

**Sea-ice melt
CO₂-carbonate
chemistry in the
western Arctic Ocean**

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Sea-ice melt CO₂-carbonate chemistry in the western Arctic Ocean: meltwater contributions to air-sea CO₂ gas exchange, mixed layer properties and rates of net community production under sea ice

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Abstract

The carbon dioxide (CO₂)-carbonate chemistry of sea-ice melt and co-located, contemporaneous seawater has rarely been studied in sea ice covered oceans. Here, we describe the CO₂-carbonate chemistry of sea-ice melt (both above sea ice as “melt ponds” and below sea ice as “interface waters”) and mixed layer properties in the western Arctic Ocean in the early summer of 2010 and 2011. At nineteen stations, the salinity (~ 0.5 to < 6.5), dissolved inorganic carbon (DIC; ~ 20 to < 550 μmol kg⁻¹) and total alkalinity (TA; ~ 30 to < 500 μmol kg⁻¹) of above-ice melt pond water was low compared to water in the underlying mixed layer. The partial pressure of CO₂ (pCO₂) in these melt ponds was highly variable (~ < 10 to > 1500 μatm) with the majority of melt ponds acting as potentially strong sources of CO₂ to the atmosphere. The pH of melt pond waters was also highly variable ranging from mildly acidic (6.1 to 7) to slightly more alkaline than underlying seawater (8 to 10.7). All of observed melt ponds had very low (< 0.1) saturation states (Ω) for calcium carbonate (CaCO₃) minerals such as aragonite (Ω_{aragonite}). Our data suggests that sea ice generated “alkaline” or “acidic” melt pond water. This melt-water chemistry dictates whether the ponds are sources of CO₂ to the atmosphere or CO₂ sinks. Below-ice interface water CO₂-carbonate chemistry data also indicated substantial generation of alkalinity, presumably owing to dissolution of calcium CaCO₃ in sea ice. The interface waters generally had lower pCO₂ and higher pH/Ω_{aragonite} than the co-located mixed layer beneath. Sea-ice melt thus contributed to the suppression of mixed layer pCO₂ enhancing the surface ocean’s capacity to uptake CO₂ from the atmosphere. Meltwater contributions to changes in mixed-layer DIC were also used to estimate net community production rates (mean of 46.9 ± 29.8 g C m⁻² for the early-season period) under sea-ice cover. Although sea-ice melt is a transient seasonal feature, above-ice melt pond coverage can be substantial (10 to > 50%) and under-ice interface melt water is ubiquitous during this spring/summer sea-ice retreat. Our observations contribute to growing evidence that sea-ice CO₂-carbonate chemistry is highly variable and its contribution to the complex factors that influence the balance

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of CO₂ sinks and sources (and thereby ocean acidification) is difficult to predict in an era of rapid warming and sea ice loss in the Arctic Ocean.

1 Introduction

Sea-ice is one of the largest biomes on the planet. It has a strong impact on climate through its modulation of heat, water vapor and momentum exchanges, and the physics (stratification, mixing) and biology (sea-ice and pelagic communities) of the polar regions (Thomas and Dieckman, 2010). In the last decade, seasonal sea-ice loss, associated with atmospheric warming, air-sea-ice feedbacks and climate modes of variability (e.g., ACIA, 2005; Serreze and Francis, 2006; Maslanik et al., 2007; Wang and Overland, 2009), has increased significantly in the Arctic Ocean since 2007. Rapid loss of summertime sea ice, combined with other synergistic impacts such as hydrological changes (e.g., increased melt and fresh water inputs to polar waters), has profound implications for the biology and physico-biogeochemical conditions of the Arctic and Southern Oceans (e.g., McGuire et al., 2006, 2009; Arrigo et al., 2008; Pabi et al., 2008).

The polar and subpolar regions of both hemispheres have large impacts on the exchange of carbon dioxide (CO₂) between atmosphere and ocean, and particularly on the ocean uptake of anthropogenic CO₂. Low temperatures and low buffering capacity of these waters facilitates ocean uptake of CO₂ from the atmosphere. In the high latitudes, ocean CO₂ sinks represent a significant contribution to the global ocean sink of $\sim 1.4 \text{ PgCyr}^{-1}$ (PgC = 10^{15} gC; e.g., Takahashi et al., 2009; Schuster et al., 2013). Quantifying and understanding the dynamics of ocean-atmosphere exchanges of CO₂ in permanently and seasonally ice covered regions has been difficult to assess owing to lack of data (e.g., Bates and Mathis, 2009) with future predictions difficult to make owing to rapid sea ice loss, particularly in the Arctic Ocean.

Over the last decade, a limited number of investigations in the Arctic and Antarctica have been conducted on sea-ice CO₂-carbonate chemistry, the impact of sea-ice on

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the carbon cycle, and ocean-atmosphere CO₂ exchanges (e.g., Semiletov et al., 2004; Zemmeling et al., 2006; Rysgaard et al., 2007; Delille et al., 2007; Miller et al., 2011a, b; Fransson et al., 2011; Geilfus et al., 2012a, b). These studies have shown large heterogeneity and variability (in time, space and within sea-ice) in CO₂-carbonate chemistry in sea-ice, and brines in both Arctic and Antarctic sea-ice environments (Fig. 1). From these studies, it appears that the dynamics of CO₂ in sea-ice and impacts on ocean-atmosphere exchanges of CO₂ appears highly complex and unpredictable. The CO₂-carbonate chemistry composition of sea ice is not only a function of physical conditions (i.e., temperature, salinity, ice thickness), and concentration/dilution processes associated with brine formation, brine rejection and ice melt, respectively. It is also a function of sea-ice biological processes such as primary production and respiration (e.g., Gosselin et al., 1986; Legendre et al., 1992; Thomas and Dieckmann, 2010; Dieckmann and Hellmer, 2010), and production of calcium carbonate (CaCO₃, e.g., Ikaite formation, Papadimitriou et al., 2004; Dieckmann et al., 2008) and its dissolution. Although few studies on sea-ice and brines have been conducted, there are even fewer studies of CO₂-carbonate chemistry from above-ice melt ponds or below-ice interface melt waters (e.g., Geilfus et al., 2012a).

Two scenarios, both of which have commonalities and differences, appear relevant to understanding variability in sea-ice CO₂-carbonate chemistry and impacts on ocean-atmosphere CO₂ exchanges across the seawater–ice–atmosphere interface (Fig. 1a and b). During freeze-up, the formation of high salinity brines appears to drive a large uptake of CO₂ from the atmosphere and downward flux of dissolved inorganic carbon with cold dense waters formed during brine rejection (Anderson et al., 2004). At the same time, very high $p\text{CO}_2$ (> 1000 to many 1000's μatm) values have been reported (Matsuo and Miyake, 1966; Tison et al., 2002; Miller et al., 2011a, b) in both brines and sea-ice. High $p\text{CO}_2$ conditions in winter sea ice appear to facilitate efflux of CO₂ from sea-ice into the atmosphere (Miller et al., 2011b). Subsequent melt water may have high $p\text{CO}_2$ concentrations with loss of CO₂ to the atmosphere from melt ponds and mixed layers highly influenced by melt water (Fig. 1a).

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An alternative scenario is that sea ice and brines have low $p\text{CO}_2$ contents during sea-ice retreat and melt (Fig. 1b) with strong influx of CO_2 into melt ponds and post-ice breakup mixed layers (Fig. 1b). Actual direct measurements of $p\text{CO}_2$ and pH were not reported in the original literature but using data from several studies (Rysgaard et al., 2007; Delille et al., 2007; Fransson et al., 2011; Sejk et al., 2011; Geilfus et al., 2012a), we compute $p\text{CO}_2$ and pH from reported salinity, temperature and carbonate chemistry data. Such data show very low $p\text{CO}_2$ ($< 100 \mu\text{atm}$) and high pH (> 8.2 to 8.3) in spring sea-ice.

In this study, we report CO_2 -carbonate chemistry data from above-ice melt ponds, below-ice interface melt water, and mixed layer seawater beneath sea-ice cover at nineteen sea-ice locations in the western Arctic Ocean. These sea-ice stations were conducted as part of the NASA ICESCAPE (Impacts of Climate on the Eco-Systems and Chemistry of the Arctic Pacific Environment) project, and represent conditions observed in early summer (i.e., July) in 2010 and 2011. Previous CO_2 -carbonate chemistry data from above-ice melt ponds and below-ice interface melt water is very limited (Miller et al., 2011a; Fransson et al., 2011; Geilfus et al., 2012a), although important to consider given their widespread distribution and global significance to the carbon cycle. For instance, during the brief sea-ice retreat period, melt ponds can constitute as much as 50 % of the surface area (e.g., Sejk et al., 2011). Furthermore, changes in sea-ice distributions associated with warming and other feedbacks in the high latitudes are rapidly changing the complex associations between sea ice, melt water and seawater in polar regions with profound implications for the global carbon cycle (e.g., Bates and Mathis, 2009). We discuss data collected as part of the ICESCAPE expedition in 2010 and 2011 in context with other studies and scenarios shown in Fig. 1 to evaluate the possible contribution of sea ice for CO_2 dynamics and ocean-atmosphere CO_2 exchanges. Estimates of rates of net community production (NCP) beneath sea-ice were also determined using changes in DIC and accounting for the contribution of below-ice interface melt waters to the upper water-column. We also discuss and compare melt pond pH and saturation states (Ω) for CaCO_3 minerals (i.e., for aragonite $\Omega_{\text{aragonite}}$

and calcite, Ω_{calcite}). The context for this latter discussion is that ocean acidification is expected to impact the polar oceans earlier than other regions (owing to low temperatures and buffer capacity of surface waters) and given recent observations of low Ω waters in surface waters of the Canada Basin (Jutterstrom et al., 2010).

2 Methods

2.1 Seawater CO₂-carbonate chemistry considerations

It is useful to briefly summarize the terms and equations governing seawater CO₂-carbonate chemistry, as this is important context for discussion of results later in the paper. DIC is the sum of bicarbonate ([HCO₃]), carbonate ([CO₃²⁻]) and CO₂ in natural waters (Dickson et al., 2007) and thus defined as:

$$\text{DIC} = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{CO}_2^*] \quad (1)$$

where [CO₂*] is equivalent to [CO₂]_{aq} + [H₂CO₃]. Total alkalinity (TA) can be defined as:

$$\text{TA} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})^-] + [\text{OH}^-] - [\text{H}^+] \quad (2)$$

where is total borate concentration in seawater. DIC, TA, pH and $p\text{CO}_2$ (partial pressure of CO₂) are the common measurable parameters. All components of the seawater CO₂-carbonate system, including [HCO₃], [CO₃²⁻] and saturation states for calcium carbonate (CaCO₃) minerals such as calcite (Ω_{calcite}) and aragonite ($\Omega_{\text{aragonite}}$), can be computed from two observed parameters. Physico-biogeochemical processes such as ocean release of CO₂ by air-sea gas exchange or primary production/respiration act to decrease DIC and $p\text{CO}_2$ and increase pH, $\Omega_{\text{aragonite}}$ and Ω_{calcite} (e.g., Zeebe and Wolf-Gladrow, 2001). In contrast, ocean uptake of CO₂ and respiration act oppositely (increasing DIC and $p\text{CO}_2$ and decreasing pH, $\Omega_{\text{aragonite}}$ and Ω_{calcite}), while TA remains

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unchanged (except for minor changes associated with nitrate uptake or release). Precipitation or calcification and dissolution of CaCO_3 is defined as:



As Eq. (3) and (4) show, calcification/ CaCO_3 precipitation decreases TA, while CaCO_3 dissolution increases TA, respectively.

2.2 Sampling and chemical analyses

2.2.1 Water column sampling

The hydrography and biogeochemistry of the western Arctic was sampled during two ICESCAPE cruises aboard the US Coast Guard Cutter *Healy* conducted in early summer in the western Arctic Ocean. In 2010, one hundred and forty hydrocast-CTD stations were occupied (18 June to 16 July 2011), while one hundred and seventy three hydrocast-CTD stations were occupied in 2011 (28 June to 24 July 2011). Water-column sampling was mainly conducted on the shallow shelf of the Chukchi Sea but also in the deep (> 200 m depth) southern Canada Basin. Core hydrography samples (e.g., salinity, temperature, inorganic nutrients) were collected as well as ~ 1600 water-column seawater samples for DIC and TA.

The majority of the sampling occurred on the shallow shelf of the Chukchi Sea (~ 30 to ~ 70 m deep, plus shelf-break samples as deep as 200 m) during the summertime sea-ice retreat period (Fig. 2). The shelf has been characterized as an inflow shelf (Carmack and Wassmann, 2006; Fig. 2 inset) where the physical and hydrographic properties are highly influenced by the northward flow of nutrient rich Pacific water associated with transports of Anadyr Water (AW), Bering Shelf (BSW) and Alaskan Coastal Current (ACC) waters from the Bering Sea to the Canada Basin.

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2.2.2 Sea-ice stations

Nineteen sea-ice stations were occupied during the ICESCAPE expedition, ten in 2010 (covering the period of 24 June to 11 July) and nine in 2011 (covering the period of 5 to 20 July; Fig. 2). Most of the sea-ice stations were located over the Chukchi Sea shelf but several were also located in the deep Canada Basin. At each of the sea-ice stations, samples were collected from above-ice melt ponds, below-ice ice–water interface and in the surface mixed layer beneath. Sampling on the ice was conducted upwind of the ship at representative ice stations (Frey et al., 2012; unpublished data). Sea-ice melt pond water was sampled for salinity, temperature, inorganic nutrients and seawater CO₂-carbonate chemistry. Nearby, ice cores were drilled and under ice seawater (at the ice–water interface within 0.1 m of the ice bottom) was sampled for water chemistry using a vertically-oriented Kemmerer water sampler. At each ice station, CTD-hydrocast (using Niskin samplers) sampling of the water-column was undertaken from the USCGC *Healy* after ice operations were completed. In situ temperature was measured at each station.

Melt pond water, interface melt water, and CTD-hydrocast salinity samples were analyzed onboard the USCGC *Healy* after with a Guildline salinometer (calibrated with seawater salinity standards) as part of the core hydrography measurement suite.

DIC and TA samples, collected in ~ 300 mL Pyrex bottles that were poisoned with 100 µL Hg₂Cl, sealed and stored in the dark before analysis, were analyzed onboard the vessel. The exception was that DIC samples from 2010 were analyzed at UAF. Replicate samples for DIC and TA were also analyzed at BIOS within a few months of sampling.

2.2.3 Chemical analyses

DIC was determined using a high precision (0.05 % CV) small-volume DIC analyzer (~ 1.5 mL sample size) using an infrared-based instrument (AIRICA; Marianda Co, Germany; Bates et al., 2012). TA was determined by a high-precision (< 0.05 % CV) poten-

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tiometric technique using a VINDTA 2S (Marianda, Germany). Both DIC and TA instruments were routinely calibrated using seawater Certified Reference Material (CRM) from A.G. Dickson, Scripps Institute of Oceanography, and the accuracy of samples compared to CRM's was less than 0.1 % ($2 \mu\text{mol kg}^{-1}$). Six samples of sea-ice (3 from multi-year and 3 from first year ice) were also collected in gas tight bags, carefully melted and analyzed for DIC onboard the vessel in 2011.

2.3 Data computations and visualization

Seawater CO_2 -carbonate system parameters including $p\text{CO}_2$ (μatm), $\Omega_{\text{aragonite}}$ and Ω_{calcite} and pH (total scale) were computed from salinity (S), temperature (T , $^{\circ}\text{C}$), TA and DIC data (using CO2calc software; Robbins et al., 2011). The carbonic acid dissociation constants pK_1 and pK_2 (Roy et al., 1993) were used to allow better calculations at low temperature present in the Arctic Ocean. We estimated the calculation error range for $p\text{CO}_2$, pH, $\Omega_{\text{aragonite}}$ and Ω_{calcite} to be $\pm 5 \mu\text{atm}$, ± 0.001 and ± 0.004 (assuming a TA error of $\pm 0.5 \mu\text{mol kg}^{-1}$), respectively. Ocean Data View 4 (ODV; Schlitzer, 2011) software was used to visualize the data. We also use reported salinity, temperature and sea-ice and seawater CO_2 -carbonate chemistry (typically DIC and TA) from the few studies of sea-ice (e.g., Rysgaard et al., 2007; Fransson et al., 2011; Miller et al., 2011a, b; Geilfus et al., 2012a) to compute $p\text{CO}_2$, pH, $\Omega_{\text{aragonite}}$ and Ω_{calcite} that was not reported in the original literature.

3 Results

3.1 Shelf hydrography and biogeochemical properties

At the time of the two cruises (late June to mid July), most of the Chukchi Sea was sea ice free with sea-ice cover restricted to northernmost regions of the shelf and slope, and southern Canada Basin (Fig. 2). Most of the Chukchi Sea shelf is shallower than

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100 m (Fig. 3a), while the Canada Basin was sampled to depths > 4000 m (Fig. 3 inset). A wide range of temperature ($\sim -1.8^{\circ}\text{C}$ to $\sim 8^{\circ}\text{C}$) and salinity (~ 27 to 33 ; Fig. 3a) was observed over the shelf in both summers of 2010 and 2011. As reported elsewhere (Bates et al., 2013), winter/early spring water (including remnant winter water on the shelf during summertime) had a narrow range of temperature ($\sim -1.8^{\circ}\text{C}$ to $< -1^{\circ}\text{C}$) and salinity (~ 32.2 to 32.8), with summertime variability in shelf water mixed layer temperature and salinity reflecting the influence of warming and sea-ice melt. The hydrographic properties of shelf water exhibited two generic water mass types, including: (1) high salinity (32 – 33) and variable temperature ($\sim -1^{\circ}\text{C}$ to 8°C); and (2) variable salinity (26 – 33) and cold temperature ($\sim -1.8^{\circ}\text{C}$ to $< 1^{\circ}\text{C}$), with variability in between these two water mass types. The freshest mixed layer salinity was about 18 (Fig. 3a).

Shelf waters generally had relatively low nitrate ($< 6\ \mu\text{mol kg}^{-1}$) and phosphate ($< 1\ \mu\text{mol kg}^{-1}$) concentrations, compared to nutrient rich winter/early spring shelf water and deep Canada Basin waters (Fig. 3b). Similar patterns were shown in silicate for shelf waters (< 5 – $10\ \mu\text{mol kg}^{-1}$) with high dissolved oxygen concentrations (350 – $450\ \mu\text{mol kg}^{-1}$), which as shown later, reflects the high rates of pelagic primary production on the Chukchi Sea shelf during summertime. In contrast to nitrate and phosphate distributions, both silicate and dissolved oxygen in the deep Canada Basin water had lower concentrations than the remnant winter/early spring water on the shelf and slope of the Chukchi Sea.

3.2 Water column seawater CO_2 -carbonate chemistry on the Chukchi Sea shelf

Winter/early spring water (including winter water remnant on the shelf during summertime) and deep Canada Basin water had a narrow range of DIC (~ 2200 – $2300\ \mu\text{mol kg}^{-1}$) and TA (~ 2250 – $2350\ \mu\text{mol kg}^{-1}$). In contrast, summertime shelf waters had a large range of seawater CO_2 -carbonate chemistry with DIC ranging from ~ 1850 – $2300\ \mu\text{mol kg}^{-1}$ and TA ranging from 1850 – $2350\ \mu\text{mol kg}^{-1}$, respectively (Fig. 3d).

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A closer inspection revealed that surface/mixed layer DIC and TA had a smaller range of $\sim 1800\text{--}2000$ and $1850\text{--}2250 \mu\text{mol kg}^{-1}$, respectively (Fig. 4a), over a salinity range of 6 (Fig. 4a inset). These shelf waters generally had high dissolved oxygen contents (~ 350 to $> 450 \mu\text{mol kg}^{-1}$) and low nitrate values ($< 3 \mu\text{mol kg}^{-1}$; Fig. 4b), reflecting uptake of nitrate in support of primary and new production and generation of oxygen as a result (e.g., Hill and Cota, 2005; Bates et al., 2005a; Arrigo et al., 2012).

Shelf surface/mixed layer seawater $p\text{CO}_2$ generally had low values (< 100 to $300 \mu\text{atm}$; Fig. 4c) relative to atmospheric $p\text{CO}_2$ concentrations of $\sim 392\text{--}398 \mu\text{atm}$. As shown in previous studies (e.g., Pipko et al., 2002; Murata et al., 2003; Bates, 2006; Bates et al., 2006; Bates and Mathis, 2009), several factors including summertime undersaturation of CO_2 relative to the atmosphere, retreat of sea-ice cover, and moderate to strong winds act in combination as strong driving forces for ocean sinks of CO_2 from the atmosphere. In contrast to shelf surface/mixed layer, deeper remnant winter water on the shelf and deep waters of the Canada Basin had higher and much larger range of seawater $p\text{CO}_2$ (~ 300 to $> 600 \mu\text{atm}$; Fig. 4c). Deeper water (particularly in halocline waters of the Canada Basin) had the highest $p\text{CO}_2$ values (up to $1300 \mu\text{atm}$).

Shelf surface/mixed layer seawater pH had a relatively large range (~ 8.2 to 8.5) in contrast to lower pH in deeper waters (< 7.8 ; Fig. 4c inset). Relatively high pH of surface water on the Chukchi Sea shelf, when compared to typical open-ocean pH values of 8.1 to 8.2 , reflected the impact of high rates of primary production on the shelf. As shown for the Chukchi Sea (e.g., Bates et al., 2009, 2013), as well as other marine environments, photosynthetic uptake of CO_2 increases pH due to adjustment of seawater CO_2 -equilibrium (e.g., Zeebe and Wolf-Gladrow, 2002; Dickson et al., 2007). The saturation state values for CaCO_3 minerals such as aragonite (i.e., $\Omega_{\text{aragonite}}$) and calcite (i.e., Ω_{calcite}) ranged from $\sim 0.5\text{--}4$ with a few values less than 1 (Fig. 4d). As shown in Fig. 4d, Ω values less than 1 for aragonite for some shelf waters and deep waters in the Canada Basin indicates that these waters are potentially corrosive for CaCO_3 .

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3.3 Above and below-ice melt seawater CO₂-carbonate chemistry

Nineteen sea-ice stations were sampled for seawater CO₂-carbonate chemistry in 2010 and 2011. Both above-ice melt ponds and below-ice interface melt waters were sampled and compared to mixed layer conditions beneath each ice station (Figs. 5–7).

3.3.1 Salinity variability

The salinity range of the sampled above-ice ponds ranged from 0.5 to 6 with one sample in the Canada Basin at ~ 16 (Fig. 6a). In comparison, below-ice interface water sampled just below the sea ice had highly variable salinity values (Fig. 5c) compared to above-ice melt pond water (i.e., salinity < 5), or the mixed layer beneath (e.g., salinity > 25; Fig. 5e). Interface waters with values in-between these end-members reflect varying proportions of mixed layer and sea-ice melt water contributions (Fig. 6a). The below-ice interface melt waters also had temperature ranges of ~ -1.6 °C to +1.6 °C.

3.3.2 TA and DIC variability

The majority of TA and DIC values for above-ice melt pond water ranged from < 50 to 600 μmol kg⁻¹ (Figs. 5b and 6a) and typically lower than interface water or mixed layer seawater values. The exception to this was the higher salinity melt pond water that had TA and DIC values at ~ 1030 and 1170 μmol kg⁻¹, respectively.

As expected from higher salinity values, the interface water had highly variable TA and DIC contents (Fig. 5d), either having similarities to above-ice melt pond water or the mixed layer beneath each ice station (Figs. 5f and 6a). The DIC content of six sea-ice samples was similar to the sea-ice melt pond data (i.e., ~ 25 to 250 μmol kg⁻¹).

3.3.3 pH and pCO₂ variability

The above-ice melt pond water had highly variable pH that ranged from 6.1 to 8.8 (Fig. 6b; Fig. 7a). Most of the above-ice melt pond water sampled over the Chukchi

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Sea shelf had much lower pH values (< 7.8) when compared to the typical range of seawater of ~ 8.1 to 8.2 , and the mixed layer at the ice stations (Fig. 7e). Several of the sampled melt ponds had pH values less than 7 and thus were mildly acidic (Fig. 7a). The exceptions were the two melt ponds in Canada Basin that had much higher pH (> 8.6), and several stations on the NE Chukchi Sea shelf.

In comparison to above-ice melt ponds, the below-ice interface water had higher pH values (> 8 ; Fig. 7c), closer to the underlying mixed layer water (Fig. 7e). Again, the lowest below-ice pH values (~ 7.8 to 8) were observed in the Canada Basin and on the NE shelf of the Chukchi Sea.

For $p\text{CO}_2$, the melt ponds and interface waters showed similar patterns to pH. In the low pH and acidic melt pond water, $p\text{CO}_2$ values ranged from ~ 350 to $> 1500 \mu\text{atm}$ (Fig. 7b) and were typically higher than atmospheric $p\text{CO}_2$ values of approximately 392 to $398 \mu\text{atm}$. The exceptions were ice stations sampled in the Canada basin and on the NE shelf of the Chukchi Sea, all of which had very $p\text{CO}_2$ low values ($< 50 \mu\text{atm}$; Fig. 6c).

Concentrations of $p\text{CO}_2$ were much lower in interface waters ($< 300 \mu\text{atm}$; Fig. 6c, Fig. 7d) than melt ponds, particularly over the Chukchi Sea shelf. As shown with TA, DIC and pH, interface water $p\text{CO}_2$ either had values similar to melt pond water or the mixed layer below (Fig. 7f). The $p\text{CO}_2$ of interface water had similar geographic patterns to contemporaneous mixed layer $p\text{CO}_2$ values observed across the region.

3.3.4 CaCO_3 saturation states

The saturation states for CaCO_3 minerals such as aragonite and calcite in melt pond and interface waters had very different values compared to mixed layer values across the Chukchi Sea shelf. All the melt ponds had $\Omega_{\text{aragonite}}$ (Fig. 6d) that were less than 0.2 . Although not shown, the Ω values for calcite (i.e., Ω_{calcite}) were also less than 0.2 . Ω values less than 1 indicate chemical conditions favoring dissolution of CaCO_3 . The ICESCAPE data indicate that all the sampled melt ponds were highly corrosive for any CaCO_3 particles present in melt water. Furthermore, nearly half the sampled interface

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waters (those with low salinity and more influenced by melt contributions) had similarly low Ω values.

4 Discussion

4.1 Sea-ice melt CO₂-carbonate chemistry

5 The ICESCAPE expeditions revealed that the CO₂-carbonate chemistry of melt pond and interface waters was highly variable, and distinctly different from the underlying water-column across the Chukchi Sea. Using these data, it is possible to constrain the chemical composition of sea ice, the melting of which contributed to both melt pond and interface waters. The contribution of sea-ice and melt water to mixed layer CO₂-carbonate chemistry under sea-ice cover (and the relative balance of CO₂ sinks and sources) can also be examined.

4.1.1 Can we determine the composition of sea-ice from which melt waters were produced?

15 Melt water present in above-ice ponds and at the sea-ice/mixed layer interface has a chemical composition that reflects the summed influence of several processes, including: (1) the initial composition of sea-ice after its formation and brine rejection during winter freeze-up; (2) any biogeochemical modification during winter, and; (3) biogeochemical modification imparted by the biological community within sea-ice, mixing with seawater and influence of gas exchange during the spring/early summer melt. While there is undoubtedly some variability in CO₂-carbonate composition in sea-ice imparted during initial formation and winter metabolism, we assume that sea-ice had a fairly uniform chemical composition before spring melt.

25 Given the above caveat, the CO₂-carbonate composition of sea ice can be constrained by backing out its chemical composition from contemporaneous summertime ice station observations of sea ice melt, the mixed layer beneath, and comparisons

to winter/early spring waters of the region. The sea ice source water CO₂-carbonate chemistry that contributed to melt water ponds is shown in Fig. 8.

In the first step of the method, the % proportion of seawater compared to melt water contributions (assuming a salinity of zero for source water) is determined. The % proportion of seawater and melt water is expressed here with a range of 0.00 to 1.00, and summed the equal 1.00.

Secondly, given the relative proportion of seawater and sea-ice melt water sampled at each ice station, the contribution of seawater to sea-ice melt water is then determined using mean winter/early spring DIC and TA observed in the western Arctic during the ICESCAPE expeditions and previous data collected on the Chukchi Sea shelf during 2002, 2004 and 2009 (Bates et al., 2013). At each ice station, the observed DIC and TA in melt water (i.e., DIC_{MELT} + TA_{MELT}) is the sum of the contributions of seawater (i.e., DIC_{SEAWATER} + TA_{SEAWATER}) and sea-ice (i.e., DIC_{SEAICE} + TA_{SEAICE});

$$\text{DIC}_{\text{MELT}} = (\text{DIC}_{\text{SEAWATER}} \bullet \%) + (\text{DIC}_{\text{SEAICE}} \bullet \%) \quad (5)$$

$$\text{TA}_{\text{MELT}} = (\text{TA}_{\text{SEAWATER}} \bullet \%) + (\text{TA}_{\text{SEAICE}} \bullet \%) \quad (6)$$

The DIC and TA values below the mixed layer at 30 m deep at each ice station were also fairly representative of winter/early spring remnant water on the shelf during summertime sampling, given that the mean DIC and TA concentrations at this depth horizon were similar (within a few $\mu\text{mol kg}^{-1}$) to the reported chemistry of winter/early spring water.

In the third step, the unknown terms (i.e., DIC_{SEAICE} and TA_{SEAICE}) in Eqs. (5) and (6) are solved, using observed winter/early spring DIC and TA values (i.e., DIC_{SEAWATER} + TA_{SEAWATER}), observed sea-ice melt water DIC and TA observations. An iterative solution is used to adjust the DIC_{SEAICE} and TA_{SEAICE} to reduce the residuals of Eqs. (5) and (6) to zero. The DIC_{SEAICE} and TA_{SEAICE} terms that constrain knowledge of the composition of sea-ice are shown in Fig. 8. The winter/early spring DIC and TA values have a standard deviation of ~ 6 and 8 %, respectively, and thus we assume an error of ~ 11 % for the DIC_{SEAICE} and TA_{SEAICE} terms.

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4.1.2 Determining the chemical anomalies of above-ice and below-ice melt pond water

The second approach provides a relative assessment of the deviation of CO₂-carbonate chemistry of sea-ice melt water (and expressed as DIC and TA anomalies; i.e., DIC_{ANOMALY} and TA_{ANOMALY}) relative to below mixed layer waters (Fig. 9). From DIC, TA and salinity relationships at 30 m deep, the salinity of interface water was used to predict DIC and TA concentrations if this water was simply diluted with freshwater (i.e., zero DIC and TA). Here, DIC and TA values below the mixed layer at 30 m deep at each ice station were assumed representative of winter/early spring water remnant on the shelf during summertime sampling.

Secondly, these predicted DIC and TA values were then compared to observed interface water concentrations to determine deficit/excess of DIC and TA relative to winter/early spring shelf water. Since ice melt water diluted the mixed layer (and decreased salinity in the upper water-column), the ice melt contribution to the mixed layer can be determined. A similar approach was used for determining the source water chemistry of above-ice melt water, but previously reported mean winter/early spring DIC and TA values were used rather than concentrations at 30 m at each ice station.

The DIC and TA anomaly of melt waters (i.e., DIC_{ANOMALY} and TA_{ANOMALY}) are determined relative to seawater, and expressed here as %difference from winter/early spring DIC and TA values (Fig. 9). It should be noted that DIC_{ANOMALY} and TA_{ANOMALY} are highly correlated with salinity normalized DIC and TA (i.e., nDIC and nTA using a salinity of 32; not shown here), respectively. nDIC and nTA concentrations also provide an indication of the melt water contribution to mixed layer CO₂-carbonate chemistry. Finally, DIC_{ANOMALY} and TA_{ANOMALY} are expressed as positive or negative values (e.g., positive DIC_{ANOMALY} and TA_{ANOMALY} values indicates that melt water has a higher DIC and TA content, respectively than winter/early spring shelf water).

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4.2 Sea-ice contributions to melt water chemistry

4.2.1 Sea-ice contributions to above-ice melt pond CO₂-carbonate chemistry

The mean above-ice melt pond source water TA and DIC concentration was $54.4 \pm 105.9 \mu\text{mol kg}^{-1}$, and 56.4 ± 45.7 respectively (variability shown in Fig. 8). This compares to an observed DIC range of 75 to 224 (mean of $148.2 \pm 54.1 \mu\text{mol kg}^{-1}$; TA was not measured) that were measured from melted sea-ice cores during ICESCAPE cruises in 2011.

All the melt pond (and interface) water also had positive DIC_{ANOMALY} (except two negative below-ice samples) and variable TA_{ANOMALY} values (Fig. 9). This observation, combined with the finding that melt pond waters had measureable DIC and TA at zero salinity end member for melt water infers that sea-ice had residual DIC and TA that is subsequently entrained into melt waters. The DIC and TA contents of sea ice are likely remnant from winter freeze-up and brine rejection, and subsequently modified by spring/early summer biogeochemical modification by active biological communities within the sea ice.

A closer inspection of Fig. 8a suggests melt pond chemical compositions reflect the influences of two types of sea ice sources to the melt water. Irrespective of whether this is due to legacy composition from sea-ice formation or subsequent sea-ice metabolism, the two types of sea-ice composition subsequently dictate the concentration of other parameters such as pH and $p\text{CO}_2$ (Fig. 8b). The mean salinity of sea ice melt types was 2.8. While the DIC (i.e., DIC_{SEAICE}) content of both types were similar, large variability of TA (or TA_{SEAICE}) infers that these melt waters were active regions of CaCO₃ precipitation (e.g., Ikaite formation, Papadimitriou et al., 2004; Dieckmann et al., 2008) or CaCO₃ dissolution within the sea ice, and its contribution to melt water.

The first type of sea-ice source water that contributes to above-ice melt ponds was “alkaline” (i.e., low $p\text{CO}_2$ /high pH) with relatively TA:DIC ratios compared to typical seawater. The sea-ice source composition had a TA and DIC of $127.7 \pm 138.6 \mu\text{mol kg}^{-1}$

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(range of 31–392 $\mu\text{mol kg}^{-1}$), and 63.7 ± 74.6 (range of 2–210 $\mu\text{mol kg}^{-1}$), respectively (Fig. 8a and b).

The mean $\text{DIC}_{\text{SEAICE}}$ and $\text{TA}_{\text{SEAICE}}$ values are equivalent to pH, $p\text{CO}_2$ and $\Omega_{\text{aragonite}}$ values of 9.65, $< 0.1 \mu\text{atm}$, and 0.35, respectively. This chemistry infers active generation of alkalinity in sea ice, presumably as a result of CaCO_3 dissolution, the signature of which is also evidenced by production of alkaline melt water. The potential generation of alkalinity in sea ice and its signature on melt water is also shown in Fig. 9a in the above-ice melt water with positive $\text{TA}_{\text{ANOMALY}}$ values. The associated melt waters had very low $p\text{CO}_2$ ($< 50 \mu\text{atm}$), high pH (> 8.6), and very low $\Omega_{\text{aragonite}}$ values (i.e., highly corrosive to CaCO_3 ; Fig. 9b; 10a).

The second type of sea-ice source water that contributes to above-ice melt ponds were mildly acidic (high $p\text{CO}_2$ /low pH) with very low TA:DIC ratios. The sea-ice source had a mean TA and DIC of $3.1 \pm 5.3 \mu\text{mol kg}^{-1}$ (range of 0 to $15 \mu\text{mol kg}^{-1}$), and 52.8 ± 26.2 (range of 34 to $127 \mu\text{mol kg}^{-1}$), respectively (Fig. 8a and b). These mean values are equivalent to a pH, $p\text{CO}_2$ and $\Omega_{\text{aragonite}}$ of 5.48, $\sim 620 \mu\text{atm}$ and < 0.1 , respectively. The above-ice melt ponds had high $p\text{CO}_2$, low pH and $\Omega_{\text{aragonite}}$ values associated with low $\text{TA}_{\text{ANOMALY}}$ values (< 0 ; Fig. 9a and b, Fig. 10a).

Unlike the *alkaline* above-ice melt ponds, in the *acidic* above-ice melt ponds, melt pond water, CO_2 -equilibria dictates that carbonate species were only present in the form of dissolved CO_2 [$\text{CO}_2 + \text{H}_2\text{CO}_3$] with negligible [HCO_3^-] and [CO_3^{2-}] present. The mildly acidic pH (6.1 to 7.5) of several sea-ice melt waters sampled during the ICESCAPE expeditions (Fig. 10a) was unusual compared to typical seawater conditions. The above-ice melt pond DIC values were close to or higher than TA, a contrary condition compared to typical seawater. At these low pH levels, comparing with Bjerrum plots of [HCO_3^-], [CO_3^{2-}] and [CO_2^*] against pH (see Butler, 1982; Zeebe and Wolfegladrow, 2001), it is evident that [CO_3^{2-}] was largely absent (or very low values) with [HCO_3^-] and [CO_2^*] being the dominant carbonate species. Equilibrium thermodynamics of the CO_2 -carbonate system dictate that DIC is greater than TA in such waters.

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Miller et al. (2011a) also found sea-ice brine values with TA:DIC ratios close to one (or in one case with DIC > TA) in the Amundsen Gulf (Beaufort Sea) indicating low pH of sea-ice brine water.

4.2.2 Sea-ice contributions to below-ice interface melt water CO₂-carbonate chemistry

The sea-ice contribution to below-ice interface melt water also appeared to be more alkaline than the underlying mixed layer seawater. This is reflected by higher TA:DIC ratios as shown in Fig. 8c, d. Similar to sea-ice contributions to some above-ice melt ponds, the sea-ice chemistry that influences below-ice melt water also shows evidence of generation of alkalinity. Again it seems highly likely that dissolution of CaCO₃ in sea ice subsequently influences the chemistry of below-ice melt water. The below-ice melt water tends to cluster into two types, the first having similarities to above-ice melt pond water, and the second type having similarities to mixed layer seawater. Both types of below-ice melt water had highly variable CO₂-carbonate chemistry (Fig. 8c and d) compared to the sea-ice composition determined from above-ice melt ponds.

The sea-ice sources that contribute to below-ice interface melt water (that have a similar chemistry to above-ice melt pond water) had a mean TA and DIC of $497.4 \pm 225.7 \mu\text{mol kg}^{-1}$ (range of 136–769 $\mu\text{mol kg}^{-1}$), and 434.0 ± 265.5 (range of 44–748 $\mu\text{mol kg}^{-1}$), respectively, as shown in Fig. 8c, d. The second type, that was most similar to seawater (Fig. 8c and d), had a mean TA and DIC of $1797.8 \pm 298.1 \mu\text{mol kg}^{-1}$ (range of 1440–2112 $\mu\text{mol kg}^{-1}$), and 1460.2 ± 487.0 (range of 940–2045 $\mu\text{mol kg}^{-1}$), respectively.

The two types of sea ice that contributed water to the below-ice melt had low $p\text{CO}_2$ and (< 50 μatm) and higher pH (> 8.23 for the fresher type and 8.89 for the seawater type). However, while the fresher type had very low $\Omega_{\text{aragonite}}$ values (< 0.4), the seawater type had high $\Omega_{\text{aragonite}}$ values of 3.7. This contrasting chemistry is also manifested in the below-ice melt water with high TA_{ANOMALY} melt water having low $p\text{CO}_2$

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(< 50 μatm ; Fig. 9c; high pH of > 8.5 not shown in figure), and high $\Omega_{\text{aragonite}}$ (> 2; Fig. 9d).

These approaches for back-calculating sea-ice compositions and their contributions to the chemistry of below-ice interface melt water infers that generation of alkalinity in sea ice has an active role in reducing $p\text{CO}_2$ contents for below-ice melt waters and in the diluted mixed-layer beneath sea-ice cover. The implication of this finding for air-sea CO_2 gas exchange is discussed later in Sect. 4.3.

4.3 Melt water chemistry and comparison to other studies: implications for air-sea CO_2 gas exchange

4.3.1 Above-ice melt pond CO_2 -carbonate chemistry and comparisons to other studies

Similar to the two types of sea-ice compositions, the above-ice melt ponds had two different chemical types. The first type had much lower $p\text{CO}_2$ and $\Omega_{\text{aragonite}}$ values (< 50 μatm and < 0.3, respectively) and higher pH (8.5 to 10.8; Fig. 10a) compared to seawater, presumably reflecting the contribution of alkalinity to melt pond water.

The second type of above-ice melt pond water had much higher $p\text{CO}_2$ (> 390 to > 1500 μatm ; Fig. 10a) and $\Omega_{\text{aragonite}}$ and pH values (< 0.3 and 6.2 to 7.5, respectively). The two ice stations sampled with above-ice melt ponds with highest $p\text{CO}_2$ /lowest pH and $\Omega_{\text{aragonite}}$ were found in the southern Canada Basin compared to the NW Chukchi Sea (lower $p\text{CO}_2$ /higher pH and $\Omega_{\text{aragonite}}$). This geographic variability in ice melt pond chemistry reflects similar geographic patterns in $p\text{CO}_2$, pH and $\Omega_{\text{aragonite}}$ in the underlying mixed layer beneath the ice (Figs. 5 and 7). These melt pond $p\text{CO}_2$ values were much higher than other melt pond data reported in the literature (79–348 μatm ; Geilfus et al., 2012a). In fact, the Geilfus et al. (2012a) melt pond, sampled in the Amundsen Gulf in the Canadian Archipelago shelf appear to have an intermediate chemistry compared to the two types found in the Chukchi Sea.

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The ICESCAPE data suggest that highly variable sea-ice biology contributes to highly variable above-ice melt pond water chemistry. As shown in other sea-ice studies, the net metabolism of the sea-ice biological community is highly likely to influence melt pond chemistry (i.e., through balance of photosynthesis/net autotrophy vs. respiration/net heterotrophy, Fig. 11a). Our data also indicate that variability in the net balance of CaCO₃ production or dissolution (contributing either a deficit or excess of alkalinity respectively) has a strong control on melt pond CO₂ carbonate chemistry.

While there is little supporting data, there does appear to be some difference in the metabolic status of sea ice over the Chukchi Sea and Canada Basin. Sea ice at the Canada Basin stations more likely to be net heterotrophic (source of CO₂ to the ice melt ponds) when compared to the Chukchi Sea shelf ice stations and other melt ponds reported in the literature (which may have been influenced by net autotrophy in the ice; Geilfus et al., 2012a).

The timing of sampling is likely an important factor to consider. Ice melt water chemistry is highly influenced by sea-ice and brine carbonate chemistry. During sea-ice advance/freeze-up, very high $p\text{CO}_2$ values have been reported in sea ice and brines (Matsuo and Miyake, 1966; Tison et al., 2002). Miller et al. (2011a) recently reported high $p\text{CO}_2$ of sea ice and brines (ranging 300 to > 12 000 μatm but mostly > 1000–2000 μatm ; Fig. 11b). Similarly high $p\text{CO}_2$ values have also reported in sea ice during wintertime (Miller et al., 2011b). As shown in Fig. 11b, in other studies of the spring sea-ice breakup, high early season $p\text{CO}_2$ (Geilfus et al., 2012a) transitions to very low $p\text{CO}_2$ values in both sea ice and brines, presumably associated with net autotrophy in the sea ice (e.g., Rysgaard et al., 2007; Fransson et al., 2011; Sejk et al., 2011).

Most of the above-ice ponds we sampled during the ICESCAPE project appear not have yet transitioned from “winter-early spring” high $p\text{CO}_2$ /low pH and $\Omega_{\text{aragonite}}$ conditions to low $p\text{CO}_2$ /high pH and $\Omega_{\text{aragonite}}$ in response to net autotrophy and alkalinity generation within the sea ice. Alternatively, since the melt water was sampled later in the season, the above-ice melt ponds may have transitioned from net autotrophy to net

heterotrophy in response to a later season increase in the microbial activity compared to autotrophic activity in sea-ice.

The other difference between above-ice melt ponds sampled in the western Arctic and other ice-covered regions is that the majority of them appear to be a potential sources of CO_2 to the atmosphere (Fig. 10a; Fig. 11a). At least 60% of the sampled above-ice melt pond waters had $p\text{CO}_2$ values higher than the atmosphere. This provides for an air-sea $p\text{CO}_2$ gradient that is favorable to the transfer of CO_2 to the atmosphere. In contrast, other sampled sea-ice melt ponds – with low $p\text{CO}_2$ relative to the atmosphere – appear to be relatively strong sinks for atmospheric CO_2 , similar to observations reported elsewhere (Semiletov et al., 2004; Geilfus et al., 2012a). Our observations suggest that both scenarios, as shown in Fig. 1 and modified in Fig. 11, exist for above-ice melt ponds in the western Arctic and that alkalinity variability and CaCO_3 precipitation/dissolution (i.e., increasing/decreasing $p\text{CO}_2$) appear highly important for controlling CO_2 gas exchange between melt ponds and the atmosphere.

4.3.2 Below-ice interface melt water CO_2 -carbonate chemistry and implications for air-sea CO_2 gas exchange

As shown earlier, the $p\text{CO}_2$ of most below-ice interface melt water (the “alkaline” type) was generally lower than the mixed layer $p\text{CO}_2$ beneath (Fig. 10b). Furthermore, the pH and $\Omega_{\text{aragonite}}$ values were also higher than the underlying mixed layer with a couple of exceptions (Fig. 10b). In general, low $p\text{CO}_2$ /high pH and $\Omega_{\text{aragonite}}$ values in below-ice melt water compared to the underlying mixed layer was observed across the Chukchi Sea shelf. In contrast, two below-ice melt waters sampled in the Canada Basin had high $p\text{CO}_2$ /low pH and $\Omega_{\text{aragonite}}$ relative to the mixed-layer beneath (Fig. 10b).

Our observations indicate that, in general, the $p\text{CO}_2$ of below-ice interface water was ~ 30 – 60 % lower than the seawater $p\text{CO}_2$ of the mixed layer beneath (Fig. 11). The average mixed layer $p\text{CO}_2$ across the Chukchi Sea shelf was $\sim 188 \pm 38 \mu\text{atm}$ lower and fresher by ~ 10 % than the mean mixed layer value. Assuming that melt water contributed to the dilution of the mixed layer, its CO_2 -carbonate chemical composition was

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estimated to reduce mean winter/early spring mixed layer water $p\text{CO}_2$ of $\sim 360 \mu\text{atm}$ by $\sim 5\%$ (or $\sim 18\text{--}20 \mu\text{atm}$). As we discuss later in Sect. 4.3, sea-ice melt has an important role in influencing seawater CO_2 -carbonate chemistry in addition to potentially impacting pelagic biological processes.

5 4.3.3 The contribution of sea ice melt to air-sea CO_2 fluxes

The contribution of sea-ice melt water to the balance of air-sea CO_2 sinks and sources in the Arctic Ocean is highly uncertain owing to observed variability shown here or in previous studies (Geilfus et al., 2012a). The marginal sea-ice zone of the Arctic is presently about 12 million km^2 (i.e., ~ 16 million km^2 sea-ice cover during the winter maxima which reduces to ~ 4.5 to 6 million km^2 at its minima in the recent past) having expanded by 50 % during the last few decades and it is expected that this will continue. Sea-ice melt ponds are transient features (a couple of weeks to 1 month) and typically cover 20 to 50 % of the sea-ice surface area.

In our study, those “acidic” above-ice melt ponds that had high $p\text{CO}_2$ should lose CO_2 to the atmosphere (conceptually shown in Fig. 11a). We estimate that to the efflux of CO_2 from melt pond water was likely to be in the range of 50 to 100 $\text{mmol m}^2 \text{d}^{-1}$ (up to 400 $\text{mmol m}^2 \text{d}^{-1}$ in those melt ponds with highest $p\text{CO}_2$). If all above-ice melt ponds exhibited similar chemical properties (i.e., high $p\text{CO}_2$), the seasonal efflux of CO_2 from above-ice melt ponds would range between ~ 22 and 216 TgCyr^{-1} , depending on their % cover and duration in a given year. This range of CO_2 sources to the atmosphere is large compared to the mean Arctic Ocean CO_2 sink of 135 Tgyr^{-1} (Schuster et al., 2013).

However, our observations also showed *alkaline* above-ice melt ponds (with very low $p\text{CO}_2$ values) that would facilitate uptake of CO_2 from the atmosphere, and counteract the impact of “acidic” melt ponds as CO_2 sources to the atmosphere (conceptually shown in Fig. 11a). Similar estimate of air-sea CO_2 gas exchanges determined using

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the CO₂-carbonate chemistry of melt ponds observed by Geilfus et al. (2012a) showed that they too would take up CO₂ from the atmosphere.

Furthermore, as shown in Sect. 4.3.2, exposure of mixed-layer water that is influenced by dilution with “alkaline” below-ice interface melt water would enhance the uptake of CO₂ into the mixed layer from the atmosphere. Clearly, any assessment of the influence of above-ice and below-ice melt water chemistry on air-sea CO₂ sinks and sources requires further investigation to examine the seasonal CO₂ behavior in many types of sea-ice melt water at different stages in the net metabolic condition of the sea ice, variability in CaCO₃ precipitation/dissolution processes, and production of excess alkalinity in melt water and assessment of the relative proportion of “alkaline” vs. “acidic” sea-ice melt water.

4.4 Below-ice determination of net community production (NCP) in the mixed layer from DIC changes

As discussed earlier, shelf waters had a DIC range of ~ 1850 to 2300 μmol kg⁻¹ with surface waters typically at the lower end of this range. Seawater pCO₂ in shelf waters were also typically lower than atmospheric pCO₂ values with surface waters having the lowest values (< 100 to 250 μatm across much of the Chukchi Sea, with slightly higher values in the southern Chukchi Sea presumably owing to warming of these waters as the summer progressed). Such summertime distributions of DIC and pCO₂ have been observed previously (e.g., Bates et al., 2006a) and appear associated with high rates of primary production (PP).

Earlier reports indicate that the rates of primary production or net community production (NCP) during the sea-ice free summertime period on the Chukchi Sea shelf are high at 340–2850 mg C m⁻² d⁻¹ (e.g., Hameedi, 1978; Cota et al., 1996; Wheeler et al., 1996; Chen et al., 2002; Hill and Cota, 2005; Bates et al., 2006a; Mathis et al., 2009) compared to other shelf environments in the Arctic. Annual rates of PP or NCP have been estimated at 35 to 364 g C m⁻² yr⁻¹ (Wheeler et al., 2005; Hill and Cota, 2005; Bates et al., 2005a). Recently, Arrigo et al. (2012) have shown high rates of primary

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production under sea-ice in the NW region of the Chukchi Sea during the ICESCAPE expeditions.

In contrast to short-term in situ ^{14}C based or deck board simulation rates of PP, time-integrated water column rates of net community production can be estimated by evaluating changes in DIC, dissolved oxygen or inorganic nutrients. Here, we determine rates of NCP using changes in DIC from winter/early spring values to summertime (i.e., $\Delta\text{DIC}^{\text{SEASONAL}}$). Thus, changes in DIC reflect changes imparted by net community production (uptake of CO_2/DIC ; $\Delta\text{DIC}^{\text{NCP}}$), and contributions from sea-ice melt ($\Delta\text{DIC}^{\text{SEAMELT}}$).

$$\Delta\text{DIC}^{\text{SEASONAL}} = \Delta\text{DIC}^{\text{NCP}} + \Delta\text{DIC}^{\text{SEAMELT}} \quad (7)$$

This approach is simplified by assumptions that sea-ice cover is a barrier to air-sea CO_2 gas exchange, and that advection of different water masses is much slower than the timeframe of changes imparted by NCP or sea-ice melt. Thus, rates of NCP are determined from the following:

$$\Delta\text{DIC}^{\text{NCP}} = \Delta\text{DIC}^{\text{SEASONAL}} - \Delta\text{DIC}^{\text{SEAMELT}} \quad (8)$$

The contributions of sea-ice melt CO_2 -carbonate chemistry to changes in DIC within the mixed layer (i.e., $\Delta\text{DIC}^{\text{SEAMELT}}$) are accounted for by: (1) using the % proportion of melt water in the mixed layer determined by changes in salinity; (2) predicting the DIC contributed from below-ice melt DIC composition determined earlier in Sect. 4.1, and; (3) comparing vertical profiles of observed DIC with winter/early spring DIC values gives an estimate of $\Delta\text{DIC}^{\text{SEASONAL}}$. The sum of both provides a residual DIC change that is equivalent to $\Delta\text{DIC}^{\text{NCP}}$. The analysis at each ice station is integrated over the upper 30 m of the water column. Here, the $\Delta\text{DIC}^{\text{NCP}}$ rates were converted to g C m^{-2} , and equivalent to the rate of NCP expressed as $\text{g C m}^{-2} \text{period}^{-1}$. Since we cannot determine the exact duration of NCP since early spring, the NCP rates reflect the integrated value from initial winter conditions until the ice station sampling date. The NCP

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rates shown in Figs. 11 and 12 are given as positive or negative values; the latter reflecting net autotrophy (i.e., net primary production > net respiration), and the former net heterotrophy.

High rates of NCP were observed across the Chukchi Sea shelf (Fig. 12a), with a maximum of $93.2 \text{ gCm}^{-2} \text{ period}^{-1}$ (i.e., negative NCP) with a mean of $46.9 \pm 29.8 \text{ gCm}^{-2} \text{ period}^{-1}$. The high rates of NCP are co-located with low nDIC (Fig. 12b) and, high, integrated chlorophyll *a* biomass (up to 400 mgCm^{-2} ; Fig. 12c). As shown in Fig. 12, the high rates of NCP are also associated with low $p\text{CO}_2$ (Fig. 13a), higher pH (~ 8.3 to 8.4 ; Fig. 12b), high, integrated chlorophyll *a* biomass (Fig. 12c) and high rates of simulated in situ primary production (up to $6 \text{ gCm}^{-2} \text{ d}^{-1}$; Fig. 13d). Previous data have shown summertime rates of primary production or NCP at 0.5 to $2.9 \text{ gCm}^{-2} \text{ d}^{-1}$ (Hameedi, 1978; Cota et al., 1996; Wheeler et al., 1996; Chen et al., 2002; Hill and Cota, 2005; Bates et al., 2005a). The annual rates of primary production or NCP have been estimated previously at 35 to $364 \text{ gCm}^{-2} \text{ yr}^{-1}$ (Hill and Cota, 2005; Walsh et al., 2005; Bates et al., 2005a; Mathis et al., 2009). Our estimates of NCP from DIC changes (accounting for contributions of sea-ice melt) are thus within the range observed for primary production or NCP for the Chukchi Sea shelf.

Across the Chukchi Sea shelf, seawater $p\text{CO}_2$ values are much lower (Fig. 12a) than atmospheric $p\text{CO}_2$ owing to the combined impact of biological production and sea-ice melt. This combination of physico-biogeochemical influences produces a strong air-sea CO_2 gradient facilitating ocean uptake of CO_2 from the atmosphere. Such observations have been observed previously in the Chukchi Sea (e.g., Murata and Takizawa, 2002; Pipko et al., 2004; Bates, 2006; Bates et al., 2006, 2011). Very low $p\text{CO}_2$ was observed in the vicinity of a large below-ice phytoplankton bloom in the NW Chukchi Sea (Arrigo et al., 2012; Fig. 12a).

In contrast to the Chukchi Sea shelf, surface waters of the Canada Basin had positive NCP values. This suggests that the mixed layer of the Canada Basin undergoes net respiration ($18.4 \pm 15.2 \text{ gCm}^{-2} \text{ period}^{-1}$). This may also indicate that Canada Basin surface waters are net heterotrophy and indicate the export of organic carbon from the

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shelf and its remineralization in Canada Basin waters. The lack of net primary production or NCP in these waters is associated with high nDIC values (Fig. 12b), low integrated chlorophyll *a* biomass ($< 20 \text{ gCm}^{-2}$; Fig. 12c, Fig. 13c) and very low rates of simulated in situ primary production ($< 0.1 \text{ gCm}^{-2} \text{ d}^{-1}$; Fig. 13d). Our low rates of NCP (i.e., net heterotrophy) appear to reflect the very low rates of PP or NCP observed previously in the Canada Basin (i.e., < 5 to $46 \text{ gCm}^{-2} \text{ d}^{-1}$; English, 1961; Cota et al., 1996; Wheeler et al., 1996; Chen et al., 2002), and the previous findings that the Canada Basin is perennially oligotrophic (e.g., English, 1961; Moran et al., 1997; Anderson et al., 2003).

The seawater $p\text{CO}_2$ values in the Canada Basin surface waters were modestly higher (~ 280 to $350 \mu\text{atm}$) than earlier observations in the early 2000's (~ 250 to $280 \mu\text{atm}$; Bates et al., 2006) and similar to observations in more recent years (Cai et al., 2010; Mathis et al., 2013; Fig. 13b). Surface pH and $\Omega_{\text{aragonite}}$ were relatively low at 8.05 to 8.1 and < 0.5 , respectively. Similarly low $\Omega_{\text{aragonite}}$ surface waters have been observed in the Canada Basin previously (Jutterstrom et al., 2010). This finding suggests that surface waters corrosive to CaCO_3 are seasonally present in the Canada Basin far earlier than model predictions have indicated (Steinacher et al., 2009).

5 Conclusions

Observations of CO_2 -carbonate chemistry in above-ice melt ponds, below-ice interface melt water, and the water column across the western Arctic Ocean in the late spring/early summer of 2010 and 2011 are presented here. Contemporaneous examination of the CO_2 -carbonate chemistry of above-ice and below-ice melt waters and collocated, mixed-layer seawater has rarely been undertaken in sea-ice covered oceans.

Our observations of CO_2 -carbonate chemistry at sea-ice stations in the western Arctic Ocean revealed that the $p\text{CO}_2$ concentrations of the majority of above-ice melt pond water was high (~ 400 to $1500 \mu\text{atm}$) compared to other ice melt ponds reported in the literature (Geilfus et al., 2012a). This finding suggests that the sampled melt

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ponds in the western Arctic Ocean were potentially strong sources of CO₂ to the atmosphere (Fig. 11a). These findings contrast with other studies that have shown ice melt ponds with low pCO₂ content acting as strong sinks for atmospheric CO₂ (Geilfus et al., 2012a). The variability of above-ice melt pond chemistry observed in the western Arctic appears to confirm the substantial variability in sea-ice pCO₂ reported by other studies (as shown in Fig. 11b).

The pH of sampled ice melt waters was also mildly acidic (6.1 to 7.5) with DIC concentrations higher than TA and very low (< 0.1) saturation states (Ω) for calcium carbonate (CaCO₃) minerals such as aragonite ($\Omega_{\text{aragonite}}$). This finding suggests that these above-ice melt ponds were potentially corrosive to CaCO₃ in the sea ice melt. It is also likely that low Ω ice melt pond values contribute to the low Ω surface waters previously observed in the Canada Basin (Yamamoto-Kawai et al., 2005; Jutterstrom et al., 2009). A few above-ice melt ponds appear to be influenced by alkaline sea-ice melt and were strong sinks for CO₂ (scenario 2 in Fig. 1). In summary, above-ice melt pond water exhibited CO₂-carbonate chemistry that corresponded to both scenarios discussed in the introduction and in Fig. 1.

In contrast to above-ice melt pond waters, the below-ice interface melt water sampled at the ice stations had lower pCO₂ and higher pH/ $\Omega_{\text{aragonite}}$ than the co-located mixed layer beneath. Our analysis indicates that alkalinity is generated in sea ice and contributes to below-ice melt water chemistry. The generation of alkalinity, presumably from dissolution of CaCO₃ in sea ice, contributes to a reduction of seawater pCO₂ in the mixed layer below, with implications for the net balance of CO₂ sinks and sources in the western Arctic. As shown in the conceptual summary of annual dynamics of CO₂-carbonate chemistry, the below-ice water has lower pCO₂ (and higher pH) than the underlying mixed layer.

Above-ice melt ponds and below-ice melt waters are brief features observed in spring prior to breakup of sea ice. While they are transient (4 to 6 weeks), sea ice melt ponds can constitute greater than 50 % of the ice surface. In addition to their impact on albedo, heat, momentum and water exchanges in the high latitudes, our observations con-

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tribute to growing evidence that the impact of sea ice on seawater carbonate chemistry is highly variable. This study, as in previous studies, confirms that further study of the dynamics and timing of all components of sea-ice chemistry (sea ice, brines, melt ponds) will be important for future assessments of the complex factors that influence the balance of CO₂ sinks and sources (and thereby ocean acidification) in the ice-covered high latitudes. With further warming and sea-ice loss in the Arctic, for example, the presence of ice melt ponds and melt waters is likely to be greater in the expanded region of seasonal sea-ice retreat.

Supplementary material related to this article is available online at
[http://www.biogeosciences-discuss.net/11/1097/2014/
bgd-11-1097-2014-supplement.pdf](http://www.biogeosciences-discuss.net/11/1097/2014/bgd-11-1097-2014-supplement.pdf).

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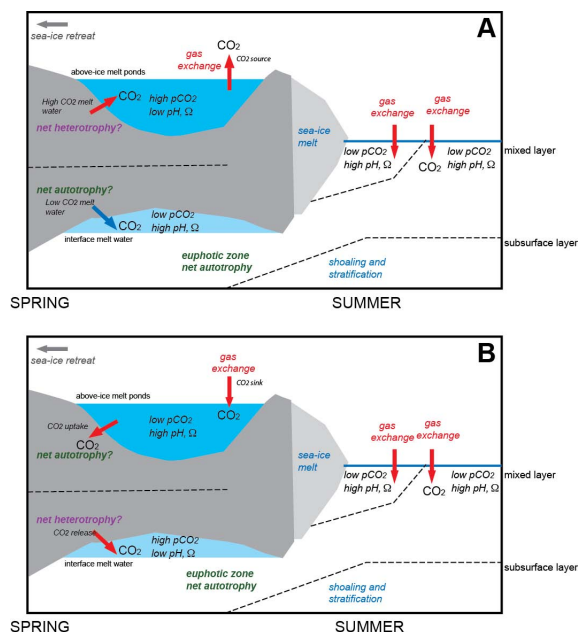


Fig. 1. Schematic of processes impacting sea-ice CO₂-carbonate chemistry. In panels **(A)** and **(B)**, the seasonal advanced (freeze-up) and retreat (melting and breakup) is shown against approximate seasonally timing for both Arctic and Antarctic studies (both shown against season rather than month). Processes that can influence the production or loss of sea ice are shown in blue and red respectively. For example, photosynthesis and calcification reduces CO₂. In the water column, generalized changes in mixed layer depth and surface water stratification are shown. Also shown in the figure are idealized surface ice melt ponds and under-ice interface melt water. In panel **(A)**, ice melt is shown to have high pCO₂/low pH, with efflux of CO₂ from melt ponds to the atmosphere. In panel **(B)**, the opposite case is shown, with ice melt ponds shown with low pCO₂/high pH conditions and as sinks for atmospheric CO₂.

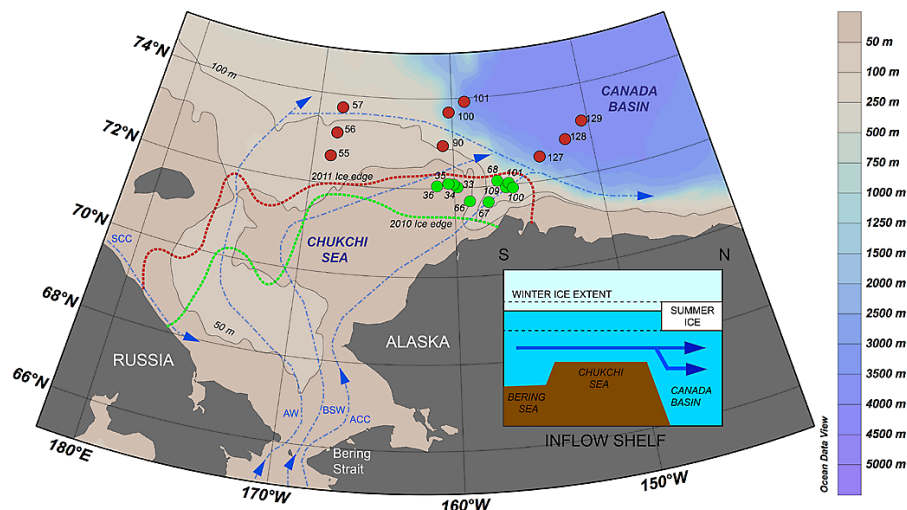


Fig. 2. Map of the western Arctic Ocean showing the sea-ice stations occupied during the ICESCAPE cruises of 2010 (red symbols) and 2011 (green symbols) with sea-ice station numbers also shown. The approximate sea-ice edge is shown for 2010 (bold dashed green line) and 2011 (bold dashed red line). Approximate streamlines (blue dashed lines) of water flow across the Chukchi Sea are shown and include the following water masses: Alaskan Coastal Current (ACC), Bering Shelf Water (BSW) and Anadyr Water (AW). The intermittent flow of the Siberian Coastal Current (SCC) through Long Strait into the Chukchi Sea is also shown. Sea ice data were retrieved from the National Sea-Ice Data Center (Cavalieri et al., 1996, updated yearly; <http://nsidc.org/data/seoice/index>). INSET. A schematic of the “inflow” shelf is shown illustrating the northward flow of water across the shelf from the Bering Sea, through Bering Strait, and across the Chukchi Sea shelf to the Canada Basin.

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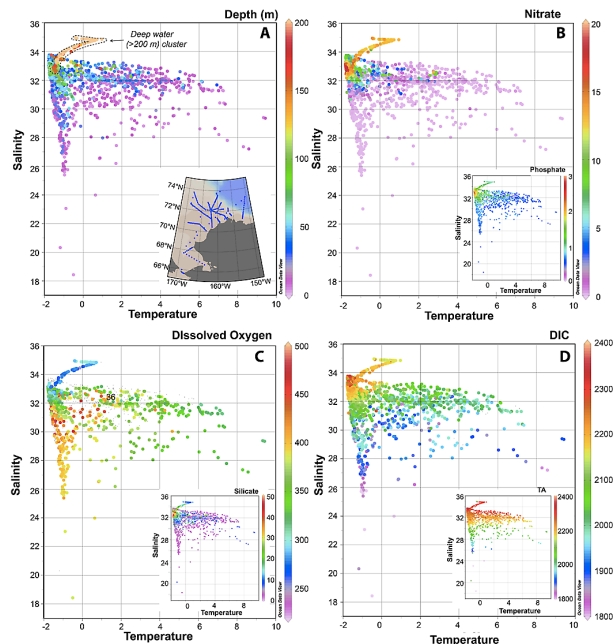


Fig. 3. Water column hydrography and marine biogeochemistry of the 2010 and 2011 ICESCAPE cruises. **(A)** Temperature ($^{\circ}\text{C}$) vs. salinity with range of color denoting depth (m), and locations of 2010 and 2011 ICESCAPE hydrocast-CTD stations shown in the inset. The depth of samples collected below 200 m deep is not differentiated colorwise, and represent water depths to > 4000 m. With this in mind, the approximate range of deep water (Canada Basin) hydrographic properties are shown within the dashed line. **(B)** Temperature ($^{\circ}\text{C}$) vs. salinity with range of color denoting nitrate concentration ($\mu\text{mol kg}^{-1}$) with phosphate ($\mu\text{mol kg}^{-1}$) shown in the inset. **(C)** Temperature ($^{\circ}\text{C}$) vs. salinity with range of color denoting dissolved oxygen concentration ($\mu\text{mol kg}^{-1}$) with silicate ($\mu\text{mol kg}^{-1}$) shown in the inset. **(D)** Temperature ($^{\circ}\text{C}$) vs. salinity with range of color denoting dissolved inorganic carbon (DIC) concentration ($\mu\text{mol kg}^{-1}$) with total alkalinity (TA; $\mu\text{mol kg}^{-1}$) shown in the inset.

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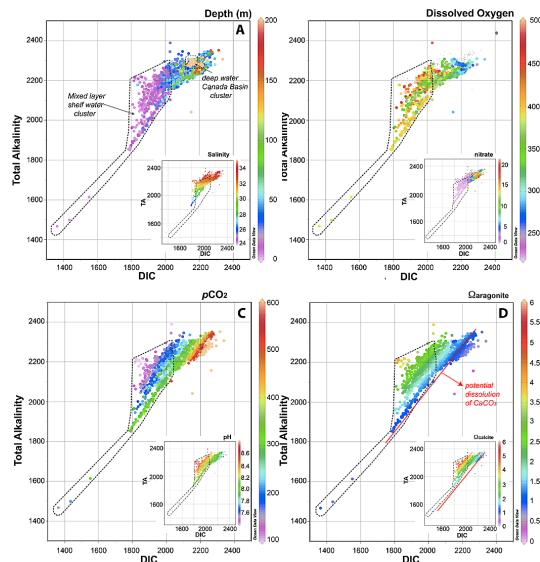


Fig. 4. Seawater CO₂-carbonate chemistry and marine biogeochemistry of the 2010 and 2011 ICESCAPE cruises. **(A)** DIC ($\mu\text{mol kg}^{-1}$) vs. total alkalinity (TA; $\mu\text{mol kg}^{-1}$) with range of color denoting depth (m), with salinity shown in the inset. The depth of samples collected below 200 m deep is not differentiated colorwise, and represents water depth to > 4000 m. With this in mind, the approximate range of deep water (Canada Basin) hydrographic properties are shown within the light dashed line. Approximate cluster of shelf mixed layer water is shown here and in all panels and insets. **(B)** DIC ($\mu\text{mol kg}^{-1}$) vs. total alkalinity (TA; $\mu\text{mol kg}^{-1}$) with range of color denoting dissolved oxygen ($\mu\text{mol kg}^{-1}$) with nitrate $\mu\text{mol kg}^{-1}$ shown in the inset. **(C)** DIC ($\mu\text{mol kg}^{-1}$) vs. total alkalinity (TA; $\mu\text{mol kg}^{-1}$) with range of color denoting $p\text{CO}_2$ (μatm) with pH (no units) shown in the inset. **(D)** DIC ($\mu\text{mol kg}^{-1}$) vs. total alkalinity (TA; $\mu\text{mol kg}^{-1}$) with range of color denoting saturation state (Ω) for aragonite (no units) with Ω_{calcite} (no units) shown in the inset. The red line denotes Ω values of 1 with potential dissolution of CaCO₃ minerals below a Ω value of 1.

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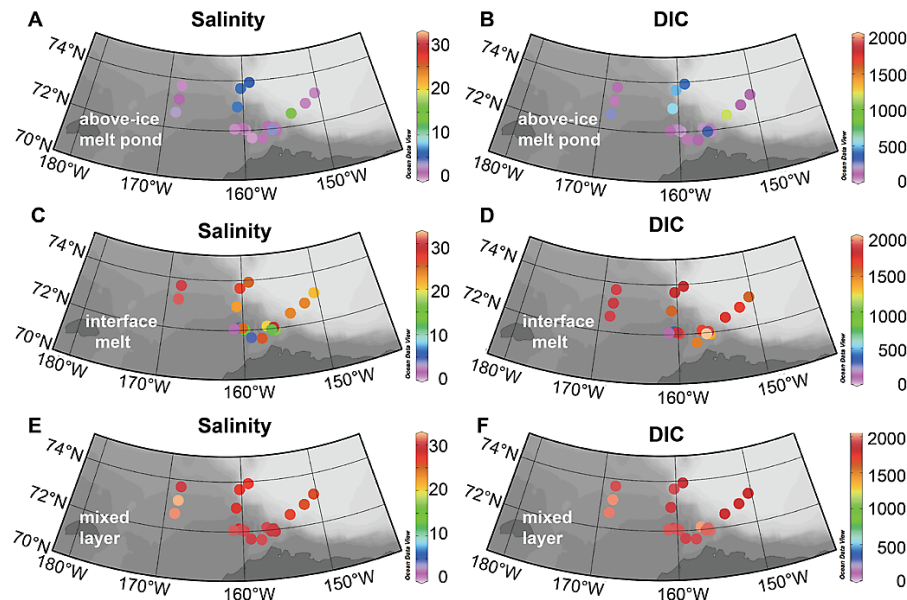


Fig. 5. Surface maps of above-ice melt ponds, below-ice interface melt water, and mixed layer values beneath each ice station sampled on 2010 and 2011 ICESCAPE cruises. **(A)** Salinity for above-ice melt ponds. **(B)** DIC ($\mu\text{mol kg}^{-1}$) for above-ice melt ponds. **(C)** Salinity for below-ice interface melt water. **(D)** DIC ($\mu\text{mol kg}^{-1}$) for below-ice interface melt water. **(E)** Salinity for mixed layer values beneath each ice station. **(F)** DIC ($\mu\text{mol kg}^{-1}$) for mixed layer values beneath each ice station.

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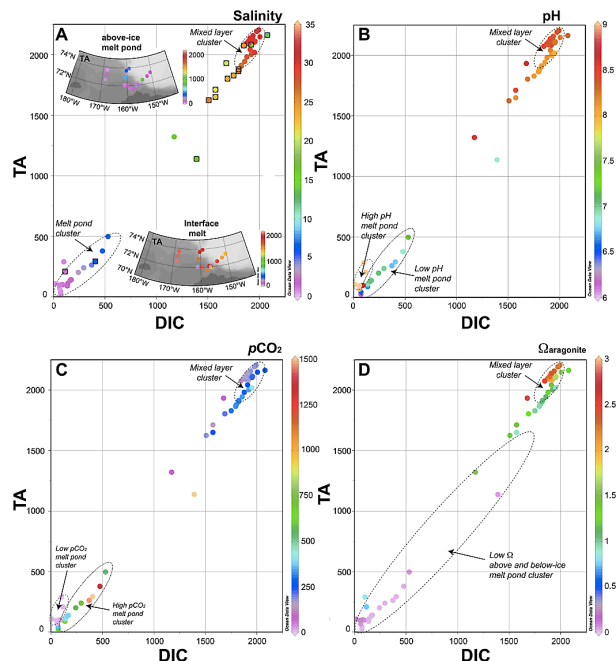


Fig. 6. Scatter plots of CO₂-carbonate chemistry for above-ice melt ponds, below-ice interface melt waters, and mixed layer values beneath each ice station sampled on 2010 and 2011 ICESCAPE cruises. **(A)** DIC (μmol kg⁻¹) vs. total alkalinity (TA; μmol kg⁻¹) with range of color denoting salinity. Surface TA is shown for above-ice melt ponds and below-ice interface melt waters in the insets. The approximate chemical clustering of above-ice melt ponds, below-ice interface melt waters, and mixed layer water is also shown. **(B)** DIC (μmol kg⁻¹) vs. total alkalinity (TA; μmol kg⁻¹) with range of color denoting pH. **(C)** DIC (μmol kg⁻¹) vs. total alkalinity (TA; μmol kg⁻¹) with range of color denoting pCO₂. **(D)** DIC (μmol kg⁻¹) vs. total alkalinity (TA; μmol kg⁻¹) with range of color denoting Ω_{aragonite} values.

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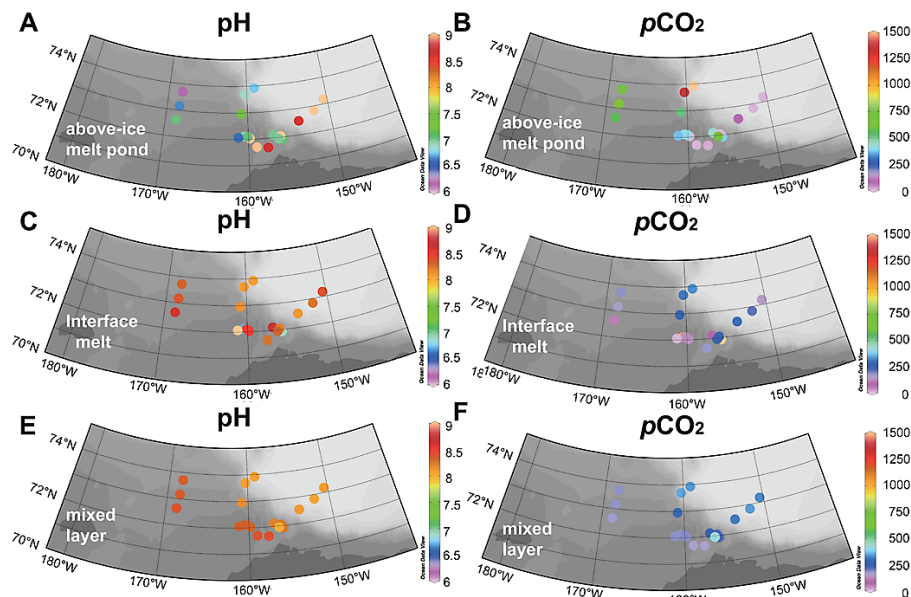


Fig. 7. Surface maps of above-ice melt ponds, below-ice interface melt water, and mixed layer values beneath each ice station sampled on 2010 and 2011 ICESCAPE cruises. **(A)** pH for above-ice melt ponds. **(B)** $p\text{CO}_2$ (μatm) for above-ice melt ponds. **(C)** pH for below-ice interface melt water. **(D)** $p\text{CO}_2$ (μatm) for below-ice interface melt water. **(E)** pH for mixed layer values beneath each ice station. **(F)** $p\text{CO}_2$ (μatm).

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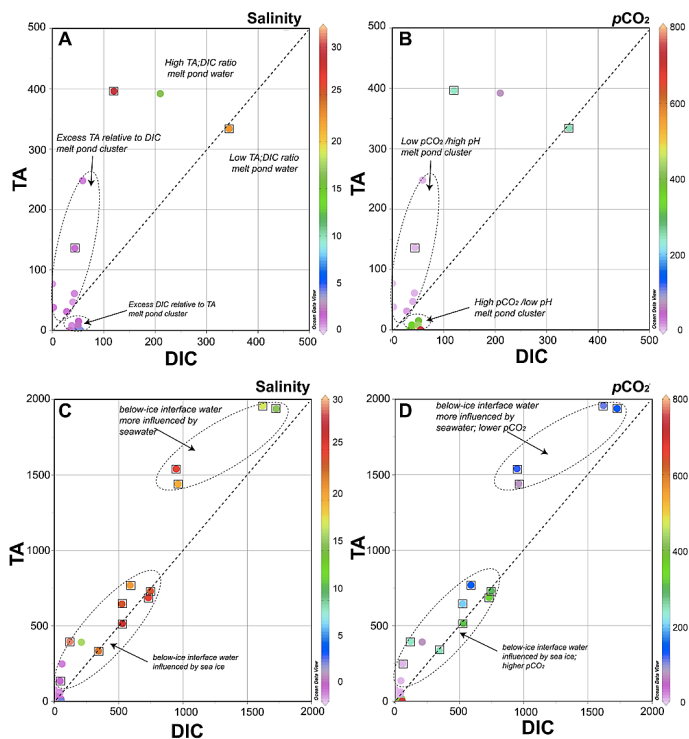


Fig. 8. Scatter plots of above-ice melt ponds and below-ice interface water for DIC and TA against salinity and $p\text{CO}_2$ each ice station sampled on 2010 and 2011 ICESCAPE cruises. **(A)** salinity for above-ice melt ponds. **(B)** $p\text{CO}_2$ (μatm) for above-ice melt ponds. **(C)** salinity for below-ice interface melt water. **(D)** $p\text{CO}_2$ (μatm) for below-ice interface melt water.

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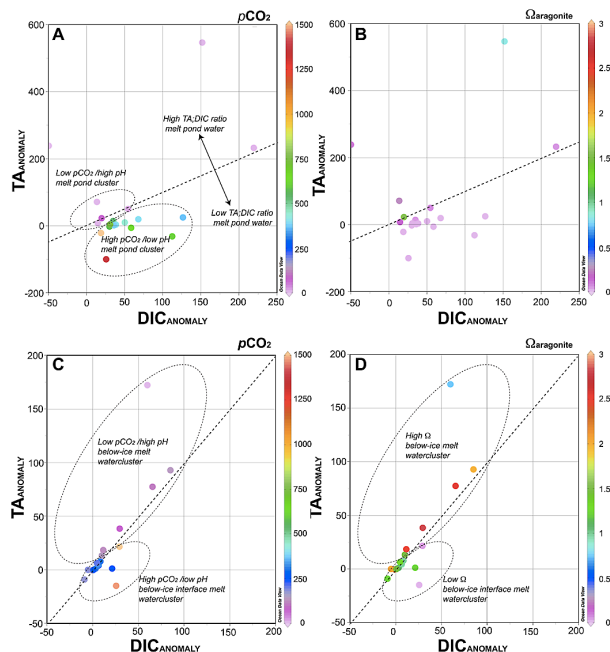


Fig. 9. Scatter plots of TA and DIC anomalies (i.e., $TA_{ANOMALY}$ and $DIC_{ANOMALY}$) for above-ice melt pond water and below-ice interface melt water, compared to CO₂-carbonate chemistry, sampled on 2010 and 2011 ICESCAPE cruises. The units for $TA_{ANOMALY}$ and $DIC_{ANOMALY}$ are % difference in concentration from winter/early spring remnant shelf water. **(A)** Above-ice melt pond water $DIC_{ANOMALY}$ vs. $TA_{ANOMALY}$ with range of color denoting pCO_2 (μatm). The approximate chemical clustering of above-ice melt pond water is shown with bold dashed line (in this and other panels) denotes the changes in TA:DIC ratio relative to $TA_{ANOMALY}$ and $DIC_{ANOMALY}$. **(B)** Above-ice melt pond water $DIC_{ANOMALY}$ vs. $TA_{ANOMALY}$ with range of color denoting $\Omega_{\text{aragonite}}$ value. **(C)** Below-ice interface melt water $DIC_{ANOMALY}$ vs. $TA_{ANOMALY}$ with range of color denoting pCO_2 (μatm). **(D)** Below-ice interface melt water $DIC_{ANOMALY}$ vs. $TA_{ANOMALY}$ with range of color denoting $\Omega_{\text{aragonite}}$ values.

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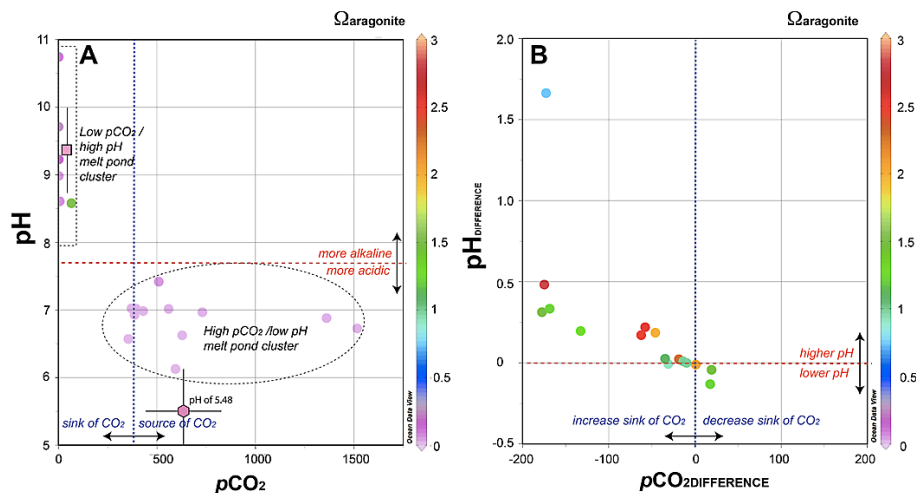


Fig. 10. Surface maps of mixed layer net community production (NCP), nDIC and chlorophyll values at each ice station sampled on 2010 and 2011 ICESCAPE cruises. **(A)** Above-ice melt pond chemistry showing $p\text{CO}_2$ (μatm) vs. pH with range of color denoting $\Omega_{\text{aragonite}}$ values. **(B)** Difference between below-ice interface melt water and mixed layer. Panel shows $p\text{CO}_2$ (μatm_{2013}) vs. pH with range of color denoting $\Omega_{\text{aragonite}}$ values. Positive values indicate that mixed layer values are high than the below-ice interface melt water.

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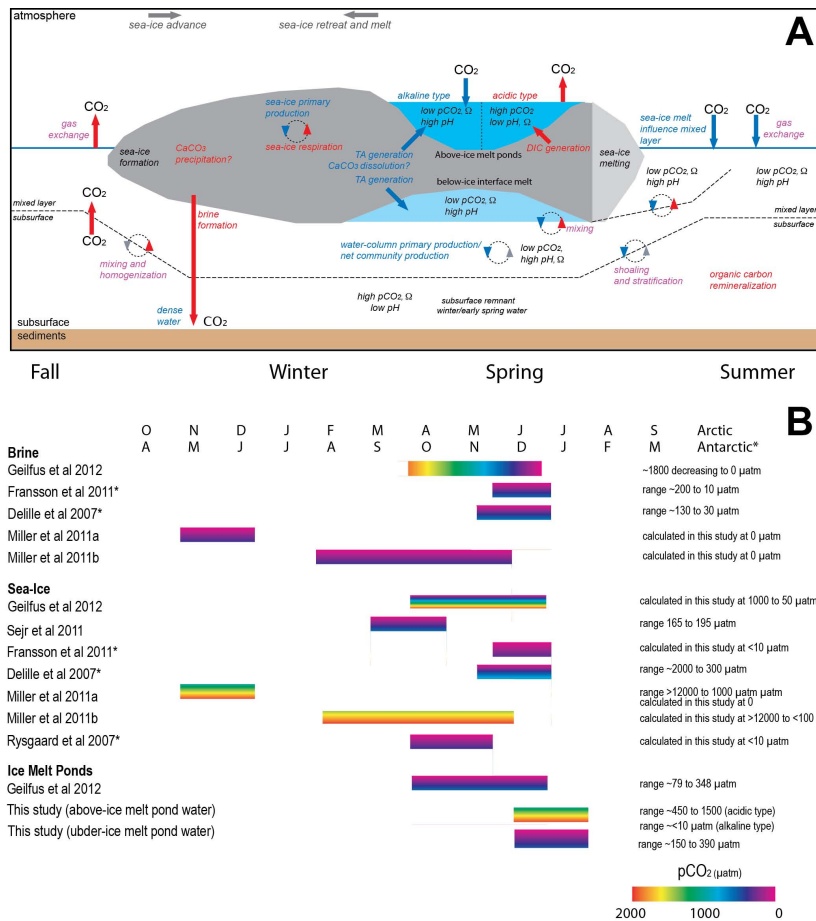


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Fig. 11. Schematic of processes impacting sea-ice and seawater CO₂-carbonate chemistry in the western Arctic Ocean. In panel **(A)** the seasonal advanced (freeze-up) and retreat (melting and breakup) is shown against approximate seasonally timing for both Arctic and Antarctic studies (both shown against season rather than month). Processes that can influence the decrease or increase of melt water or seawater $p\text{CO}_2$ are shown in blue and red respectively. For example, photosynthesis and calcification reduces CO₂. In the water column, generalized changes in mixed layer depth and surface water stratification are shown. Also shown in the figure are idealized surface ice melt ponds and below-ice interface melt water. In panel **(B)** timing of study and approximate ranges of $p\text{CO}_2$ are shown for sea ice brines, sea ice, and sea ice melt. The color spectrum, representing range of $p\text{CO}_2$, is shown either horizontally or vertically. For example, the horizontal changes in $p\text{CO}_2$ shown for the Geilfus et al. (2012) study approximate the seasonal changes observed in their study. The vertically aligned color spectrum reflects the approximately range of data reported for that study (i.e., with no seasonal change shown).

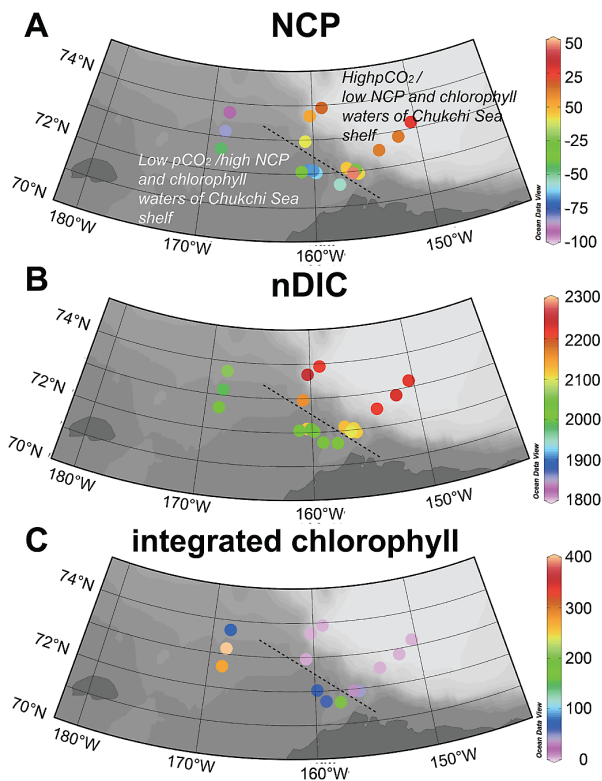


Fig. 12. Surface maps of mixed layer net community production (NCP), nDIC and chlorophyll values at each ice station sampled on 2010 and 2011 ICESCAPE cruises. **(A)** Rate of NCP at each ice station (unit of $\text{gC m}^{-2} \text{ period}^{-1}$; i.e., spring to time of sampling in summertime). The NCP rate is integrated over the upper 30 m of the water column. **(B)** Mixed layer nDIC (i.e., DIC value normalized to a salinity of 32; $\mu\text{mol kg}^{-1}$) at each ice station. **(C)** integrated chlorophyll-*a* biomass at each ice station (i.e., mg C m^{-2} integrated over the upper 30 m).

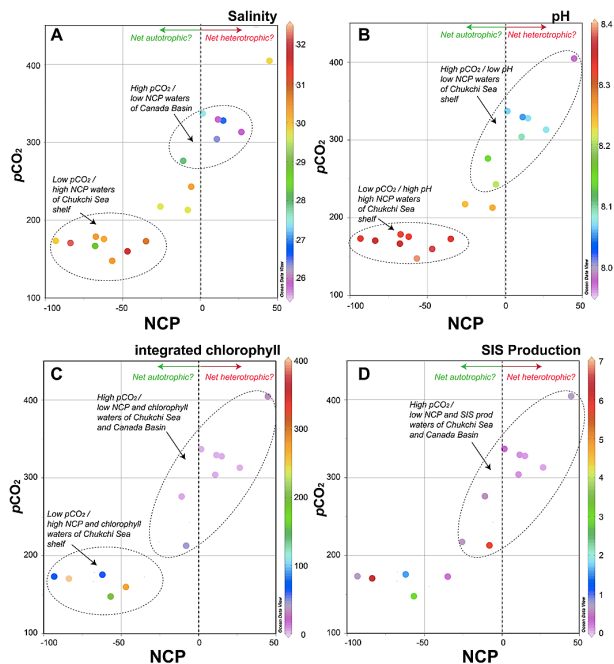


Fig. 13. Scatter plots of NCP (unit of $\text{gCm}^{-2}\text{period}^{-1}$; i.e., spring to time of sampling in summertime) against $p\text{CO}_2$ (μatm) compared with salinity, pH, integrated chlorophyll-*a* and simulated in situ production rates from the 2010 and 2011 ICESCAPE cruises. **(A)** NCP vs. $p\text{CO}_2$, with range of color denoting salinity. The approximate chemical clustering of mixed layer shelf waters is shown in this and other panels. **(B)** NCP vs. $p\text{CO}_2$, with range of color denoting pH. **(C)** NCP vs. $p\text{CO}_2$, with range of color denoting integrated chlorophyll-*a* (integrated over the upper 30 m; mgCm^{-2}). **(D)** NCP vs. $p\text{CO}_2$, with range of color denoting simulated in situ production (SIS) rates (integrated over the upper 30 m; $\text{gCm}^{-2}\text{d}^{-1}$).