Seasonal calcium carbonate undersaturation in shelf waters of the Western Arctic Ocean; how biological processes exacerbate the impact of ocean acidification

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Abstract

The Arctic Ocean accounts for only 4% of the global ocean area but it contributes significantly to the global carbon cycle. Recent observations of seawater carbonate chemistry in shelf waters of the Western Arctic from 2009 to 2011 indicate that extensive areas of the benthos are exposed to bottom waters that are seasonally undersaturated with respect to calcium carbonate (CaCO$_3$) minerals, particularly aragonite. Our observations indicate seasonal reduction of saturation states (Ω) for calcite ($\Omega_{\text{calcite}}$) and aragonite ($\Omega_{\text{aragonite}}$) in the subsurface in the Western Arctic by as much as 0.9 and 0.6, respectively. Such data indicates that bottom waters of the Western Arctic shelves are already potentially corrosive for biogenic and sedimentary CaCO$_3$ for several months each year. Seasonal changes in Ω are imparted by a variety of factors such as phytoplankton photosynthesis, respiration/remineralization of organic matter and air-sea gas exchange of CO$_2$ – combined these processes either increase or enhance Ω in surface and subsurface waters, respectively. These seasonal physical and biological processes also act to mitigate or enhance the impact of Anthropocene ocean acidification (OA) on Ω in surface and subsurface waters, respectively. Future monitoring of the Western Arctic shelves is warranted to assess the present and future impact on Ω values from ocean acidification and seasonal biological/physical processes on Arctic marine ecosystems.

1 Introduction

The release of anthropogenic carbon dioxide (CO$_2$) to the atmosphere and its uptake by the global ocean has significant implications for ocean chemistry and marine organisms and ecosystems. While the ocean remains mildly basic (pH > 7) at present, the uptake of anthropogenic CO$_2$ from the atmosphere into the ocean changes the chemical balance of seawater resulting in gradual acidification of seawater in a process termed ocean acidification (OA; Caldeira et al., 2003, 2005; Doney et al., 2009;
Feely et al., 2009). As the CO$_2$ content of seawater increases, the pH, carbonate ion concentration [CO$_3^{2-}$] and saturation state (Ω) of calcium carbonate (CaCO$_3$) minerals such as calcite and aragonite decreases. Semi-continuous records of seawater carbonate chemistry show that the CO$_2$ partial pressure (pCO$_2$) of surface seawater has increased by > 30%, while pH has decreased by ~0.1 over the last twenty to thirty years (Bates and Peters, 2007; Santana-Casiano et al., 2007; Dore et al. 2009; Gonzalez-Davila et al., 2010; Olafsson et al., 2010; Byrne et al., 2010; Bates et al., 2012). In the open ocean of the Pacific, uptake of anthropogenic CO$_2$ has been shown to reduce the saturation state of CaCO$_3$ minerals and resulted in the shoaling of the lysoline depth (where Ω = 1) by up to 100 m (Feely et al., 2004). In the coastal ocean, upwelling has also been shown to bring low pH and Ω onto adjacent shelves (e.g. Feely et al., 2008; Fassbender et al., 2011; Mathis et al., 2012).

The future impact of ocean acidification on marine organisms and ecosystems remains highly uncertain at present. A growing number of experimental and field studies show a variety of responses of marine organisms – even within individual taxa depending on life stage and other physico-biogeochemical factors – such as corals, echinoderms, bivalves and mollusks that secrete biogenic CaCO$_3$ as shells, skeletons or framework structures (e.g. Buddemeier et al., 2004; Fabry et al., 2008; Doney et al., 2009; Smith, 2009; Bűdenbender et al., 2011; Ries, 2011) Seawater with low pH and saturation state less than one (i.e. Ω < 1) is potentially corrosive to biogenic and sedimentary forms of CaCO$_3$ such as calcite, high-Mg calcite and aragonite. Ocean acidification thus increases the potential for dissolution of CaCO$_3$ (Andersson et al., 2010) particularly in shallow shelf environments where dissolution of calcareous sediments can alter the buffer capacity of waters overlying such sediments. However, despite the emergence of ocean acidification as a potential problem of global significance, integrated studies of the interaction and feedbacks between ocean acidification, seawater carbonate chemistry, and naturally/anthropogenically influenced physico-biogeochemical processes are in their infancy, particularly in the coastal ocean.
The Arctic Ocean – including the deep central basin and surrounding shallow shelf seas – has been identified as vulnerable to the impacts of ocean acidification (e.g. Yamamoto-Kawai et al., 2009; Bates and Mathis, 2009; Anderson et al., 2011). Recent observations, syntheses and model studies indicate that naturally low temperatures, pH and $\Omega$ values of surface waters in the Arctic are conducive to earlier onset of ocean acidification this century – especially given anticipated further release of anthropogenic CO$_2$ to the atmosphere and its uptake by the global ocean (IPCC, 2007) – when compared to other open ocean and coastal waters (e.g. Orr et al., 2005; Steinacher et al., 2009). The impact of ocean acidification on the Arctic Ocean is also likely to be highly synergistic with environmental changes associated with warming, rapid sea-ice loss and sea-ice meltwater/freshwater inputs to the Arctic, and increased coastal erosion (e.g. ACIA, 2005; Serreze and Francis, 2006; Maslanik et al., 2007; McGuire et al., 2006, Arrigo et al., 2008; Pabi et al., 2008; WWF Climate Feedbacks Report, 2009; McGuire et al., 2009; Wang and Overland, 2009).

Assessment of the present and future impact of ocean acidification in the Arctic is complicated by contradictory responses and feedbacks within the region (Bates and Mathis, 2009). Field expeditions are difficult to conduct in the Arctic but, nonetheless, there is growing evidence that low pH and $\Omega$ conditions exist in the Arctic Ocean at present. In the Arctic Ocean, low $\Omega$ values have been observed in the subsurface halocline layer of the central basin waters for both calcite ($\Omega_{\text{calcite}}$) and aragonite ($\Omega_{\text{aragonite}}$; Jutterstrom and Anderson, 2005; Yamamoto-Kawai et al., 2009; Chierici and Fransson, 2009). Low $\Omega$ values and reduced buffering capacity of surface waters due to sea-ice melt water has also been observed in the central basin during summertime (Yamamoto-Kawai et al., 2009). On the surrounding polar shelves, low $\Omega$ waters that are potentially corrosive to CaCO$_3$ (i.e. $\Omega < 1$) have been seasonally observed in several regions, including: (1) slope waters of the Northern Chukchi Sea (e.g. Bates et al., 2009) and Beaufort Sea (Mathis et al., 2012); (2) in outflow waters of the Arctic in the Canadian Arctic Archipelago (Azetsu-Scott et al., 2010), and; (3) as far south as the Bering Sea shelf (Mathis et al., 2009, 2011a, b).
In this study, we assess the present state of $\Omega_{\text{calcite}}$ and $\Omega_{\text{aragonite}}$ conditions within surface and subsurface waters across the Western Arctic including the Eastern East Siberian Sea, Chukchi Sea, and Western Beaufort Sea shelves between 2009 and 2011. We use data collected as part of the recent RUSALCA (Russian-American Long Term Census of the Arctic) and ICESCAPE (Impacts of Climate on the Eco-Systems and Chemistry of the Arctic Pacific Environment) expeditions to the Western Arctic Ocean. These data are used to assess if shelf bottom waters of the Western Arctic are potentially corrosive to CaCO$_3$ minerals. In the early 2000s, repeat seasonal observations during the Shelf-Basin Interactions (SBI) project showed that pH values were lower than 8.0 and values for $\Omega_{\text{aragonite}}$ were $< 1$ in subsurface waters on the northern slope of the Chukchi Sea but not across the shelf (Bates et al., 2009). We examine whether bottom waters with low pH and $\Omega$ are present across much of the shelf areas of the Western Arctic Ocean, thereby providing an assessment of the present-day seasonal exposure of the seafloor benthos to bottom waters that are corrosive for CaCO$_3$ shells and skeletons.

Furthermore, we examine the interactions and feedbacks between seawater carbonate chemistry and physical, biological and chemical processes in the Western Arctic. Such physico-biogeochemical processes significantly impact seawater carbonate chemistry (e.g. $p$CO$_2$, pH and $\Omega$) and include the following: marine ecosystem photosynthesis and respiration (or net community production that includes primary production and remineralization of organic carbon); air-sea CO$_2$ gas exchange; warming and sea-ice loss, and; changes in the inputs of terrestrial freshwater and organic carbon. When integrated, these processes act to either mitigate or enhance the impact of anthropogenic ocean acidification – resulting from uptake of anthropogenic CO$_2$ from the atmosphere – in surface and subsurface waters, respectively, of the Arctic Ocean.
2 Methods

2.1 Sampling

Summer seawater carbonate chemistry samples were collected on multiple CTD-hydrocasts from the East Siberian, Chukchi, Beaufort Sea shelves and at Bering Strait from 2009 to 2011. These three expeditions included: (1) RUSALCA 2009 (4–29 September 2009); (2) ICESCAPE 2010 (18 June to 16 July 2010), and; (3) ICESCAPE 2011 (28 June to 24 July 2011). At each CTD-hydrocasts, profiles of salinity, temperature, depth, total alkalinity (TA) and dissolved inorganic carbon (DIC) were measured. Samples for TA and DIC were collected according to Dickson et al. (2007).

2.2 Sample analyses

Samples from the RUSALCA 2009 cruise were analyzed at Bermuda Institute of Ocean Sciences (BIOS), while ICESCAPE cruise samples were analyzed on board (TA in 2010; TA and DIC in 2011). Replicate samples for all 3 cruises were also analyzed at BIOS. TA and DIC analyses followed methods described by Dickson et al. (2007). TA was determined by a potentiometric technique using a VINDTA 2S (Marianda, Germany). DIC was determined using a standard coulometric technique on the VINDTA 3C and SOMMA system (Bates et al., 1996) and also using a small-volume (~1 ml sample size) using an infrared based instrument (AIRICA; Marianda Co, Germany). The 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 µmol kg\(^{-1}\)).

2.3 Data computations and visualization

Seawater carbonate system parameters including \(p\text{CO}_2\) (µatm), \(\Omega_{\text{aragonite}}\) and \(\Omega_{\text{calcite}}\) and pH (total scale) were computed using CO2calc software (Robbins et al., 2011) and salinity (S), temperature (T) [°C], TA and DIC data. 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 $\Omega_{\text{aragonite}}$ and $\Omega_{\text{calcite}}$ to be $+0.02$ (assuming a DIC and TA error of $\pm2 \mu$mol kg$^{-1}$).

Ocean Data View 4 (ODV; Schlitzer, 2011) software was used to visualize the data. Both composite scatter and contour plots of 2009–2011 data are shown in addition to individual years of data. In the paper we show surface data (typically 0–10 m depth and represents the uppermost Niskin sampler tripped at each CTD-Hydrocast station). The bottom water data represents samples typically within 5 m of the seafloor (deepest Niskin sampler tripped at each CTD-Hydrocast station) at shelf and slope stations with water depths less than 200 m. Data from the 2002–2004 Shelf-Basin Interactions project in the Chukchi Sea (e.g. Bates et al., 2005a, b; Bates, 2006) are also examined for comparison.

3 Results

The physical and biochemical conditions of the Western Arctic Ocean are strongly influenced by northward transport of Pacific Ocean through Bering Strait (Woodgate and Aagaard, 2005a; Cooper et al., 1997) and freshwater runoff from the rivers into the Arctic (Anderson et al., 2011). The inflow of Pacific Ocean water ($\sim 1$ Sv during summer; $1$ Sv $= 10^6$ m$^3$ s$^{-1}$) into the Chukchi Sea is comprised of Alaskan Coastal Current (ACC), Bering Sea shelf and Anadyr Current waters, with subsequent outflow through submarine canyons such as Herald Valley and Barrow Canyon, partly into the Canada Basin and partly eastward along the narrow Beaufort Sea shelf. There is also an episodic inflow into the Chukchi Sea from the East Siberian Sea through Long Strait via the Siberian Coastal Current (SCC; Weingartner, 1999). During our observations from 2009–2011, summertime temperatures varied from $-1.8$ to $7.5$°C and salinity from 24–34 (Fig. 2).
3.1 Seawater carbonate chemistry variability across the Western Arctic

Seawater carbonate chemistry variability across the Western Arctic. Seawater carbonate chemistry was also highly variable across this region. Seawater TA and DIC concentrations from the three expeditions generally varied between 1400–2300 µmol kg\(^{-1}\) (Fig. 2b; DIC only shown in the paper). Surface water values typically ranged from 1850–2250 µmol kg\(^{-1}\) for TA and 1800–2200 µmol kg\(^{-1}\) for DIC with higher values in the Chukchi Sea compared to the East Siberian Sea, Beaufort Sea and offshore in the Canada Basin (Fig. 2a). The lowest TA and DIC concentrations were generally observed in Long Strait close to the Russian coastline. These waters originate in the East Siberian Sea and are carried eastward into the Chukchi Sea with the Siberian Sea Current (SSC). The low TA and DIC contents of the SSC waters result from considerable freshwater input from river runoff into the ESS and sea-ice melt (Semiletov et al., 2004). Very low TA and DIC concentrations were also observed on the Western Beaufort Sea shelf, and likely reflect waters with seawater carbonate chemistry diluted by very low TA and DIC in Mackenzie River freshwater outflow onto the shelf and into the Canada Basin (Macdonald et al., 2002). Subsurface values on the shelves and in the halocline of the Canada Basin ranged between 2150–2300 µmol kg\(^{-1}\) for TA and 2050–2250 µmol kg\(^{-1}\) for DIC (Fig. 3a).

3.2 Surface \(pCO_2\) and pH variability

Seawater \(pCO_2\) and pH conditions across the Western Arctic were highly variable ranging from < 100 to > 900 µatm and 7 to 8.5, respectively (Figs. 2c, d, 3b, 4). Surface waters had \(pCO_2\) values typically lower than atmospheric values (\(~ 150–300\) µatm) across much of the Chukchi Sea in 2009–2011 (Fig. 4a, c, e). The lowest seawater \(pCO_2\) values were observed close to Herald Valley in the Westernmost Chukchi Sea in 2009 (Fig. 4a: < 200 µatm) and across the Chukchi Sea in 2010 and 2011 (Fig. 4c, e: < 200 µatm). Extremely low seawater \(pCO_2\) concentrations (< 80 µatm) were observed in the region of the under sea-ice phytoplankton bloom observed in the NW Chukchi
Sea in 2010 and 2011 (Arrigo et al., 2012; Fig. 4c, e). These values represent some of the lowest seawater $pCO_2$ values observed anywhere in the global ocean. Seawater pH ranged from 8.2 to 8.4 in most surface waters (Fig. 2d). The exceptions were very high $pCO_2$ (> 600 µatm) and low pH (7 to 7.5) observed in the East Siberian Sea north of Wrangel Island and in the Siberian Sea Current outflowing from the East Siberian Sea into the Chukchi Sea through Long Strait in 2009 (Figs. 2c, d, 3b). High $pCO_2$ has been observed in the Siberian Sea Current previously (Fransson et al., 2009). This finding is not surprising given the very high seawater $pCO_2$ values (~ 500 to ~ 1500 µatm) in the near-shore bays and estuaries of the East Siberian Sea (e.g. Tiksi Bay) and Kolyma River outflow (Semiletov et al., 1999, 2007; Pipko et al., 2008).

3.3 Subsurface $pCO_2$ and pH variability

Subsurface seawater $pCO_2$ was much higher (~350–900) and pH much lower (~7.3–7.8) when compared to surface waters (Figs. 2c, d, 3b, 4b, d, f). Seawater carbonate chemistry differences between surface and bottom waters were as much as 600–800 µatm for seawater $pCO_2$ and 1 to 1.5 for pH, respectively. This reflects strong physical stratification between the surface mixed layer and subsurface waters. High seawater $pCO_2$ values greater than 400 µatm were observed in bottom waters close to the seafloor across the Southern Chukchi Sea and East Siberian Sea in 2009 (Fig. 4b), and in the Northern Chukchi Sea in 2010 and 2011 (Fig. 4d, f). Interestingly relatively low subsurface $pCO_2$ (~250–400 µatm) was observed at Bering Strait and Southern Chukchi Sea, presumably reflecting inflow of low $pCO_2$ water from the Bering Sea shelf (Bates et al., 2011a).

3.4 Saturation states of $\Omega_{\text{calcite}}$ and $\Omega_{\text{aragonite}}$

The saturation states of $\Omega_{\text{calcite}}$ and $\Omega_{\text{aragonite}}$ are useful indicators of the status of ocean acidification on the Western Arctic shelves. The $\Omega$ values were highly variable with $\Omega_{\text{calcite}}$ and $\Omega_{\text{aragonite}}$ ranging from < 0.5 to 5.5 and < 0.5 to 4, respectively (Figs. 2e,
f, 3c, d). In surface waters across the Western Arctic, $\Omega_{\text{calcite}}$ and $\Omega_{\text{aragonite}}$ values were typically greater than 1 (Fig. 5a, c). Across much of the Chukchi Sea, $\Omega_{\text{calcite}}$ and $\Omega_{\text{aragonite}}$ values ranged from 3.5–5 and 2 to 3 (Fig. 5) with surface waters highly oversaturated with respect to CaCO$_3$ minerals. Elsewhere, $\Omega_{\text{calcite}}$ and $\Omega_{\text{aragonite}}$ values were lower in the Westernmost Chukchi Sea and East Siberian Sea ranging from 2–3 and 1.5 to 2, respectively (Fig. 5), with lower values in Long Strait. The low $\Omega_{\text{calcite}}$ and $\Omega_{\text{aragonite}}$ values in the East Siberian Sea are not unexpected (Anderson et al., 2010, 2011) given that surface waters have high seawater $pCO_2$ (and low pH) values that have been attributed primarily to the remineralization of organic matter introduced to the ESS from Siberian Rivers (e.g. Anderson et al., 1990; Cauwet and Sidorov, 1996; Kattner et al., 1999; Anderson et al., 2009). In contrast to surface waters of the Western Arctic shelves, surface/mixed layer waters in the Canada Basin were close to 1 to 1.5 for $\Omega_{\text{calcite}}$ and even below 1 for $\Omega_{\text{aragonite}}$. Such low saturation states, especially for aragonite, have been observed in polar mixed layer waters of the Canada Basin previously (Jütterstrom and Anderson, 2010) and reflect contributions of high $pCO_2$, low pH/$\Omega$ sea-ice melt waters and freshwaters from the Mackenzie River.

The saturation states of calcite and aragonite in subsurface waters were much lower than surface water values. Across much of the Chukchi Sea, $\Omega_{\text{calcite}}$ and $\Omega_{\text{aragonite}}$ values ranged from 1 to 1.5 and <1 to 2, respectively (Figs. 5b, d, 6). In many regions of the Chukchi Sea and East Siberian Sea, the near seafloor $\Omega_{\text{calcite}}$ were close to 1 while $\Omega_{\text{aragonite}}$ was often <1. This was particularly evident in the East Siberian Sea with remineralization of organic matter back to CO$_2$ in subsurface waters the likely primary cause for reducing $\Omega$ values. In the Northern Chukchi Sea, the low $\Omega$ values are co-located in areas with high rates of euphotic zone marine phytoplankton primary production and thus likely reflect subsurface remineralization of vertically exported organic matter. Elsewhere in the Southern Chukchi Sea, the near seafloor $\Omega$ values were higher (Fig. 6), and presumably reflect input of relatively lower $pCO_2$ and higher pH/$\Omega$ waters inflowing from the Bering Sea shelf.
4 Discussion

4.1 Surface enhancement and subsurface suppression of \( \text{CaCO}_3 \) saturation states

The 2009–2011 RUSALCA and ICESCAPE expeditions into the Western Arctic revealed that the saturation states for \( \Omega_{\text{calcite}} \) and \( \Omega_{\text{aragonite}} \) of bottom waters were seasonally close to or lower than 1 during the sea-ice free summertime in the Western Arctic. As with previous observations from the early 2000’s during the SBI project (Bates et al., 2009), surface water enhancement and subsurface water suppression of \( \Omega \) was observed, respectively. The causes for the seasonal divergence in \( \Omega \) values for surface and subsurface waters of the Western Arctic have been previously ascribed to feedbacks between biological processes and seawater carbonate chemistry and as evidence for a Phytoplankton-Carbonate Saturation State (“PhyCaSS”) interaction (Bates et al., 2009). Similar seasonal interactions between biological processes and seawater carbonate chemistry have subsequently been observed on the Bering Sea shelf (Mathis et al., 2010). Interactions between seawater carbonate chemistry and biological processes have also been observed in other environments, including the open ocean Pacific (Feely et al., 1988), in coral reefs (Bates et al., 2010) and anthropogenically perturbed estuaries (Feely et al., 2010).

In the PhyCaSS interaction, the seasonal uptake of \( \text{CO}_2 \) by phytoplankton photosynthesis in surface waters – in those areas with very high rates of marine phytoplankton primary production measured during the sea-ice free period (Hill and Cota, 2005) – substantially reduce seawater DIC and \( p\text{CO}_2 \). Photosynthesis or phytoplankton primary production thus acts to increase the pH and \( \Omega \) of surface waters, thereby seasonally mitigating the long-term reduction of \( \Omega \) due to gradual ocean acidification (Bates et al., 2009). In the Western Arctic, summertime high rates of phytoplankton primary production also result in large vertical and horizontal export of organic carbon on polar shelves such as the Chukchi Sea (Moran et al., 2005; Bates et al., 2005). Remineralization of organic matter back to \( \text{CO}_2 \) was invoked as explanation for the
seasonal subsurface reduction of pH and Ω in subsurface waters, with this biological process adding to the reduction of Ω due to gradual ocean acidification (Bates et al., 2009). In this study, as explanation for observations collected during the RUSALCA and ICESCAPE projects, we expand on the simple PhyCaSS treatment to include other physico-biogeochemical processes that can impact seawater carbonate chemistry, pH and Ω, including: air-sea CO₂ gas exchange, and sea-ice melt and freshening. Potential changes in physico-biogeochemical conditions are discussed later in light of the apparent expansion of the low Ω bottom water in the Western Arctic during the last decade.

Seawater carbonate chemistry, pH and saturation states for CaCO₃ can be influenced by several physical, chemical, and biological factors (Fig. 7a). Those processes that act to reduce DIC and pCO₂, and increase pH and Ω include the following: (a) photosynthesis or primary production (i.e. net ecosystem production, NEP), and; (b) loss of CO₂ from surface waters due to air-sea gas exchange of CO₂ in those areas that are sources of CO₂ to the atmosphere (see Fig. 7a). Those processes that act to increase DIC and pCO₂, and decrease pH and Ω include the following: (c) respiration or remineralization of organic carbon back to CO₂, and; (d) gain of CO₂ in surface waters due to air-sea gas exchange of CO₂ in those areas that are oceanic sinks of CO₂ from the atmosphere (Fig. 7a). Other processes having relatively minor impacts on pH and Ω include: (e) calcification and dissolution of CaCO₃; (f) warming or cooling (for example, a 10°C temperature change imparts a 0.1 change in Ω), and; (g) freshening of the mixed layer due to sea-ice melt (Fig. 7a).

Here, we examine changes in Ω for surface and subsurface waters that are imparted by ocean acidification due to anthropogenic CO₂ uptake (δΩOA). Superimposed on gradual changes in Ω caused by ocean acidification are seasonal changes influenced by the following; (1) biological processes in the water column during the sea-ice free growing season (i.e. δΩBIOL) which includes photosynthesis/respiration, expressed as rate terms of primary production or net community production; (2) air-sea gas exchange
of CO₂ (δΩGASEX), and; (3) warming/cooling of waters during the sea-ice free summertime and sea-ice covered period (δΩTEMP).

In surface waters, the potential changes due to long-term and seasonal forcings of Ω values (ΔΩSURFACE) can be expressed by the following:

$$\Delta \Omega_{SURFACE} = \delta \Omega_{OA} + \delta \Omega_{BIOL} + \delta \Omega_{GASEX} + \delta \Omega_{TEMP} \quad (1)$$

In Fig. 8, δΩTEMP is shown as δΩWARM and δΩCOOL to reflect the impact of warming and cooling on surface waters. Other factors, thought to have minor impacts on surface Ω are discussed later. In subsurface waters of the Western Arctic, air-sea CO₂ gas exchange and temperature changes are less important and changes in Ω (i.e. ΔΩSUBSURFACE) expressed as:

$$\Delta \Omega_{SUBSURFACE} = \delta \Omega_{OA} + \delta \Omega_{BIOL} \quad (2)$$

We thus compare and contrast changes in Ω in surface and subsurface waters to determine if potentially corrosive subsurface waters are a signal of the Anthropocene (i.e. ocean acidification) that is compounded by natural physico-biogeochemical processes (Figs. 7a, 8a; albeit that these processes are likely anthropogenically perturbed).

The contribution of ocean acidification (δΩOA) to Ω changes in the Western Arctic. We estimate the present-day contribution of ocean acidification due to uptake of anthropogenic CO₂ (i.e. δΩOA) as follows. Recent estimates of the global ocean inventory of anthropogenic CO₂ range from 120 to 160 Pg C (Sabine et al., 2004; Khatiwala et al., 2009). In the Arctic Ocean, the inventory of anthropogenic CO₂ is approximately 2.5 to 3.3 Pg C or about 2 % of the global ocean inventory (Tanhua et al., 2009). Previous studies have indicated that the inventory of anthropogenic CO₂ in the upper ocean of the Arctic is approximately 35–40 µmol kg⁻¹ of DIC. Stated another way, the mean DIC content of polar surface water is estimated to be 35–40 µmol kg⁻¹ higher at present compared to pre-industrial times with the consequence of reducing pH and Ω. Given typical salinity, temperature, DIC and TA values for surface and subsurface waters observed during summertime of 2009 to 2011, we estimate that ocean acidification due
to anthropogenic CO$_2$ uptake has reduced $\Omega$ values by $\sim$ 0.4 to 0.6 for $\Omega_{\text{calcite}}$ and $\sim$ 0.3 to 0.4 for $\Omega_{\text{aragonite}}$ since pre-industrial times. A schematic seasonal time series for $\Omega_{\text{aragonite}}$ is shown with $\delta \Omega_{\text{OA}}$ denoted by the dashed blue line for both surface and subsurface waters (Fig. 8b, c; a similar time series for $\Omega_{\text{calcite}}$ is not shown but would be scaled by approximately 150%). Superimposed on the long-term changes due to ocean acidification are changes in $\Omega$ imparted by seasonal processes (Fig. 8).

Potential physical and biological factors influencing seasonal changes in $\Omega$ in surface waters. In surface waters, marine phytoplankton primary production or net community production during the sea-ice free growing season (i.e. $\delta \Omega_{\text{BIOL}}$) increase $\Omega$ values (Fig. 8a, b). In the Chukchi Sea, very high rates of marine phytoplankton primary production or net community production (NCP; 0.8–1.2 g C m$^{-2}$ d$^{-1}$ and greater than 4 g C m$^{-2}$ d$^{-1}$; Bates et al., 2005, references therein) have been observed in the early 2000s, and similarly during the 2009–2011 period (Arrigo et al., 2012). In the early 2000s, the net summertime drawdown in salinity normalized DIC due to NCP typically ranged from 100–200 µmol kg$^{-1}$ in the Chukchi Sea. During the 2009–2011 period, we estimated that the DIC drawdown due to NCP similarly ranged from 100–200 µmol kg$^{-1}$ (average of $\sim$ 130 µmol kg$^{-1}$ lower DIC values in surface waters compared to our best estimates of earliest season winter/spring DIC values below the mixed layer). This drawdown of DIC is equivalent to an average increase of $\Omega_{\text{aragonite}}$ by approximately 1.3 (Fig. 8a, b).

There are, however, counteracting processes reducing $\Omega$ in surface waters, such as ocean uptake of CO$_2$ from the atmosphere during the sea-ice free period (i.e. $\delta \Omega_{\text{GASEX}}$). Previous estimates of air–sea CO$_2$ flux range from 10 to 40 mmol CO$_2$ m$^{-2}$ d$^{-1}$ (Bates and Mathis, 2009, references therein). This uptake is equivalent to an increase in DIC of surface waters (i.e. 0–30 m deep) of $\sim$ 30–130 µmol kg$^{-1}$ with the average equivalent to a reduction in $\Omega_{\text{aragonite}}$ of $\sim$ 0.7. A minor contributor is seasonal warming of surface waters ($\delta \Omega_{\text{TEMP}}$ or denoted as $\delta \Omega_{\text{WARM}}$ in Fig. 8b) during sea-ice retreat and melt which is estimated to increase $\Omega_{\text{aragonite}}$ by...
~ 0.01 per °C. With surface waters exhibiting warming by ~ 1 °C to ~ 8 °C, the maximum increase in $\Omega_{\text{aragonite}}$ due to warming is likely less than 0.1 (Fig. 8b).

Other potential physical and biological factors have negligible or undetermined impact on $\Omega$. Calcification or dissolution of CaCO$_3$ within the benthic community has minor impact on $\Omega$ (Fig. 7a) and there is little evidence for water-column phytoplankton calcification. Vertical mixing or diffusion is likely to reduce the $\Omega$ of surface waters through entrainment of high $p$CO$_2$, low pH/$\Omega$ subsurface waters is assumed here to have minor impact on $\Omega$. Strong physical stratification of the water-column is likely to suppress vertical mixing and diffusion during the sea-ice free period while strong mixing and homogenization during sea-ice advance in September and October will “reset” seasonally imparted changes in pH and $\Omega$ to “winter” conditions (Fig. 8a). The contribution of sea-ice melt to surface waters also appears to have minor impact on $\Omega$. In Fig. 5, the $\Omega$ values of surface waters does not change substantially despite considerable freshening. Sea-ice melt water TA and DIC values observed in the Chukchi Sea tend to be low (~ 80 to 500 µmol kg$^{-1}$) with very low $\Omega$ values of < 0.1 (N. R. Bates, unpublished data). This suggests that sea-ice melt should reduce surface water $\Omega$ (Fig. 7a), but the relative contribution of sea-ice melt water TA and DIC compared to the TA and DIC content of surface seawater is quite small (< few %).

Summing these potential forcings, it appears that there is a net increase in $\Omega_{\text{aragonite}}$ of ~ +0.3 primarily driven by NCP (i.e. $\Delta\Omega_{\text{SURFACE}}[+0.3] = \delta\Omega_{\text{OA}}[-0.3] + \delta\Omega_{\text{BIOL}}[+1.3] + \delta\Omega_{\text{GASEX}}[-0.7] + \delta\Omega_{\text{TEMP}}[-0.1]$). Thus, seasonal summertime biological production appears to more than offset the reduction in $\Omega_{\text{aragonite}}$ values due to ocean acidification (Figs. 7b, 8b).

Potential physical and biological factors influencing seasonal changes in $\Omega$ in subsurface waters: in subsurface waters of the Western Arctic, the DIC content of subsurface waters appears to increase by about 20–30 µmol kg$^{-1}$, equivalent to a reduction in $\Omega_{\text{aragonite}}$ of about 0.2 to 0.3. Summing these potential forcings, it appears that there is a net decrease in $\Omega_{\text{aragonite}}$ of approximately ~0.6 compared to preindustrial times primarily driven by ocean acidification and remineralization (i.e. $\Delta\Omega_{\text{SUBSURFACE}}[-0.6] =$
δΩ_{OA} [-0.3] + δΩ_{BIOL} [-0.3]). On seasonal timescales, it seems that while ocean acidification brings subsurface water Ω values close to a value of one, it is biologically mediated suppression of Ω values that tips the balance and reduces Ω values below a value of one. Thus, it is likely that the presence of corrosive waters on the Western Arctic shelves is a recent phenomenon, a signal of the Anthropocene, and one that is exacerbated by natural biological processes. Such seasonal transitions in Ω that are compounded by natural biological processes have also been shown to occur in the Bering Sea (Mathis et al., 2009, 2011a, b) and in the East Siberian Sea (Anderson et al., 2010).

This analysis also suggests that there is an imbalance of the δΩ_{BIOL} term for surface and subsurface waters of the Western Arctic (i.e. ΔΩ_{BIOL} [+1.0] = δΩ_{SURFACE}^{BIOL} [+1.3] + δΩ_{SUBSURFACE}^{BIOL} [-0.3]). This imbalance is likely driven by unquantified terms such as the slow release of CO_{2} from shelf sediments (due to remineralization of sedimentary organic carbon and benthic ecosystem respiration; e.g. Grebmeier et al., 2008) and offshore horizontal export of organic carbon. The former process is likely to reduce Ω in bottom waters over the sea-ice covered period when the water column on the shelf is well mixed. For the latter process, previous studies have shown large plumes of suspended particulate organic matter being exported off the Chukchi Sea shelf into the halocline of the Canada Basin (e.g. Bates et al., 2005). The implication of these observations is that the Ω values of halocline waters in the Canada Basin are reduced from remineralization of shelf derived, allochthonous organic carbon.

Is there any change in the distribution of low Ω bottom water in the Western Arctic? The 2009 to 2011 RUSALCA/ICESCAPE data revealed large areas of Ω_{aragonite} undersaturation across the Chukchi Sea (Fig. 5). The summer Ω_{aragonite} values decreased to levels lower than observed in previous years in the early 2000’s during the SBI project (Bates et al., 2009). In the early 2000’s, undersaturated bottom waters were only observed on the northern slope of the Chukchi Sea rather than across the shelf at present. It appears that low Ω bottom water has expanded across much of the Western
Arctic but given the paucity of survey and time-series data, it is difficult to assess if this is a recent phenomena driven by environmental change in the Arctic.

In the early 2000s, the decrease in DIC contents in surface waters due to phytoplankton primary production increased $\Omega_{\text{aragonite}}$ by a mean value of $\sim 0.3$ (Bates et al., 2009). In the late 2000s, the average increase of $\Omega_{\text{aragonite}}$ in surface water was approximately $\sim 0.6$ (although not shown, the net impact on $\Omega_{\text{calcite}}$ is about 0.9), presumably reflecting increases in NCP (Arrigo et al., 2012) and reduction in ocean uptake of CO$_2$ (Cai et al., 2010, 2012) and thus the balance of $\delta \Omega_{\text{BIOL}}$ and $\delta \Omega_{\text{GASEX}}$. Arrigo et al., 2008 have shown significant increases in rates of summertime phytoplankton primary production (and a longer growing season) in surface waters across the Arctic over the last two decades. Model studies also suggest that coastal shelf phytoplankton primary production has increased over the last few decades (e.g. Manizza et al., 2011). The ICESCAPE expeditions in 2010 and 2011 found extensive blooms of phytoplankton under the sea-ice of the Central Chukchi Sea (Arrigo et al., 2012) while some of the lowest seawater values of seawater $p$CO$_2$ ever observed in the global ocean (i.e. $< 100 \mu$atm) have been measured in this area (e.g. Bates et al., 2011). The implications of these studies are that if rates of primary production are higher in the Western Arctic, then surface water enhancement of $\Omega$ is likely as well as concomitant reduction of $\Omega$ values – presumably linked to increased vertical export of organic carbon and subsequent benthic respiration and remineralization – in bottom waters present on the shelf. Potentially counteracting this phenomena is the likelihood that a longer growing season, lower surface seawater $p$CO$_2$ and expanded areas of seasonal ice free areas may have enhanced the uptake of CO$_2$ from the atmosphere through gas exchange. In the central basin of the Arctic, increases in surface seawater $p$CO$_2$ – and presumably reduction in $\Omega$ – due to enhanced air-sea CO$_2$ gas exchange since the major sea-ice loss event in 2007 appears to have reduced the sink of CO$_2$ into surface waters over the last few years (Cai et al., 2010, 2012). It seems clear that the geographic distribution and seasonal timings of seawater carbonate chemistry, pH and $\Omega$ variability is rapidly changing in a transitioning Arctic Ocean.
4.2 Potential impact on marine ecosystems

Considering the fact that $\Omega_{\text{aragonite}}$ and $\Omega_{\text{calcite}}$ are generally lower in the high-latitude regions (Doney et al., 2009), gradual ocean acidification in the future may have an earlier impact on polar and subpolar benthic calcifying organisms compared to temperate and tropical species (e.g. Doney, 2009; Bates et al., 2009; Mathis et al., 2011a, b). The seasonal presence of potentially corrosive bottom waters for CaCO$_3$ may have a variety of direct impacts on juvenile to adult benthic calcifying organisms, and their associated ecosystems. For example, CaCO$_3$ undersaturation can be harmful especially in early development stages of calcifying organisms (Lischka et al., 2011). Rapid changes in seawater chemistry of the Arctic Ocean might cause a decrease in diversity of calcifying organisms (both benthic and planktonic), with consequences for trophic flow/ecosystem structure (Walther, 2010). The most recent study on mineralogy of skeletons of bimineralic calcifiers exposed to seawater high-CO$_2$ conditions showed increases of calcite to aragonite ratio (Ries, 2011), favoring calcitic organisms. Experimental calcification studies on Arctic Ocean pteropods (which secrete aragonite shells) showed a 28% decrease in calcification projected for 2100 (Comeau et al., 2009). Higher solubility of aragonite compared to calcite makes this form of CaCO$_3$ mineral more vulnerable to dissolution in higher pH/lower $\Omega$ conditions. Given that the seawater chemistry of the Arctic Ocean is controlled by complex physical and biological processes that are vulnerable to change (Kaltin and Anderson, 2005), quantifying the responses of calcifying organisms to ocean acidification and seasonally changing $\Omega_{\text{aragonite}}$ has great importance in the future (Orr et al., 2005; Walther et al., 2009; Comeau et al., 2009; Smith, 2009; Lischa et al., 2011).

5 Conclusions

Previous models predict that undersaturation with respect to aragonite will occur in the polar mixed layer of the Arctic by 2016, with the polar shelves transitioning later
this century (Steinacher et al., 2009). Observations have shown previously that the polar mixed layer (Yamamoto-Kawai et al., 2009) and small areas of the Chukchi Sea shelf (Bates et al., 2009) already exhibit \( \Omega \) values less than one. In this study, we find that large areas of the shelf benthos in the Western Arctic are seasonally exposed to bottom waters that are undersaturated with respect to CaCO\(_3\) minerals and thus potentially corrosive for biogenic or sedimentary CaCO\(_3\). These results suggest that the area of undersaturation for aragonite and even calcite has expanded to most of the Western Arctic shelf.

The potential causes for these changes in seawater chemistry in the Western Arctic relate to ocean acidification and seasonal biological/physical processes in the region. Ocean acidification due to anthropogenic CO\(_2\) uptake appears to have reduced \( \Omega \) values by \(~0.4\) to \(0.6\) for \( \Omega_{\text{calcite}} \) and \(~0.3\) to \(0.4\) for \( \Omega_{\text{aragonite}} \) since pre-industrial times. However, superimposed on the ocean acidification influence on \( \Omega \), are seasonal biological and physical processes that drive \( \Omega \) values in different directions for surface and subsurface waters. As such, these processes mitigate and enhance the impact of ocean acidification seasonally in surface and subsurface waters, respectively. Future changes in \( \Omega \) values on the Western Arctic shelves appear unpredictable due to uncertainties about the extent of sea-ice loss, warming, changes in marine phytoplankton production and air-sea CO\(_2\) gas exchange in the region. Expansion of the sea-ice free region, increased surface water warming and increased growing season may facilitate future increases in marine phytoplankton primary production/NCP that in turn could exacerbate subsurface suppression of \( \Omega \) values due to increased vertical export of organic carbon. Counteracting this may be increased air-sea CO\(_2\) gas exchange in the region (due to longer sea-ice free periods and increased marine phytoplankton primary production/NCP) that would act to increase \( \Omega \) values. Such predictions are difficult to make given that air-sea CO\(_2\) gas exchange rates appear to be rapidly changing in the Arctic Ocean (Bates and Mathis, 2009). The deep Arctic Ocean basins (Canada and Eurasian basins) and surrounding shallow coastal seas (e.g. Barents, Laptev, Kara, East Siberian, Chukchi, and Beaufort Seas, and Canadian Archipelago) constitutes
only ~ 4% of global ocean area (Pipko et al., 2011). In the last couple of decades, the summertime retreat of summer sea-ice from the Arctic polar shelves due to enhanced melting has exposed surface waters to the atmosphere and allowed the shallow coastal seas of the Arctic Ocean such as the Chukchi and Barents Sea (and Bering Sea) to become significant sinks for atmospheric CO₂ (Murata and Takizawa, 2003; Bates, 2006; Chen and Borges, 2009). Such changes may have temporarily increased the ocean uptake of CO₂ into the Arctic (Bates et al., 2006) such that the Arctic Ocean now contributes approximately 5–14% of the annual global CO₂ uptake (Bates and Mathis, 2009) and as a consequence suppressed Ω values on the shelves. However, since the major sea-ice loss event in 2007, observations indicate that the Arctic may have transitioned back to a smaller sink for CO₂ (Cai et al., 2010, 2012) with potentially less impact on Ω, illustrating the dynamic and rapidly changing nature of the Arctic environment.

In this study, we have not addressed any observed impact on benthic organisms or ecosystems, but, it is clear that the combination of ocean acidification and seasonal biological/physical processes combine to seasonally produce conditions that are potentially unfavorable for calcifying organisms and merit future monitoring of the Western Arctic shelves.

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Fig. 1. Map of the Arctic Ocean showing the stations occupied during the cruises according to the cruise year: RUSALCA 2009 (4–29 September 2009; purple); ICESCAPE 2010 (18 June to 16 July 2010; green) and ICESCAPE 2011 (28 June to 24 July 2011; red).
Fig. 2. Summertime scatter plots of depth and seawater carbonate chemistry superimposed on temperature versus salinity compiled for years 2009–2011 in the Western Arctic Ocean. The panels include: (A) depth (m); samples from depths greater than 200 m are denoted as a uniform color and represent offshelf samples in the Canada Basin; (B) dissolved inorganic carbon (DIC; µmol kg$^{-1}$); (C) $p$CO$_2$ (µatm); (D) pH; (E) $\Omega$$_{\text{calcite}}$, and; (F) $\Omega$$_{\text{aragonite}}$. The TS diagram shows the envelope of surface water in the Western Arctic (T: $-1.5–7.5^\circ$C; S: 33–24), while subsurface waters on the Chukchi Sea were more confined with regard to physical properties (T: $-1.5–1^\circ$C; S: 34–32). Both panels also show the influence of the Atlantic Intermediate Waters (AIW; Emery, 2003) observed in the Canada Basin (T: $-1.5–3^\circ$C; S: 34.7–34.9).
Fig. 3. Summertime scatter plots of depth, $p$CO$_2$, $\Omega_{\text{calcite}}$, and $\Omega_{\text{aragonite}}$ superimposed on DIC versus TA compiled for years 2009–2011 in the Western Arctic Ocean. The panels include: (A) depth (m); samples from depths greater than 200 m are denoted as a uniform color and represent offshelf samples in the Canada Basin; (B) $p$CO$_2$ (µatm); (D) pH; (C) $\Omega_{\text{calcite}}$, and; (D) $\Omega_{\text{aragonite}}$. 

Shelf water undersaturation of CaCO$_3$ in the western Arctic; July 27, 2012.
Fig. 4. Summertime surface and bottom water maps of seawater $p$CO$_2$ (µatm) for individual years in 2009, 2010 and 2011 in the Western Arctic Ocean. Surface seawater $p$CO$_2$ data is plotted in panels (A), (C) and (E) while bottom water seawater $p$CO$_2$ is plotted in panels (B), (D) and (F).
Fig. 5. Composite (2009–2011) summertime maps of surface and bottom water $\Omega_{\text{calcite}}$ and $\Omega_{\text{aragonite}}$ in the Western Arctic Ocean. The panels include: (A) surface $\Omega_{\text{calcite}}$; (B) bottom water $\Omega_{\text{calcite}}$; (C) surface $\Omega_{\text{aragonite}}$ and; (D) bottom water $\Omega_{\text{aragonite}}$. 
Fig. 6. Summertime maps of bottom water $\Omega_{\text{calcite}}$ and $\Omega_{\text{aragonite}}$ for individual years in 2009, 2010 and 2011 in the Western Arctic Ocean. $\Omega_{\text{calcite}}$ data is plotted in panels (A), (C) and (E) while $\Omega_{\text{aragonite}}$ is plotted in panels (B), (D) and (F).
Fig. 7. Schematic of Ω changes due to physical and biological processes superimposed onto typical Western Arctic TA and DIC variability (A) and with net seasonal changes (B). The arrows denote direction of Ω change due to individual/combined processes but arrow length does not denote magnitude of Ω change. Photosynthesis, primary production and loss of CO₂ from surface waters due to gas exchange increase Ω. Calcification/dissolution of CaCO₃, warming and cooling, and freshening of the mixed layer have minor impact on Ω. Respiration, remineralization of organic carbon to CO₂ and gain of CO₂ by surface waters due to gas exchange decrease Ω. The purple, blue, dark green, light green and yellow lines denote Ωaragonite values of 0.5, 1, 2, 3, and 4, respectively. The dashed line encompasses the typical TA and DIC values of Western Arctic seawater from 2009–2011.
Fig. 8. Schematic annual time-series of seawater chemistry on the Western Arctic shelves to show the impact of ocean acidification and biological/physical processes on $\Omega$ values for aragonite. In all three panels, bottom axis J to D denotes January to December. (A) annual schematic of changes in $\Omega_{\text{aragonite}}$ on shelf waters of the Western Arctic Ocean. The sea-ice free period is approximately 3–4 months. Shelf waters are well mixed during the sea-ice covered period with mixed layer developing in late spring due to warming and sea-ice melt, and erosion of the mixed layer in September–October due to convective mixing and homogenization of shelf waters during fall cooling and sea-ice advance. The $\delta\Omega_{\text{OA}}$, $\delta\Omega_{\text{BIOL}}$, $\delta\Omega_{\text{GASEX}}$, and $\delta\Omega_{\text{TEMP}}$ terms are shown in the figure with general direction of forcing of $\Omega$. (B) annual schematic changes in $\Omega_{\text{aragonite}}$ of surface waters. The red line denotes total change in $\Omega$ (i.e. $\Delta\Omega_{\text{SURFACE}}$) while other terms are denoted as follows: $\delta\Omega_{\text{OA}}$ (cyan), $\delta\Omega_{\text{BIOL}}$ (green), $\delta\Omega_{\text{GASEX}}$ (orange), and $\delta\Omega_{\text{TEMP}}$ (purple) terms. (C) annual schematic changes in $\Omega_{\text{aragonite}}$ of subsurface waters. The red line denotes total change in $\Omega$ (i.e. $\Delta\Omega_{\text{SUBSURFACE}}$) while other terms are denoted as follows: $\delta\Omega_{\text{OA}}$ (cyan), $\delta\Omega_{\text{BIOL}}$ (green).