

**Seasonal Observations of carbonate chemistry and ocean acidification in 2012**

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FINAL REPORT

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## EXECUTIVE SUMMARY

Samples were collected and analyzed for dissolved inorganic carbon (DIC) and total alkalinity (TA) in August and September in Burger, Klondike, and Statoil study areas, as well as the expanded study area in the northeastern and southwestern Chukchi Sea. These samples were used to calculate the pH, partial pressure of carbon dioxide ( $p\text{CO}_2$ ), and carbonate mineral saturation states ( $\Omega$ ) for calcite and aragonite in the water column. The data were consistent with recent studies in the region that showed primary production from phytoplankton 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  $\text{CO}_2$ . 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. Data from 2012 show a definitive seasonal progression of aragonite becoming undersaturated along the bottom in September. While carbonate saturation states would naturally be suppressed by high rates of export production, penetration of anthropogenic  $\text{CO}_2$  into the water column (ocean acidification) has caused the observed undersaturations. These undersaturations will likely expand as  $\text{CO}_2$  levels in the atmosphere continue to rise in the coming decades. It is unclear what the implications of ocean acidification will be with respect to benthic calcifying organisms.

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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 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 (CO<sub>2</sub>). Currently, the Arctic basin is an important sink for atmospheric CO<sub>2</sub> with recent estimates suggesting that the region contributes between 5 to 14% to the global ocean's net uptake of CO<sub>2</sub> (Bates and Mathis, 2009). In the lease areas being studied as part of the CSESP, the Chukchi Sea appears to be a strong seasonal sink for atmospheric CO<sub>2</sub>.

The uptake of CO<sub>2</sub> by the Arctic Ocean is of particular importance because since the Industrial Revolution the oceans have absorbed approximately 127 Petagram (Pg) (Pg = 10<sup>15</sup> g C) of CO<sub>2</sub> from the atmosphere (Sabine and Feely, 2007). While this has mitigated the increase in atmospheric CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> levels have risen sharply, with a subsequent decrease in the availability of carbonate ions (CO<sub>3</sub><sup>2-</sup>) and a suppression of the saturation states ( $\Omega$ ) of calcium carbonate minerals (CaCO<sub>3</sub>), 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 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<sub>2</sub> (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 CO<sub>2</sub> 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, 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 eastern 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 the year, the Arctic Ocean is almost completely covered by sea-ice with only small areas of open water in the form of 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 marginal 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., 1995; Woodgate et al., 2005). As such, the physics and carbon biogeochemistry of the Chukchi Sea are 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  $\sim 0.8\text{-}1.0 \text{ Pg C yr}^{-1}$  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  $\sim 135 \text{ Tg C yr}^{-1}$  ( $\text{Tg} = 10^{12} \text{ g}$ ) 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; Among, 2004; Rachold *et al.*, 2004; Guo and Macdonald, 2006; Raymond *et al.*, 2007; Holmes *et al.*, 2008). Pan-arctic river inputs of carbon have been estimated by McGuire *et al.* (2009) at  $33 \text{ Tg C yr}^{-1}$  of DOC and  $43.2 \text{ Tg C yr}^{-1}$  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  $\sim 12 \text{ Tg C yr}^{-1}$  (e.g., Rachold *et al.*, 2004; Macdonald *et al.*, 2010). 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 marine carbon cycle in the Arctic Ocean 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,  $\text{CO}_2$  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 shelves of the Arctic Ocean (Cota et al., 1996; Hill and Cota, 2005) where nutrients are more limited. Occupying the base of the food web, primary production rates of phytoplankton 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., 2005; Mathis et al., 2009; Macdonald et al., 2010). Intense seasonal growth of marine phytoplankton supports a large zooplankton biomass that in turn supports diverse open water 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., gray whale, walrus, and 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.*, 2005; Moran et al., 2005; Lepore et al., 2007) (Figure 1). High concentrations of sPOC have been observed (up to  $2000 \text{ mg C L}^{-1}$ ; 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 bottom waters over the shelf.

Pigment analysis of phytoplankton is a well-established technique to map phytoplankton populations and distributions, and to monitor their abundance and composition (Wright, 2005). In the past, these parameters have been determined by microscopy. However, microscopy is time-consuming and some species are too small to be identified via microscopy. Pigments are used as biomarkers of phytoplankton groups and while some pigments are unique markers of one phytoplankton group (such as peridinin for dinoflagellates), most of the pigments are shared between groups (such as fucoxanthin for diatoms and prymnesiophytes) (Jeffrey, 1994). Pigment concentrations, which are used in this study, provide a qualitative abundance of each phytoplankton group.

## *Air-Sea Fluxes of CO<sub>2</sub>*

The export character of the shelf conditions the surface waters of the Chukchi Sea to be a strong sink for atmospheric CO<sub>2</sub>. Early studies of the Chukchi Sea (Semiletov 1999) showed that seawater  $p\text{CO}_2$  (~200-350  $\mu\text{atm}$ ) ( $\mu\text{atm} = 10^{-6} \text{ atm}$ ) values were lower than the atmosphere (~365-380  $\mu\text{atm}$  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 summer (~150-350  $\mu\text{atm}$ ; 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 is the main 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 primary production of phytoplankton or net community production (Bates et al., 2005; Mathis et al., 2007), especially in the vicinity of Barrow Canyon (at the northern edge of the Chukchi Sea shelf; Bates et al., 2005; 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<sub>2</sub> from the atmosphere and winter mixing induced from brine rejection (Anderson et al., 2004; Omar et al., 2007). 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  $\mu\text{atm}$  relative to the atmosphere, creating a strong driving force for air-sea exchange. Previous estimates of the rates of air-sea CO<sub>2</sub> exchange during the sea-ice free period in the summertime have ranged from approximately -20 to -90 mmol CO<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> (mmol = 10<sup>-3</sup> 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<sub>2</sub> (Kaltin and Anderson, 2005). The annual ocean CO<sub>2</sub> uptake for the Chukchi Sea shelf has been estimated at 2-9 mmol C m<sup>-2</sup> yr<sup>-1</sup> (Katlin and Anderson, 2005; Bates, 2006), or approximately 11 to 53 Tg C yr<sup>-1</sup>. These studies show that the Chukchi Sea shelf dominates air-sea CO<sub>2</sub> 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  $\Omega$ , 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 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  $\text{CO}_2$  into the oceans, particularly in high latitude regions. The decrease in seawater pH due to the uptake of  $\text{CO}_2$  (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  $\text{CO}_2$  has already decreased surface water pH by 0.1 units when averaged across the global ocean. Intergovernmental Panel on Climate Change (IPCC) scenarios, based on present-day  $\text{CO}_2$  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  $\text{CaCO}_3$  production by calcifying fauna (Buddemeier et al., 2004; Fabry et al., 2008) and increased  $\text{CaCO}_3$  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, 2010; Yamamoto-Kawai et al., 2009; Chierici 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  $\text{CaCO}_3$  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  $\text{CO}_2$  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  $\text{CO}_2$  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 (1202, 1203, and 1204) to the study area in August and September of 2012 (Figure 2). Samples for DIC and TA were collected at all three studies sites in August and only at the expanded study sites in September. 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 ( $\text{HgCl}_2$ ) 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). Pigment (phytoplankton) samples were collected by filtering three liters of seawater through 47mm glass fiber filters. The filters were stored in liquid nitrogen.

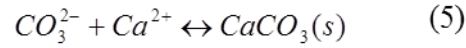
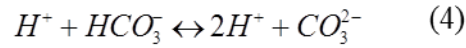
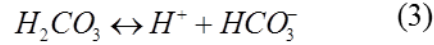
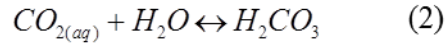
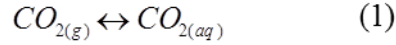
### *Laboratory Analysis and Calculation of Carbonate Parameters*

DIC and TA samples were analyzed using 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<sub>2</sub> 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% ( $\sim 1 \mu\text{mol kg}^{-1}$ ,  $\mu\text{mol} = 10^{-6} \text{ mol}$ ) and stable over time. Seawater  $p\text{CO}_2$ , pH and CaCO<sub>3</sub> saturation states for calcite ( $\Omega_{\text{calcite}}$ ) and aragonite ( $\Omega_{\text{aragonite}}$ ) 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 CO<sub>2</sub> 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  $\Omega_{\text{calcite}}$  and  $\Omega_{\text{aragonite}}$  were  $\sim 0.02$ .

Pigment samples were analyzed using High Performance Liquid Chromatography (HPLC). The filters were extracted into acetone for 16 hours in a -20 °C freezer. The samples were filtered and 1000  $\mu\text{L}$  were mixed with 300  $\mu\text{L}$  of milliQ water and 200  $\mu\text{L}$  of the mixed solution were injected into the Agilent HPLC instrument. Pigment concentrations were calculated from peak areas obtained from the phytoplankton pigment standards.

## *Basis of the Arctic Marine Carbonate System*

As CO<sub>2</sub> levels rise in the atmosphere, the increased pCO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>3</sub><sup>2-</sup> (Eq. 5) decreases the saturation states of both aragonite and calcite:

$$\Omega_{aragonite} = \frac{[Ca^{2+}][CO_3^{2-}]}{K^*_{SP_{aragonite}}} \quad (6)$$

$$\Omega_{calcite} = \frac{[Ca^{2+}][CO_3^{2-}]}{K^*_{SP_{calcite}}} \quad (7)$$

Cold ocean temperatures increase the solubility of CO<sub>2</sub> 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 sub-polar 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.*, 2010) 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  $\Omega$  in the mixed layer while an accumulation of DIC in subsurface waters through remineralization suppresses  $\Omega$  (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. Further decreases in pH and  $\Omega$  could have significant consequences for the benthic and pelagic ecosystems in a region where organisms are already struggling to adapt to changing environmental conditions (Løvorn *et al.*, 2003; Moore *et al.*, 2003; Overland and Stabeno, 2004; Grebmeier *et al.*, 2006).

## RESULTS

### *August cruise (Cruise 1202)*

Bottom DIC and TA gradually increased in concentration from the southernmost stations of Klondike to the northernmost stations of Burger and Statoil, while bottom pH and  $\Omega_{\text{arag}}$  decreased (Figure 3). The lowest bottom DIC and TA concentrations were found at Klondike ( $\text{DIC}^{\text{min}} = 2003 \mu\text{moles kg}^{-1}$ ;  $\text{TA}^{\text{min}} = 2217 \mu\text{moles kg}^{-1}$ ). The average bottom DIC and TA were higher at Statoil ( $\text{DIC}^{\text{mean}} = 2226 \mu\text{moles kg}^{-1}$ ;  $\text{TA}^{\text{mean}} = 2287 \mu\text{moles kg}^{-1}$ ) than at Burger ( $\text{DIC}^{\text{mean}} = 2189 \mu\text{moles kg}^{-1}$ ;  $\text{TA}^{\text{mean}} = 2275 \mu\text{moles kg}^{-1}$ ), while maximum concentrations of DIC and TA were found at Burger, reaching  $2298 \mu\text{moles kg}^{-1}$  and  $2318 \mu\text{moles kg}^{-1}$ , respectively. Salinity was also highest at Burger ( $S^{\text{max}} = 33.37$ ), with a small decrease towards the south at Klondike ( $S^{\text{min}} = 32.28$ ). Temperature was negatively correlated with DIC, TA and salinity and progressively decreased from south Klondike to north Statoil ( $T^{\text{max}} = 4.6^{\circ}\text{C}$ ,  $T^{\text{min}} = -1.7^{\circ}\text{C}$ ) (Figure 4).

This pattern was accompanied by highest  $p\text{CO}_2$ , and lowest pH and  $\Omega_{\text{arag}}$  values at Burger ( $p\text{CO}_2^{\text{max}} = 920 \mu\text{atm}$ ;  $\text{pH}^{\text{min}} = 7.68$ ;  $\Omega_{\text{arag}}^{\text{min}} = 0.58$ ). Bottom waters undersaturated with respect to aragonite were found at Burger and Statoil, while  $\Omega_{\text{arag}}$  remained oversaturated in Klondike, ranging between 1.73 and 2.35. Bottom waters at Burger were also undersaturated with regard to calcite ( $\Omega_{\text{calc}}^{\text{min}} = 0.93$ ) and were very close to calcite undersaturation ( $\Omega_{\text{calc}}^{\text{min}} = 1.01$ ) at Statoil.

At the surface, the carbonate chemistry followed an opposite pattern than was observed at the bottom (Figure 5). The highest values of DIC and TA were found at Klondike, with a maximum of  $1992 \mu\text{moles kg}^{-1}$  and  $2118 \mu\text{moles kg}^{-1}$ , respectively. At Statoil, surface DIC and TA concentrations were lowest ( $\text{DIC}^{\text{min}} = 1734 \mu\text{moles kg}^{-1}$ ;  $\text{TA}^{\text{min}} = 1951 \mu\text{moles kg}^{-1}$ ). Temperature was also lowest at Statoil and highest at Klondike, ranging from  $-0.18^\circ\text{C}$  to  $6.6^\circ\text{C}$  (Figure 6). A  $p\text{CO}_2$  minimum value of  $86.6 \mu\text{atm}$  was observed at Statoil, while the maximum value of  $266.9 \mu\text{atm}$  was measured at Burger. pH and  $\Omega_{\text{arag}}$  increased from Klondike to Statoil. All surface waters were supersaturated with regard to aragonite, with lowest levels of 1.71 found at Burger. The highest chlorophyll-*a* concentrations were found north of Burger and Statoil ( $\text{chl } a^{\text{max}} = 376.2 \text{ ng L}^{-1}$ ), which was accompanied by high fucoxanthin and alloxanthin concentrations ( $\text{fux}^{\text{max}} = 98.7 \text{ ng L}^{-1}$ ;  $\text{alx}^{\text{max}} = 16.4 \text{ ng L}^{-1}$ ), suggesting the presence of diatoms and cryptophytes (Figure 11).

### *September cruises (Cruises 1203 and 1204)*

September bottom observation showed a similar pattern as in August with an increase of DIC and TA concentrations from south to north while pH and  $\Omega_{\text{arag}}$  decreased. The highest bottom DIC and TA concentrations,  $2302 \mu\text{moles kg}^{-1}$  and  $2299 \mu\text{moles kg}^{-1}$  respectively, were found in the northern part of Hanna Shoal, along with the lowest temperatures ranging between  $-1.7$  and  $-1.2^\circ\text{C}$  (Figures 7 and 8). TA concentrations in Herald Shoal and the central area showed little variability, ranging between  $2250$  and  $2260 \mu\text{moles kg}^{-1}$  respectively, whereas DIC values were more variable, ranging between  $2106$  and  $2156 \mu\text{moles kg}^{-1}$ . This pattern was followed by the highest  $p\text{CO}_2$  levels ( $p\text{CO}_2^{\text{max}} = 1157.8 \mu\text{atm}$ ), highest salinities ( $S^{\text{max}} = 33.31$ ) and lowest pH and  $\Omega_{\text{arag}}$  ( $\text{pH}^{\text{min}} = 7.58$ ;  $\Omega_{\text{arag}}^{\text{min}} = 0.47$ ) in Hanna Shoal. Bottom waters undersaturated with regard to

aragonite were found in Hanna Shoal, while  $\Omega_{\text{arag}}$  remained supersaturated in Herald Shoal, ranging from 1.17 to 2.10. Waters remained oversaturated with regard to calcite, except in Hanna Shoal, where  $\Omega_{\text{calc}}$  reached a minimum of 0.75.

At the surface, the DIC and TA followed an opposite pattern than was observed at the bottom (Figure 9). The lowest surface DIC and TA concentrations were found in Hanna Shoal, with a minimum of 1736  $\mu\text{moles kg}^{-1}$  and 1882  $\mu\text{moles kg}^{-1}$  respectively, accompanied by the lowest temperatures and salinities with minima of 0.2°C and 26.77 respectively (Figure 10). The highest concentrations of TA and DIC were found in Herald Shoal, where surface water is warm and salty ( $\text{DIC}^{\text{max}} = 2011 \mu\text{moles kg}^{-1}$ ;  $\text{TA}^{\text{max}} = 2211 \mu\text{moles kg}^{-1}$ ;  $T^{\text{max}} = 5.4^\circ\text{C}$ ;  $S^{\text{max}} = 32.04$ ). Surface pH averaged 8.25 in the whole study area, and ranged between  $\text{pH}^{\text{min}} = 8.18$ , close to the coast, and  $\text{pH}^{\text{max}} = 8.66$ , in north Hanna Shoal. The lowest pH and  $\Omega_{\text{arag}}$  values were found in Hanna Shoal ( $\text{pH}^{\text{min}} = 8.18$ ;  $\Omega_{\text{arag}}^{\text{min}} = 1.37$ ). All surface waters were supersaturated with regard to aragonite, with a maximum of 2.37 found in Herald Shoal area. The high  $\Omega_{\text{arag}}$  were accompanied by high chlorophyll a concentrations ( $\text{chl}^{\text{a max}} = 2039 \text{ ng.L}^{-1}$ ), with highest concentrations of fucoxanthin and 19'-hexfucoxanthin ( $\text{fux}^{\text{max}} = 806 \text{ ng.L}^{-1}$ ;  $19\text{hex}^{\text{max}} = 238 \text{ ng.L}^{-1}$ ), which correspond to high abundance of diatoms and prymnesiophytes respectively (Figure 12).

Depth profiles showed a gradual increase of  $p\text{CO}_2$ , DIC and TA in both months, while pH and  $\Omega_{\text{arag}}$  decrease (Figures 13-17). In August, TA and DIC reached maximum concentrations below 30 m depth ( $\text{DIC}^{\text{max}} = 2348 \mu\text{moles kg}^{-1}$ ;  $\text{TA}^{\text{max}} = 2318 \mu\text{moles kg}^{-1}$ ). At the surface, TA ranged between 1887 and 2210  $\mu\text{moles kg}^{-1}$ , whereas TA only varied between 2210 and 2308  $\mu\text{moles kg}^{-1}$  along the seafloor.  $p\text{CO}_2$  showed an opposite pattern and ranged between and 124.0 and 924.1  $\mu\text{atm}$  near the bottom.

September observations along the DBO line showed that surface DIC concentrations increased slightly from Wainwright to Burger, with a minimum concentration of 1821  $\mu\text{moles kg}^{-1}$  close to the coast to a maximum of 2028  $\mu\text{mol.kg}^{-1}$  offshore, while the highest TA,  $p\text{CO}_2$  and salinities were found close to Wainwright ( $\text{TA}^{\text{max}} = 2142 \mu\text{moles kg}$ ;  $p\text{CO}_2 = 262.4 \mu\text{atm}$ ;  $S^{\text{max}} = 31.8$ ) (Figure 9). This pattern was followed by a decrease of temperature with a maximum of 4.2°C close to shore and a minimum of 0.4 off shore (Figure 10). This pattern was accompanied by the lowest pH values found near-shore ( $\text{pH}^{\text{min}} = 8.18$ ). The aragonite saturation state was similar

through the water column close to the coast and at the surface to Burger ( $\Omega_{\text{arag}} = 2$ ). Undersaturated waters with respect to aragonite were found further off shore below 30m depth with  $\Omega_{\text{arag}}$  decreasing gradually and reaching a minimum at Burger ( $\Omega_{\text{arag}}^{\text{min}} = 0.70$ ). After 30m depth, DIC and TA reach the highest values 2266 and 2287  $\mu\text{moles kg}^{-1}$  respectively, corresponding to a lower pH ( $\text{pH}^{\text{min}} = 7.8$ ) and water close to undersaturation (Figure 16). Salinity and temperature showed the same feature with cold water after 30 m ( $T^{\text{min}} = -1.4^{\circ}\text{C}$ ) and higher salinity ( $S^{\text{max}} = 33.07$ ) (Figure 18).

## DISCUSSION

The combination of several biological and physical drivers, such as production and remineralization of organic matter, changes in temperature, intrusion of different water masses, sea ice melt and riverine input all induced the large observed variability in the carbonate parameters. High biological productivity along the sea ice margin counteracted the effect of sea ice melt water, resulting in relatively high pH and  $\Omega_{\text{arag}}$  at the northern most stations in both August and September (Figures 5 and 6). The low salinity, temperature and TA levels at the northern sites suggest that a significant amount of sea ice melt water was present. These sites also showed a high chlorophyll-*a* concentration, mostly due to high abundances of diatoms and cryptophytes right at the sea ice edge. High productivity decreased DIC and counteracted the TA-reducing sea ice melt effect, resulting in higher pH and carbonate mineral saturation states at these ice affected locations.

The combination of respiration of organic matter, water depth and some upwelling of deep Canada Basin water strongly influenced the northern part of the Chukchi Shelf with  $\text{CO}_2$ -rich water, leading to undersaturation with regard to aragonite (Figure 18). High salinity, DIC and TA concentrations were well correlated with the cold-water signal observed along the seafloor in the Hanna Shoal region and along the DBO line. The overall increase of bottom DIC and  $\text{pCO}_2$  between August and September is most likely due to remineralization of organic material at depth. However, additional oxygen measurements, or any other sort of data describing remineralization processes, would need to be taken in order to confirm this hypothesis.



A comparison of the last two field seasons suggests that in 2012, conditions in the northern Chukchi Sea were characterized by a strong sea-ice melt signal, enhancing stratification; whereas in 2011, waters were well mixed. 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. Surface values for  $p\text{CO}_2$  in 2011 were higher than in 2012, most likely due to mixing of remineralized  $\text{CO}_2$  from the bottom to the surface. These findings highlight the dynamic nature of this marine ecosystem, especially on an interannual timescale.

### *Timing of Ice Retreat*

As a strong low salinity and cold water signal in the surface waters from ice melt was present in 2012, 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 on seasonal production is minimal during blooms associated with colder surface water temperatures. This is favorable for 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 of 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  $\text{CO}_2$  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, 2011 and 2012 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 during the subsequent ice-free period. The consumption of DIC derived 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  $\text{CO}_2$ . 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 primary production of phytoplankton and zooplankton grazing cause large quantities of organic matter to be exported from the mixed layer to the seafloor. When this organic matter is remineralized by bacteria, it adds DIC back to the water column, lowering 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 are natural phenomena. However, the rising inventory of  $\text{CO}_2$  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 dominate the Chukchi Sea fauna. While ocean acidification is a global issue, 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 of how the global ocean will respond.

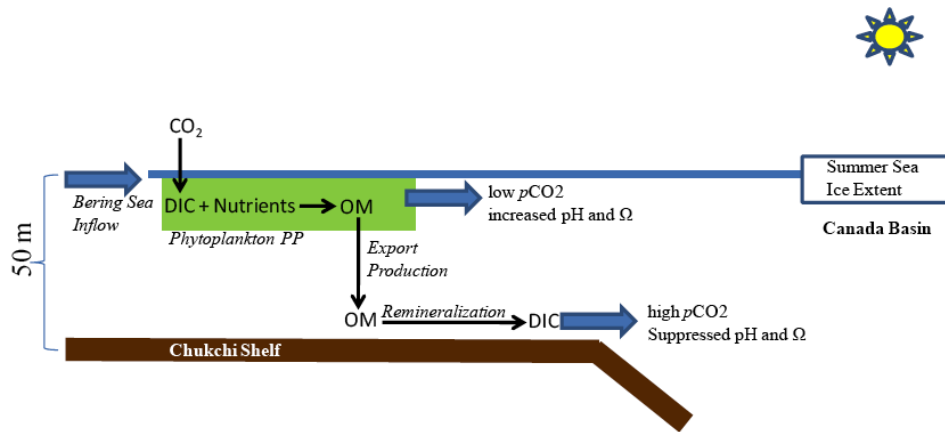


Figure 1. Schematic of the influences on the carbon cycle in the Chukchi Sea. High rates of primary production (green box) consumes DIC, lowering the  $p\text{CO}_2$  of the surface waters and promoting air-sea exchange. However, air-sea exchange happens much slower than primary production leaving the surface waters undersaturated with respect to atmospheric  $\text{CO}_2$  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  $\text{CO}_2$  and the upper halocline of the western Arctic Ocean to be undersaturated in aragonite.

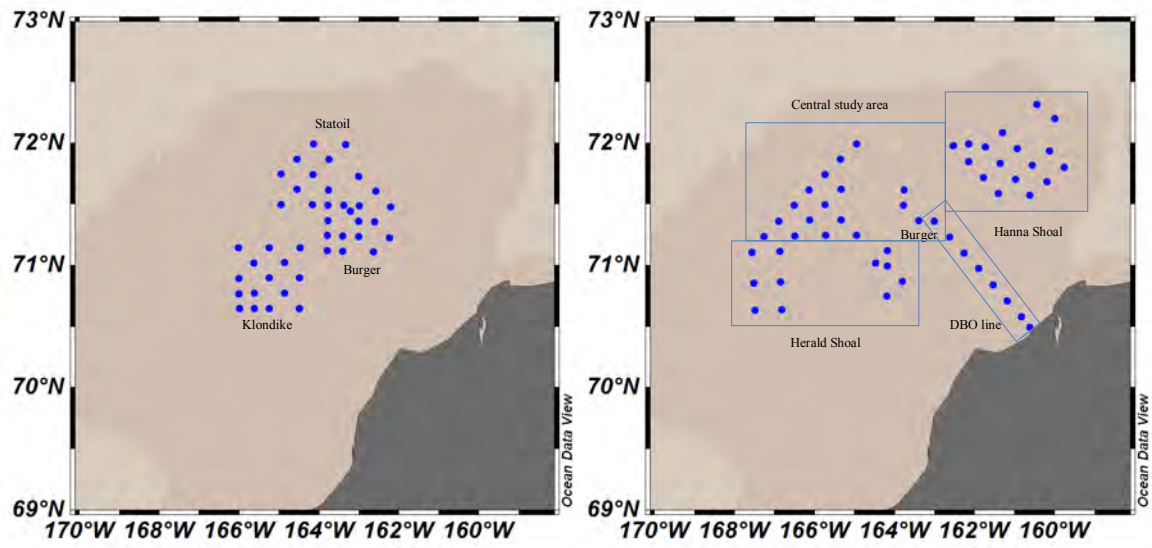


Figure 2. Location of the study areas where carbon measurements were taken in 2012 (Cruises 1202, 1203, and 1204).

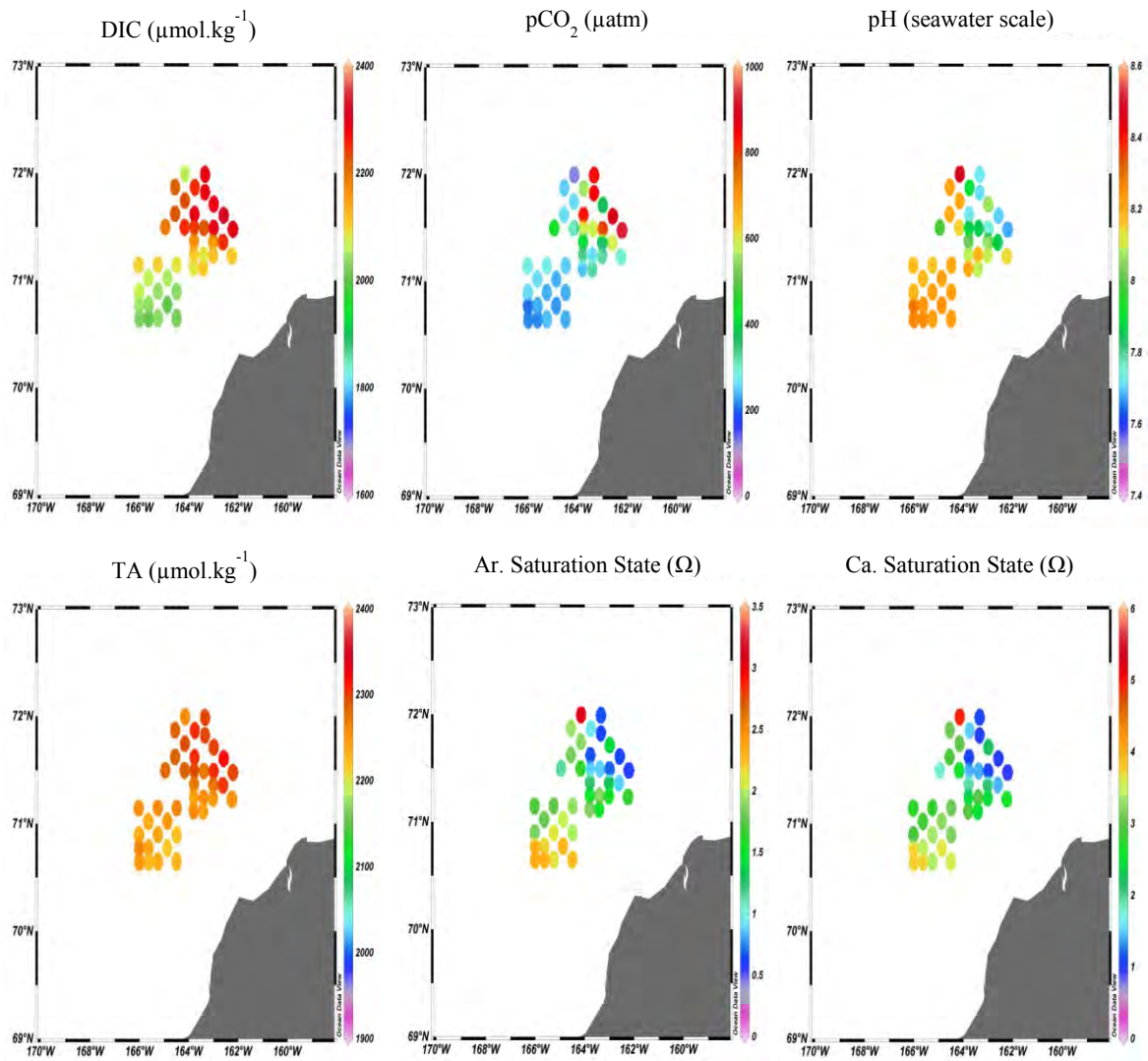


Figure 3. Observations of DIC and TA ( $\mu\text{mol.kg}^{-1}$ ) and calculated values for  $p\text{CO}_2$  ( $\mu\text{atm}$ ), pH (seawater scale), calcite saturation state ( $\Omega$ ), and aragonite saturation state ( $\Omega$ ) along the bottom in August (cruise 1202).

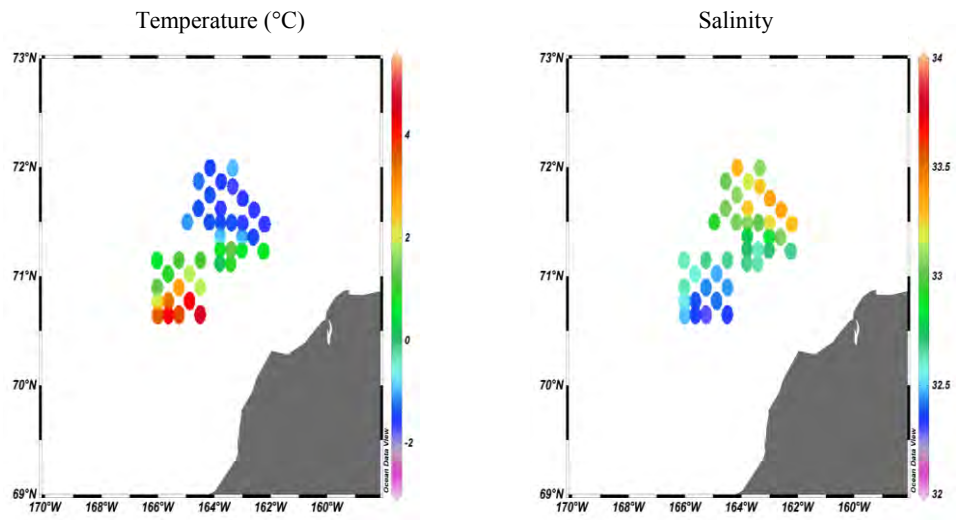


Figure 4. Observations of temperature (°C) and salinity along the bottom in August.

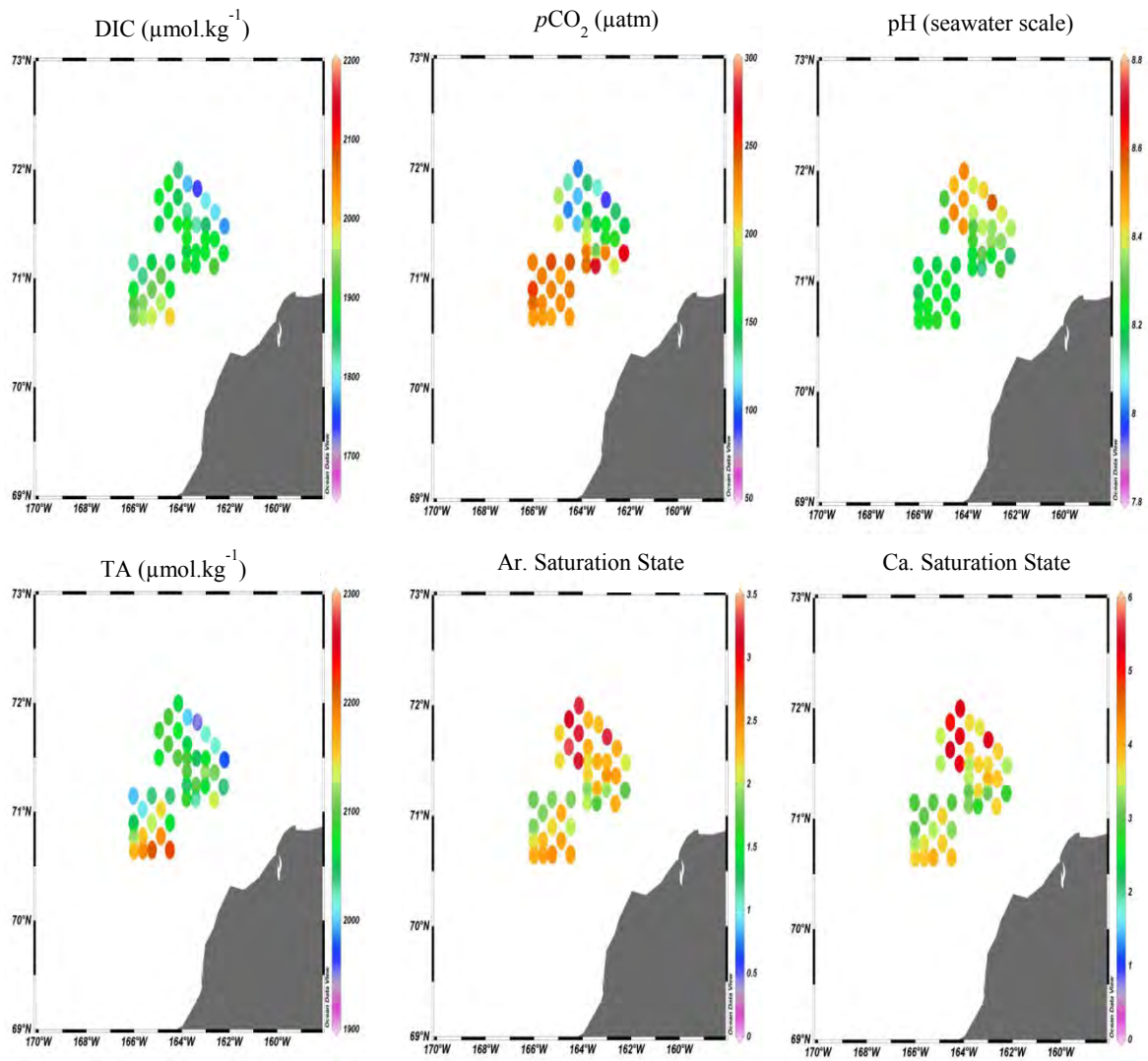


Figure 5. Observations of DIC and TA ( $\mu\text{mol.kg}^{-1}$ ) and calculated values for  $p\text{CO}_2$  ( $\mu\text{atm}$ ), pH (seawater scale), calcite saturation state ( $\Omega$ ), and aragonite saturation state ( $\Omega$ ) at the surface in August.

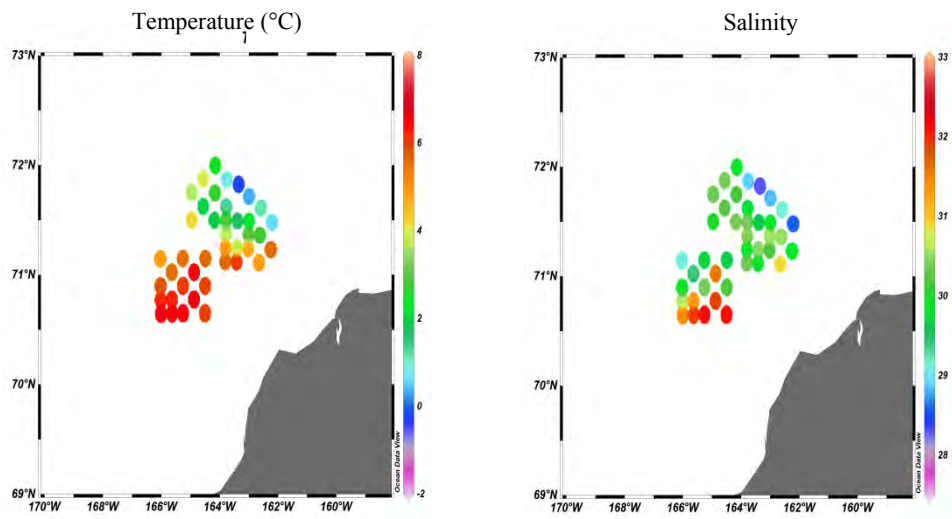


Figure 6. Observations of temperature (°C) and salinity along the surface in August.



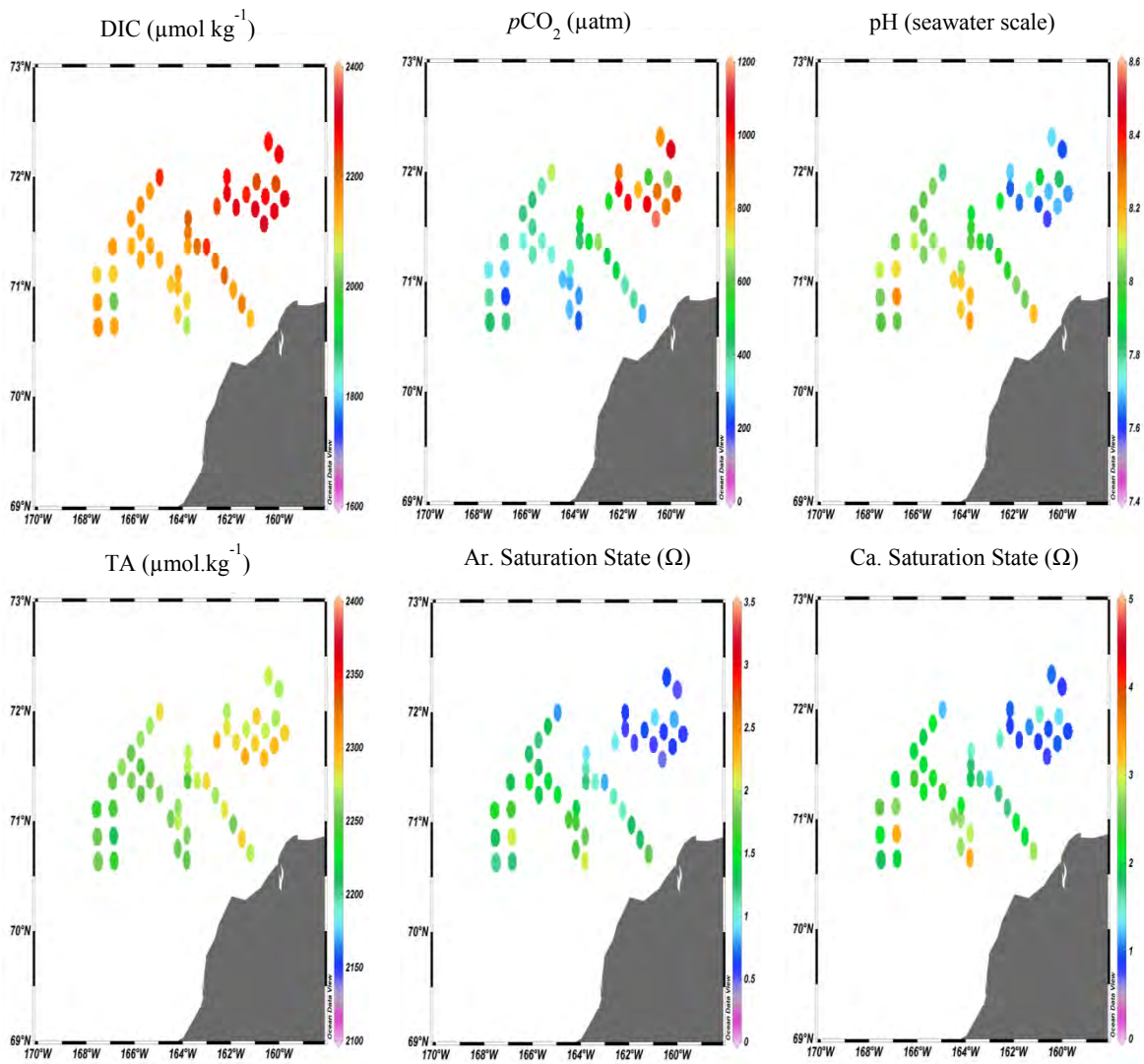


Figure 7. Observations of DIC and TA ( $\mu\text{mol kg}^{-1}$ ) and calculated values for  $p\text{CO}_2$  ( $\mu\text{atm}$ ), pH (seawater scale), calcite saturation state ( $\Omega$ ), and aragonite saturation state ( $\Omega$ ) along the bottom in September.

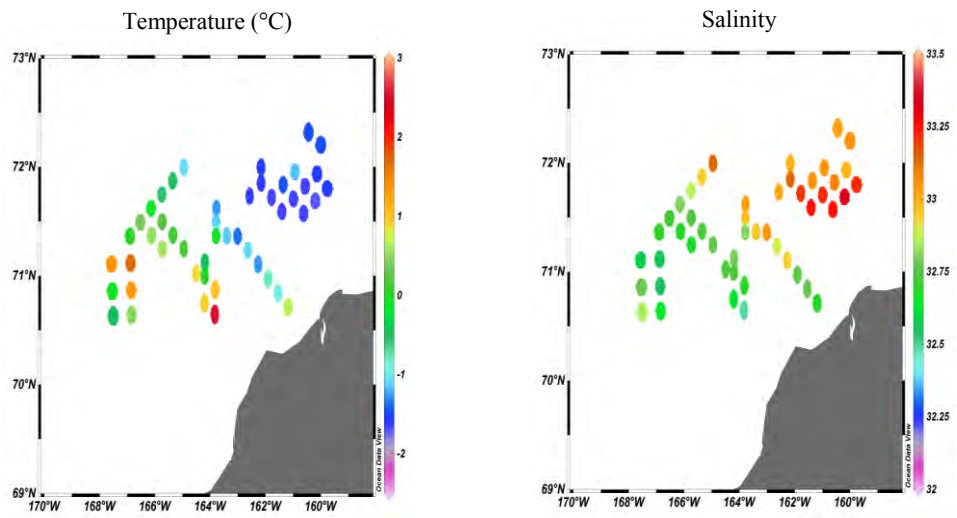


Figure 8. Observations of temperature (°C) and salinity along the bottom in September.

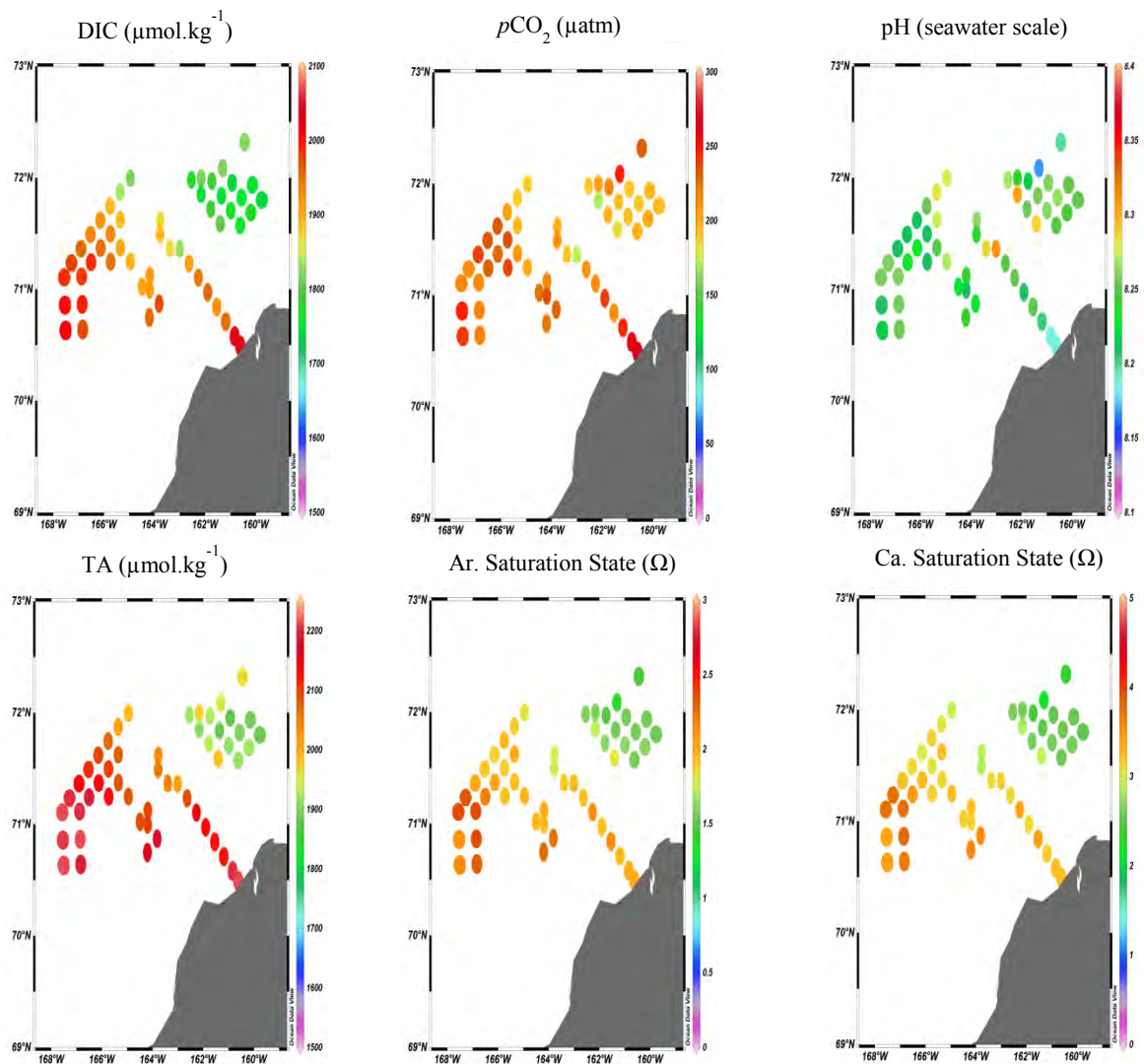


Figure 9. Observations of DIC and TA ( $\mu\text{mol.kg}^{-1}$ ) and calculated values for  $p\text{CO}_2$  ( $\mu\text{atm}$ ), pH (seawater scale), calcite saturation state ( $\Omega$ ), and aragonite saturation state ( $\Omega$ ) along the surface in September (cruises 1203 and 1204).

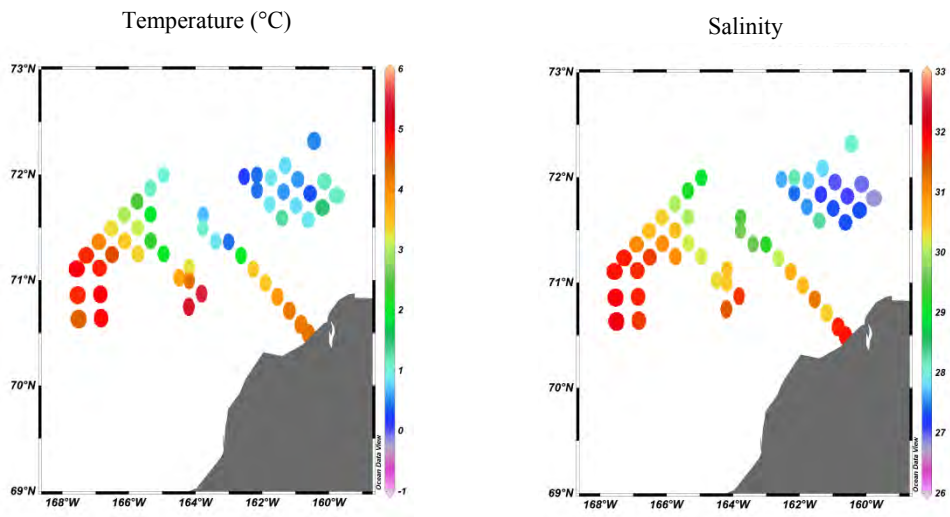


Figure 10. Observations of temperature (°C) and salinity along the surface in September.

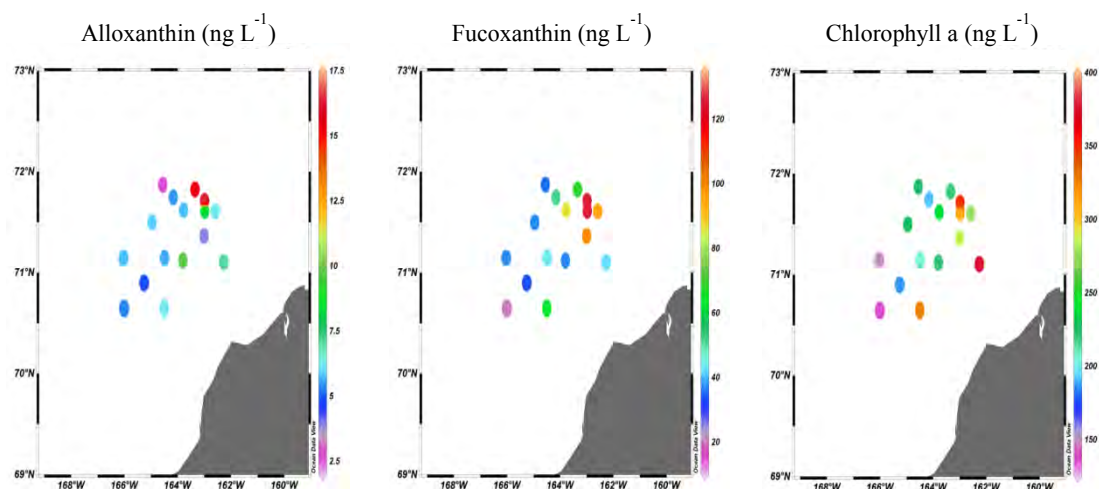


Figure 11. Observations of alloxanthin, fucoxanthin, and chlorophyll a concentrations (ng L<sup>-1</sup>) along the surface in August (cruise 1202).

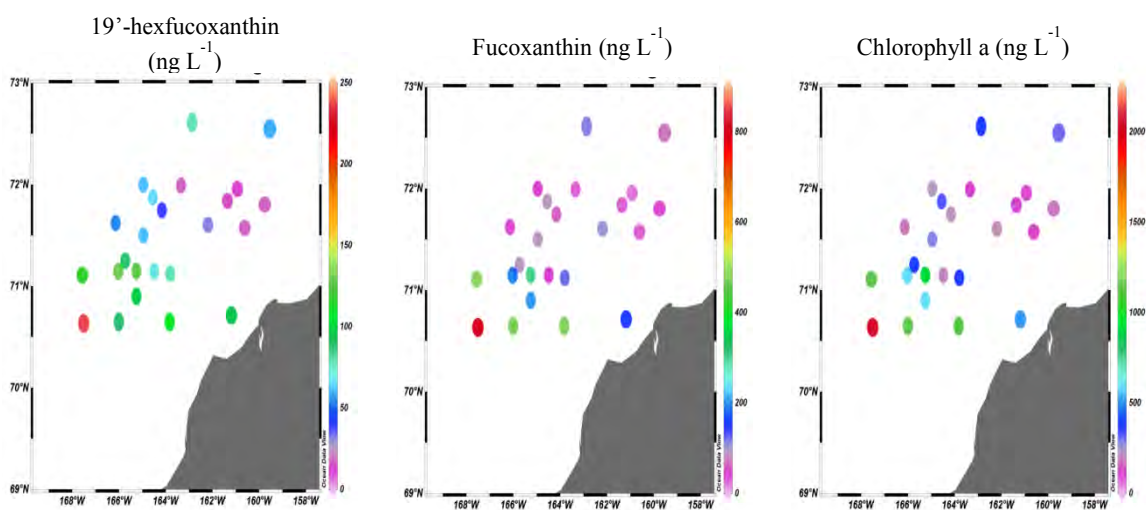


Figure 12. Observations of (a) 19'-hexfucoxanthin, fucoxanthin, and chlorophyll a concentrations (ng L<sup>-1</sup>) along the surface in September (cruises 1203 and 1204).

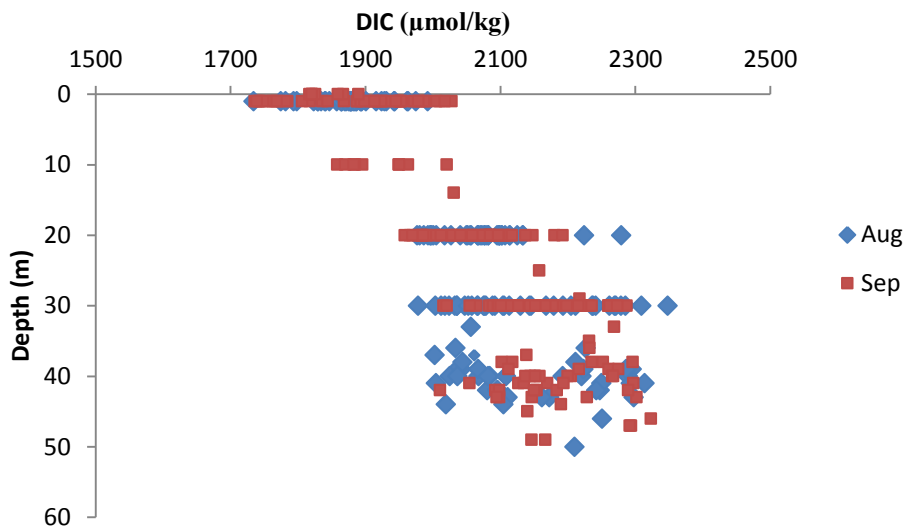


Figure 13. Observed DIC ( $\mu\text{mol.kg}^{-1}$ ) vs. depth (m) in August and September in the study area.

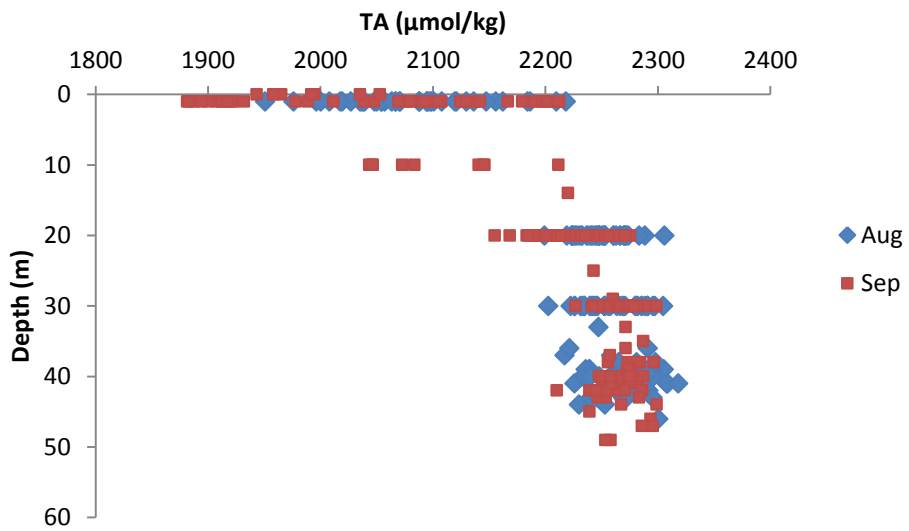


Figure 14. Observed TA ( $\mu\text{mol kg}^{-1}$ ) vs. depth (m) in August and September in the study area.

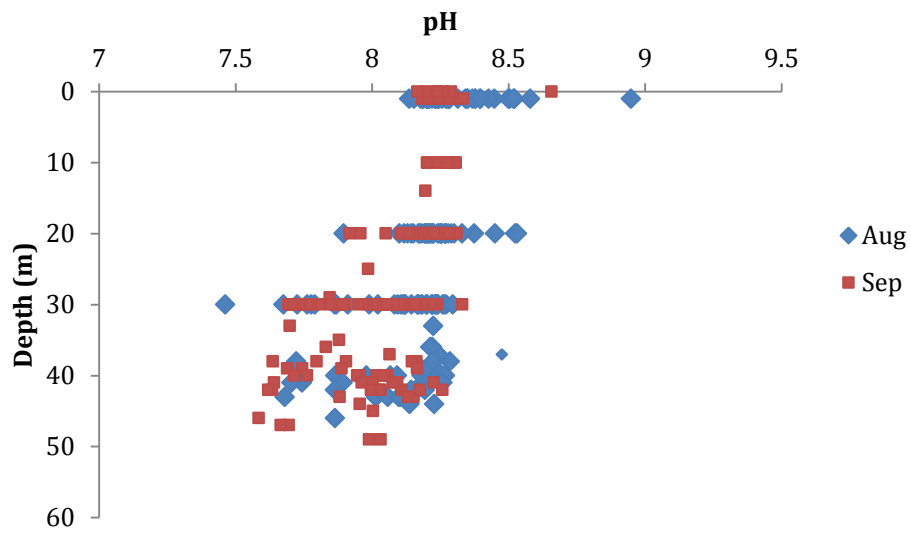


Figure 15. Calculated pH (seawater scale) vs. depth (m) in August and September in the study area.

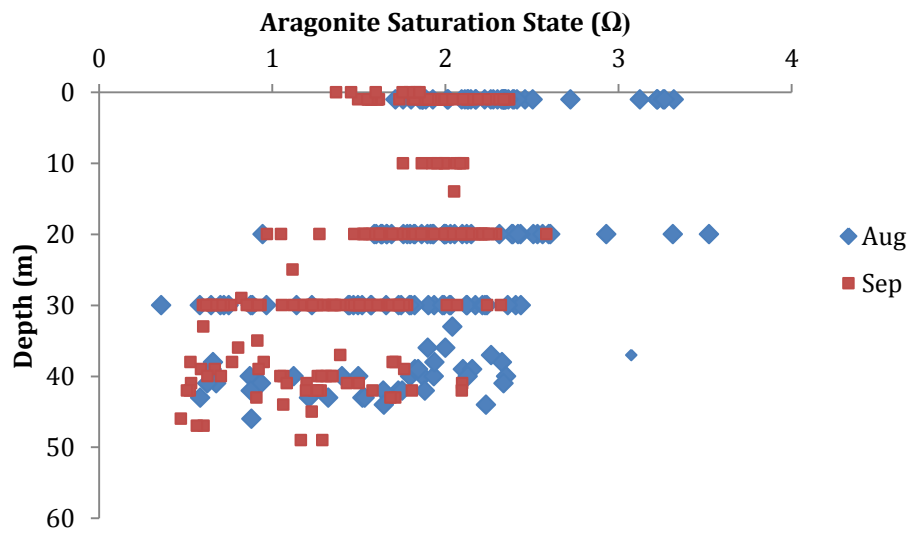


Figure 16. Calculated aragonite saturation state ( $\Omega$ ) vs. depth (m) in August and September in the study area.

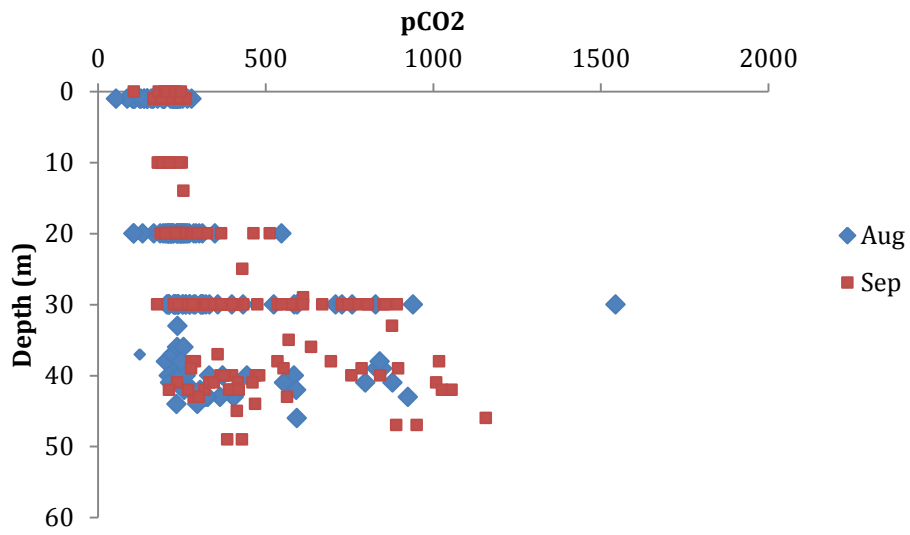


Figure 17. Calculated  $pCO_2$  ( $\mu atm$ ) vs. depth (m) in August and September in the study area.



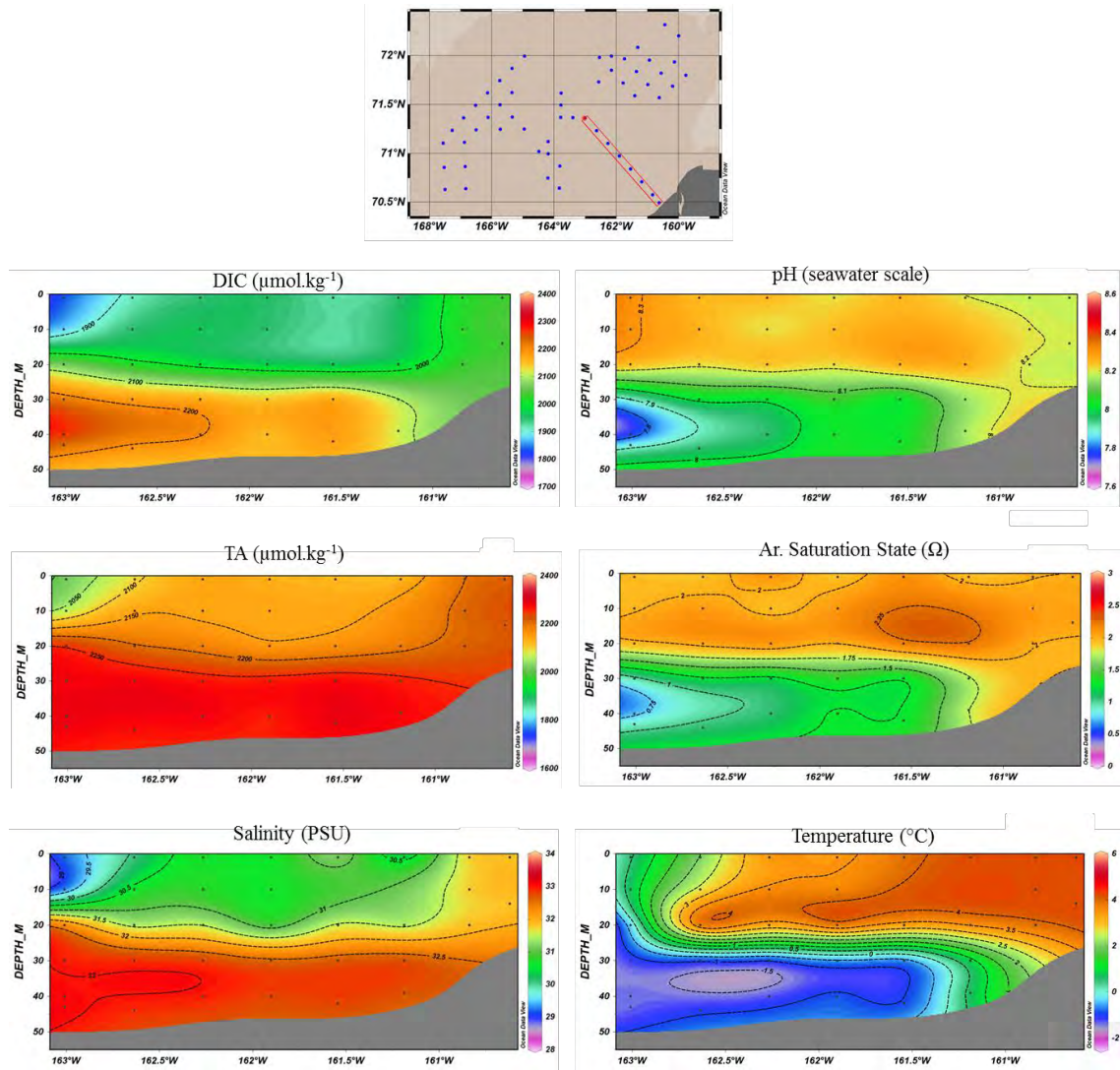


Figure 18. Observations of DIC and TA ( $\mu\text{mol.kg}^{-1}$ ) along with salinity and temperature ( $^{\circ}\text{C}$ ) with calculated values for pH (seawater scale) and aragonite saturation state ( $\Omega$ ) in a section of the DBO line in September.

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