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BGD

6, 4963–4991, 2009

**Calcium carbonate
undersaturation in
Arctic shelves**

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Calcium carbonate saturation in the surface water of the Arctic Ocean: undersaturation in freshwater influenced shelves

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Abstract

In the summer of 2005, we sampled surface water and measured pH and total alkalinity (A_T) underway aboard *IB Oden* along the Northwest Passage from Cape Farwell (South Greenland) to the Chukchi Sea. We investigated variability of carbonate system parameters, focusing particularly on carbonate concentration [CO_3^{2-}] and calcium carbonate saturation states, as related to freshwater addition, biological processes and physical upwelling. Measurements on A_T, pH at 15°C, salinity (S) and sea surface temperature (SST), were used to calculate total dissolved inorganic carbon (DIC), [CO_3^{2-}] and saturation of aragonite (ΩAr) and calcite (ΩCa) in the surface water. The same parameters were measured in the water column of the Bering Strait. Some surface waters in the Canadian Arctic Archipelago (CAA) and on the Mackenzie shelf (MS) were found to be undersaturated with respect to aragonite (ΩAr<1). In these areas, surface water was low in A_T and DIC (<1500 μmol kg^{-1}) relative to seawater and showed low [CO_3^{2-}]. The low saturation states were probably due to the effect of dilution due from freshwater addition by sea ice melt (CAA) and river runoff (MS). High A_T and DIC and low pH, corresponded with the lowest [CO_3^{2-}], ΩAr and ΩCa, observed near Cape Bathurst and along the South Chukchi Peninsula. This was linked to physical upwelling of subsurface water with elevated CO_2. Highest surface ΩAr and ΩCa of 3.0 and 4.5, respectively, were found on the Chukchi Sea shelf and in the cold water north of Wrangel Island, which is heavily influenced by high CO_2 drawdown and lower DIC from intense biological production. In the western Bering Strait, the cold and saline Anadyr Current carries water that is enriched in A_T and DIC from enhanced organic matter remineralization, resulting in the lowest ΩAr (~1.2) of the area.

1 Introduction

The gradual CO_2 increase in the ocean due to the uptake of anthropogenic CO_2 is of major concern, due to the changes in the oceanic CO_2 system and the effect on marine

life (Raven et al., 2005). The matter of ocean acidification caused by the CO_2 uptake was discussed as early as in the 1970's (e.g. Skirrow and Whitfield, 1975; Broecker and Takahashi, 1977), and has gained increased attention during the 21st century. The CO_2 in itself is an "acidic" molecule, which means that the dissolved CO_2 gas re-

5 acts with water to form carbonic acid (H_2CO_3, Eq. 1). The increased atmospheric CO_2 uptake by the oceans has lead to a decrease in pH and a decrease in the concentration of carbonate ions ($[CO_3^{2-}]$). Since the industrial revolution, the surface ocean pH has dropped by 0.1 units (Caldeira and Wickett, 2003) and is projected to drop another 0.3 to 0.4 units by 2100 (Feely et al., 2004; Orr et al., 2005). The increase of anthro-

10 pogenic CO_2 has lead to a shallower carbonate dissolution horizon of several hundred of meters in the Japan Sea (Park et al., 2006). Several laboratory studies have shown that reduction in levels of $CaCO_3$ saturation reduces calcification in marine calcifiers, such as calcifying phytoplankton (e.g. Riebesell et al., 2000) and coral reefs (Gattuso et al., 1998). However, the complexity of the marine biogeochemical processes and

15 the lack of a complete knowledge of the effect on oceanic CO_2 chemistry have lead to difficulties in predicting the consequences for marine life. It has also been difficult to set the appropriate threshold levels for a tolerable pH change (Zeebe et al., 2008). For a complete understanding of the effects of acidification, we need to assess all aspects of the forcing of the marine CO_2 system. Model results have shown that the high lati-

20 tude oceans will be the first to become undersaturated with respect to calcite and the aragonite (Orr et al., 2005).

The carbonate saturation (Ω) does not only depend on the $[CO_3^{2-}]$ but also on other factors such as pressure, temperature, salinity, and pH. Ocean pH is affected by biological primary production and respiration, physical mixing, air-sea CO_2 exchange, and

25 ocean CO_2 chemistry. The CO_2 uptake during formation of soft organic matter during photosynthesis increases the pH of surrounding water, whereas respiration of organic matter releases CO_2, leading to a pH decrease. Consequently, the balance between production and respiration and sinking of organic matter could be a major control of the $[CO_3^{2-}]$ saturation state in the whole water column. In the surface ocean, biological

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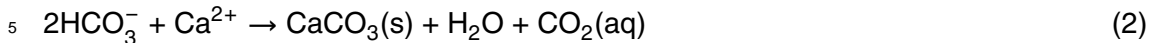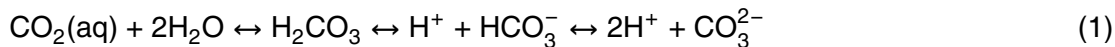
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production of hard parts, such as shells and skeletons, is the major process leading to $CaCO_3$ formation and takes place in the upper part of the ocean. This process produces CO_2 thus lowering pH according to Eqs. (1) and (2).

$$CO_2(aq) + 2H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-} \tag{1}$$

$$2HCO_3^- + Ca^{2+} \rightarrow CaCO_3(s) + H_2O + CO_2(aq) \tag{2}$$

Surface waters are generally supersaturated with respect to $CaCO_3$. However it is rare that chemical formation of $CaCO_3$ takes place due to complex ion-ion interactions, preventing a sufficient binding to the Ca^{2+} ion. Magnesium (Mg^{2+}) is one of the "competing" ions that depress a spontaneous thermodynamical $CaCO_3$ formation (e.g. Rushdi et al., 1992). It is only through biological processes that $CaCO_3(s)$ is formed. Aragonite (Ar) and calcite (Ca) are the two most common forms of $CaCO_3$ found in the ocean, with aragonite being the metastable form and calcite the stable form. Recently, there has been a report of undersaturation with respect to aragonite in the surface waters off the Oregon-California coast. This undersaturation was attributed to the natural upwelling of CO_2 rich subsurface waters in combination with increased ocean CO_2 concentrations from uptake of anthropogenic CO_2 (Feely et al., 2008). Cold and fresh water promotes $CaCO_3$ lower saturation states (Mucci et al., 1983). The Baltic Sea is a brackish and relatively cold enclosed ocean, entailing naturally low pH values and low carbonate saturation states in winter (Tyrrell et al., 2008). However, the Black Sea, another brackish water system, is strongly supersaturated year-round and has a presence of the calcifying phytoplankton *Emiliania huxleyi*. They suggest that the difference between these two brackish water systems may be due to differences in salinity and/or silicate concentration (Tyrrell et al., 2008). The combined effect of cold and relatively fresh water, and the highly biologically productive shelf seas, makes the Arctic Ocean one of the more sensitive areas for a continuing uptake of anthropogenic CO_2. Jutterström and Anderson (2005) investigated the carbonate saturation and the saturation horizon in the deeper ocean basins of the Arctic Ocean. They found that

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the saturation horizons of calcite (ΩCa=1) and aragonite (ΩAr=1) in the Arctic Ocean were located at approximately 4000 m and 2500 m, respectively. In a recent study by Azetsu-Scott et al. (2008), the saturation horizon for aragonite was revealed at 800 m in the Davis Strait and at 2500 m in the Labrador Sea.

5   In this study, we focus on the variability of the carbonate system in the coastal environment of the Arctic Ocean. We use measured total alkalinity (A_T), pH, salinity and temperature, collected by underway sampling on the cruise track along the Northwest Passage, to the Bering and the Chukchi seas in the summer of 2005. We also present a cross section of these parameters obtained from water column sampling in the Bering

10   Strait. Based on chemical equilibrium equations and sea surface salinity (S) and temperature (SST), we calculated the concentrations of the carbonate ion ($[CO_3^{2-}]$) and the calcite (ΩCa) and aragonite saturation states (ΩAr). The results are discussed with regard to the variability in the sea-ice cover, freshwater, and hydrography. One of our goals is to use the large natural variability of the marine carbonate system in this study

15   area, to provide basic information needed to predict the response to future changes in the $CaCO_3$ saturation of the upper Arctic Ocean due to changes in sea ice extent and temperature. We also provide methods to use underway sampling of seawater to study the CO_2 system and facilitate future monitoring of changes due to ocean acidification.

2 Study area

20   The *IB Oden* cruise track followed the Northwest Passage from Cape Farwell (South Greenland), passing through the Canadian Arctic Archipelago (CAA), the Mackenzie shelf (MS) and the Beaufort Sea shelf, the Chukchi Sea, the Bering Strait, and in the western East Siberian Sea (ESS), and northeast of Wrangler Island, WI, (Fig. 1). In these regions, the water is modified by mixing, seasonal freezing and melting, river

25   runoff and by biogeochemical processes. Carmack et al. (2006) summarizes the different characteristics of our study area and we have used their definitions to describe the physical state along the cruise track. Figure 1 shows the water sampling locations

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together with an illustration of the major surface currents in the study area.

Along the transect we encountered both ice-free areas and other areas with extensive ice cover throughout the summer. Sea-ice conditions are based on observations during the cruise, ice charts and the report from the Canadian Ice Services (CISA,
5 2005). Also, Fransson et al. (2009) describe the ice conditions and relative fractions of sea ice melt and river runoff computed from the A_T-S relationship. In our study area, the CAA and the area north of Wrangel Island were ice covered, whereas open water was found on the Mackenzie shelf, in the Bering Sea and over large parts of the Chukchi Sea. The southern Beaufort Sea was mainly ice-free.
10 Surface water salinity and temperature varied along the ship track (Fig. 2a and b). Relatively warm (∼4°C) and saline (∼33.9) Atlantic water enters the Labrador Sea. This water meets fresh and cold water from the Arctic Ocean that enters the Labrador Sea from the north, through the channels between the islands in the CAA. The coldest water of −1.5°C was observed in the CAA, in association with sea-ice cover. South of Banks
15 Island, we encountered open water and a dramatic temperature change from below 0 to 6°C, which coincided with a salinity increase from 27 to 32. This was probably associated with upwelling of warm, salty subsurface water around the Cape Bathurst Peninsula, where the shelf break in the Amundsen Gulf creates a polynya, which recurs annually (Barber and Hanesiak, 2004). At this same location, Fransson et al. (2009)
20 found elevated fugacity of CO_2 (fCO_2) in the surface water, which indicates upwelling of CO_2-rich subsurface water. Polynyas along the coast are sites of dense water production on the shelf (e.g. Shimada et al., 2005) and they are also important due to their large biological productivity (e.g. Grebmeier et al., 1988) and impact on the local carbon cycle.
25 The Mackenzie shelf was influenced by warm runoff from the Mackenzie River, where we observed a SST increase from about 4°C to 7°C and a salinity decrease from 30 to 11.9. The cruise passed over the shallow shelves of the southern Beaufort Sea and Chukchi Sea to the Bering Strait, where the Chukchi Sea is bounded on the south by the Bering Strait, on the west by Wrangel Island (WI), and on the east by Barrow

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Canyon. The warmest water of 8.9°C was measured in the southern part of the Chukchi Sea, close to the Siberian coast and at the southern coast of the Chukchi Peninsula. The Chukchi Sea is strongly forced, both physically and biologically, by the inflow of Pacific waters (0.8 Sv) and freshwater in the Alaskan Coast Current (ACC), entering through the Bering Strait (i.e. Weingartner et al., 2005). The Chukchi Sea also has seasonal ice cover that is highly variable from year to year.

The Diomede Islands divide the Bering Strait into two channels. A cross section of the temperature (T) and salinity (S) of the Bering Strait shows the influence of the cold and saline water in the western channel, originating from the Anadyr Current from the south (Fig. 3). On the eastern side (the Alaskan side), the Alaskan Coastal Current brings warm and fresh water, influenced heavily by the Alaskan rivers, which flows into the Arctic Ocean through the Bering Strait (Woodgate and Aagaard, 2005).

3   Data and methods

The *IB Oden* expedition took place from 12 July to 16 August 2005. Surface sea water was pumped to the main laboratory through stainless steel tubing from the ship's water intake, located at the bow at a depth of about 8 m. We collected discrete surface-water samples when the ship was in transit when ice conditions did not prevent sampling from the seawater intake. There was no sampling during 8 days, when the ship was awaiting other scientific missions and during exchange of scientists, when the ship was in Barrow (2 days). Also, no samples were taken when the ship sailed in parts of very heavy ice conditions because the seawater flow was not secure. At other times we sampled every 2 h, and in some areas (e.g. Mackenzie shelf, Bering Strait) every hour, measuring A_T and pH from the seawater intake. We obtained a total number of 242 discrete surface sampling locations which provided reliable samples. In the Bering Strait, water column samples were collected from a 12-bottle rosette attached to a Conductivity-Temperature-Depth (CTD)-sensor. Table 1 shows the date and location of the stations in the Bering Strait. Surface water sea surface salinity and temperature

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were continuously measured using a thermosalinograph SBE-21 (Seabird Electronics Inc.). A temperature sensor was also located at the sea water intake for temperature measurements of the incoming water (SST).

A_T was determined by potentiometric titration in an open cell with 0.05 M HCl, according to Haraldsson et al. (1997). The precision was computed from three replicate analyses of one sample at least twice daily and was determined to $\pm 2\,\mu mol\,kg^{-1}$ (~0.1%). The accuracy was controlled against a certified reference material (CRM) supplied by Andrew Dickson (Scripps Institution of Oceanography, San Diego, USA) at the beginning and at the end of 20 samples. The correction factor was approximately 1.002, corresponding to a difference of about $5\,\mu mol\,kg^{-1}$. The variation in the CRM measurements was $\pm 8\,\mu mol\,kg^{-1}$ for the whole cruise. pH was determined spectrophotometrically using the sulphonephtalein dye, m-cresol purple, as indicator (Clayton and Byrne, 1993; Lee and Millero, 1995). Prior to analysis the samples were thermostated to the temperature of 15°C. Samples were measured in a 1-cm flow cell. The temperature was measured in the sample upstream of the flow cell. The analytical precision was estimated to ± 0.001 pH units, which was determined by triplicate analysis of one sample every day. The accuracy was computed from the accuracy of the temperature measurements and, the accuracy in the determination of the equilibrium constants of the dye, which was approximately ± 0.002 pH units (Dickson, 1993). The magnitude of the perturbation of seawater pH caused by addition of the indicator solution was calculated and corrected for by the using the method described in Chierici et al. (1999).

3.1 Calculations

We used A_T, pH at 15°C, salinity and SST for each sample and a CO_2 calculation program CO2SYS (Lewis and Wallace, 1998) to calculate, total dissolved inorganic carbon (DIC), in situ pH, the concentration of CO_3^{2-}, $[CO_3^{2-}]$, and the saturation state of aragonite (ΩAr) and calcite (ΩCa). DIC is defined as the sum of $[CO_2^*]+[HCO_3^-]+[CO_3^{2-}]$

and A_T is defined as $[HCO_3^-]+2[CO_3^{2-}]+[B(OH)_4^-]+[OH^-]-[H^+]$, where $[CO_2^*]$ is the sum of carbonic acid $[H_2CO_3]$ and $[CO_2(aq)]$, $[HCO_3^-]$ is bicarbonate, $[B(OH)_4^-]$ is borate, $[OH^-]$ is hydrate ion, and $[H^+]$ is the hydrogen ion. We used the K1 and K2 equilibrium constants from Roy et al. (1993, 1994), and the calculations were made on the total

5 hydrogen ion scale (pH_T). We used these constants according to the findings from Mojica Prieto and Millero (2002), who found better internal consistency between pH and A_T in water temperatures near 0°C, compared to other reported constants. For KSO_4 we used that determined by Dickson (1990). Based on the analytical precision for A_T and pH, the error in the calculated $[CO_3^{2-}]$ is reported to be approximately 2%

10 by Dickson (2008). Due to the few data points of measured nutrient data we used neither phosphate (PO_4) nor silicic acid ($SiOH_4$) in our calculations. This introduced an error of 0.04% in our estimates of $[CO_3^{2-}]$, (ΩAr) and (ΩCa), based on the mean PO_4 and $SiOH_4$ concentration of 1 μM and 7 μM, respectively (unpublished data from Beringia 2005). The concentration of calcium, $[Ca^{2+}]$, is assumed to be proportional to

15 the salinity according to ($10.28 \times S/35$ μmol/kg). The thermodynamic solubility products for aragonite and calcite (Ksp) are from Mucci (1983). The CO2SYS program uses the pressure correction of Ksp by Ingle (1975). Ksp was calculated for both calcite and aragonite and the saturations states were given in terms $\Omega=[CO_3^{2-}]\times[Ca^{2+}]/Ksp$. Values of $\Omega<1$ represent undersaturated conditions, whereas values of $\Omega>1$ represent

20 conditions of supersaturation.

In the Bering Strait, we used the high resolution temperature (T) and salinity (S) data along with lower resolution data on A_T and pH[15] to construct salinity relationships for A_T and pH[15]. A_T in the Bering Strait (A_{TBeS}) was calculated using the equation $A_{TBeStr}=58.854 \times S+303.99$ ($r^2=0.974$, $N=21$) and the $pH^{15BeStr}$ using the equation

25 $pH^{15BeStr}=-0.215 \times S^2+13.622 \times S-207.65$ ($r^2=0.947$, $N=19$), obtained from the polynomial relationship with S. The polynomial pH-S dependency was likely due to the non linear CO_2 dependency. Figure 4 shows the salinity relationship with A_{TBeStr} and $pH^{15BeStr}$.

4 Results

The Atlantic water in the Labrador Sea has a relatively high A_T of >2200 μmol kg^{-1}, which is diluted as it enters the CAA when it meets low A_T sea ice melt water (Fig. 5). This is manifested by the generally low A_T values in the CAA ($\sim$1800 μmol kg^{-1}), and in the southeastern Beaufort Sea, where there is a strong influence of the Mackenzie River. Strong gradients in all study parameters were observed between the CAA and the area south of the Banks Island. In this relatively short distance, A_T increased by more than 300 μmol kg^{-1}, salinity from 27 to 32, and temperature rose from 0 to 6 °C. Other areas with high A_T and low pH were observed around the Chukchi Peninsula and the Chukchi Plateau, probably due to the effect of upwelling, as suggested by the elevated salinity at these locations (Fig. 2). Large A_T variability was observed in the Chukchi Sea and in the area surrounding the Wrangel Island, where the A_T decreased from 2200 μmol kg^{-1} to 1800 μmol kg$^{-1,}$ in the northern area.

The in situ pH (Fig. 6) varied between 7.933 and 8.515. Low pH was observed in the freshwater-rich regions (CAA and the Mackenzie shelf area). The lowest in situ pH value of 7.933 was observed at the upwelling sites around Cape Bathurst (CB, Fig. 1) and south of the Chukchi Peninsula (ChP, Fig. 1). Relative to other areas, in situ pH was reduced by 0.2 pH units or more particularly around the Chukchi Peninsula. The driver of these low pH waters was probably upwelling of saline subsurface waters that are highly enriched in CO_2 from remineralization of organic matter. The area of highest pH (>8.35 in in situ pH) was observed north of the Wrangel Island. Here we also found low DIC (Fig. 5), probably owing to a combination of sea-ice melt water and intense CO_2 drawdown by primary production. The calculated CO_3^{2-} concentrations varied from 50 to 220 μmol kg^{-1}, with the lowest values in the CAA, Mackenzie area, and southern ChP (Fig. 6). For all parameters, the Chukchi Sea had the largest regional variability of CO_3^{2-}, exhibiting both the lowest and the highest CO_3^{2-}. The influence of the Atlantic water explained the high CO_3^{2-} in the Labrador Sea.

The saturation values of ΩCa varied between 1.3 and 4.9, and for ΩAr ranged from

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0.8 and 3.1 (Fig. 7). The lowest saturation in the CAA and on the Mackenzie shelf as well as the lowest CO_3^{2-} were associated with the relatively high concentrations of cold and fresh water. At 11 locations in the CAA and the MS we observed aragonite undersaturation ($\Omega Ar < 1$) in the surface water.

5   In the Bering Strait (BeS), there were clear A_T, pH and DIC gradients, both vertically and horizontally (Fig. 8). Highest A_T and DIC values were observed in the west and lowest A_T and DIC values in the east. Highest DIC and A_T and lowest pH (in situ pH~7.97) were observed in the western channel below 10 m, and lowest DIC and highest pH were found below 10 m in the eastern channel. The high A_T and high DIC

10 (2150 μmol kg^{-1}) in combination with low pH suggested that CO_2-rich subsurface water explained the low $[CO_3^{2-}]$ and, the low ΩCa and ΩAr (1.4 and 1.2, respectively; Fig. 9). However, no undersaturation ($\Omega < 1$) was observed in the water column of the Bering Strait.

5   Discussion

15 In the upper ocean, the ΩCa and the ΩAr are affected by processes such as air-sea CO_2 exchange, biological production and respiration, physical mixing, and the effect of temperature. In this section we discuss the variability in ΩCa and ΩAr values due to these processes using A_T:DIC ratio (Fig. 10). The A_T:DIC ratio varied in the studied area due to the different processes. High AT:DIC ratios were found in the Labrador

20 Sea (LaS), indicating the influence of Atlantic water inflow which caries relatively high levels of $[CO_3^{2-}]$. The prominent aragonite undersaturation (ΩAr~0.9) that we found in the ice covered CAA was likely a result of the gradual dilution of the $[CO_3^{2-}]$ due to the addition of sea-ice meltwater, which has a very low A_T and DIC. The A_T:DIC ratio was close to one in the river influenced Mackenzie shelf, which means that A_T and DIC have about the same concentrations, and consequently $[CO_3^{2-}]$ is low. These undersaturated

25 waters may impose severe constraints on organisms that secrete aragonite to build

their skeletal material.

The highest pH values were observed north of the Wrangel Island (WI), which coincided with low DIC values and relatively high A_T:DIC ratio (Fig. 13). During biological production DIC is consumed (increase in pH) which increases $[CO_3^{2-}]$ and the saturation state for aragonite and calcite. Substantial primary production was indicated by enhanced chlorophyll-*a* (Fransson et al., 2009), suggesting that associated biological CO_2 drawdown was responsible for this region's high $[CO_3^{2-}]$ (Fig. 6) and saturation states (Fig. 7) during August 2005. The large variability of the carbonate system parameters in the Chukchi Sea appears to result from a combination of varying sea ice cover, physical mixing, and inflow of Pacific water through the Bering Strait. The Pacific water supplies nutrients that support one of the highest rates of biological production in the world ocean (Walsh et al., 1989). In the Bering Strait, the cold and saline Anadyr Current (AC) brings in water with high A_T, and high DIC, and low pH, probably derived largely from intense remineralization of organic matter. As a result this water has the lowest ΩAr (~1.25) found in the Bering Strait.

At several locations we found the signature of upwelling of subsurface waters to the surface, such as the area close to Cape Bathurst (Barber and Hanesiak, 2004) and the southern Chukchi Peninsula. In this area salinity, A_T and DIC were relatively high, and pH was low, implying upwelling of CO_2-rich subsurface water containing high DIC due to extensive remineralization of organic matter deeper in subsurface waters. This was indicated by the high $f CO_2$ values measured in this area by Fransson et al. (2009). The A_T:DIC ratio was low in both upwelling areas, especially in the Chukchi Peninsula where the lowest pH and highest DIC were measured, explaining the low $[CO_3^{2-}]$ and the ΩAr and ΩCa values (ΩAr=1 to1.5, ΩCa~2).

Macdonald et al. (2002) found that the eastward diversion of Eurasian river runoff to the western Arctic Ocean is linked to high North Atlantic Oscillation (NAO), which explained most of the recent freshening of the CAA. A fresher Arctic Ocean would affect the marine CO_2 system by reducing formation of $CaCO_3$, particularly less stable forms.

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The Arctic Ocean and its marginal seas are warming faster than other areas (Comiso, 2003; IPCC, 2007). Ice coverage in summer 2007 reached a record minimum, with ice extent declining by 42% compared to conditions in the 1980s (Maslanik et al., 2007). More sea ice melt during summer will lead to more stratification of the surface. Although the light penetration of the water column will increase as well as the growing season, favourable for phytoplankton growth, the freshening of the surface water would lead to less $[CO_3^{2-}]$ due to dilution, hampering $CaCO_3$ formation. Increased sea-ice melt could also have implications for the benthic organisms living in the sediments of the shallow shelf seas in the Arctic Ocean, such as echinoderms and molluscs (Shirayama and Thornton, 2005). In our study we observed the lowest $[CO_3^{2-}]$ in areas with large sea-ice melt water fractions, computed by Fransson et al., (in press). A future increase in the sea-ice melt water fraction would decrease $[CO_3^{2-}]$, thereby reducing $CaCO_3$ saturation.

Changes in the input of A_T by river runoff will also likely affect Arctic Ocean $[CO_3^2]$. Although the A_T and DIC values in the Arctic rivers are typically above 1000 mmol kg^{-1} (Olsson and Anderson, 1997), owing to a combination of decaying organic matter (mainly carbohydrates) and dissolution of metal (mainly calcium) carbonates in the drainage basin (Eq. 3),

$$CaCO_3(s) + CH_2O(org) + O_2 \rightarrow Ca^{2+} + HCO_3^- \tag{3}$$
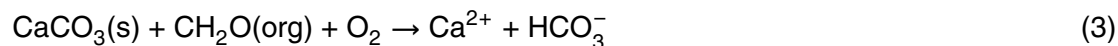
Nonetheless, riverine concentrations remain less than those in seawater, so that river input will still dilute seawater $[CO_3^2]$. The rivers draining the American continent are significantly higher in A_T and DIC relative to the Siberian rivers (Olsson and Anderson 1997). This is a result of the different minerologies of the drainage basins (Naidu, 1974). On the sandy, terraced banks of the Mackenzie and the Yukon Rivers there is enhanced erosion, whereas Siberian rivers pass through huge marsh lowlands, which favours deposition (Pocklington, 1987). The Mackenzie River has a relatively high A_T of ~1500 μmol kg^{-1} (Fransson et al., 2009) compared to other Arctic rivers, which are similar to the rivers draining into southern Baltic Sea (Hjalmarsson et al., 2008). A

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recent study investigating the trends of A_T in the rivers entering the Baltic Sea, showed that during the last century, A_T has increased in rivers flowing over drainage basins that contain metal carbonates, whereas A_T has decreased in rivers flowing over low carbonate environment, such as granite (Hjalmarsson et al., 2008). Future increases in more freshwater addition to the Arctic Ocean will decrease its surface [CO_3^{2-}] as well as its buffer capacity.

References

Azetsu-Scott, K., Slauenwhite, D., and Yeats, P.: Saturation state of sea water for calcite and aragonite in the Canadian Arctic Archipelago and the Labrador Sea. The 2nd International Symposium on the "The Ocean in a high-CO_2 world", Monaco, 6–9 October, 2008.

Barber, D. G. and Hanesiak, J. M.: Meterological forcing of sea ice concentrations in the southern Beaufort Sea over the period 1979 to 2000, J. Geophys. Res., 109, C06014, doi:10.1029/2003JC002027, 2004.

Broecker, W. S. and Takahashi, T.: Neutralization of fossil fuel CO_2 by marine calcium carbonate. In The Fate of Fossil Fuel in the Oceans, edited by: Andersen, N. R. and Malahoff, A., 213–241, Plenum Press. New York, 1977.

Caldeira, K. and Wickett, M. E.: Anthropogenic carbon and oceanic pH, Nature, 425, p. 365, 2003.

Carmack, E., Barber, D., Christensen, J., Macdonald, R., Rudels, B., and Sakshaug, E.: Climate variability and physical forcing of the food webs and the carbon budget on panarctic shelves, Progr. Oceanogr., 71, 145–181, 2006.

Chierici, M., Fransson, A., and Anderson, L. G.: Influence of m-cresol purple indicator additions

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on the pH of seawater samples: correction factors evaluated from a chemical speciation model, Mar. Chem., 65, 281–290, 1999.

CISA report: Seasonal summary for Canadian Arctic waters – summer 2005, Canadian Ice Service, 2005.

Clayton, T. D. and Byrne, R. H.: Spectrophotometric seawater pH measurements: total hydrogen ion concentration scale calibration of m-cresol purple and at-sea results, Deep-Sea Res. I, 40(10), 2115–2129, 1993.

Comiso, J. C.: Warming Trends in the Arctic, J. Clim., 16(21), 3498–3510, 2003.

Dickson, A. G. and Millero, F. J.: A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media, Deep-Sea Res. I, 34, 1733–1743, 1987.

Dickson, A. G.: Standard potential of the reaction: AgCl (s)+O H$_2$ (g)=Ag (s)+HCl (aq), and the standard acidity constant of the ion HSO$_4$ in synthetic seawater from 273.15 to 318.15 K, J. Chem. Thermodyn., 22, 113–127, 1990.

Dickson, A. G.: The measurement of sea water pH, Mar. Chem., 44, 131-142, 1993.

Dickson, A. G.: CO$_2$ in seawater, Guide for best practices in ocean acidification research and data reporting, www.epoca-project.eu/images/stories/bestpractices/s1/dickson.pdf, Kiel, Germany, 19–21 November, 2008.

Feely, R. A., Sabine, C. L., Lee, K., Berelson, W., Kleypas, J., Fabry, V. J., and Millero, F. J.: Impact of anthropogenic CO$_2$ on the CaCO$_3$ system in the ocean, Science, 305, 362–366, 2004.

Feely, R. A., Sabine, C. L., Martin Hernandez-Ayon, J., Ianson, D., and Hales, B.: Evidence for Upwelling of Corrosive "Acidified" Water onto the Continental Shelf, Science, 320(5882), 1490–1492, doi:10.1126/science.1155676, 2008.

Fransson, A., Chierici, M., and Nojiri, Y.: New insights into the spatial variability of the surface water carbon dioxide in varying sea ice conditions in the Arctic Ocean, in press, Continental Shelf Research, 29(10), 1317–1328, 2009.

Gattuso, J.-P., Frankignoulle, M., Bourge, I., Romaine, S., and Buddmeier, R. W.: Effect of calcium carbonate saturation of seawater on coral calcification, Glob. Plant. Change 18, 37–46, 1998.

Grebmaier, J. M., McRoy, C. P., and Feder, H. M.: Pelagic-benthic coupling on the shelf of the northern Bering and Chukchi Seas. I. Food supply source and benthic biomass, Mar. Ecol. Progress Ser., 48, 57–67, 1988.

Haraldsson, C., Anderson, L. G., Hasselöv, M., Hulth, S., and Olsson, K.: Rapid, high-precision

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potentiometric titration of alkalinity in the ocean and sediment pore waters, Deep-Sea Res. I, 44, 2031–2044, 1997.

Hjalmarsson, S., Wesslander, K., Anderson, L. G., Omstedt, A., Pertillä, M., and Mintrop, L.: Distribution, long-term development and mass balance calculation of total alkalinity in the Baltic Sea, Continental Shelf Research, 28, 593–601, 2008.

Ingle, S. E.: Solubility of calcite in the ocean, Mar. Chem., 3, 301–319, 1975.

Jutterström, S. and Anderson, L. G.: The saturation of calcite and aragonite in the Arctic Ocean, Mari. Chem., 94, 101–110, 2005.

Lewis, E. and Wallace, D. W. R.: Program Developed for CO_2 Systems Calculations, ORNL/CDIAC-105, Carbon Dioxide Information Analysis Centre, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, Tennessee, 1998.

Macdonald, R. W., McLaughlin, F. A., and Carmack, E. C.: Fresh water and its sources during the SHEBA drift in the Canada Basin of the Arctic Ocean, Deep-Sea Res. I, 49, 1769–1785, 2002.

Maslanik, J. A., Fowler, C., Stroeve, J., Drobot, S., Zwally, J., Yi, D., and Emery, W.: A younger, thinner Arctic ice cover: Increased potential for rapid, extensive sea-ice loss, Geophys. Res. Lett., 34(24), L24501, doi:10.1029/2006GL028269, 2007.

Mojica Prieto, F. J. and Millero, F. J.: The values of pK1+pK2 for the dissociation of carbonic acid in seawater, Geochimica Cosmochimica Acta, 66(14), 2529–2540, 2002.

Mucci, A.: The solubility of calcite and aragonite in seawater at various salinities, temperatures and at one atmosphere pressure, Am. J. Sci., 283, 781–799, 1983.

Naidu, A. S.: Sedimentation in the Beaufort Sea: a synthesis. In Marine Geology and Oceanography of the Arctic Seas, edited by: Rosenberg-Herman, Y., 173–190, Springer, Berlin, 1974.

Olsson, K. and Anderson, L. G.: Input and biogeochemical transformation of dissolved carbon in the Siberian shelf seas, Continental Shelf Research, 17(7), 819–833, 1997.

Orr, J. C., Fabry, V. J., Aumont, O., Bopp, L., Doney, S. C., et al.: Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms, Nature, 437, doi:10.1038/nature04095, 2005.

Park, G. H., Kitack, L., Tischenko, P., Min, D. H., Warner, M. J., Talley, L. D., Kang, D. J., and Kim, K. R.: Large accumulation of anthropogenic CO_2 in the East (Japan) Sea and its significant impact on carbonate chemistry, Global Biogeochem. Cy., 20(4), GB4013, doi:10.1029/2005GB002676, 2006.

Pocklington, R.: Arctic Rivers and their Discharges. Mitt. Geol.-Pal∼iont. Inst. Univ. Hamburg,

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SCOPE UNEP Sonderbd. 52, 355–356, 1987.

Raven, J. Caldeira, K., Elderfield, H., et al.: Ocean acidification due to increasing atmospheric carbon dioxide, The Royal Society, Policy Document, London, UK, 2005.

Riebesell, U., Zondervan, I., Rost, B., Tortell, P.D., Zeebe, R., and Morel, F. M. M.: Reduced calcification of marine plankton in response to increased atmospheric CO_2, Nature, 407, 364–367, 2000.

Roy, R. N., Roy, L. N., Vogel, K. M., Porter-Moore, C., Pearson, T., Good, C. E., Millero, F. J., and Campbell, D. M.: The dissociation constants of carbonic acid in seawater at salinities 5 to 45 and temperatures 0 to 46°C, Mar. Chem., 44, 249–267, 1993.

Roy, R. N., Roy, L. N., Vogel, K. M., Porter-Moore, C., Pearson, T., Good, C. E., Millero, F. J., and Campbell, D. M.: Erratum for: The dissociation constants of carbonic acid in seawater at salinities 5–45 and temperatures 0–45°C, Mar. Chem., 44, p. 337, 1994.

Rushdi, A. I., Pytkowicz, R. M., Suess, E., and Chen, C. T.: The effects of magnesium-to-calcium ratios in artificial seawater, at different ionic products, upon the induction time, and the mineralogy of calcium carbonate: a laboratory study, Geologische Rundschau, 81, 21571–21578, 1992.

Schlitzer, R.: Interactive analysis and visualization of geoscience data with Ocean Data View, Computers & Geosciences, 28, 1211–1218, 2002.

Shimada, K., Carmack, E. C., Hatakeyama, K., and Takizawa, T.: Varieties of shallow temperature maximum waters in the western Canadian Basin of the Arctic Ocean, Geophys. Res. Lett., 28, 3441–3444, 2001.

Shirayama, Y. and Thornton, H.: Effect of increased atmospheric CO_2 on shallow water marine benthos, J. Geophys. Res., 110, C09S08, doi:10.1029/2004JC002618, 2005.

Skirrow, G. and Whitfield, M.: The effect of increases in the atmospheric carbon dioxide content on the carbonate ion concentration of surface water at 25°C, Limnol. Oceanogr., 20, 103–108, 1975.

Tyrrell, T., Schneider, B., Charalampopoulou, A., and Riebesell, U.: Coccolithophores and calcite saturation state in the Baltic and Black Seas, Biogeosciences, 5, 485–494, 2008, http://www.biogeosciences.net/5/485/2008/.

Walsh, J. J., McRoy, C. P., Coachman, L. K., Georing, J. J., Nihoul, J. J., Whitledge, T. E., Blackburn, T. H., Parker, P. L., Wirick, C. D., Shuert, P. G., Grebmeier, J. M., Springer, A. M., Tripp, R. D., Hansell, D. A., Djenidi, S., Deleersnijder, E., Henriksen, K., Lund, B. A., Andersen, P., Muller-Karger, F. E., and Dean, K.: Carbon and nitrogen recycling with the

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Bering/Chukchi Seas: source regions for organic matter effecting AOU demands of the Arctic Ocean, Progr. Oceanogr., 22, 277–359, 1989.

Weingartner, T. J., Danielson, S. L., and Royer, T. C.: Freshwater variability and predictability in the Alaskan Coastal Current, Deep Sea Res. Part II, 52(1–2), 169–191, 2005.

5   Woodgate, R. A. and Aagaard, K.: Revising the Bering Strait freshwater flux into the Arctic Ocean, Geophys. Res. Lett., 32, L02602, doi:10.1029/2004GL021747, 2005.

Zeebe, R. E., Zachos, J. C., Caldeira, K., and Tyrrell, T.: Carbon emissions and acidification, Science, 321, 51–52, doi:10.1126/science.1159124, 2008.

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Table 1. The locations of the water column sampling stations in the Bering Strait (BeStr). E denotes east, and W denotes west of the Bering Strait.

Station#	Sampling sites	Position (Latitude, Longitude)
6	E. Bering Strait Vicinity of the Diomede Islands	65 45.3° N, 168 41.6° W
7	E. Bering Strait	65 45.4° N, 168 28.6° W
8	E. Bering Strait, Alaska channel	65 42° N, 168 16° W
9	South of E. Bering Strait	65 33.3° N, 168 36° W
10	W. Bering Strait, Russia	65 57° N, 169 36° W
11	W. Bering Strait, Russia	65 57° N, 169 26° W
12	W. Bering Strait Vicinity of the Diomede Islands	65 51° N, 169 24° W

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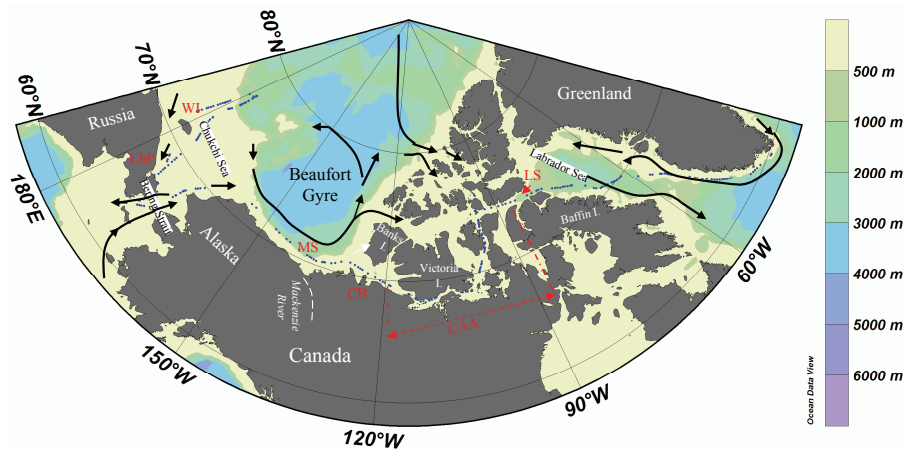
Fig. 1. The location for water sampling performed onboard the *IB Oden* during summer 2005 (blue dots). In this study we used a total number of 242 surface water measurements. The seven CTD/rosette stations in the Bering Strait are indicated individually in Figs. 3, 11, and 12. The black arrows indicate the major surface circulation. In red, MS denotes Mackenzie shelf, CB=Cape Bathurst, ChP=Chukchi Peninsula, WI=Wrangel Island. The approximate area of the Canadian Arctic Archipelago (red, CAA, 84° W to 120° W) is marked with red dashed lines. The colour scale bar illustrates the depth contours in meter.
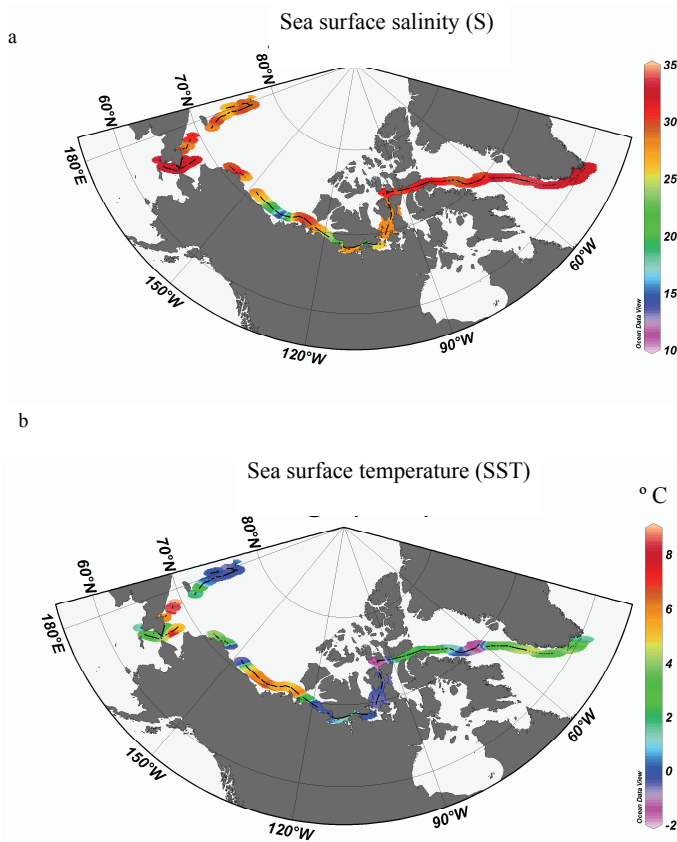
Fig. 2. The 1-min data of sea surface salinity **(a)** and, **(b)** sea surface temperature (SST, °C) along the cruise track. The colour bar illustrates the scale in salinity and temperature, respectively.
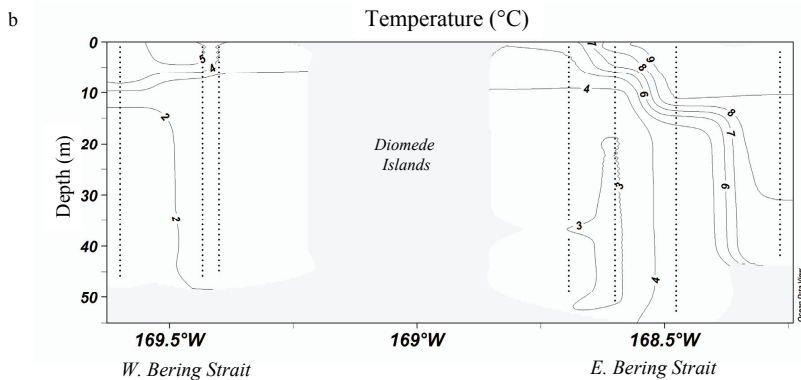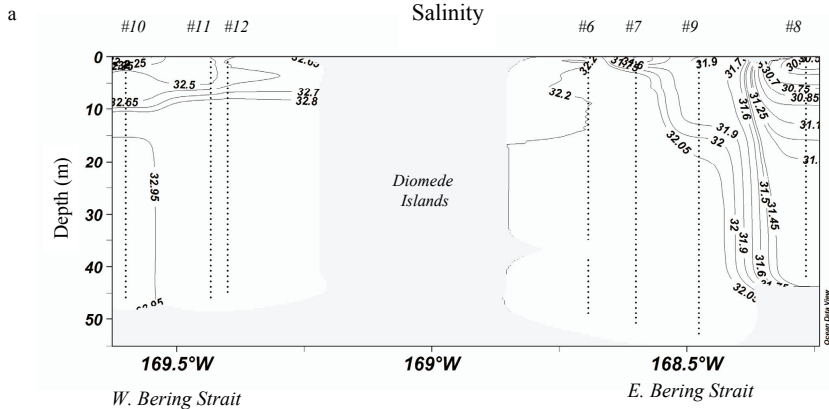
Fig. 3. A cross section of salinity and temperature (˚C) in the Bering Strait based on the seven water column stations (#6 to #12, for positions see Table 1). The Diomede Islands separate the strait into two channels.
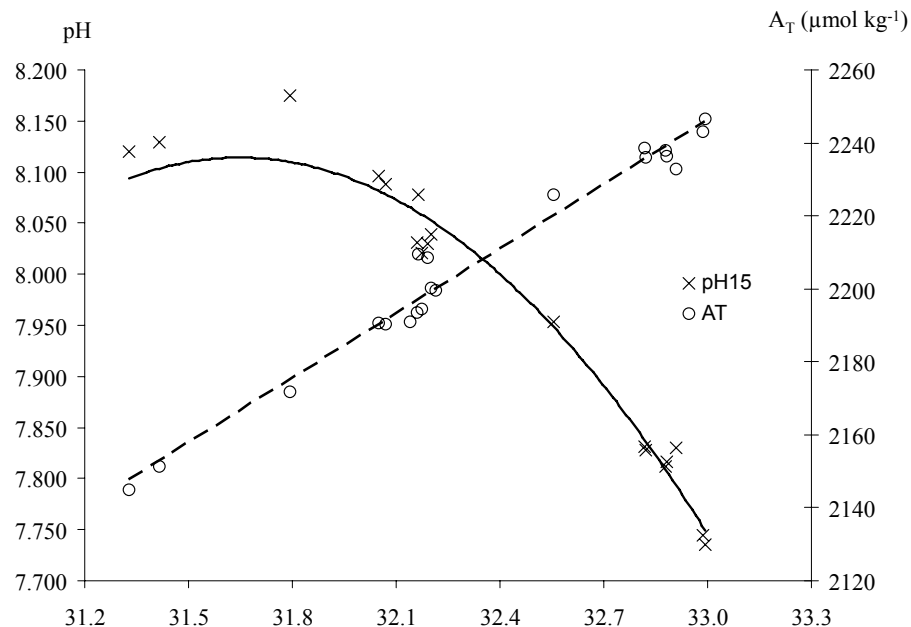
Fig. 4. The relationship of A_T (cross) and pH^{15} (open rings) with salinity is shown. For $A_{TBeStr}=58.854 \times S+303.99$ ($r^2=0.974$, $N=21$), and $pH^{15BeStr}=-0.215 \times S^2+13.622 \times S-207.65$, ($r^2=0.947$, $N=19$).
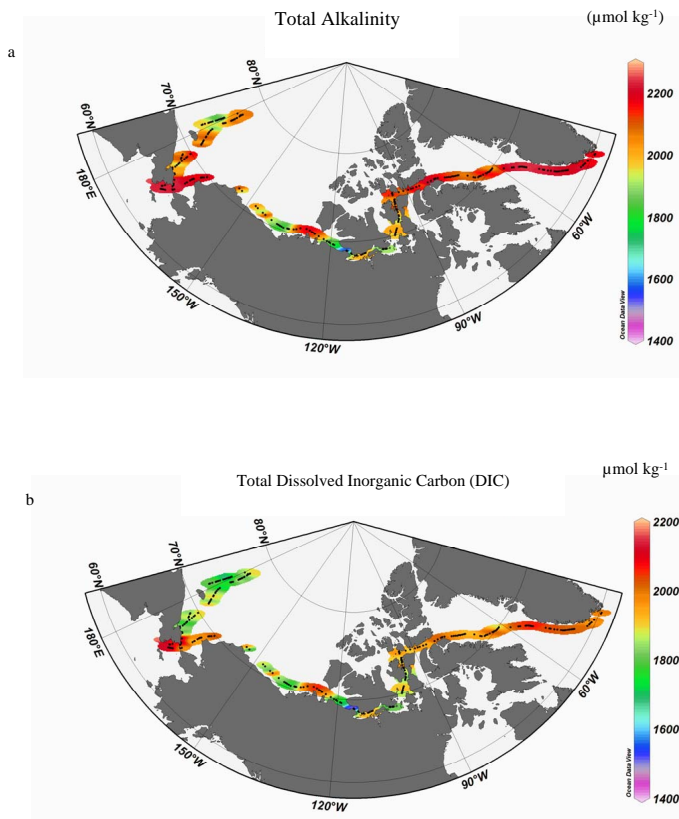
Fig. 5. The measured surface water **(a)** total alkalinity (A_T, μmol kg^{-1}), and **(b)** total dissolved inorganic carbon (DIC, μmol kg^{-1}) calculated from A_T and pH at 15°C.
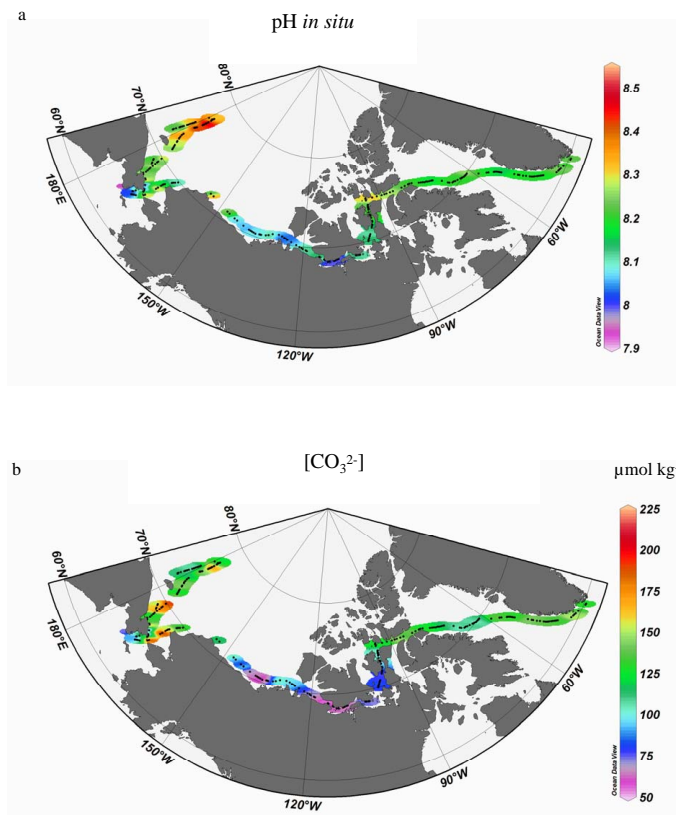
Fig. 6. The surface water **(a)** in situ pH, and **(b)** the carbonate concentration (CO_3^{2-}, μmol kg^{-1}), both calculated from A_T and pH at 15°C.
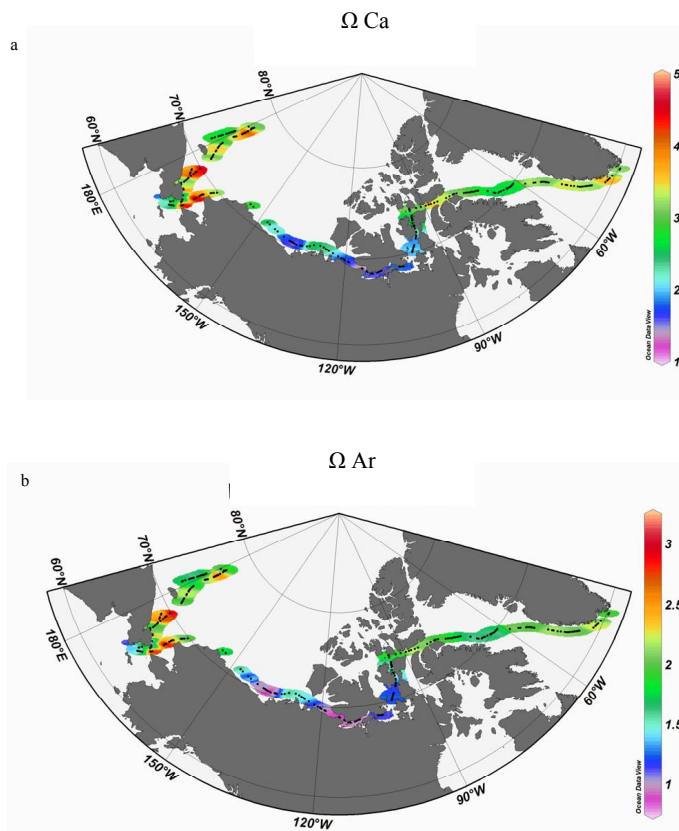
Fig. 7. The saturation of CaCO$_3$ (Ω) for **(a)** calcite, ΩCa, and **(b)** aragonite, ΩAr.
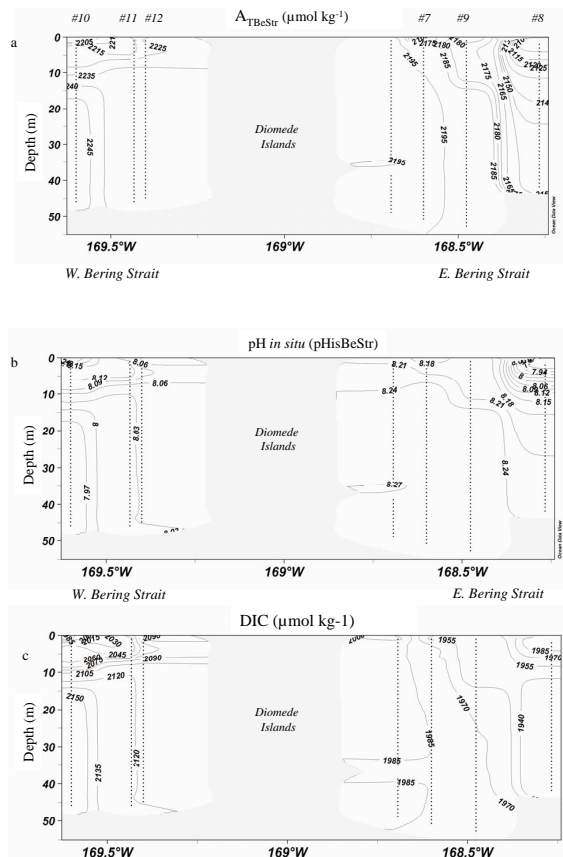
Fig. 8. A cross section of **(a)** A_{TBeStr} (μmol kg^{-1}), **(b)** pH^{isBeStr} , and **(c)** DIC (μmol kg^{-1}) in the Bering Strait. The values were calculated based on the salinity relationships with measured A_T and pH^{15} (see Fig. 4). DIC is calculated from A_{TbeStr} and pH$^{(15)BeStr}$. The sampling stations are indicated by station numbers #6 to #12, for positions see Table 1.
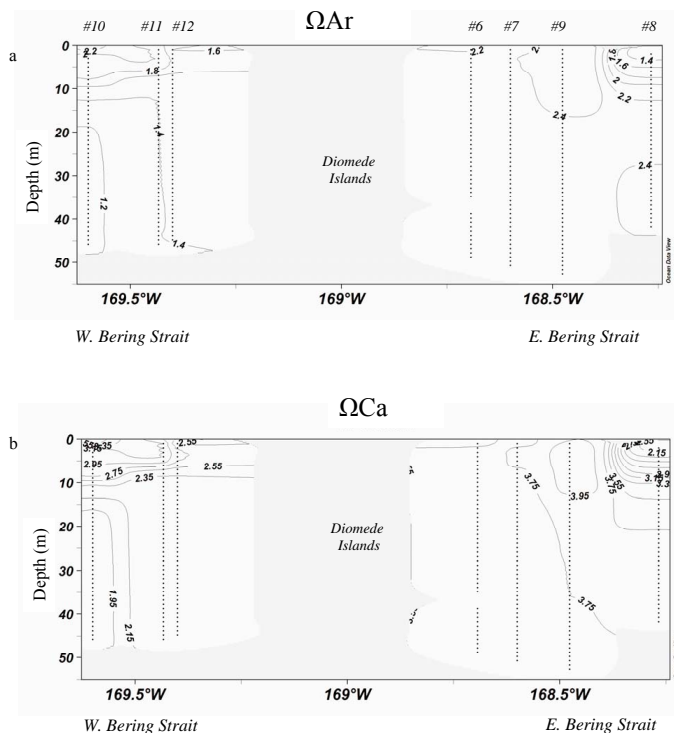
Fig. 9. The saturation of **(a)** aragonite, ΩAr), and **(b)** calcite, ΩCa, in the Bering Strait. Values of Ω<1 represent undersaturated conditions, and values of Ω>1 represent conditions of over-saturation. The sampling stations are indicated by station numbers #6 to #12, for positions see Table 1.
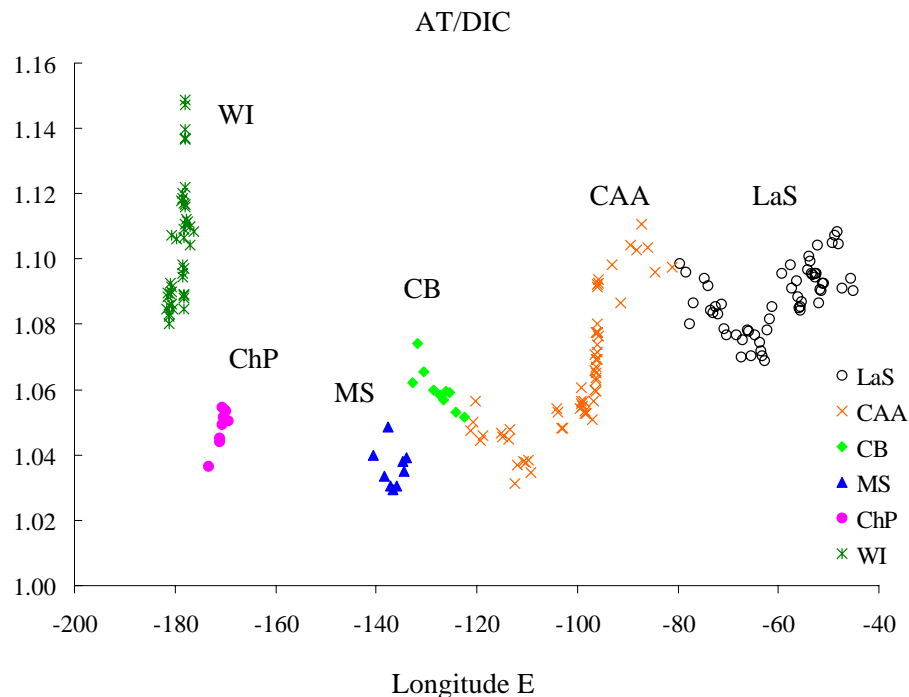
Fig. 10. A_T:DIC ratio versus longitude in Labrador Sea (LaS; black open circle), Canadian Arctic Archipelago (CAA; orange cross), Cape Bathurst (CB; green closed diamond), Mackenzie shelf (MS; blue filled triangle), South Chukchi Peninsula (ChP; purple closed circle), and Wrangler Island (WI; dark green cross).