

RESEARCH/REVIEW ARTICLE

Changes in the marine carbonate system of the western Arctic: patterns in a rescued data set

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Abstract

A recently recovered and compiled set of inorganic carbon data collected in the Canadian Arctic since the 1970s has revealed substantial change, as well as variability, in the carbonate system of the Beaufort Sea and Canada Basin. Whereas the role of this area as a net atmospheric carbon sink has been confirmed, high $p\text{CO}_2$ values in the upper halocline underscore the potential for CO_2 outgassing as sea ice retreats and upwelling increases. In addition, increasing total inorganic carbon and decreasing alkalinity are increasing $p\text{CO}_2$ and decreasing CaCO_3 saturation states, such that undersaturation with respect to aragonite now occurs regularly in both deep waters and the upper halocline.

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As we witness dramatic changes in the Arctic Ocean and its drainage basin, with rising temperatures, summer and multi-year sea-ice loss, permafrost thawing and coastal erosion, our attempts to understand what is occurring and deconvolute the results of natural versus anthropogenic processes are confounded by the lack of long time-series data that describe not only the climatic, but also the biogeochemical, state of the system. Numerical climate models (e.g., Meehl et al. 2007) indicate that the impacts of anthropogenic global warming are proceeding fastest in the Arctic, and the satellite sea-ice record (e.g., Perovich & Richter-Menge 2009; Stroeve et al. 2012) appears to confirm that prediction. Nevertheless, our ability to accurately project those changes into the future is still limited by our fragmented understanding of biogeochemical and physical processes in the Arctic (Stroeve et al. 2007; Schiermeier 2012; Stroeve et al. 2012), as well as by our inability to predict future human behaviour.

Although ocean carbonate system research has accelerated over the last two decades in response to public and political concern about climate change and ocean acidification, chemical oceanographers have been studying the marine inorganic carbon cycle for much longer.

The Institute of Ocean Sciences began measuring total inorganic carbon (TIC) and total alkalinity (A_T) in the Arctic Ocean in 1974. Logistics, protocols, and analytical methods have obviously changed since that time, hopefully improving data quality, but nonetheless, the early data are a valuable resource and contribute insight into how the system has evolved.

In this paper, we discuss what this 40-year time series tells us about the variability in the carbonate system of the Beaufort Sea, with particular reference to the atmospheric CO_2 sink and CaCO_3 stability. The data set, itself, has been compiled from both paper and electronic sources at the Institute of Ocean Sciences (Giesbrecht et al. 2014) and includes data from the Gulf of Alaska, through Bering Strait and the Canadian Archipelago, and into the Gulf of St. Lawrence. However, the bulk of the data, with multiple observations of the same stations and water masses over many years, are from the Beaufort Sea, and therefore, we focus our discussion on the western Canadian Arctic, including the Canada Basin, the Mackenzie Shelf and Amundsen Gulf (Fig. 1), using the data collected between 120 and 156°W. For insights into the carbonate system oceanography of the other North American polar and subpolar seas, see, for example, Wong et al. (2007;

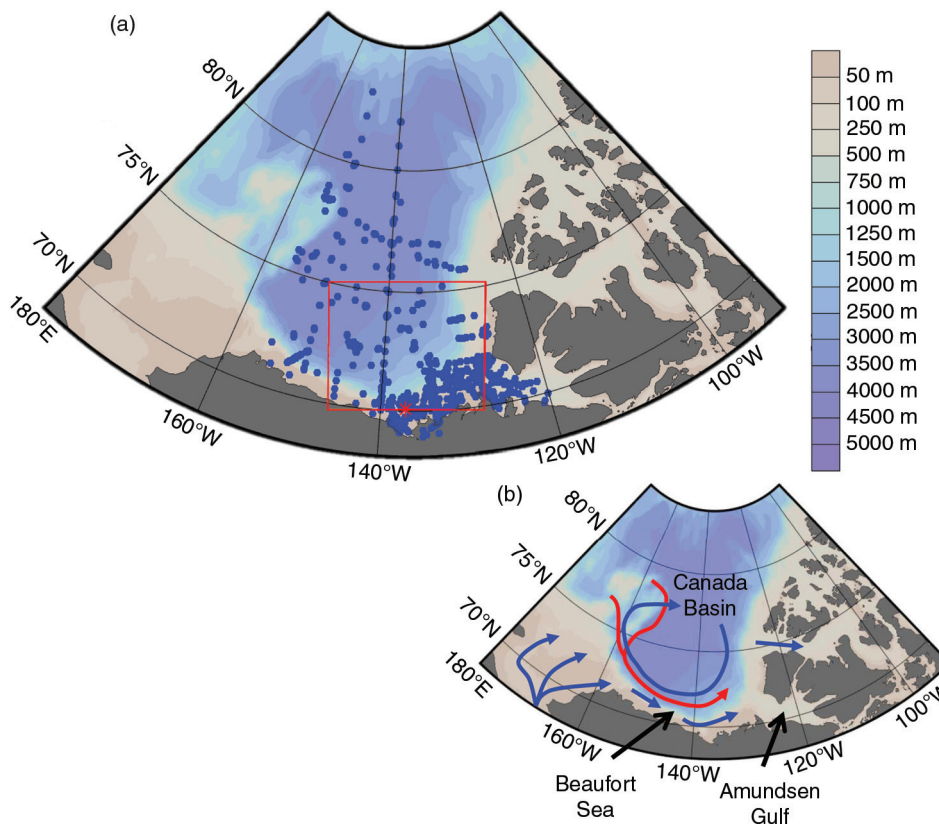


Fig. 1 Map of the western Arctic Ocean showing (a) sampling stations in (b) the Canada Basin, Beaufort Sea and Amundsen Gulf included in the discussion. The colour bar shows bathymetry, the red box in (a) represents the area used in Figs. 6 and 8–10, and in (b) dominant surface currents are represented by blue arrows and subsurface currents by red arrows.

Gulf of Alaska), Kaltin & Anderson (2005; Bering Sea), Bates et al. (2013; Chukchi Sea), Azetsu-Scott et al. (2010; Canadian Archipelago and Labrador Sea), and Mucci et al. (2011; St. Lawrence Estuary). Parts of this data set have already been published within the context of specific process studies (Yamamoto-Kawai et al. 2009; Mucci et al. 2010; Miller et al. 2011; Yamamoto-Kawai et al. 2011; Lansard et al. 2012), but this paper is the first to look at this internally consistent time series as a whole.

The Western Canadian Arctic

The southern Beaufort Sea, including the Mackenzie Shelf and Amundsen Gulf, has been studied more extensively for a longer period and is better understood than the Canada Basin. This is primarily a function of logistics and historical access, and is reflected in the distribution of our inorganic carbon data set (Table 1). For overviews of the oceanographic and meteorological conditions of this area, see Carmack et al. (1997), Melling (1998), Carmack & Macdonald (2002), McLaughlin et al. (2002), McLaughlin et al. (2004), Barber & Hanesiak (2004), Overland (2009) and Bringué & Rochon (2012).

Briefly, the circulation of surface waters and sea ice within the Canada Basin is generally clockwise (Fig. 1b), although the strength of this circulation, which defines the Beaufort Gyre, varies in time (McLaughlin et al. 2002; Asplin et al. 2009), apparently in response to the Arctic Oscillation (e.g., Thompson & Wallace 1998). The currents over the Beaufort Shelf and upper slope are variable, with frequent wind-driven reversals, although the mean flow is generally towards the east (Melling 1993). The upper water column, down to about 200 m, is primarily derived from Pacific Ocean waters (Fig. 1b) which are modified as they pass through the Bering and Chukchi

Table 1 Number of carbonate system data points (individual bottle samples for total inorganic carbon, total alkalinity and/or pH) included in the data set by date and latitude.

Latitude	1974–79	1980–89	1990–99	2000–02	2003–04	2005–09
81–84N	0	0	0	0	0	76
78–81N	0	0	67	0	21	275
75–78N	0	0	65	44	48	932
72–75N	0	0	105	47	65	1367
69–72N	240	146	185	580	1391	884

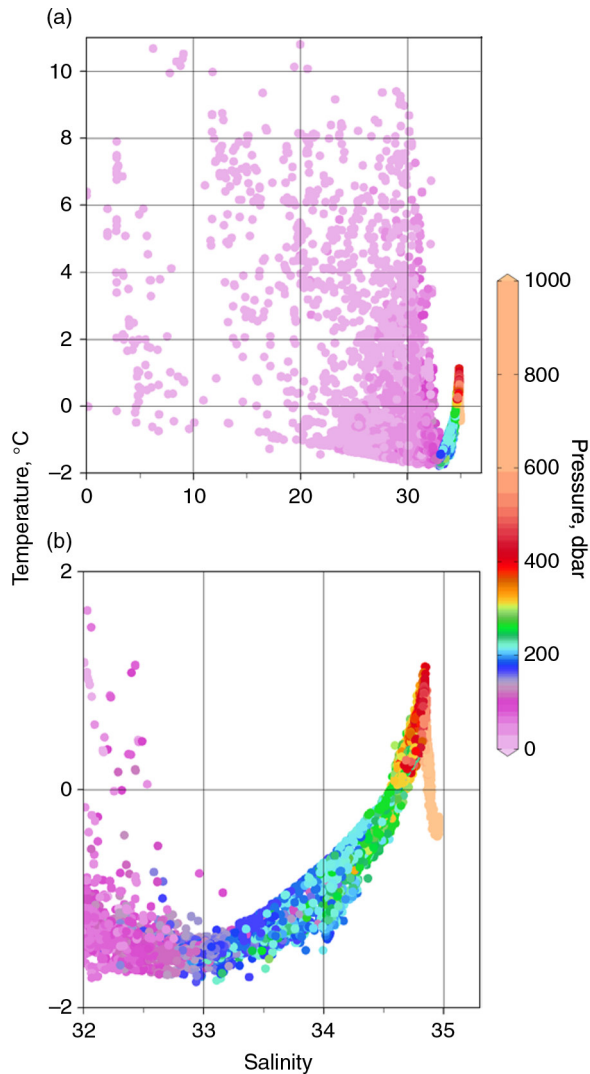


Fig. 2 Temperature–salinity diagrams for all stations shown in Fig. 1a. Note different temperature and salinity scales between (a) and (b). Salinity is given as the practical salinity (S_p). Although the data set and the plot contain data from below 1000 dbar, the colour bar is truncated at that depth to maintain the higher resolution at shallower depths.

seas and by seasonal local processes, specifically by mixing with river waters (both the Mackenzie River and Siberian rivers) and by sea-ice formation and melt (Fig. 2a; Coachman & Barnes 1961; Carmack & Macdonald 2002). The wide and shallow continental shelf, with the 80-m shelf break approximately 140 km from shore, is a crucial feature: a winter sea-ice stamukhi zone confines the Mackenzie River outflow in an extensive freshwater estuary over the inner shelf, and sea-ice formation in a shallow flaw-lead polynya on the middle shelf produces brine that promotes mixing and convection (Macdonald et al. 1995; Melling & Moore 1995; Carmack & Macdonald 2002). In summer, the complete loss of ice cover enables

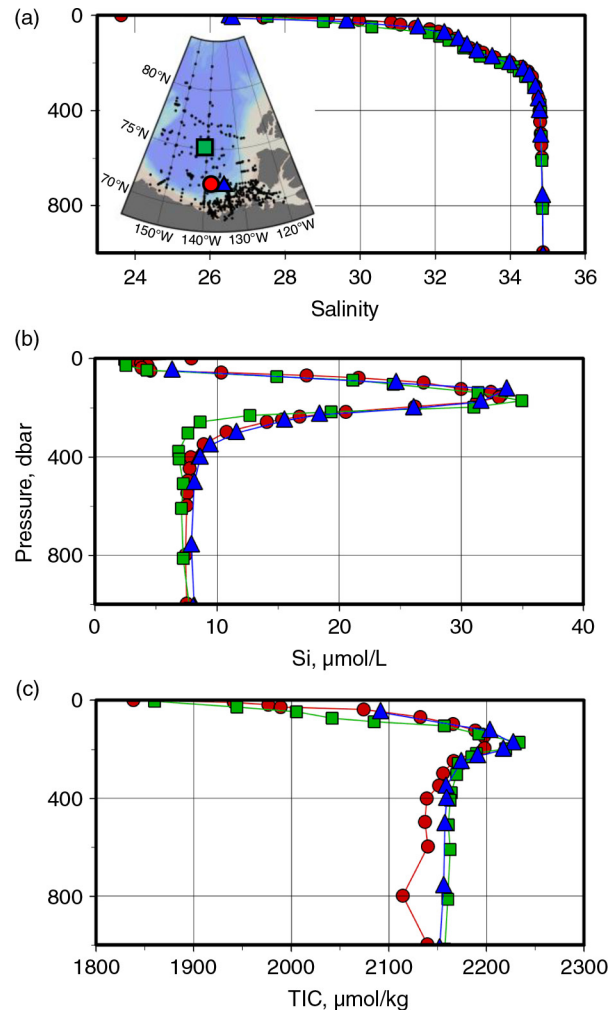


Fig. 3 Typical (a) salinity (S_p), (b) silicate and (c) total inorganic carbon (TIC) profiles at depths above 1000 dbar from representative stations in the Beaufort Sea. The map inset in (a) shows the station locations: red circles, 71.87°N, 141.67°W, 24 August 1995; blue triangles, 71.70°N, 134.68°W, 18 August 2002; and green squares, 75.06°N, 140.37°W, 27 August 2005.

wind-influenced events, such as sediment resuspension (Lintern et al. 2005) and upwelling, particularly at shelf-edge canyons and headlands (Williams et al. 2006; Williams & Carmack 2008).

Below the surface layer, the upper halocline hosts nutrient and TIC maxima (Fig. 3) originating from high-nutrient and high-TIC Pacific waters that have been further modified by organic matter remineralization beneath the high-productivity surface waters of the Chukchi Shelf (Bates et al. 2005; Bates et al. 2013) and possibly also the Bering Sea (Mathis et al. 2011). Below the upper halocline, the lower halocline overlays warmer Atlantic waters ($T > 0^\circ\text{C}$), the core of which is represented by a temperature maximum at 400–500 m (Fig. 2b).

Below the temperature maximum, the deep Atlantic layer waters are the product of complex mixing between the high-salinity Atlantic waters and cold, brine-enriched waters derived from dense water production in the shallow flaw-lead polynyas of the pan-Arctic shelves (Östlund et al. 1987; Carmack et al. 1997; Swift et al. 1997; Anderson et al. 1999). The bottom waters of the Canada Basin below 2700 m are isolated, with warmer temperatures and older inorganic ^{14}C values than are observed in the Eurasian Basin (Schlosser et al. 1994). At least some of the surface waters from the Beaufort Gyre exit through the Canadian Archipelago (Melling et al. 1984; McLaughlin et al. 2006), and the carbonate system signal of the Pacific waters can be identified throughout the archipelago and into Baffin Bay (Azetsu-Scott et al. 2010).

The Arctic carbonate system

Our ability to recover information about the state of the marine carbonate system in the past is facilitated by the fact that the carbonate system parameters (dissolved inorganic carbon [DIC]; A_{T} ; carbon dioxide partial pressure [$p\text{CO}_2$]; and pH) are interdependent, and in seawater, only two need to be measured to fully characterize the system (e.g., Dickson et al. 2007), including calcium carbonate saturation states (Ω). Carbonate system chemistry in seawater, the global marine carbon cycle and many of the pitfalls of working in this field have been exhaustively reviewed by a number of people (in addition to Dickson et al. (2007), Zeebe & Wolf-Gladrow (2001) and Emerson & Hedges (2008) are useful texts), but the Arctic Ocean has unique characteristics that need to be considered when trying to understand air–sea CO_2 exchange and acidification processes.

The presence of sea ice has profound impacts on inorganic carbon geochemistry in the Arctic Ocean beyond the discredited paradigm that sea ice is a barrier to gas exchange (e.g., Loose et al. 2011). Arguably, one of the most important discoveries in the polar carbon cycle over recent years is that hydrodynamic processes associated with sea-ice formation and heat exchange in leads and polynyas appear to enhance direct air–sea gas exchange in the presence of a broken, mobile ice cover (Loose et al. 2009; Else et al. 2011). Therefore, as the relatively solid multi-year pack ice of the Arctic is replaced with a thinner, more mobile and more seasonal ice cover, atmospheric CO_2 drawdown into cold, undersaturated surface waters continues throughout the year and could be increasing (e.g., Steiner et al. 2013). An important caveat to that potential increase in the sink of atmospheric CO_2 is that summertime sea-ice melt and river outflow stratify the

surface waters, limiting the capacity for sustained CO_2 drawdown. Not only are many Arctic river waters supersaturated in CO_2 (e.g., Pipko et al. 2008; Vallières et al. 2008), but thin fresh surface mixed layers quickly equilibrate with the atmosphere and then release CO_2 as the temperature rises in late summer (Bates & Mathis 2009; Cai et al. 2010; Mucci et al. 2010; Else et al. 2013). In addition, when low-salinity surface waters refreeze the following winter, the brine released is insufficient to substantially deepen the mixed layer or form dense shelf waters that can be exported into the deep basins (Melling & Moore 1995). On the other hand, greater fetch associated with reduced ice coverage increases the potential for wind mixing, which could offset melt-induced stratification. Finally, as the area of seasonal sea ice increases, total annual sea-ice production also increases, potentially enhancing dense water export to intermediate and deep waters in some areas. How intermediate- and deep-water formation rates respond to the changing ice environment in the Arctic is a critical question in the Arctic carbon cycle: only through deep convection can a more efficient air–sea gas exchange contribute to the solubility pump.

The impact of changing sea-ice conditions on the biological pump is even more ambiguous. On one hand, increasing light availability to surface pelagic communities in the presence of thinner ice and more open water, along with increasing nutrient inputs from upwelling and rivers would be expected to increase primary production (e.g., Bates & Mathis 2009). On the other hand, increased stratification limits nutrient supply from subsurface waters (e.g., Tremblay et al. 2008; Cai et al. 2010; McLaughlin & Carmack 2010). In addition, while enhanced river flows may increase nutrient inputs, rivers contribute only a small fraction of the total nutrients supplied to Arctic Ocean surface waters (Macdonald et al. 2010), and any benefit from additional nutrients provided by rivers could be offset by the associated increase in turbidity (Macdonald et al. 1987) or shading by coloured dissolved organic matter (Granskog et al. 2007). Also, much of the primary production in the Arctic Ocean, particularly in the Canadian Arctic, appears to occur below the low-nutrient, relatively fresh surface waters, in subsurface chlorophyll maxima (Carmack et al. 2004; Martin et al. 2010), where the carbon consumption cannot draw down atmospheric CO_2 unless the stratification is eroded by high winds or freezing. Presently, the biological pump in the interior of the Canada Basin seems to be exceptionally weak (Honjo et al. 2010), with low productivity and low export, although the south-east Beaufort Sea appears to export a substantial fraction of locally produced biogenic carbon, despite relatively low productivity in the surface waters (Shadwick et al. 2011).

Because the biological pump is based on carbon removal from surface into deep waters, a vigorous but recycling ecosystem that retains carbon in the surface waters does not contribute to CO₂ drawdown over timescales longer than a few months. Therefore, even if primary production in the Arctic Ocean does increase, a sustained increase in atmospheric CO₂ drawdown requires a concomitant increase in export production, and it is not clear whether that will happen (e.g., Honjo et al. 2010).

As a whole, the Arctic Ocean currently appears to serve as a net atmospheric CO₂ sink, with cold surface waters able to absorb carbon dioxide when sea-ice and meteorological conditions allow (e.g., Miller & DiTullio 2007; Bates & Mathis 2009). Notable localized exceptions, where CO₂ outgassing occurs, include the waters along the Siberian coast, where large quantities of terrigenous organic matter are delivered and metabolized (e.g., Semiletov et al. 2012) and upwelling areas along coasts and ice edges (Mucci et al. 2010; Mathis et al. 2012). The geographic diversity of the Arctic Ocean, with different processes dominating carbon cycling in different areas, coupled with opposing climate-change feedbacks, make it difficult to predict how the Arctic Ocean CO₂ source/sink balance will change as the climate warms.

The data set

Giesbrecht et al. (2014) give a detailed description of the data set, including quality control and discussions

of the analytical methods used and how they changed through time, as well as the temporal and spatial distribution of the data. In brief, because of the high variability in Arctic water masses, coupled with a dearth of deep samples, the internal consistency of this data set is based mainly on the fact that all the TIC and alkalinity measurements were conducted by the same laboratory, with careful intercalibrations whenever methods changed. Although the total data set spans 35 years, from 1974 to 2009, the sampling intensity increased dramatically through that period, from 65 stations during the 1970s to more than 1400 during the period from 2000 to 2009. Most of the samples were analysed for TIC and A_T, with pH analyses only from 2003–04. Although more samples were analysed for A_T, TIC has a greater temporal coverage. The vast majority of the data is from the summer months (July, August and September) and the only winter data (January, February and March) included are from 1987 and 2004. This data set therefore carries a strong summer bias, and any further analysis and interpretation, particularly if focussed on surface waters, needs to take that bias into consideration.

The total inorganic carbon time series

The total inorganic carbon (TIC; in seawater, generally assumed to be primarily DIC) data are the most complete in our data set, with coverage in all four decades between 1974 and the present (Fig. 4). The most striking

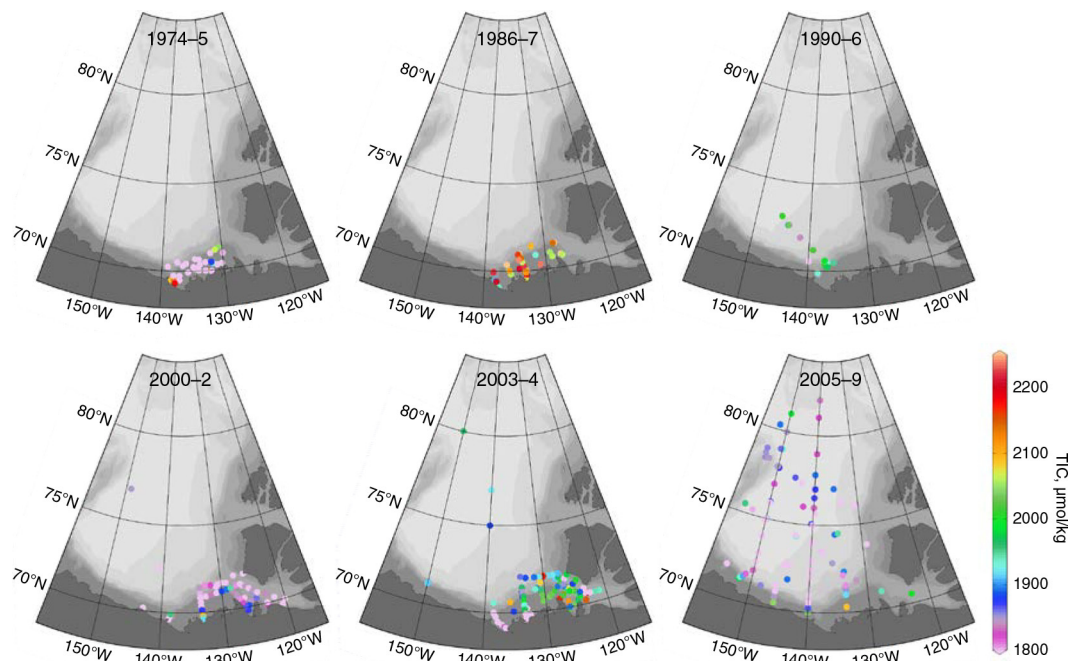


Fig. 4 Maps of surface (0–20 dbar) total inorganic carbon (TIC) by date intervals.

characteristic of this data set is how the sampling coverage has expanded through time, both in terms of sampling frequency and area. In addition, the surface values are extremely variable, which is largely a product of the complex hydrography of the region, but also of a large interannual variability coupled with varying cruise dates between years. The surface TIC concentrations have generally decreased as we entered the 21st century, mainly as a result of freshening and dilution due to sea-ice melt and river runoff (Fig. 5; Yamamoto-Kawai et al. 2009). The large number of low TIC values from 1974 and 1975 primarily reflects a dominance of low-salinity river waters at the stations sampled during those mid-summer expeditions. Note that during the 1986–87 and 2003–04 periods, when winter data are included, a number of higher TIC and salinity values were measured.

The characteristic profiles for the Beaufort Sea and southern Canada Basin (based on the box in Fig. 1a) show substantial variability in the TIC maximum within the upper halocline, with TIC concentrations intermittently varying by up to 50 $\mu\text{mol/kg}$ (Fig. 6a). The change from high values in 1990–92 to lower values in 1995 is coincident with observations of large-scale water-mass changes, with an increasing Atlantic Water volume and attendant shoaling of the upper halocline in the Canada Basin, as described by McLaughlin et al. (2002). They attributed those changes to atmospheric circulation patterns associated with a positive shift in the Arctic Oscillation that

occurred around 1990. However, despite another TIC peak in the upper halocline following an increase in the Arctic Oscillation (AO) index at the turn of the millennium (Fig. 6a), there does not appear to be a relationship between upper halocline TIC and the AO index after that time, and this data set does not support a strong relationship between the AO and the CO_2 system chemistry of the halocline. A plot showing TIC at the core of the Pacific Winter Water layer (Fig. 6b) reveals that although TIC is generally increasing, there is no clear geographical pattern in that increase.

pCO₂ Variations

The CO_2 partial pressure in seawater, $p\text{CO}_{2\text{SW}}$ is defined as the CO_2 partial pressure in a volume of air in equilibrium with that water. Thus, $p\text{CO}_{2\text{SW}}$ represents the potential for the water to either absorb CO_2 from or release it to the atmosphere. The actual air–sea CO_2 flux is not only dependent on the partial pressure gradient between the air and the seawater (i.e., the thermodynamic forcing) but also on the rate at which CO_2 molecules are able to cross the air–sea boundary (the kinetic control), which is in turn dependent on boundary turbulence and the myriad factors that control it (e.g., Nightingale 2009). Although our data set does not contain any direct $p\text{CO}_{2\text{SW}}$ measurements, $p\text{CO}_{2\text{SW}}$ can be calculated from TIC, alkalinity, and/or pH with reasonable

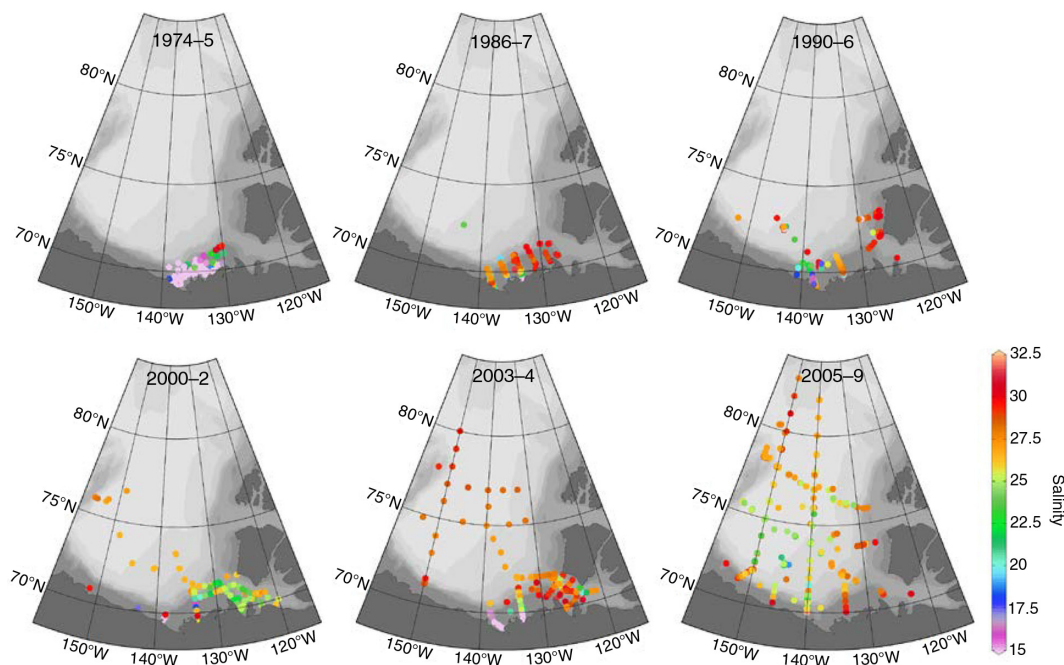


Fig. 5 Maps of surface (0–20 dbar) salinity (S_p), by date intervals.

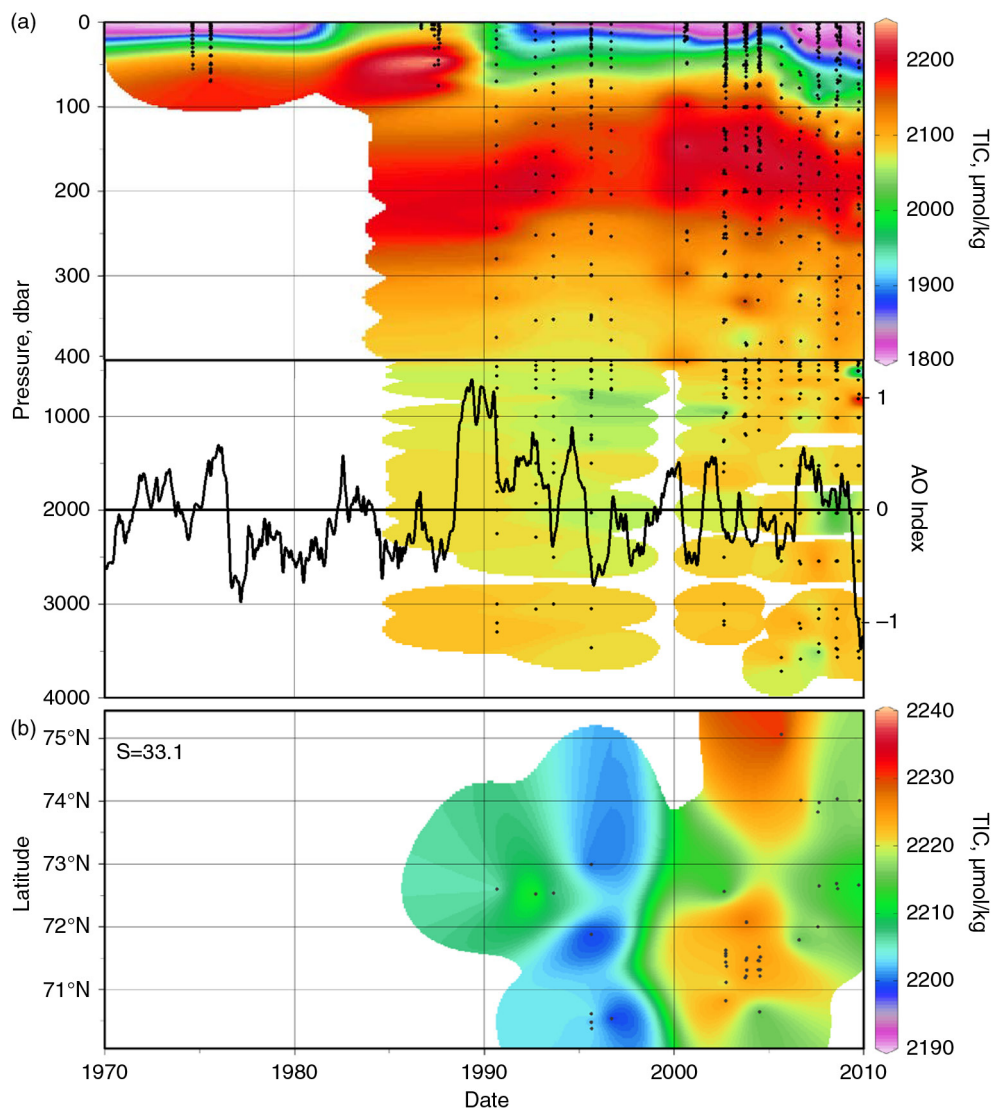


Fig. 6 (a) Vertical total inorganic carbon (TIC) distributions in the Beaufort Sea and Canada Basin (within red box on Fig. 1a) through time overlaid with the Arctic Oscillation (AO) index, defined as the difference in sea-level atmospheric pressure anomalies of opposite sign between the Arctic and 37–45°N (data from the US National Oceanic and Atmospheric Administration Climate Prediction Center). (b) TIC on the 33.1 salinity surface, corresponding to the Pacific Water core and defined as salinities between 32.9 and 33.3. Note the different TIC colour scales between (a) and (b).

confidence (e.g., Dickson et al. 2007), and we have calculated $p\text{CO}_{2\text{SW}}$ for all the samples for which we have both TIC and A_T measurements.

The surface waters in this area have been consistently undersaturated with respect to the atmosphere (Fig. 7). We note that this data set includes samples covering the full annual cycle (as described by Lansard et al. 2012), confirming the net CO_2 drawdown potential of these waters postulated by other studies (Mucci et al. 2010; Shadwick et al. 2011; Else et al. 2012). Isolated instances of oversaturation are associated with warming ice-melt, coastal and ice-edge upwelling, or river waters, whereas stations showing severe undersaturation accompany

phytoplankton blooms. Any trends in these surface $p\text{CO}_2$ data associated with climate change are overshadowed by interannual variability and the seasonal distributions of the sampling programs; that is, this data set, alone, is too short and too seasonally biased to identify a climate-change signal in the surface waters.

Perhaps more informative, from a climate-change perspective, are the variations in the subsurface waters. Figure 8 shows that although a $p\text{CO}_{2\text{SW}}$ maximum occurs in the upper halocline, at the same depths as the TIC maximum (Fig. 6a), the two parameters are at least somewhat decoupled. Alkalinity variations in this area are also important in setting $p\text{CO}_{2\text{SW}}$ and alkalinity appears

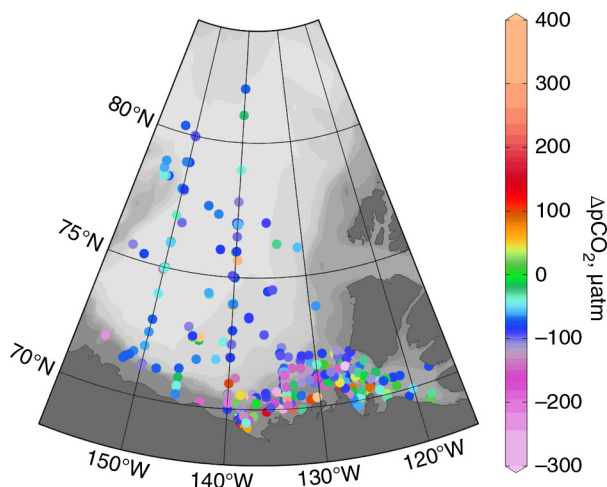


Fig. 7 Air–sea $p\text{CO}_2$ gradient, $\Delta p\text{CO}_2$, 1974–2009, where negative values indicate surface water (0–20 dbar) undersaturation, with respect to the atmosphere. $p\text{CO}_{2\text{SW}}$ calculated from measured total inorganic carbon and total alkalinity using the CO2SYS MatLab version (van Heuven et al. 2011), with the carbonate system constants of Mehrbach et al. (1973), refit by Dickson & Millero (1987), and the KSO_4 constant of Dickson (1990). Atmospheric $p\text{CO}_2$ measured at Barrow, Alaska (Keeling et al. 2001); in the absence of atmospheric pressure data, mole fraction (in ppm) assumed to be equivalent to partial pressure (in μatm).

to have been generally decreasing in the halocline since at least 1994 (Fig. 9). As discussed by Giesbrecht et al. (2014), the alkalinity data from the 1990s may be somewhat high, but that cannot be confirmed, and we have no reason to doubt the changes observed during the first decade of the 2000s. Assuming that the alkalinity data are generally robust, other possible explanations for the observed variations in the halocline include water-mass changes (as per McLaughlin et al. 2002) and variations in rates of transport and remineralization of shelf-derived organic carbon (e.g., Bates et al. 2013) or of sea-ice formation and brine rejection (as hypothesized by Rysgaard et al. 2011).

A deconstruction analysis, building on previous approaches pioneered by Takahashi et al. (1993) and more recently used by Metzl et al. (2010), provides additional insight into the causes of the $p\text{CO}_2$ variations in the halocline. We parameterized the sensitivity of the calculated $p\text{CO}_2$ to variations in temperature, salinity, TIC and A_T over the ranges observed in the halocline of the Beaufort Sea using the CO2SYS program (Table 2). Using these sensitivity equations, we calculated the fractional impact of the average changes in T, S, TIC and A_T between the time intervals 1990–96, 2000–04, and

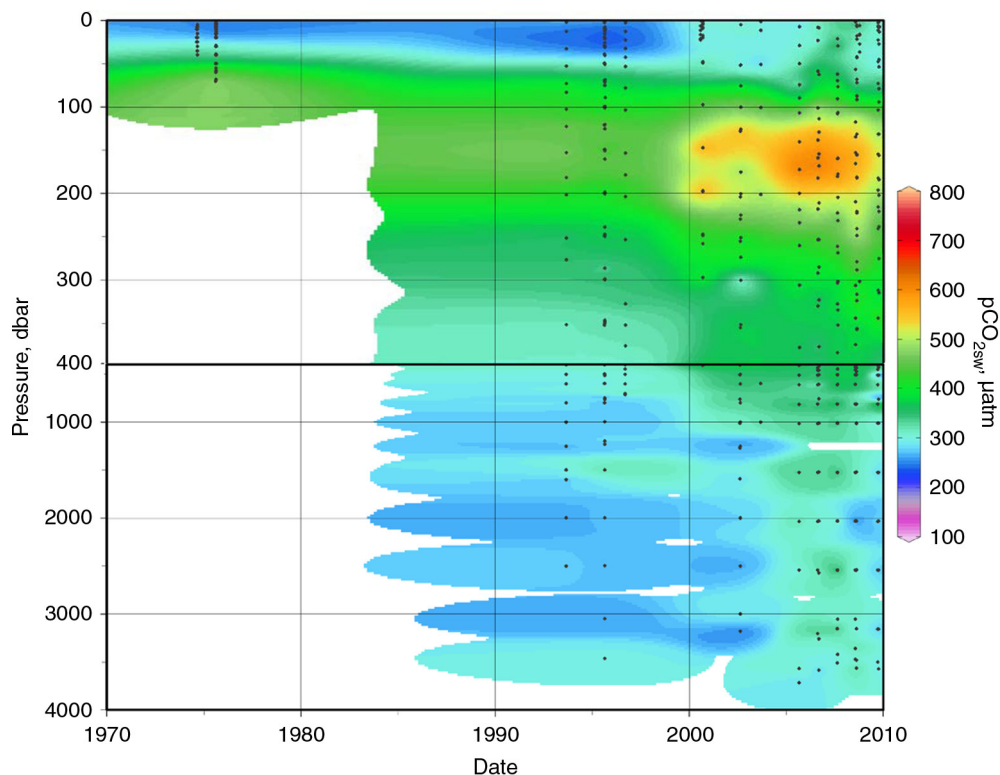


Fig. 8 Vertical $p\text{CO}_{2\text{SW}}$ distributions in the Beaufort Sea and Canada Basin (within red box on Fig. 1a) through time. Calculated from measured total inorganic carbon and total alkalinity using the CO2SYS MatLab version (van Heuven et al. 2011), with the carbonate system constants of Mehrbach et al. (1973), refit by Dickson & Millero (1987), and the KSO_4 constant of Dickson (1990).

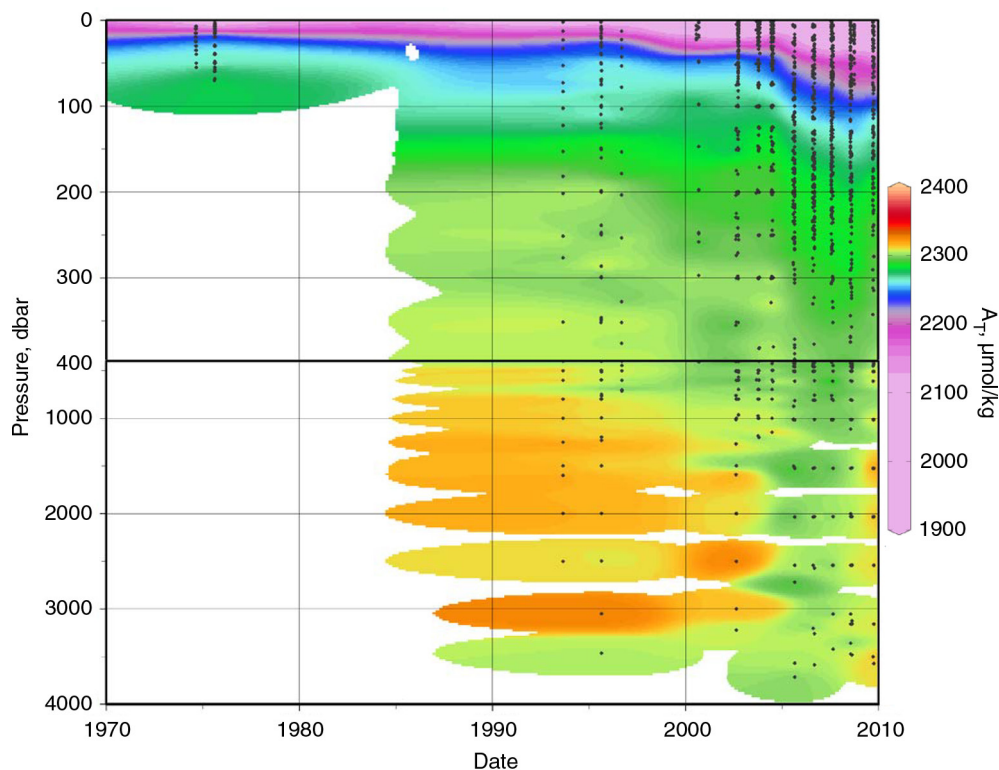


Fig. 9 Vertical distributions of total alkalinity (A_T) in the Beaufort Sea and Canada Basin (within red box on Fig. 1a) through time.

2005–09 (Table 3). The observed changes in temperature and salinity played a negligible role in the $p\text{CO}_{2\text{SW}}$ increase (Table 3b), while both increasing TIC and decreasing alkalinity were important. Although the overall changes between the early 1990s and the 2005–09 period indicate that decreasing alkalinity was the dominant factor in increasing $p\text{CO}_{2\text{SW}}$, dividing that time period into smaller intervals shows that increasing TIC concentrations were more important between the early 1990s and the 2000–04 period, and it was only during the first decade of the 2000s that decreasing alkalinity dominated the $p\text{CO}_{2\text{SW}}$ increase. We note that if the alkalinity data from the 1990s have been overestimated, the actual impact of

alkalinity changes on $p\text{CO}_{2\text{SW}}$ between the 1990–95 and 2000–04 periods would be even lower than shown in Table 3b.

Resolving the specific physical and biogeochemical mechanisms of these changes in TIC and alkalinity within the halocline will require a focussed, station-by-station analysis of the data set, which we leave for future papers. Nonetheless, because the upper halocline waters feed coastal and ice-edge upwelling, further increases in $p\text{CO}_{2\text{SW}}$ in these waters could have significant implications for the net atmospheric CO_2 sink in the Arctic, particularly if upwelling rates also increase with ice retreat (Carmack & Chapman 2003).

Table 2 Sensitivity of calculated $p\text{CO}_{2\text{SW}}$ to variations in temperature (T), salinity (S), total inorganic carbon (TIC) and total alkalinity (A_T) in the Beaufort Sea halocline. We calculated $p\text{CO}_{2\text{SW}}$ using CO2SYS (Pierrot et al. [2006]; carbonate system constants of Mehrbach et al. [1973], refit by Dickson & Millero [1987] and the KSO_4 constant of Dickson [1990]) by varying each parameter over the given range of values observed between 100 and 200 dbar and within the area of 70–75°N, 128–145°W, while holding the other three parameters constant at their average values. Regression lines were fit to plots of calculated $p\text{CO}_{2\text{SW}}$ versus each parameter to generate the sensitivity equations; second order regressions substantially improved the fits for TIC and A_T , but not for T and S. Note that these sensitivity equations are only valid for conditions in the halocline of the Beaufort Sea.

Parameter	Average	Range	$p\text{CO}_2$ sensitivity	r^2
T, °C	−1.4	−1.7 to −0.3	$p\text{CO}_2 = 539 + 23.8T$	0.9999
S (‰)	33.1	31.9 to 34.5	$p\text{CO}_2 = 137 + 11.2S$	1.0000
TIC, μmol/kg	2200	2070 to 2260	$p\text{CO}_2 = 65\,600 - 63.4\text{TIC} + 0.0154\text{TIC}^2$	0.9983
A_T , μmol/kg	2270	2170 to 2350	$p\text{CO}_2 = 124\,000 - 104A_T + 0.0221A_T^2$	0.9993

Table 3 (a) Changes in average values of measured parameters and directly calculated $p\text{CO}_{2\text{SW}}$ within the Beaufort Sea halocline (100–200 dbar). (b) Changes in $p\text{CO}_{2\text{SW}}$ (μatm) calculated from the changes in measured parameters in (a) and sensitivities in Table 2. Comparison between $\Delta p\text{CO}_{2\text{SW}}$ in (a) and $\Delta p\text{CO}_{2\text{SW}}(\text{Sum})$ in (b) indicates the error in our approach to estimating the independent effects of changes in temperature (T), salinity (S), total inorganic carbon (TIC) and total alkalinity (A_T) on $p\text{CO}_{2\text{SW}}$.

(a) Date range	ΔT , °C	ΔS (PSU)	ΔTIC , $\mu\text{mol/kg}$	ΔA_T , $\mu\text{mol/kg}$	$\Delta p\text{CO}_{2\text{SW}}$, μatm
(2005–09)–(1990–96)	0.0285	0.090	5.0	–25.6	118
(2000–04)–(1990–96)	–0.0075	0.045	19.1	–3.6	87
(2005–09)–(2000–04)	0.0361	0.045	–14.1	–22.0	31
(b) Date range	$\Delta p\text{CO}_2(\text{T})$	$\Delta p\text{CO}_2(\text{S})$	$\Delta p\text{CO}_2(\text{TIC})$	$\Delta p\text{CO}_2(\text{A}_T)$	$\Delta p\text{CO}_{2\text{SW}}(\text{sum})$
(2005–09)–(1990–96)	0.678	1.01	20	112	134
(2000–04)–(1990–96)	–0.179	0.51	82	14	96
(2005–09)–(2000–04)	0.858	0.50	–62	98	37

Carbonate mineral saturation state

While the oceanic CO_2 source-versus-sink balance in individual Arctic Ocean regions may change in intensity or direction, the net inorganic carbon content of the oceans is increasing along with atmospheric CO_2 levels. Consequently, both seawater pH and calcium carbonate mineral saturation states are decreasing, in a process termed ocean acidification (e.g., Gattuso & Hansson 2011). The calcium carbonate saturation state is defined as:

$$\Omega = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K'_{\text{sp}}} \quad (1)$$

where the brackets indicate molar concentrations and K'_{sp} is the conditional solubility product of the CaCO_3 mineral. Of the two most common CaCO_3 polymorphs secreted by marine organisms, aragonite has a higher K'_{sp} and higher solubility than calcite (Mucci 1983). Therefore, despite the fact that fewer organisms secrete aragonite than calcite, the aragonite saturation state, Ω_{Ar} is often used as an indicator of seawater corrosiveness and acidification (both natural and anthropogenic).

In the Arctic Ocean, acidification caused by increasing CO_2 is exacerbated by freshening resulting from sea-ice melt and river runoff, which also reduce CaCO_3 saturation states in surface waters. Because of the relatively high CO_2 solubility in the cold Arctic surface waters, in combination with the already high CO_2 concentrations in the subsurface Pacific inflow waters, many Arctic Ocean waters are naturally more acidic than is typical of the global ocean, and waters undersaturated with respect to aragonite have already been identified at the surface in the Beaufort Sea (Yamamoto-Kawai et al. 2011) and the Canadian Archipelago (Chierici & Fransson 2009).

As noted in those earlier studies (Chierici & Fransson 2009; Yamamoto-Kawai et al. 2011), the Beaufort Sea/Canada Basin area is particularly inclined towards low CaCO_3 saturation states, because of sea-ice melt and the high- $p\text{CO}_{2\text{SW}}$ Pacific water inflow. Therefore, even small direct anthropogenic acidification effects could tip the area into a biologically stressful state. Our time series (Fig. 10) shows that the aragonite saturation state (Ω_{Ar}) is highly variable but has generally been decreasing in both the upper halocline and deep waters. Not surprisingly, the vertical Ω_{Ar} profiles mainly parallel those for $p\text{CO}_{2\text{SW}}$ and an analysis similar to that shown in Tables 2 and 3 for $p\text{CO}_{2\text{SW}}$ gave the same results for Ω_{Ar} . Bottom water saturation states, which are also depressed by high hydrostatic pressure, are of particular concern, because benthic communities are generally less mobile than their pelagic neighbours, and organic matter remineralization in oxic surface sediments releases additional CO_2 to the bottom waters (Anderson et al. 2011).

Sustaining future observations

This data set results from the vision and tenacity of a handful of scientists, who have been driven to collect samples whenever they could, regardless of an explicit mandate or lack thereof. The effort has often been limited by budgetary and logistical constraints, and the benefits of the substantial upturn in resources (financial and infrastructure) and access (due to reduced coverage by thick ice) to conduct this research over the last decade are obvious; recent intensive process studies, including those during the 2007–08 International Polar Year, have dramatically increased our understanding of what currently controls the inorganic carbon system of the Arctic (e.g., Mucci et al. 2010; Anderson et al. 2011; Shadwick et al. 2011; Yamamoto-Kawai et al. 2011;

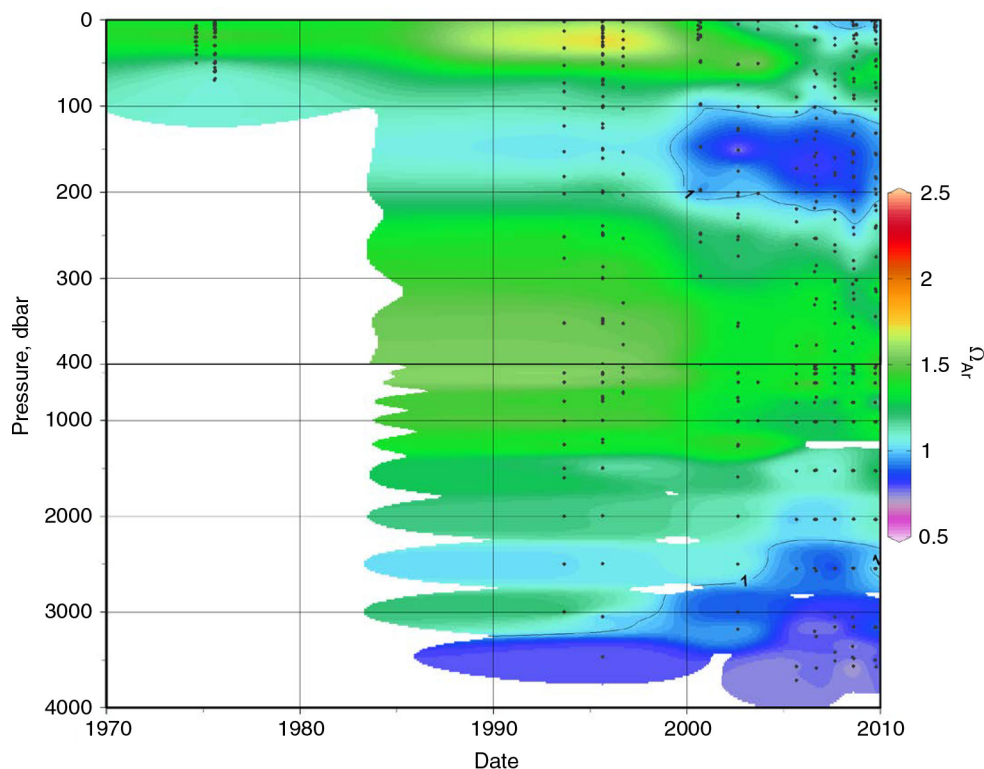


Fig. 10 Vertical distributions of aragonite saturation state (Ω_{Ar} ; Eqn. 1) in the Beaufort Sea and Canada Basin (within red box in Fig. 1a) through time. $\Omega_{Ar} = 1$ contour shown, indicating undersaturated zones in dark blue and purple. Ω_{Ar} calculated from measured total inorganic carbon and total alkalinity using the CO2SYS MatLab version (van Heuven et al. 2011), with the carbonate system constants of Mehrbach et al. (1973), refit by Dickson & Millero (1987), and the KSO_4 constant of Dickson (1990).

Else et al. 2012; Semiletov et al. 2012). Nevertheless, although the insights derived from new data, traditional knowledge (e.g., Barber et al. 2012) and historical data, such as those presented here, are improving how processes are represented and parameterized in predictive models (Deal et al. 2014), the observations to date are still insufficient to distinguish between natural variability and climate change-associated trends (e.g., Burroughs 2007). For that, we need to systematically collect high-resolution (both in space and time) data, not only for the inorganic carbon system, but also for all the ancillary parameters necessary to understand those carbon data (e.g., $\delta^{18}O$, $\delta^{13}C$, $\Delta^{14}C$, dissolved and particulate organic carbon, vertical flux).

Although sea-ice retreat is easing our logistical constraints in some ways, in other ways, the loss of a stable ice cover is making it more difficult to access both coastal and open ocean waters, especially during the winter and shoulder seasons, periods that are still poorly represented in our data sets, resulting in a strong “summer” bias in our understanding of the Arctic Ocean. The high

financial costs associated with research in remote areas also continue to be a limiting factor. Collecting the kind of data required to understand and ultimately predict carbonate system changes in the Arctic will require implementation of an extensive network of automated instruments (e.g., Dickson 2006). The stability and precision of in situ pCO_{2SW} and pH sensors are approaching thresholds necessary for effective seawater monitoring, and although a more mobile ice pack continues to complicate bottom mooring deployments in the Arctic, ice-tethered profilers and gliders show promise (e.g., Jackson et al. 2012). Shipboard work will continue to be required for servicing the instrument network, ground-truthing the in situ data, and conducting process studies, but as is evident from the difficulty in interpreting the data set we present here, ship-based sampling, alone, will not generate the quantity and resolution of data required to answer the pressing questions we will face in the coming decades and centuries about how the Arctic is responding to climate change.

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