics have been identified based on physical parameters: (i) super-saturation in the upper half of sea ice (stations YRS5-6) was observed during the winter-spring transition when brine contraction occurred due to cooling, leading to the concentration of salts, CO₂ and other gases associated with brine rejection and upward transport. (ii) Surface under-saturation developed when the top layers become permeable, i.e., when the BrV exceeded 5%, the theoretical permeability threshold for fluid transport through sea ice, according to Golden et al. (1998). pCO₂ at the ice surface decreases below saturation as a first consequence (YRS9 and 10). (iii) Complete under-saturation of the ice column (stations YRS11, 12, and 3 even if preceded by 1 year) was observed by mid-November, with low sea ice pCO₂ as a consequence of ice melting and subsequent brine dilution, brine volume expansion and increase in sea ice permeability.

4.3 The surface of the sea ice cover

4.3.1 Carbon content

The dissolved inorganic carbon content of sea ice is affected by CO₂ exchanges. DIC₆ concentrations remained low (< 351 μmol kg⁻¹) at the top of the ice (first 5 cm), compared to the ice interior. Such a depletion at the top of the ice has been repeatedly observed (Geilfus et al., 2013; Kotovitch et al., 2016; Moreau et al., 2015). This depletion can be ascribed to the CO₂ release to the atmosphere since most primary production was concentrated at the bottom of the ice, and no significant CaCO₃ precipitation occurred at the sea ice surface except potentially at stations YRS11 and YRS12 (Figure 5c,d). CO₂ releases from the ice to the atmosphere occurred throughout all seasons, as explained in the next section.

Precipitation of CaCO₃ at the surface in warm conditions has been rarely reported. It has rather been reported at the surface in cold ice (Nomura et al., 2013; Rysgaard et al., 2013). However, the slight increase of CaCO₃ content at station YRS11 and YRS12 (Figure 5c,d) indicates that precipitation develops at the ice surface consistently with omega ikaite above 1. During the rest of the survey, no precipitation was detected at the surface, while omega ikaite was lower and below 1 in cold surface ice (YRS5-YRS10).

4.3.2 pCO₂ and air-snow-ice CO₂ fluxes

CO₂ fluxes exhibited seasonal and diel variations and were likely affected by the thin wet and salty surface snow cover.

4.3.2.1 Seasonal variations

The seasonal pattern of air-ice CO₂ fluxes direction was consistent with the pCO₂ evolution at the sea ice surface. CO₂ release generally occurred during the sea ice growth when pCO₂ was

supersaturated (Figure 10). CO₂ uptake occurred mainly later in the season, during ice decay, when ice became permeable (BrV > 5%), and pCO₂ was undersaturated. This seasonal pattern has also been reported by others (Delille et al., 2014; Miller et al., 2011; Nomura et al., 2010b; Papakyriakou & Miller, 2011). In late spring, fluxes were alternating between release and uptake on a short-time scale.

When the ice was expected to be impermeable during winter, i.e. with brine volume at the sea ice surface below the permeability threshold for fluid transport of 5% (Golden et al., 1998), air-ice fluxes were generally close to zero. However, some significant CO₂ releases over snow-covered ice were observed. These significant winter CO₂ releases have been reported by others using eddy-correlation techniques (Miller et al., 2011; Sievers et al., 2015). This questions the permeability threshold for gas transport in sea ice, permeability being a major control of CO₂ fluxes (Buckley & Trodahl, 1987; Delille et al., 2014). The gas permeability threshold is still debated and has been assessed for brine volumes ranging between 7.5% and 10% according to field observations (Zhou et al., 2013), while models suggest a threshold around 10% of brine volume (Moreau et al., 2014). However, at a smaller scale, the absence of discontinuity in the pCO₂ profiles (Figure S3) can argue for a permeability threshold below 5%.

Indeed, the principle of the pCO₂ measurement method is based on the equilibrium between the ice sample and the gas phase. Hence, the equilibrium depends on the ice permeability for gases. A first-order estimate of this permeability range is the same as the one for liquids (i.e. BrV>5%). The method should not work below this threshold as reported by Geilfus et al (2012b) in sea ice from Barrow (AK) where pCO₂ in impermeable layers were constant around the concentration of the standard gas. Still, in this study, we carried out pCO₂ measurements for BrV<5%. The trend was consistent below and within the range of liquid permeability and the pCO₂ exceeded the standard gas concentration in impermeable layers, especially above 130 cm at stations YRS5 and YRS6 (Figure S3). As we did not observe the obvious bias reported by Geilfus et al (2012b) or any significant discontinuity in our pCO₂ profiles, our measurements seem to be valid below the 5% permeability threshold. This would suggest the BrV threshold for gas permeability to be lower than 5% in sea ice of McMurdo sound. This calls for a better constraint of the permeability threshold for gases.

An alternative explanation for winter CO₂ efflux is the formation of micro-cracks in the landfast sea ice cover. Microcracking has been observed through acoustic studies in the Arctic (Dempsey et al., 2018; Milne, 1972) and Antarctica, especially in McMurdo Sound (Cole & Dempsey, 2004; Dempsey et al., 2018; Langhorne & Haskell, 1996). Ice cracking in the Arctic has been ascribed by Milne (1972) to thermal stress - temperature drop - in winter or spring. Temperature drops induce heat loss at the sea ice surface and subsequent tensile stresses (Ganton & Milne, 1965; Milne, 1972). Cracks, which relieve some of the stresses, are in turn produced along vertical planes and over tens of centimeters (Milne, 1972). Accordingly, visual observations carried out by Light et al.(2003) suggested large changes in microstructure as samples were cooled to -30°C and the presence of microcracks around inclusions while the ice cools and brines are expelled upward. This is consistent with the increase of pressure in sea ice related to ice cooling (Crabeck et al., 2016).

In this study, in late winter (27 September 2012), a sharp air temperature decrease (from -17°C to -25°C) was observed during the night (Figure 13). Ice temperatures followed the same trend and dropped from -17°C to -21°C. Simultaneously, CO₂ efflux up to 6 mmol m⁻² d⁻¹ occurred over

the snow and the ice. This event is potentially linked to ice cracking. This calls for further investigation of the effect of microcracking on CO₂ release too.

4.3.2.2 Diel variations in CO₂ fluxes

In late spring, both release and uptake of CO₂ occurred over a 24-hour period. Uptake occurred when air and ice temperatures were above 0°C and -5°C, respectively, while release took place when temperatures dropped again below these levels at nighttime (Figure 11).

This diurnal pattern of CO₂ fluxes may be related to an increase of NCP during daylight and a decrease of NCP during nighttime. However, nighttime heterotrophy is questionable since solar irradiance was above 0.4 MJ m⁻² h⁻¹ (Figure 11). Then CO₂ release at nighttime should also be ascribed to physical processes. The CO₂ release and uptake sequences could be related to diel temperature variations and the surface freeze-thaw cycles.

Atmospheric temperature variations were mainly affecting the top 6 cm of the ice (Figure 11). We assumed that the surface melt of sea ice was most likely occurring during day time. The subsequent brine dilution can lead to a large decrease of surface pCO₂ as observed at station YRS11 (sampled around midday) and allowed uptake of atmospheric CO₂. The nocturnal refreezing of the ice skin potentially induced CO₂ release to the atmosphere. Similarly, Papakyriakou and Miller (2011) observed prominent diurnal shifts from CO₂ release to CO₂ uptake over landfast sea ice using the eddy covariance technique. The uptake corresponded to local peaks in surface net radiation and air temperature while the release was associated with night-time minima in net radiation and temperature. These authors ascribed the diel variations to cooling and freezing of the brines during the night.

Our results suggest that fluxes are highly variable on a diel cycle and that changes from release to uptake within 24 hours are likely linked to diel changes in NCP or freeze-thaw cycles during spring and summer.

4.3.2.3 Effect of thin brine-wetted snow on CO₂ fluxes

To date, only a few studies distinguished the snow-air interface and the ice-air interface. We observed larger CO₂ release and uptake over snow than over bare sea ice. Some studies have reported larger fluxes at the snow-air interface (Fischer, 2013; Geilfus et al., 2012a; Nomura et al., 2013), but in opposite others pointed out impeded CO₂ diffusion over snow-covered sea ice (Geilfus et al., 2012a; Meiners et al., 2018; Nomura et al., 2010a). Indeed, deep snow cover may decrease the magnitude of the fluxes compared to bare ice, especially if superimposed ice -a fresh ice layer formed from snow meltwater- is forming (Delille et al., 2014; Geilfus et al., 2012a; Nomura et al., 2010a; Zemmeling et al., 2006).

Early studies about fresh snow (i.e., snow without salt) over inland terrestrial ecosystems considered snow as an inert layer storing CO₂ and paid little attention to processes within the snow (Brooks et al., 2005; Takagi et al., 2005). Only the impact of biological processes (i.e. microbial respiration) has been studied and was reported not to be significant (Pirk et al., 2016). However, in terrestrial ecosystems close to the sea and even for sea ice, several studies reported chemical and photochemical reactions (see Bartels-Rausch et al., 2014 for a review). Sea salts in snow promote the formation of a surface liquid layer with a high ionic concentration that hosts chemical reactions (Domine & Shespon, 2002).

During this survey, neither snow ice nor superimposed ice formation that could act as a physical barrier to gas exchange were observed. The snow cover was characterized by high salinity (7.4 - 24.5), low thickness (below 4 cm), and high wetness due to brine wicking, i.e. the upward migration of sea salt enriched brines from the sea ice to the snowpack (Domine et al., 2004). Compared to previous studies (Delille et al., 2014; Geilfus et al., 2012a; Nomura et al., 2010a; Papakyriakou & Miller, 2011; Zemmelen et al., 2006), the snow cover was saltier and thinner during our survey. Wet and salty base snow can be viewed as solid snow crystals partially surrounded by liquid (i.e. brine) or disordered air-ice interface (Bartels-Rausch et al., 2014). Such a multiphase medium potentially modifies ice-gas interactions. First, gas adsorption or desorption on snow crystals is proportional to the specific surface area (SSA) – the surface area of snow accessible to gases per mass unit (Legagneux et al., 2002). SSA is changing with snow properties and types (e.g. temperature, density, morphology, crystal structure). Gas interactions within wet snow cover are thus expected to be different from those within dry snow. In addition, CO₂ can dissolve within this multiphase medium. Higher salinity increases the CO₂ buffer capacity of liquids or disordered layers, so that salty snow is likely to have a larger CO₂ storage capacity compared to fresh snow. The CO₂ storage capacity of salty base snow would add up to the total sea ice CO₂ storage capacity so that sea ice with a salty snow cover should have a larger CO₂ storage capacity compared to bare ice. We therefore suggest that the thin salty snow layer observed during the survey allowed CO₂ transport due to its shallowness and provided an enhanced CO₂ storage capacity compared to bare ice and related enhanced CO₂ fluxes.

5 Conclusions

We investigated the inorganic carbon dynamics in Antarctic landfast sea ice. Besides the first long-term monitoring of both pCO₂ and CO₂ fluxes at sea ice interfaces from winter to summer, this study also investigated the trophic status of sea ice and proposed a mechanism for CaCO₃ precipitation within the biofilm formed at the bottom of the ice.

Results revealed a succession of heterotrophic and autotrophic phases in the sea ice interior during spring. However, the seasonal pattern of CO₂ fluxes at the air-snow-ice interface was decoupled from the trophic status observed in the ice interior. This seasonal pattern of CO₂ fluxes was mainly driven by changes in pCO₂ at the surface that were related to physical processes. In late spring, diel variations of CO₂ fluxes were superimposed on seasonal variations. It appeared that both biotic and abiotic processes dominated the inorganic carbon dynamics at the sea ice surface in late spring. Diel variations potentially correspond to diel changes in NCP or to freeze-thaw cycles affecting basal snow and ice skin temperatures. As a result, a robust budget of air-snow-ice CO₂ fluxes would require both long term and high-frequency measurements to capture both seasonal and diel patterns.

McMurdo landfast ice is known to accumulate a substantial amount of biomass and is recognized as one of the most productive biotopes of the global ocean. Accordingly, we observed a large biomass build-up at the bottom of the ice but, strikingly associated with transient heterotrophic activity and nitrate plus nitrite accumulation. This counterintuitive observation is likely due to the presence of a biofilm (microbial assemblages embedded in extracellular polymeric substances) where remineralization and accumulation of nutrients are taking place. Our results further suggest that such biofilm also promotes CaCO₃ precipitation, which develops in parallel with an increase of salinity-normalized TA, another counterintuitive observation. EPS functional groups within a biofilm can bind substantial amounts of free calcium. Sequential EPS

degradation due to microbial activity create nucleation sites for CaCO₃ precipitation and provide bicarbonate ions within the biofilm that increase alkalinity. These observations call for further studies on the implication of biofilm formation at the bottom of sea ice.

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The data used within this work are available on the Institutional Repository set up by the University of Liège (<https://orbi.uliege.be>) and will be accessible with a permanent link.

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Figure 1: Location of the YROSLAE year-round sea ice biogeochemistry station, along Ross Island, Ross Sea, Antarctica. The satellite picture is a visible image from NASA's Moderate Resolution Imaging Spectroradiometer (MODIS) Terra on November 29, 2012.

Figure 2: Ice texture of Yrosiae (YRS) stations from 2011 and 2012.

Figure 3: Evolution of air temperature recorded by the Ice-T buoy in 2012 (brown line), air temperature (orange line) and solar radiation (grey line) in 2011 and 2012 recorded by the weather station at Arrival Heights (23 km away from sampling location).

Figure 4: Temporal evolution of (a) temperature, (b) salinity, (c) brine volume fraction and (d) Rayleigh number. Plots were produced using the radial basis function method for interpolation in Surfer 8 software. Black dots are data points from field sampling.

Figure 5: Temporal evolution of (a) Taf_6 , (b) DIC_6 , (c) CaCO_3 concentrations and (d) omega ikaite. Black dots are data points from field sampling. Horizontal blue lines mark the limits between the surface, interior and bottom layers of the ice. Plots were produced using the radial basis function method for interpolation in Surfer 8 software.

Figure 6: Temporal evolution of (a) chlorophyll *a* and (b) POC concentrations in sea ice. Plots were produced using the radial basis function method for interpolation in Surfer 8 software. Grey dots are data points from field sampling.

Figure 7: Temporal changes of (a) nitrate plus nitrite concentrations and (b) POC concentrations in surface, bottom and interior ice layers. Net community production derived from (c,d) O_2/Ar and (e) DIC.

Figure 8: Vertical profiles of (a) O_2 concentrations in bulk ice, (b) $[\text{O}_2]_{\text{bio}}$ calculated from Eq.(5) and (c) $\text{O}_2\text{bio}/\text{O}_2$ ratio.

Figure 9: Temporal evolution of pCO_2 . Samples were analyzed with a standard gas of 300 ppm. Black dots are data points from field sampling. This plot was produced using the radial basis function method for interpolation in Surfer 8 software.

Figure 10: Temporal evolution of a) mean pCO_2 (ppm, red symbols, left axis) for the top 15 cm of the and the corresponding mean BrV (% , green symbols, right axis) b) daily mean CO_2 fluxes ($\text{mmol m}^{-2} \text{ j}^{-1}$) over the ice (light blue open circles) and the snow (dark blue crosses). Positive values indicate CO_2 release to the atmosphere, and negative values indicate CO_2 uptake.

Figure 11: CO_2 fluxes in late spring (crosses for snow-atm and open circles for ice-atm), air temperature (brown line, recorded at 6 cm above ice surface with Ice-T buoy), ice temperatures (orange, yellow and green lines, recorded at 6, 11 and 18 cm below the ice surface with Ice-T buoy) and irradiance recorded at Arrival Heights (grey line).

Figure 12: Conceptual model of CaCO_3 precipitation in the biofilm from Braissant et al. (2009). Step 1: EPS functional groups (A and B); step 2: calcium binding more or less tightly to functional groups A and B; step 3: complex formation between LMW organic carbon compound and calcium; step 4: Release of LMW organic carbon by microbial activity and oxidation to HCO_3^- which in turn increase TA within the biofilm; step 5: CaCO_3 formation either on EPS or in pockets within the biofilm. Permission of Federation of European Microbiological Societies.

Figure 13: CO₂ fluxes in early spring, air temperature (brown line, recorded at 6 cm above ice surface with Ice-T buoy) and ice temperature (orange line, recorded at 6 cm below ice surface with Ice-T buoy).

Table 1: Sampling dates

Station	Sampling date	Mean snow depth (cm)
YRS1	28 November 2011	2.5
YRS2	3 December 2011	1.6
YRS3	8 December 2011	0.9
YRS4	19 September 2012	1.2
YRS5	5 October 2012	1.5
YRS6	18 October 2012	0.8
YRS7	25 October 2012	0.8
YRS8	1 November 2012	0.6
YRS9	7 November 2012	0.8
YRS10	13 November 2012	0.8
YRS11	22 November 2012	0.7
YRS12	30 November 2012	0

Table 2: Primary production and community production rates for landfast sea ice of the Arctic and Southern oceans.

Location	Layer	Method	NCP ($\mu\text{mol L}^{-1} \text{d}^{-1}$)	NCP ($\text{mg C m}^{-2} \text{d}^{-1}$)	References
Arctic Ocean					
Barrow, Alaska	Surface – Internal	O ₂ /Ar	-6.6–3.6		Zhou et al. (2014)
Malene Bight, SW Greenland	Surface	Oxygen incubations	0.8 ± 3.5		Søgaard et al. (2010)
	Bottom		6.3 ± 2.3		
Nunavut, Canada	Bottom	Optode incubations	1.6–2.8		Campbell et al. (2017)
Southern Ocean					
McMurdo Sound	Bottom	O ₂ /Ar	-4.3–3.8	-10.6–9.3	This study
McMurdo Sound	Bottom, platelet	Standing crop of Chl- <i>a</i>		170–1200	Arrigo et al. (1995)
Casey Station (East Antarctica)	Bottom	O ₂ microelectrode		103–163	McMinn et al. (2012)
McMurdo Sound	Internal	O ₂ /Ar	-0.1–1.1	-0.5–9.8	This study
	Surface		-0.3–0.9	-2–2.6	

Table 3: Summarized data for bulk and brine pCO₂ records in the Arctic and Southern oceans as well as in Saroma-ko.

Location	Ice type	Method	Season	pCO ₂ (ppm)	References
Saroma-ko, Japan	Landfast ice	Computed from brine DIC/TA	Winter	2.7–195	Nomura et al. (2010a)
Arctic Ocean					
Resolute Passage, Nunavut	Landfast ice (1 st year)	Computed from brine DIC/TA	Spring	200–1128	Brown et al. (2015)
		Brine pCO ₂ computed from bulk DIC/TA		2–3326	
		In situ brine (peepers)		230–1280	
Resolute Passage, Nunavut	Landfast ice (1 st year)	In situ bulk	Late Spring	6–182	Geilfus et al. (2015)
		Bulk computed from DIC/TA		0–32	
		In situ brine		20–389	
Point Barrow, Alaska	Landfast ice (1 st year)	In situ bulk	Spring	23–442	Geilfus et al. (2012b)
Amundsen Gulf, Beaufort Sea	Pack ice and landfast ice	In-situ brines	Spring	0–1839	Geilfus et al. (2012a)
Nuuk, Greenland	Landfast ice	In situ bulk	Spring	77–330	Crabeck et al. (2014)
Southern Ocean					
Bellingshausen Sea, Antarctica	Pack ice (1 st year)	In situ bulk	Spring	9–193	Geilfus et al. (2014)
Bellingshausen Sea, Weddell Sea, Indian sector of the SO	Pack ice (1 st year)	In situ brine	Spring-Summer	28–921	Delille et al. (2014)
Cape Evans (Ross Sea)	Landfast ice	In situ bulk	Spring-Summer	2–810	This study