

Seasonal Observations of carbonate chemistry and ocean acidification in 2011

Prepared for

ConocoPhillips Company
P.O. Box 100360
Anchorage, AK 99510-0360

Shell Exploration & Production Company
3601 C Street, Suite 1334
Anchorage, AK 99503

And

Statoil USA E & P, Inc
2700 Gambell St
Anchorage, AK 99507

Final Report

Prepared by:

Jeremy T. Mathis
Assistant Professor
Chemical Oceanography
University of Alaska Fairbanks
School of Fisheries and Ocean Sciences
245 O'Neill BLDG
Fairbanks, AK 99775-7220
Phone: (907) 474-5926
jtmathis@alaska.edu

October 2012

Executive Summary

Samples were collected and analyzed for dissolved inorganic carbon and total alkalinity in August, September, and October in the Berger, Klondike, Statoil, as well as the expanded study area in the eastern Chukchi Sea. These samples were used to calculate the pH, partial pressure of CO₂, and carbonate mineral saturation states for calcite and aragonite in the water column. The data was consistent with recent studies in the region that showed that phytoplankton primary production in late spring significantly alters the carbon biogeochemistry of the water column throughout the year. Early in the ice-free period, primary production consumes DIC in the euphotic zone causing pH and carbonate mineral saturation states to increase. However, much of the organic matter that is produced is exported from the surface making the eastern Chukchi Sea a strong sink for atmospheric CO₂. As the organic matter settles near the bottom and is broken down by bacteria, DIC concentrations increase sharply, particularly later in the year, driving down pH and suppressing the concentrations of important carbonate minerals that are necessary for shell growth in benthic calcifying organisms. The data from 2011 was consistent with data collected in 2010 and showed a definitive seasonal progression of aragonite becoming undersaturated along the bottom in September, and broadly undersaturated in October. While carbonate saturation states would naturally be suppressed by the high rates of export production, the penetration of anthropogenic CO₂ into water column (ocean acidification) has caused the observed undersaturations and these will likely expand as CO₂ levels in the atmosphere continue to rise in the coming decades. It is unclear at this time what the implications to the benthic calcifying ecosystem will be due to ocean acidification.

Table of Contents

Executive Summary.....	3
Introduction.....	4
Background.....	5
<i>Biological Production</i>	7
<i>Air-Sea Fluxes of CO₂</i>	7
<i>Ocean Acidification</i>	8
Methods	
<i>Cruise Information and Water Column Sampling</i>	9
<i>Laboratory Analysis and Calculation of Carbonate Parameters</i>	11
<i>Basis of the Arctic Marine Carbonate System</i>	11
Results	
<i>1102 – The August Cruise</i>	13
<i>1104 – The September Cruise</i>	14
<i>1104 – The October Cruise</i>	15
Discussion.....	15
Concluding Remarks.....	17
Figure 1.....	19
Figure 2.....	20
Figure 3.....	21
Figure 4.....	22
Figure 5.....	23
Figure 6.....	24
Figure 7.....	25
Figure 8.....	26
Figure 9.....	27
Figure 10.....	28
Figure 11.....	29
Figure 12.....	30
Figure 13.....	31
Figure 14.....	32
Figure 15.....	33
Figure 16.....	34
Figure 17.....	35
Figure 18.....	36
Table 1.....	37
Table 2.....	38
Table 3.....	39
Table 4.....	40
Table 5.....	41
Table 6.....	42
References.....	43

Introduction

The Arctic Ocean plays an important and likely increasing role in both the regional and global climate system with complex and poorly constrained interactions and feedbacks between sea-ice, the ocean and atmosphere, and the hydrological cycle. Some of these interactions have a significant impact on the global balance and atmospheric concentrations of greenhouse gases such as carbon dioxide (CO₂). Currently, the Arctic basin is an important sink for atmospheric CO₂ with recent estimates suggesting that the region contributes between 5 to 14% to the global ocean's net uptake of CO₂ (Bates and Mathis, 2009). The Chukchi Sea is a strong seasonal sink for atmospheric CO₂. The uptake of CO₂ by the Arctic Ocean is of particular importance because since the Industrial Revolution the oceans have absorbed approximately 127 Pg (Pg = 10¹⁵ g C) of anthropogenically produced CO₂ from the atmosphere (Sabine and Feely, 2007). While this has mitigated the increase in atmospheric CO₂ concentrations by ~55% (Sabine et al., 2004; Sabine and Feely, 2007), it has changed the carbonate chemistry of seawater chemical speciation (e.g.,

Caldiera and Wickett, 2003; Andersson and Mackenzie, 2004; Feely et al., 2004; Orr et al., 2005; Millero, 2007) with unknown, but potentially significant impacts to current and future marine ecosystems (Fabry et al., 2008, 2009; Cooley and Doney, 2009). The absorption of atmospheric CO₂ by the ocean has resulted in a lowering of pH, especially over the last few decades (e.g., Bates, 2007; Byrne et al., 2010) as atmospheric CO₂ levels have risen sharply, with a subsequent decrease in the availability of carbonate ions (CO₃²⁻) and a suppression of the saturation states (Ω) of calcium carbonate minerals (CaCO₃), which could result in a reduction of suitable habitat for marine calcifiers. These processes, collectively termed "ocean acidification" (OA), have occurred naturally over geologic time scales (e.g. Zachos et al., 2005) but have been accelerated due to anthropogenic emissions from industrial processes and changes in land use (Feely et al., 2004; Sabine et al. 2004; Orr et al., 2005; Caldiera and Wickett, 2005). Because of these rapid environmental changes, the Arctic marine carbon cycle will likely enter a transition period in the coming decades, with large uncertainties in the exchange of atmosphere-

ocean CO₂ (Anderson and Kaltin, 2001; Bates et al., 2006; Bates and Mathis, 2009; Cai et al., 2010; Jutterstrom and Anderson, 2010) in response to sea-ice loss and other climate change induced processes, such as warming temperatures and changes in primary production. Furthermore, the Arctic marine carbon cycle and marine ecosystems are also vulnerable to ocean acidification that results from the uptake of anthropogenic CO₂ from the atmosphere (Orr et al., 2005; Steinacher et al., 2009; Bates et al., 2009; Yamamoto-Kawai et al., 2009).

Background

The Arctic Ocean occupies ~2.6% of the surface area of the global ocean, but contains <1% of the total ocean volume. It is a Mediterranean type sea that is almost completely surrounded by landmasses, with only few communication points with other ocean basins. Given its geographical layout, it is disproportionately impacted by terrestrial fluxes and receives almost 10% of the total global river runoff annually from an extensive system of rivers and smaller coastal streams that drain the watersheds of Siberia and northern North America (McGuire et al., 2006; Cooper et al., 2008). However, these discharges are episodic, with the majority of the total flux occurring in late spring and summer. The landmasses surrounding the Arctic basin contain large stores of terrestrial carbon and strongly influence the biogeochemical dynamics of the marine carbon cycle. For half the year, the Arctic Ocean is almost completely covered by sea-ice with only small areas of open water in the form polynyas and flaw-leads. This seasonal sea-ice cover plays a major role in controlling the carbon cycle through vertical homogenization of the water-column by physical processes such as ventilation, brine rejection and convective mixing. In the western Arctic (i.e. Chukchi Sea), seasonal atmospheric warming and the inflow of warm, lower salinity waters from Pacific sources leave the broad Chukchi shelf nearly sea-ice free for most of the summer months. The wide and shallow Chukchi Sea occupies a particularly extensive portion of the western Arctic Ocean. Relatively warm and nutrient-rich Pacific Ocean waters enter the Chukchi Sea, flowing northward through Bering Strait from the Bering Sea (Coachman et al., 1975; Roach et al., 1975; Woodgate et al., 2005). As such, the physics and carbon

biogeochemistry of the Chukchi Sea is highly influenced by this inflow and can be characterized as an "inflow" shelf (Carmack and Wassmann, 2006; Bates and Mathis, 2009). Inflow of Pacific Ocean water through Bering Strait into the Chukchi Sea delivers ~0.8-1.0 Pg C year⁻¹ (Pg = 10¹⁵ g) of inorganic carbon into the Arctic Ocean (Bates and Mathis, 2009), with outflow from the western Arctic primarily through the Canadian Archipelago. In comparison, rates of primary production from marine phytoplankton and ice algae have been determined to be ~135 Tg C yr⁻¹ (Tg = 10¹² g) in the entire Arctic Ocean, although there are large uncertainties in these estimates (Macdonald *et al.*, 2010). The Arctic landmasses contain even larger stores of carbon compared to the marine environment, and there are significant river inputs of organic carbon to the Arctic shelves (e.g., Lobbes *et al.*, 2000; Amon, 2004; Rachold *et al.*, 2004; Guo and Macdonald, 2006; Raymond *et al.*, 2007; Holmes *et al.*, 2011). Pan-arctic river inputs of carbon have been estimated by McGuire *et al.* (2009) at 33 Tg C yr⁻¹ of DOC and 43.2 Tg C yr⁻¹ DIC, which are 7.1% and 10.6% of their respective total global total river fluxes (Cai *et al.*, 2011). River inputs of particulate organic carbon (POC) and coastal erosion of terrestrial carbon (mostly refractory organic carbon) have also been estimated at ~12 Tg C yr⁻¹ (e.g., Rachold *et al.*, 2004; Macdonald *et al.*, 2009). Arctic rivers thus contribute disproportionately large amounts of carbon to the Arctic Ocean compared to other ocean basins. Compared to many other open-ocean and coastal environments, relatively few studies of the marine carbon cycle have been conducted in the western Arctic. The harsh polar climate and difficult logistical support have limited most studies to opportunistic icebreaker surveys conducted on the Arctic Ocean shelves during the summertime sea-ice retreat. Even with large scale, multiyear projects such as the Shelf-Basin Interactions (SBI II) (Grebmeier *et al.*, 2008), spring and summer observations of the Arctic Ocean marine carbon cycle are highly limited and virtually absent during fall and winter. Thus, there are considerable uncertainties about the physical and biological controls on the marine carbon cycle, natural and human perturbed seasonal and interannual variability, CO₂ sinks and sources in the Arctic Ocean and ocean acidification.

Biological Production

The inflow of nutrient-rich water from the Pacific Ocean into the Chukchi Sea (Codispoti *et al.*, 2005), coupled with near constant light in summer supports a brief, but intensive period of marine phytoplankton photosynthesis and growth compared to other Arctic Ocean shelves (Cota *et al.*, 1996; Hill and Cota, 2005) where nutrients are more limited. Occupying the base of the food web, phytoplankton primary production rates on the Chukchi Sea shelf can exceed $>300 \text{ g C m}^2 \text{ y}^{-1}$ or $0.3\text{-}2.8 \text{ g C m}^2 \text{ d}^{-1}$ (e.g., Hameedi, 1978; Cota *et al.*, 1996; Gosselin *et al.*, 1997; Hill and Cota, 2005; Bates *et al.*, 2005a; Mathis *et al.*, 2009; Macdonald *et al.*, 2009). Intense seasonal growth of marine phytoplankton supports a large zooplankton (e.g., copepods; see Hopcroft report for description in the study area) biomass that in turn supports diverse openwater and seafloor ecosystems (Feder *et al.*, 2005; Grebmeier *et al.*, 2008). Both pelagic and benthic ecosystems on the Chukchi Sea shelf support marine mammal (e.g., grey whale, walrus, polar bears), seabird and human populations in the region. In the Chukchi Sea, the brief period of high rates of marine phytoplankton primary production results in the formation of high concentrations of suspended particulate organic carbon (sPOC) (Bates *et al.*, 2005b; Moran *et al.*, 2005; Lepore *et al.*, 2007) (**Figure 1**). High concentrations of sPOC have been observed (up to 2000 mg C L^{-1} ; average of $\sim 200\text{-}300 \text{ mg C L}^{-1}$) across the shelf, with considerable export of sPOC off the shelf into the Canada Basin (Bates *et al.*, 2005b), and relatively high rates of vertical export of organic carbon to shelf, slope and basin sediments (Moran *et al.*, 2005; Lepore *et al.*, 2007). The ecosystem is dominated by large sized phytoplankton (Grebmeier *et al.*, 2008) that produce a relatively large size class of organic matter (i.e., as POC) that is rapidly exported to the bottom waters over the shelf.

Air-Sea Fluxes of CO₂

The export character of the shelf is what conditions the surface waters of the Chukchi Sea to be a strong sink for atmospheric CO₂. Early studies of the Chukchi Sea (Semiletov 1999) showed that seawater $p\text{CO}_2$ ($\sim 200\text{-}350 \text{ }\mu\text{atm}$) values were lower than the

atmosphere (~365-380 μatm at the time of observation) during the sea-ice free period. Since then, other studies have observed similarly low seawater $p\text{CO}_2$ conditions on the Chukchi Sea shelf during summertime (~150-350 μatm ; Pipko et al., 2002; Murata and Takizawa, 2003; Bates et al., 2005a; 2006; Bates, 2006; Chen and Gao, 2007; Fransson et al., 2009; Andreev et al., 2009). Large drawdowns of surface water DIC from primary production is the primary controller of $p\text{CO}_2$ values in summer (Bates et al., 2005; Bates, 2006; Cai et al., 2010). The seasonal changes in DIC have been largely attributed to high rates of summertime phytoplankton primary production or net community production (Bates *et al.*, 2005; Mathis *et al.*, 2007a), especially in the vicinity of Barrow Canyon (at the northern edge of the Chukchi Sea shelf; Bates et al., 2005a; Hill and Cota, 2005) which is close to the lease areas. However, the seasonal decrease in $p\text{CO}_2$ values is somewhat moderated by warming temperatures that drive $p\text{CO}_2$ values higher. The seasonal rebound of seawater $p\text{CO}_2$ and DIC during wintertime likely results from the uptake of CO_2 from the atmosphere and winter mixing induced from brine rejection (Anderson et al., 2004; Omar et al., 2005). Early season observations in the Chukchi Sea indicate that these processes return the surface waters to near saturation compared to atmospheric $p\text{CO}_2$ values before ice retreat and the onset of the spring bloom. After the bloom, summertime $p\text{CO}_2$ values are typically in the range of -50 to -200 μatm relative to the atmosphere, creating a strong driving force for air-sea exchange. Previous estimates of the rates of air-sea CO_2 exchange during the sea-ice free period in the summertime have ranged from ~ -20 to -90 $\text{mmol CO}_2 \text{ m}^{-2} \text{ d}^{-1}$ (Wang et al., 2003; Murata and Takizawa, 2003; Bates, 2006; Fransson et al., 2009) indicating that the surface waters of the Chukchi Sea shelf have the potential to be a strong sink of atmospheric CO_2 (Kaltin and Anderson, 2005). The annual ocean CO_2 uptake for the Chukchi Sea shelf has been estimated at $2-9$ $\text{mmol C m}^{-2} \text{ y}^{-1}$ (Katlin and Anderson, 2005; Bates, 2006), or approximately 11 to 53 Tg C yr^{-1} . These studies show that the Chukchi Sea shelf dominates air-sea CO_2 fluxes in the western Arctic region.

Ocean Acidification

The drawdown of DIC during the spring phytoplankton bloom has a significant

impact on water column pH and the saturation states of the two most important carbonate minerals (calcite and aragonite). As DIC is consumed, $p\text{CO}_2$ drops in the surface layer causing pH to increase, raising the saturation states of calcite and aragonite. In response to high export production, the remineralization of organic matter increases the concentration of DIC and $p\text{CO}_2$ in bottom waters and suppresses carbonate mineral saturation states to a varying degree across the Chukchi shelf. In the region near the head of Barrow Canyon, export production is highest and this is where the strongest seasonal suppression of aragonite in subsurface water has been observed. This suppression of carbonate mineral saturation states corresponds to high apparent oxygen utilization (AOU) rates and elevated silicate in the bottom waters indicating both pelagic and benthic remineralization. The subsurface effects of remineralization can be especially significant during periods of intense production when saturation states increase at the surface. These biologically driven, seasonally divergent trajectories of Ω , or the “Phytoplankton-Carbonate Saturation State” (PhyCaSS) Interaction, have been observed in the Chukchi Sea (Bates *et al.*, 2009; Bates and Mathis, 2009), and are likely typical of highly productive polar and sub-polar shelves. The PhyCaSS Interaction could be particularly influential on benthic calcifiers in the Chukchi Sea because the lowest saturation states coincide with areas of highest export production. It appears that the export production, which provides the food source at the bottom, is causing the undersaturation that could inhibit shell and test growth in calcifying organisms. This PhyCaSS interaction is now being exacerbated by the penetration of anthropogenic CO_2 into the oceans, particularly in high latitude regions. The decrease in seawater pH due to the uptake of anthropogenic CO_2 (Bindoff *et al.*, 2007; Bates, 2007) has been termed “ocean acidification” and has been observed at several open ocean time-series locations (e.g. Bermuda Atlantic Time Series (BATS) and the Hawaii Ocean Time Series (HOTS)). The uptake of anthropogenic CO_2 has already decreased surface water pH by 0.1 units when averaged across the global ocean. IPCC scenarios, based on present-day CO_2 emissions, predict a further decrease in seawater pH by 0.3 to 0.5 units over the next century and beyond (Caldeira and Wickett, 2003). Ocean acidification and decreased pH reduces the saturation states of calcium carbonate minerals such as aragonite and

calcite, with many studies showing decreased CaCO_3 production by calcifying fauna (Buddemeier et al., 2004; Fabry et al., 2008) and increased CaCO_3 dissolution. The Arctic Ocean is particularly vulnerable to ocean acidification due to relatively low pH and low temperature of polar waters compared to other waters (Orr et al., 2005; Steinacher et al., 2009) and low buffer capacity of sea-ice melt waters (Yamamoto-Kawai et al., 2009). In the Arctic Ocean, potentially corrosive waters are found in the subsurface layer of the central basin (Jutterstrom and Anderson, 2004; Yamamoto-Kawai et al., 2009; Cheirici and Fransson, 2009), on the Chukchi Sea shelf (Bates et al., 2009) and in outflow waters of the Arctic found on the Canadian Arctic Archipelago shelf (Azetsu-Scott et al., 2010). On the Chukchi Sea, waters corrosive to CaCO_3 occur seasonally in the bottom waters with unknown impacts to benthic organisms. As described above, the seasonally high rates of summertime phytoplankton primary production in the Chukchi Sea drives a downward export of organic carbon, which is remineralized back to CO_2 which in turn increases seawater $p\text{CO}_2$ (and decreasing pH) of subsurface waters. Such a seasonal biological influence on the pH of subsurface waters amplifies existing impacts of ocean acidification induced by the uptake of anthropogenic CO_2 over the last century (Bates et al., 2009). Given the scenarios for pH changes in the Arctic, the Arctic Ocean and adjacent Arctic shelves including the western Arctic, will be increasingly affected by ocean acidification, with potentially negative implications for shelled benthic organisms as well as those animals that rely on the shelf seafloor ecosystem.

Methods

Cruise Information and Water Column Sampling

Physical, chemical and biological measurements were made during cruises to the study area in August, September, and October of 2011 (**Figure 2**). Samples for dissolved inorganic carbon (DIC) and total alkalinity (TA) were collected at all three studies sites in August and September and only at the expanded study sites in October. Seawater samples for DIC/TA were drawn from Niskin bottles into pre-cleaned ~300 mL borosilicate bottles. These samples were subsequently poisoned with mercuric chloride (HgCl_2) to

halt biological activity, sealed, and returned to the laboratory for analysis. All sampling and analysis was performed in compliance with the guide to best practices for ocean acidification research and reporting (Riebesell *et al.*, 2010).

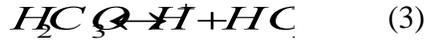
Laboratory Analysis and Calculation of Carbonate Parameters

DIC and TA samples were analyzed using a highly precise and accurate gas extraction/coulometric detection system (Bates, 2001). The analytical system consists of a VINDTA 3C (Versatile Instrument for the Detection of Total Alkalinity; <http://www.marianda.com>) coupled to a CO₂ coulometer (model 5012; UIC Coulometrics). TA samples were also determined by potentiometric titration using the VINDTA 3C. Routine analyses of Certified Reference Materials (CRMs, provided by A.G. Dickson, Scripps Institution of Oceanography) ensured that the accuracy of the DIC and TA measurements were within 0.05% (~1 μmoles kg⁻¹) and stable over time. Seawater pCO₂, pH and CaCO₃ saturation states for calcite (Ω_{calcite}) and aragonite (Ω_{aragonite}) were calculated from DIC, TA, temperature, salinity, phosphate, and silicate data using the thermodynamic model of Lewis and Wallace [1995]. The carbonic acid dissociation constants of Mehrbach *et al.* (1973) [refit by (Dickson and Millero, 1987); i.e., pK₁ and pK₂] were used to determine the carbonate parameters. The CO₂ solubility equations of Weiss (1974), and dissociation constants for borate (Dickson, 1990), silicate and phosphate (Dickson and Goyet, 1994) were used as part of the calculations. Uncertainty in the calculation of Ω_{calcite} and Ω_{aragonite} were ~0.02.

Basis of the Arctic Marine Carbonate System

As CO₂ levels rise in the atmosphere, the increased partial pressure of carbon dioxide (pCO₂) in seawater contributes to OA and the suppression of biologically important carbonate mineral concentrations, such as calcite and aragonite, through a series of well-known reactions:





Following dissolution (Eq. 1), dissolved CO₂ undergoes hydration reactions to form carbonic acid (Eq. 2), which rapidly dissociates to form carbonate and releases hydrogen ions (Eqs. 3, 4). Almost all of the produced carbonate ions react with calcium to form mineral solids (Eq. 5), preventing this reaction from contributing to dissolved alkalinity. Further, most of the free hydrogen ions produced react with the naturally dissolved alkalinity in seawater, reducing carbonate ion concentrations. The remaining hydrogen ions contribute to the lowering of pH. Carbonate mineral saturation states are dependent on the concentration of free carbonate ions according to the following equations, such that a reduction in available CO₃²⁻ (Eq. 5) decreases the saturation states of both aragonite and calcite:

$$\Omega_{aragonite} = \frac{[Ca^{2+}][CO_3^{2-}]}{K_{sp,aragonite}^*} \quad (7)$$

$$\Omega_{calcite} = \frac{[Ca^{2+}][CO_3^{2-}]}{K_{sp,calcite}^*} \quad (8)$$

Cold ocean temperatures increase the solubility of CO₂ and precondition the seawater to have lower calcium carbonate concentrations and saturation states compared to more temperate ocean environments, leaving polar and sub-polar shelves particularly vulnerable to OA (Orr *et al.*, 2005; Bates and Mathis, 2009; Fabry *et al.*, 2009; Steinacher *et al.*, 2009). In addition to this temperature effect, several other processes affect the carbonate system and can contribute to the intensification of OA in polar and subpolar regions, including seasonally high rates of primary production, river runoff, and sea-ice formation and melt processes (e.g. Bates and Mathis, 2009; Bates *et al.*, 2009). For example, seasonally intense periods of primary production are uncoupled from grazing in most polar environments (e.g., Springer *et al.*, 1996; Macdonald *et al.*, 2009) leading to high rates of organic matter export from the surface layer (e.g. Mathis *et al.*, 2007). While this export production supports the biologically diverse benthic communities in these

regions it leads to elevated rates of remineralization in bottom waters and sediments. Thus, ocean biology tends to drive seasonally divergent trajectories for seawater chemistry, with primary production in the euphotic zone increasing Ω in the mixed layer while an accumulation of DIC in subsurface waters through remineralization suppresses Ω (e.g. Bates et al., 2009). The reduction and undersaturation of carbonate minerals, particularly in bottom waters of polar and subpolar seas could have implications for benthic ecosystems. Further decreases in pH and Ω could have significant consequences for the benthic and pelagic ecosystems in a region where organisms are already struggling to adapt to changing environmental conditions (Løvrvorn *et al.*, 2003; Moore *et al.*, 2003; Overland and Stabeno, 2004; Grebmeier *et al.*, 2006).

Results

1102- The August Cruise

At the time of the August occupation, the most intense period of primary production in the Chukchi had already passed, and as such, DIC concentrations had been drawn down in the mixed layer by the bloom. Observations from the summer occupation (1102) in the lease sites showed that DIC was coupled to salinity (**Figure 3**). Surface conditions at the Klondike, Burger, and Statoil sites were relatively uniform (**Figure 9**), with DIC concentrations $\sim 2000 \mu\text{moles kg}^{-1}$ and TA concentrations $\sim 2100 \mu\text{moles kg}^{-1}$ (**Table 2**). The removal of DIC from the surface later by primary producers in late spring and summer resulted in a marked decrease in the partial pressure of CO_2 ($p\text{CO}_2$) in the mixed layer ($\sim 271 \mu\text{atm}$ to $\sim 320 \mu\text{atm}$; **Table 2**) from atmospheric values ($385 \mu\text{atm}$). The utilization of DIC at the surface strongly influenced pH, lowering values in the surface layer (**Figure 6**) after the bloom (~ 8.1 ; **Table 2**). Calcite (~ 2.9) and aragonite (~ 1.8) were supersaturated throughout the water column (**Figure 9**) at this time.

In the deeper levels of the water column at each of the study sites, DIC accumulated (**Figure 10**) off the shelf most likely due to the remineralization of exported organic matter. TA exhibited a high correlation with salinity (Figure 4) with maximum values of $\sim 2190 \mu\text{moles kg}^{-1}$ (**Tables 1, 2, 3**). Here, $p\text{CO}_2$ values increased sharply to

>400 μatm in response to the DIC accumulation from remineralization (**Figure 5; Tables 1,2,3**). The higher DIC concentrations raised $p\text{CO}_2$ values in the deeper levels of the water column, ($\sim 400 \mu\text{atm}$; **Table 1; Figure 10**) while simultaneously lowering pH and Ω (**Table 1; Figure 10**).

1104- The September Cruise

During the September cruise, DIC concentrations in the surface layer were higher than those observed in August (**Tables 4, 5 and 6**), and were again fairly well correlated with salinity (**Figure 3**). TA also increased compared to August values and maintained a tight correlation with salinity (**Tables 4, 5, 6; Figure 4**). This seasonal increase in DIC is most likely due to the uptake of CO_2 from the atmosphere, although a small percentage is also due to the remineralization of dissolved organic carbon (DOC) in the surface layer that was too light to sink. The combination of these two processes caused $p\text{CO}_2$ at the surface to increase significantly (**Tables 4,5, 6**) and at some locations the water became supersaturated with respect to atmospheric CO_2 (**Figure 5**). pH and the saturation states of calcite and aragonite responded to these changes in $p\text{CO}_2$, with supersaturations of both calcite and aragonite at the surface (**Tables 1, 2, 3; Figure 11**); however, pH had the lowest observed values of the season (~ 8.0 ; **Figure 11**).

Concentrations of DIC in the bottom waters were higher than at the surface, ($\sim 2150 \mu\text{moles kg}^{-1}$), while TA was fairly consistent ($\sim 2200 \mu\text{moles kg}^{-1}$; **Table 1; Figure 12**). This seasonal increase can be explained by storm systems that induce upwelling of high salinity, high DIC/TA water up onto the shelf in the fall. Near the bottom, $p\text{CO}_2$ values also increased sharply compared to observations made in August (**Tables 4, 5, 6**). The saturation states of both calcite and aragonite and pH dropped sharply in response to the increase in $p\text{CO}_2$ with aragonite becoming undersaturated ($\Omega < 1$) at several stations (**Figure 8**).

Spatially, the various parameters of the carbonate system were less uniform compared to August (**Figure 11**). There are several low DIC/TA features present at this time, most likely due to ice melt and river run off. This caused $p\text{CO}_2$ to be lower at these locations and pH and carbonate mineral saturation states to be higher. Near the bottom,

the increase in DIC concentrations compared to the summer occupation can be easily seen (**Figure 18**) as were the higher values of $p\text{CO}_2$ in the southern part of the study area. This increase in $p\text{CO}_2$ is most likely related to an increase in temperature along the bottom in that region, where the lowest saturation states for calcite and aragonite can be found as well.

1104- The October Cruise

In these northern most sites (**Figure 2**), the same patterns in the distribution of the carbonate parameter that were observed in September were measured here as well. In general, DIC/TA concentrations were lower at the surface, with DIC $\sim 1990 \mu\text{moles kg}^{-1}$ (**Table 4; Figure 13**) and TA concentrations $\sim 2100 \mu\text{moles kg}^{-1}$ (**Table 4; Figure 13**). The processes of atmospheric uptake of CO_2 coupled with the remineralization of DOC at the surface gave $p\text{CO}_2$ a fairly large range from $\sim 290 \mu\text{atm}$ to $\sim 610 \mu\text{atm}$ (**Table 4; Figure 13**). Surface pH values were ~ 8.0 (**Table 4; Figure 13**). Ω_{calcite} and $\Omega_{\text{aragonite}}$ values ranged at these sites from ~ 1.5 to ~ 3.0 , and ~ 0.94 and ~ 1.8 , respectively (**Table 4; Figure 13**). In the bottom waters, DIC concentrations were higher than at the surface, (**Table 4; Figure 14**) and TA concentrations varied over $\sim 100 \mu\text{moles kg}^{-1}$ (**Table 4; Figure 13**). Remineralization of organic material at depth and the upwelling of high DIC water onto the shelf caused an increase of $p\text{CO}_2$ (**Table 4; Figure 13**). Deep water pH values were between ~ 7.8 and ~ 8.1 , while Ω_{calcite} and $\Omega_{\text{aragonite}}$ values ranged from ~ 1.3 to ~ 2.5 , and ~ 0.8 to ~ 1.5 , respectively (**Table 4; Figure 14**).

Discussion

As compared to 2010, conditions in the Chukchi in 2011 were well mixed (**Figures 15-18**). No strong sea-ice melt signal was present in the surface layer at any of the lease sites, and concentrations of DIC and TA in the bottom waters were only slightly higher than at the surface. Surface values for $p\text{CO}_2$ in August in 2011 were higher than in 2010, as was pH (**Figure 9**). In September 2011, the water column was more stratified than in August, and higher concentrations of DIC and TA were present in the bottom

waters (**Figure 18**). This caused a corresponding drop in pH, and undersaturations of calcite and aragonite at the Burger and Klondike sites (**Figure 18**).

By contrast, in 2010, surface waters at the Klondike site showed a strong longitudinal gradient from west to east at the surface, and higher concentrations of DIC and TA in the bottom waters in August. A low salinity feature, most likely from ice melt, was present in the surface waters as well. In September 2010, this feature was absent even though the water column was more strongly stratified at this time of year than in 2011. Another key difference between 2010 and 2011 was the salinity gradient, which was observable in 2010, but nearly absent in 2011 (**Figures 15-18**), with the water column looking more well-mixed than the year previous. It is thus reasonable to assume that stronger physical processes, such as increased wind mixing and seasonal storm events, had a greater impact on the water column of the Chukchi shelf in 2011 than in 2010. These results highlight the dynamic nature of this marine ecosystem, especially on an interannual timescale.

The Impact of Anthropogenic CO₂

Ideally, the amount of anthropogenic CO₂ in a given system can be estimated by directly calculating the age of the water mass, but a paucity of data in this region prevents this approach. However, based on the origin of the water on the Chukchi Sea shelf and the observed density constraints, we can approximate anthropogenic CO₂ inventories to evaluate the pre-industrial state of the carbon cycle in the region. Sabine *et al.* (2004) estimated that $\sim 35 \mu\text{moles kg}^{-1}$ anthropogenic CO₂ has penetrated into waters of the North Pacific Ocean to the 26 kg m^{-3} isopycnal surface. Because the source waters of the western Arctic Ocean are derived from the Bering Sea Shelf/North Pacific a conservative assumption can be made that there is $\sim 35 \mu\text{moles kg}^{-1}$ of anthropogenic CO₂ in the water column of the Chukchi Sea.

To determine the impact of OA due to the uptake of anthropogenic CO₂, that $35 \mu\text{moles kg}^{-1}$ can be subtracted from the DIC observations made during the cruises while keeping the remaining variables (TA, salinity, temperature) consistent with observations. The remaining carbonate parameters (specifically the saturation states for calcite and

aragonite) can be recalculated using the thermodynamic model of Lewis and Wallace [1995]. When this was done for the 2011 data, the entire water column over the shelf was supersaturated with respect to aragonite during all three months and in all areas. While there are a number of weaknesses associated with this first order approximation, the calculation suggests that OA has resulted in the persistent aragonite undersaturations that have been observed in the Chukchi Sea. As atmospheric CO₂ concentrations increase, it is likely that these undersaturations will spread across the bottom waters of the shelf for at least parts of the year.

Timing of Ice Retreat

Even though a low salinity signal in the surface waters from ice melt was absent in 2011, the timing of sea-ice retreat has a substantial effect on carbonate chemistry in subsurface waters. Ice retreat exerts a significant control on the fate of the organic matter produced during the phytoplankton blooms. Zooplankton grazing of seasonal production is minimal during blooms associated with colder surface water temperatures favoring the benthic ecosystem. In contrast, warmer years increase zooplankton production by up to 50%. Thus, colder waters are expected to be associated with higher export production to the benthos, and large remineralization signals will be generated at depth, corresponding to increases in $p\text{CO}_2$ and decreases in carbonate mineral saturation states. Warmer water blooms will retain carbon in the mixed layer and contribute to increased pelagic production and reduced bottom water remineralization. Variation in the timing of sea-ice retreat could change the mode of production over the shelf. The earlier retreat of sea ice in recent years indicates that the blooms have been occurring in colder water, favoring export production. If ice continues to retreat earlier in the spring it could lead to a dichotomy for benthic organisms. On the one hand, higher rates of export production should lead to increased food supply and an expansion of biomass. However, if high rates of export production coupled to increasing anthropogenic CO₂ inventories over the shelf cause expanded aragonite undersaturations it could lead to a reduction in habitat.

Concluding Remarks

The carbonate datasets collected during the 2010 and 2011 surveys of the lease sites in the Chukchi Sea show the dynamic nature of the carbon cycle of the western Arctic Ocean. Brief, but intense periods of primary production in the surface layer in late spring sets the stage for most of the processes that occur for the remainder of the ice-free period. The consumption of DIC from phytoplankton dramatically lower the $p\text{CO}_2$ of the surface waters promoting broad regions of air-sea exchange and making the Chukchi Sea a strong sink for atmospheric CO_2 . The removal of DIC also raises the pH and carbonate mineral saturation states, counteracting the effects of ocean acidification in the surface waters. However, the disconnects between phytoplankton primary production and zooplankton grazing causes large quantities of organic matter to be exported from the mixed layer. When this organic matter is remineralized by bacteria, it adds DIC back to the water column, lower pH and suppressing carbonate mineral saturation states near the bottom.

The Chukchi Sea has been productive for thousands of years and the remineralization of organic matter and the seasonal suppression of carbonate mineral saturation states is a natural phenomenon. However, the rising inventories of anthropogenic CO_2 in the water column has begun to drive saturation states past a threshold that will likely be detrimental to some marine calcifiers, particularly the diverse benthic organisms that dominates the Chukchi Sea. While ocean acidification is a global problem, the Arctic Ocean will likely experience the physical manifestations and potential impacts of it much sooner than more temperate regions and may be a bellwether for how the global ocean will respond. Over the last decade, numerous new datasets and insights have elucidated the complexities in the feedbacks of the Arctic carbon cycle, but they have also provided exciting new insights and enhanced our understanding of the region. It is critical that these investments in infrastructure and data gather efforts continue as the Arctic becomes open for more commercial development.

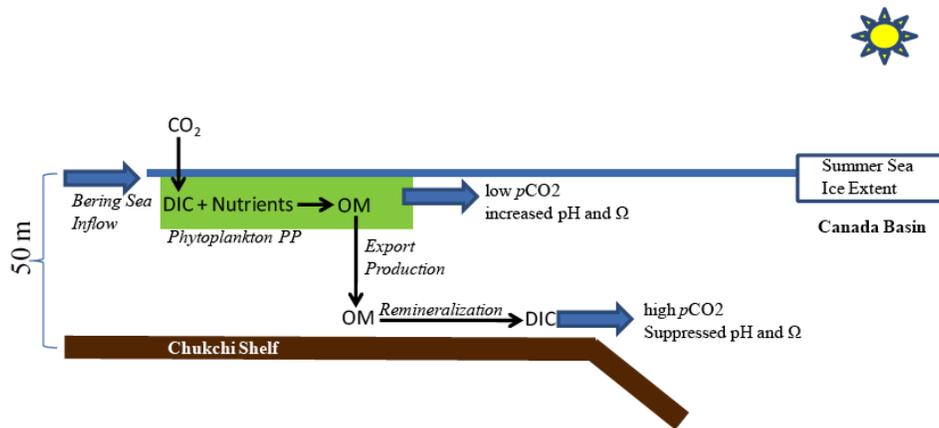


Figure 1. Schematic of the influences on the carbon cycle in the Chukchi Sea. High rates of primary production (green box) consumes DIC, lowering the $p\text{CO}_2$ of the surface waters and promoting air-sea exchange. However, air-sea exchange happens much slower than primary production leaving the surface waters undersaturated with respect to atmospheric CO_2 for most of the summer. The removal of DIC from the surface water causes pH and carbonate mineral saturation states to increase. Due to limited grazing in the water column, most of the organic matter produced by the phytoplankton is exported to depth where it is remineralized back into DIC, increasing the $p\text{CO}_2$ of the bottom waters while lowering pH and suppressing carbonate mineral saturation states. Both the surface and bottom water masses are exported off of the Chukchi shelf conditioning the surface waters under the ice in the deep Canada Basin to be undersaturated with respect to atmospheric CO_2 and the upper halocline of the western Arctic Ocean to be undersaturated in aragonite.

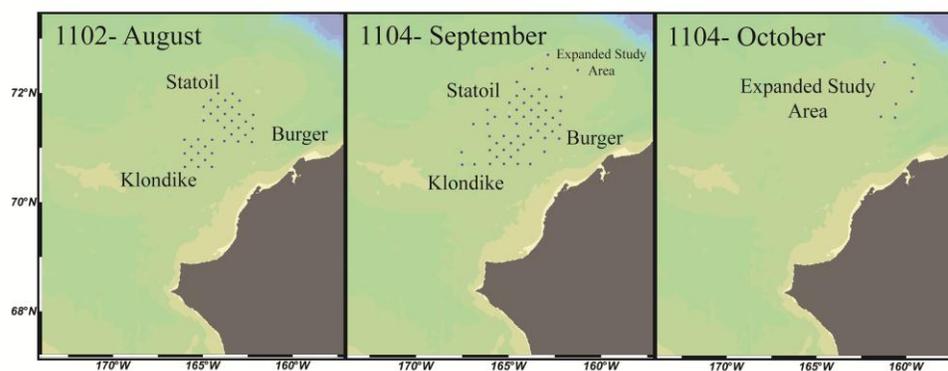


Figure 2. Location of the study areas where carbon measurements were taken in 2011. Samples for DIC and TA were collected mostly at odd numbered stations in each of the lease areas.

