Seasonal observations of carbonate chemistry and ocean acidification in the northeastern Chukchi Sea in September 2014

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Final REPORT

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EXECUTIVE SUMMARY

Observations of the marine carbonate system during the 2014 CSESP field program in the northeastern Chukchi Sea show that there are large gradients in carbonate parameters between the surface mixed-layer and bottom waters. These gradients are due to biological processes including the uncoupling of primary production and pelagic grazing of organic material. Results from 2014 are consistent with those made in 2010-2013 and showed that aragonite becomes undersaturated in the bottom waters at some stations and calcite approaches the saturation horizon. Although the underlying biological nature of the Chukchi Sea is the dominant driver of this process, the intrusion of anthropogenic CO$_2$ into these waters has likely increased the duration, extent and intensity of bottom-water undersaturations; this trend will continue as levels of anthropogenic CO$_2$ rise in the coming decades. It is unknown at this time what, if any, impact the bottom-water undersaturation will have on calcifying organisms in the region.
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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 among 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 (CO$_2$). Currently, the Arctic Basin is an important sink for atmospheric CO$_2$. Recent estimates suggest that the region contributes between 5 and 14% of the global oceans’ net uptake of CO$_2$ (Bates and Mathis, 2009). In the area being studied as part of the Chukchi Sea Environmental Studies Program (CSESP), the Chukchi Sea appears to be a strong seasonal sink for atmospheric CO$_2$.

Uptake of CO$_2$ by the Arctic Ocean is of particular importance because the oceans have absorbed ~127 Pentagrams (Pg; 1 Pg =10$^{15}$ g C) of CO$_2$ from the atmosphere since the Industrial Revolution (Sabine and Feely, 2007). While greater oceanic uptake has mitigated the global increase in atmospheric CO$_2$ concentration by 55% (Sabine et al., 2004; Sabine and Feely, 2007), it has caused the carbonate chemistry of seawater speciation (e.g., Caldiera and Wickett, 2003; Andersson and Mackenzie, 2004; Feely et al., 2004; Orr et al., 2005; Millero, 2007) to change 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 CO$_2$ by the ocean has resulted in a lowering of pH, especially over the last few decades (e.g., Bates, 2007; Byrne et al., 2010). Concurrently, atmospheric CO$_2$ levels have risen sharply, with a subsequent decrease in the availability of carbonate ions (CO$_3^{2-}$) and a suppression of the saturation states ($\Omega$) of calcium carbonate (CaCO$_3$) minerals in seawater, which could result in a reduction of suitable habitat for marine calcifiers. These processes, which collectively are termed “ocean acidification” (OA), have occurred naturally over geological time scales (e.g., Zachos et al., 2005) but have been accelerated due to increasing 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 CO$_2$ (Anderson and Kaltin, 2001; Bates et al., 2005b; Bates and Mathis, 2009; Cai et al., 2010; Jutterstrom and Anderson, 2010) in response to the loss of sea-ice and other climate-change-induced processes such as warming temperatures and changes in primary
production. The arctic marine carbon cycle and marine ecosystems also are vulnerable to ocean acidification that results from the uptake of 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 approximately 2.6% of the surface area of the global ocean and contains <1% of the total ocean volume. It is a Mediterranean-type sea that is almost completely surrounded by landmasses and has few communication points with other ocean basins. Because of 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 northwestern 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 of the year, the Arctic Ocean is covered almost completely by sea-ice, with only small areas of open water in the form of polynyas and flaw leads. The 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 free of sea-ice during most of the summer.

The wide and shallow Chukchi Sea occupies a particularly extensive portion of the marginal western Arctic Ocean. Warm and nutrient-rich Pacific Ocean water enters the Chukchi Sea, flowing northward from the Bering Sea through Bering Strait (Coachman et al., 1975; Roach et al., 1995; Woodgate et al., 2005). Consequently, the physics and carbon biogeochemistry of the Chukchi Sea are influenced greatly by this inflow, and the Chukchi shelf 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 of inorganic carbon into the Arctic Ocean (Bates and Mathis, 2009), with outflow from the western Arctic occurring primarily through the Canadian Archipelago. In comparison, rates of primary production from marine phytoplankton and ice algae were calculated to be ~135
Tg C yr\(^{-1}\) (Tg = 10\(^{12}\) g) in the entire Arctic Ocean, although there are large uncertainties in these estimates (Macdonald et al., 2010). The arctic land-masses contain even larger stores of carbon than the ocean does, and there are significant river inputs of organic carbon to the arctic shelves (e.g., Lobbes et al., 2000; Among, 2004; Raymond et al., 2004; Guo and Macdonald, 2006; Holmes et al., 2008). Pan-arctic river inputs of carbon have been estimated by McGuire et al. (2009) at 33 Tg C yr\(^{-1}\) of dissolved organic carbon (DOC) and 43.2 Tg C yr\(^{-1}\) of dissolved inorganic carbon (DIC), which are 7.1% and 10.6% of their respective total global river fluxes (Cai, 2011). In addition, riverine inputs of particulate organic carbon (POC) and coastal erosion of terrestrial carbon (mostly refractory organic carbon) have been estimated at ~12 Tg C yr\(^{-1}\) (e.g., Raymond et al., 2004; Macdonald et al., 2010). Arctic rivers thus contribute disproportionately large amounts of carbon to the Arctic Ocean than do other ocean basins compared with many other open-ocean and coastal environments. 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 marine carbon cycle in the Arctic Ocean are greatly limited and virtually absent during the fall and winter seasons. Thus, there are considerable uncertainties about the physical and biological controls on the marine carbon cycle, natural and human-perturbed seasonal and interannual variability, CO\(_2\) sinks and sources in the Arctic Ocean, and ocean acidification.

Air–Sea Fluxes of CO\(_2\)

The export character of the shelf conditions the surface waters of the Chukchi Sea to be a strong sink for atmospheric CO\(_2\). Early studies of the Chukchi Sea showed that the partial pressure of carbon dioxide (pCO\(_2\)) in seawater (~200–350 μatm; 1 μatm = 10^{-6} atm) values were lower than in the atmosphere (~400 μatm at the time of observation) during the ice-free period (Semiletov, 1999). Since then, other studies have reported similarly low seawater pCO\(_2\) conditions on the Chukchi Sea shelf during the summer (~150–350 μatm; Pipko et al., 2008; Murata and Takizawa, 2003; Bates et al., 2005a; Bates, 2006; Chen and Gao, 2007; Fransson et al., 2009; Andreev et al., 2010). Large drawdowns of surface water DIC from primary
production are the main controller of $pCO_2$ values in summer (Bates et al., 2005a; Bates, 2006; Cai et al., 2010). The seasonal changes in DIC have been attributed largely to high rates of primary production of phytoplankton, or to net community production (Bates et al., 2005a; Mathis et al., 2007), especially in the vicinity of Barrow Canyon (at the northeastern 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 of $pCO_2$ values is moderated somewhat by warming temperatures that drive $pCO_2$ values higher. The seasonal rebound of seawater $pCO_2$ and DIC in the winter likely results from the uptake of CO$_2$ from the atmosphere and winter mixing of seawater induced from brine rejection (Andersson et al., 2004; Omar et al., 2007). Late winter observations in the Chukchi Sea indicate that these processes return the surface waters to near saturation compared to atmospheric $pCO_2$ values before ice retreat and the onset of the spring phytoplankton bloom. After the bloom, summertime $pCO_2$ 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 ice-free period in the summertime have ranged from approximately −20 to −90 mmol CO$_2$ m$^{-2}$ d$^{-1}$ (1 mmol = 10$^{-3}$ mol; 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 mmol C m$^{-2}$ yr$^{-1}$ (Kaltin and Anderson, 2005; Bates, 2006), or approximately 11–53 Tg C yr$^{-1}$. Those studies show that the Chukchi Sea shelf dominates air–sea CO$_2$ fluxes in the western Arctic region (Figure 1).

**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, $pCO_2$ drops in the surface layer, causing pH to increase and 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 $pCO_2$ in bottom waters and suppresses carbonate mineral saturation states to varying degrees across the Chukchi shelf. Export production is highest in the region near the head of Barrow Canyon and this is where the strongest seasonal suppression of aragonite in subsurface water has been recorded. This
suppression of carbonate mineral saturation states corresponds to high apparent oxygen utilization (AOU) rates and elevated silicate in the bottom waters, indicating that both pelagic and benthic remineralization are occurring. The subsurface effects of remineralization can be especially significant during periods of intense biological production, when saturation states increase at the surface. These biologically driven, seasonally divergent trajectories of $\Omega$, 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 for organisms on and in the seafloor, causes the undersaturation that could inhibit shell and test growth in many calcifying organisms.

This PhyCaSS Interaction is now being exacerbated by the penetration of CO$_2$ into the oceans, particularly in high-latitude regions. The decrease in seawater pH due to the ocean’s uptake of CO$_2$ (Bindoff et al., 2007; Bates, 2007) has been termed “ocean acidification” and has been observed at open ocean locations during time-series studies (e.g., Bermuda Atlantic Time Series [BATS], Hawaii Ocean Time Series [HOTS]). The uptake of CO$_2$ has already decreased surface-water pH by 0.1 unit when averaged across the global ocean. Intergovernmental Panel on Climate Change (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 reduce 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 its low pH, low temperature of polar waters (Orr et al., 2005; Steinacher et al., 2009,) and low buffering capacity of waters from melted sea-ice (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, 2010; Yamamoto-Kawai et al., 2009; Chierici and Fransson, 2009), on the Chukchi Sea shelf (Bates et al., 2009), and in outflow waters from the Arctic found on the shelf of the Canadian Arctic Archipelago (Azetsu-Scott et al., 2010). In the Chukchi Sea, waters corrosive to CaCO$_3$ occur seasonally in the bottom waters, but with
unknown impacts to benthic organisms. As described above, the seasonally high rates of summertime primary production by phytoplankton in the Chukchi Sea drive a downward export of organic carbon, which is remineralized back to CO$_2$. This, in turn, increases the $p$CO$_2$ (and decreases the pH) of subsurface seawater. Such a seasonal biological influence on the pH of subsurface waters amplifies existing impacts of ocean acidification induced by the uptake of 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 those of the Chukchi Sea, will be increasingly affected by ocean acidification, with potentially negative implications for both shelled benthic organisms and other animals that rely on the shelf’s benthic ecosystem.

METHODS

Cruise Information and Water-column Sampling

Physical, chemical, and biological measurements were made during Cruise WW1404 on the Westward Wind September 8-25, 2014 (Figure 2). At each station, samples for DIC and Total Alkalinity (TA) were collected at four depths: near-surface 2 m, 20 m, 30 m, and 40 m. Seawater samples for DIC/TA were drawn from Niskin bottles into pre-cleaned 250 mL borosilicate bottles, poisoned with mercuric chloride (HgCl$_2$) to halt biological activity, sealed, and returned to the laboratory for analysis. All sampling and analyses were conducted 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 with a 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 CO$_2$ coulometer (model 5012; UIC Coulometrics). TA samples also were determined by potentiometric titration with 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 μmol kg$^{-1}$; 1 μmol = 10$^{-6}$ mol) and were stable over time. Seawater $p$CO$_2$, pH, and CaCO$_3$ saturation states for calcite ($\Omega_{Ca}$, data not shown) and aragonite ($\Omega_{Ar}$) were calculated from DIC, TA, temperature, salinity, phosphate, and silicate data with the thermodynamic model of Lewis and Wallace (1995). The carbonic acid dissociation constants of Mehrbach et al.
(1973), which were 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 the
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_{Ca} and Ω_{Ar} is
~0.02.

Basis of the Arctic Marine Carbonate System

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

\[ \text{CO}_2(g) \leftrightarrow \text{CO}_2(aq) \] (1)
\[ \text{CO}_2(aq) + H_2O \leftrightarrow H_2\text{CO}_3 \] (2)
\[ H_2\text{CO}_3 \leftrightarrow H^+ + \text{HCO}_3^- \] (3)
\[ H^+ + \text{HCO}_3^- \leftrightarrow 2H^+ + \text{CO}_3^{2-} \] (4)
\[ \text{CO}_3^{2-} + Ca^{2+} \leftrightarrow Ca\text{CO}_3(s) \] (5)

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 and
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 alkaline constituents 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 CO₃^{2−} (Eq. 5)
decreases the saturation states of both aragonite and calcite (Eqs. 6 and 7):

\[ \Omega_{\text{aragonite}} = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K^*_{\text{pH,aragonite}}} \] (6)
\[ \Omega_{\text{calcite}} = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K^*_{\text{pH,calcite}}} \] (7)
Cold ocean temperatures increase solubility of CO$_2$ and precondition seawater to have lower calcium carbonate concentrations and saturation states than occur in more temperate ocean environments, thus making polar and sub-polar shelves particularly vulnerable to OA (Orr et al., 2005; Bates and Mathis, 2009; Fabry et al., 2009; Mathis et al., 2009; Steinacher et al., 2009). In addition to this temperature-driven effect, several other processes affect the carbonate system and can contribute to the intensification of OA in polar and sub-polar regions, including seasonally high rates of primary production, river runoff, and sea-ice formation and melting processes (e.g., Bates and Mathis, 2009; Bates et al., 2009). For example, seasonally intense periods of primary production are not coupled with grazing in most high latitude environments (e.g., Springer et al., 1996; Macdonald et al., 2010) leading to high rates of export of organic matter from the surface layer (e.g., Mathis et al., 2007). While this export production supports the biologically diverse benthic communities in these regions, it also leads to elevated rates of remineralization in bottom waters and sediments. Thus, biological processes tend to drive seasonally divergent trajectories for seawater chemistry, with primary production in the euphotic zone increasing Ω in the mixed layer, whereas 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 sub-polar seas, could have implications for benthic ecosystems, in that further decreases in pH and Ω could have significant consequences for both benthic and pelagic ecosystems in a region where organisms are already struggling to adapt to changing environmental conditions (Lovvorn et al., 2003; Moore et al., 2003; Overland and Stabeno, 2004; Grebmeier et al., 2006).

RESULTS

Ocean Acidification samples were analyzed from 45 stations during cruise WW1404. DIC values ranged from 1847 to 2240 µmol kg$^{-1}$ and generally increased with increased water depth: near-surface DIC $\bar{x}$ = 1979 µmol kg$^{-1}$; 20m DIC $\bar{x}$ = 2020 µmol kg$^{-1}$; 30m DIC $\bar{x}$ = 2054 µmol kg$^{-1}$; 40m DIC $\bar{x}$ = 2108 µmol kg$^{-1}$ (Figure 3). TA ranged from 1996 to 2267 µmol kg$^{-1}$ and also increased with water depth: near-surface TA $\bar{x}$ = 2132 µmol kg$^{-1}$; 20m TA $\bar{x}$ = 2171 µmol kg$^{-1}$; 30m TA $\bar{x}$ = 2196 µmol kg$^{-1}$; 40m TA $\bar{x}$ = 2215 µmol kg$^{-1}$. For the calculated OA parameters, $p$CO$_2$ ranged from 178 to 906 µatm, pH ranged from 7.66 to 8.32, and Ω$_{Ar}$ ranged from 0.6 to 2.3.
Salinity values ranged from 28.76 to 32.64 practical salinity units (PSU) and increased with depth. DIC values are positively correlated with salinity; with a higher salinity value (e.g., 32 PSU) having a higher DIC value (e.g., 2240 µmol kg\(^{-1}\)). TA values are also positively correlated with salinity; with a higher TA value (e.g., 2267 µmol kg\(^{-1}\)) also having a higher salinity value.

On WW1404, OA samples were analyzed from the inner shelf for the first time, labeled as “Inner” in Figure 2. These samples exhibit nearly the same range as the total study area sampled during WW1404 for all depths: DIC ranged from 1847 to 2240 µmol kg\(^{-1}\), TA ranged from 1996 to 2267 µmol kg\(^{-1}\), pH ranged from 7.66 to 8.22, pCO\(_2\) ranged from 225 to 906 µatm, \(\Omega_{\text{Ar}}\) ranged from 0.6 to 2.1, salinity ranged from 28.76 to 32.64 PSU, and temperature ranged from -1.63 to 6.28. At 40m water depth (Figure 4) at the inner stations: DIC \(\bar{x} = 2149\) µmol kg\(^{-1}\), TA \(\bar{x} = 2222\) µmol kg\(^{-1}\), pCO\(_2\) \(\bar{x} = 554\) µatm, pH \(\bar{x} = 7.90\), and \(\Omega_{\text{Ar}}\) \(\bar{x} = 1.1\). Near-surface depths (Figure 5) at the inner stations: DIC \(\bar{x} = 1980\) µmol kg\(^{-1}\), TA \(\bar{x} = 2125\) µmol kg\(^{-1}\), pCO\(_2\) \(\bar{x} = 327\) µatm, pH \(\bar{x} = 8.08\), and \(\Omega_{\text{Ar}}\) \(\bar{x} = 1.6\).

DISCUSSION

After five years of observations in the lease area, we have shown that bottom waters of the northeastern Chukchi Sea are undersaturated in the carbonate mineral aragonite for at least parts of the open-water season every year and probably are so into the fall and winter months. Although there are still limitations in our understanding due to the short duration of the time-series, a clear trend is emerging. It shows that aragonite saturation states are decreasing (Mathis 2012). This decrease in saturation states may be due to variable or even increasing rates of primary production in the region. However, the fact that anthropogenic CO\(_2\) inventories are increasing by 1.5–2.0 µatm yr\(^{-1}\) cannot be ignored.

High rates of primary production during the open water season delays the onset of low saturation states in surface waters of the study region. However, the combined effect of the PhyCaSS Interaction and the intrusion of anthropogenic CO\(_2\) will exacerbate OA at depth. It is unclear what impact these processes will have on benthic organisms, but it will be critical to continue to monitor the water chemistry as well as benthic biomass and health to identify any changes due to potential OA.
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Figure 1. Schematic of the influences on the carbon cycle in the Chukchi Sea. High rates of primary production (green box) consume DIC, lowering the $p$CO$_2$ of the surface waters and promoting air–sea exchange. However, air–sea exchange happens much more slowly than primary production does, leaving 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. Because grazing in the water-column is limited, most of the organic matter produced by the phytoplankton is exported to depth, where it is remineralized back into DIC, increasing the $p$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 causing the upper halocline of the western Arctic Ocean to be undersaturated in aragonite.
Figure 2. Location of the study area in the northeastern Chukchi Sea where carbon measurements were taken September 8-25, 2014 (Cruise WW1404). Klondike, Burger, and Statoil refer to the three typical study areas, with the inner stations highlighted.
Figure 3. Observations of temperature (°C), TA (µmol kg$^{-1}$), and DIC (µmol kg$^{-1}$) vs. salinity (PSU) and calculated values of pH, $pCO_2$ (µatm), and aragonite saturation states ($Ω_{Ar}$) vs. salinity.
Figure 4. Salinity (PSU), Temperature (°C), TA (µmol kg⁻¹), DIC (µmol kg⁻¹), pCO₂ (µatm), pH, and Ω_{Ar} values at the bottom (water depth 40 m).
Figure 5. Salinity (PSU), Temperature (°C), TA (µmol kg⁻¹), DIC (µmol kg⁻¹), pCO₂ (µatm), pH, and Ω_Ar values at the near-surface (water depth 2 m).