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Processes of multibathyal aragonite undersaturation in the Arctic Ocean

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Abstract

During 3 years of study (2010–2012), the western Arctic Ocean was found to have unique aragonite saturation profiles with up to three distinct aragonite undersaturation zones. This complexity is produced as inflow of Atlantic-derived and Pacific-derived water masses mix with Arctic-derived waters, which are further modified by physiochemical and biological processes. The shallowest aragonite undersaturation zone, from the surface to ∼30 m depth is characterized by relatively low alkalinity and other dissolved ions. Besides local influence of biological processes on aragonite undersaturation of shallow coastal waters, the nature of this zone is consistent with dilution by sea-ice melt and invasion of anthropogenic CO2 from the atmosphere. A second undersaturated zone at ∼90–220 m depth (salinity ∼31.8–35.4) occurs within the Arctic Halocline and is characterized by elevated pCO2 and nutrients. The nature of this horizon is consistent with remineralization of organic matter on shallow continental shelves bordering the Canada Basin and the input of the nutrients and CO2 entrained by currents from the Pacific Inlet. Finally, the deepest aragonite undersaturation zone is at greater than 2000 m depth and is controlled by similar processes as deep aragonite saturation horizons in the Atlantic and Pacific Oceans. The comparatively shallow depth of this deepest aragonite saturation horizon in the Arctic is maintained by relatively low temperatures, and stable chemical composition. Understanding the mechanisms controlling the distribution of these aragonite undersaturation zones, and the time scales over which they operate will be crucial to refine predictive models.

1. Introduction

The chemistry of the Arctic Ocean is changing rapidly as a result of increasing surface temperature, extensive melting of multiyear sea-ice, uptake of atmospheric CO2 [Cai et al., 2010; Mathis et al., 2011; Bates et al., 2013; Robbins et al., 2013a; Yamamoto-Kawai et al., 2013], increasing terrestrial runoff of freshwater and its influx of terrigenous carbon [Serreze, 2011; Wadham, 2012; Fichot and Kaiser, 2013], and thawing of methane hydrates [Shakhova et al., 2005; Zimov et al., 2006; Biastoch et al., 2011]. Because mean residence time of surface waters in the Arctic Ocean is short (<2.6–14.2 years) [Ekwurzel et al., 2001], changes within these time scales may result in rapid changes in stratification of properties such as salinity and carbonate saturation state.

Carbonate saturation state (Ω) is an index of the mineral saturation of the water and is described by a solubility ratio:

\[ \Omega_{\text{CaCO}_3} = \frac{[\text{CO}_3^{2-}] \times [\text{Ca}^{2+}]}{K_{sp}} \]

where \( K_{sp} \) is the solubility product for a specific mineral (e.g., calcite or aragonite, a function of salinity, temperature, and pressure) and \([\text{CO}_3^{2-}]\) and \([\text{Ca}^{2+}]\) are the concentrations of carbonate and calcium ions, respectively. Values of \( \Omega_{\text{CaCO}_3} \) less than 1 indicate undersaturated conditions that will dissolve the mineral. The carbonate saturation horizon is often a useful parameter to describe the saturation state profile, and is defined as the depth at which \( \Omega_{\text{CaCO}_3} \) transitions from supersaturated conditions to undersaturated conditions [Feely et al., 2009; Pälike et al., 2012].

There are large differences in the nature of calcite and aragonite saturation horizons between the Atlantic, Pacific, and Indian Oceans [Berger and Winterer, 1974], each having at least one major saturation...
horizon at depth. For example, aragonite saturation horizons in the North Pacific and the North Atlantic are at depths of ~500 m and ~1500 m, respectively [Millero, 2013]. Generally, the main saturation horizon is deeper in the tropics and shallower at higher latitudes, although minor horizons may occur locally coincident with oxygen minimum zones [e.g., Bianucci and Denman, 2012; Murata et al., 2015]. A recent synthesis of 14 years data from the North Pacific Ocean has shown an upward migration of the aragonite saturation horizon at ~1–2 m/yr due to increases in anthropogenic CO₂ in the water column [Feely et al., 2012].

1.1. Multibathyal Saturation Zones
In many high-latitude waters, aragonite saturation state profiles may be more complex than can be represented by a single horizon depth. For example, in the Southern Ocean two aragonite saturation horizons have been identified: a horizon at ~300 m on the inner shelf and a deeper horizon at 2100–2800 m on the outer slope and rise [Hillenbrand et al., 2003]. The Arctic Ocean also demonstrates multibathyal undersaturation, with more than one aragonite saturation horizon observed in the Canadian Archipelago and Labrador Sea [Azetsu-Scott et al., 2010] and throughout much of the Canada Basin [Jutterström and Anderson, 2005; Anderson et al., 2013]. Due to the multibathyal nature of aragonite saturation profiles in high-latitude waters, below we use the term “aragonite undersaturation zone” to refer to a stratum of aragonite-undersaturated water bounded by aragonite-saturated waters. Thus, an aragonite undersaturation zone includes waters below the aragonite saturation horizon.

The nature of aragonite saturation state profiles in the Arctic Ocean is driven by very different processes than those of the typically unibathyal saturation profile in the Atlantic and Pacific Oceans, for which the aragonite saturation horizon depth is largely a function of temperature and large-scale variation of pCO₂ driven by parameters of global circulation patterns, such as residence time. The additional complexity of aragonite saturation in Arctic Ocean largely occurs in shallow waters, and is due to its unique circulation and stratification resulting from significant variation of the inputs of freshwater and large variations in sea-ice coverage, biological activity, and temperature of inflow waters. For example, areas of declining sea-ice cover and increased absorption of CO₂ in a highly stratified water column are creating a rapid decline of saturation state of increasingly fresh surface waters [Yamamoto-Kawai et al., 2009b; Cai et al., 2010; Yamamoto et al., 2012]. This trend has recently resulted in an area greater than 307,000 km² aragonite undersaturated surface water observed during 2010–2011 [Robbins et al., 2013a]. Sea-ice formation can also reduce pCO₂ of surface waters through brine pumping [Rysgaard et al., 2011; Fransson et al., 2013].

Building on previous studies in the Canadian Basin and Archipelago [Jutterström and Anderson, 2005; Bates et al., 2006; Anderson et al., 2010; Azetsu-Scott et al., 2010; Cai et al., 2010; Chierici et al., 2011; Shadwick et al., 2011; Bates et al., 2013], and using data collected over a 3 year time span (2010–2012), we analyzed water column aragonite saturation state (Ωa) in the Canada and Makarov Basins. We combined this analysis of trends in Ωa with tracer data to elucidate the major processes contributing to the nature of three aragonite saturation zones that are presently observed. These data demonstrate spatial and temporal complexity, provide insight into the mechanisms contributing to the multiple aragonite saturation depths in the Arctic Ocean, and provide a basis for longer-term projections.

2. Methods
2.1. Sampling
Station and surface water samples were collected during late summer peak sea-ice melting seasons (August–September) of 2010, 2011, and 2012 onboard the USCGC Healy (HLY1002, HLY1102, and HLY1202). Figure 1 shows station locations from these three cruises, combined with data from stations collected during the 2005 cruise of the Swedish icebreaker Oden (AOS05) [Anderson et al., 2010; Newton et al., 2013]. As part of the methodology of the 2010–2012 Healy cruises, surface water samples were collected at high-spatial resolution (~0.24 to 10 km between samples). Thus, the sampling frequency of surface waters differs between the two compared data sets. Additional methodological details for samples used in this study are contained in supporting information, and full details of cruise reports and data collected are in Robbins et al. [2013b, 2013c, 2014].
2.2. Analyses

Seawater pH measurements were made shipboard, whereby approximately 30 milliliters (ml) of seawater was collected directly into cylindrical optical glass cuvettes following the procedure of SOP6b [Dickson, 1990b]. These cells were warmed to 25°C for approximately 30 min and subsequently analyzed on either an Agilent 8453 UV-Visible spectrophotometer or USB-4000 fiber optic spectrometer (Ocean Optics, Inc., USA), using purified metacresol purple indicator dye, and method and equations of Liu et al. [2011]. The precision for these methods was 0.002. Water samples from rosettes or from the underway throughflow system were collected for total alkalinity (TA) and total dissolved inorganic carbon (T\textsubscript{CO_2}) in 300 ml borosilicate glass bottles and preserved with saturated HgCl\textsubscript{2} solution. TA was measured using a single-point spectrophotometric titration method with bromocresol purple (BCP) [Liu et al., 2015]. The titration system consisted of a USB-4000 fiber optic spectrometer (Ocean Optics, Inc., USA), a 665 Dosimat auto-titrator with stir plate (Metrohm AG, Switzerland), and a purging system with high-purity N\textsubscript{2} gas. Certified reference material (CRM) obtained from A.G. Dickson Scripps Institute of Oceanography was used to determine that the analytical precision of the TA measurements was ±1 μmol kg\textsuperscript{-1}. Samples were analyzed for dissolved inorganic carbon (T\textsubscript{CO_2}) using the methods of Dickson et al. [2007] using either CMS015 CO\textsubscript{2} coulometer (UIC, Inc., USA) at the University of South Florida or a CMS014 and CMS130 acidification module (UIC, Inc., USA) at the USGS St. Petersburg, FL. Through the use of CRM [Dickson et al., 2003], the precision of the T\textsubscript{CO_2} measurements was measured at ±2 μmol kg\textsuperscript{-1}. Oxygen isotopic composition (δ\textsuperscript{18}O) was measured from separate samples using a Thermo Finnigan Delta V mass spectrometer at the University of South Florida, Tampa, FL. Values are reported with respect to the SMOW reference scale, with precision of 0.1‰. Nutrient concentrations (phosphate, nitrate + nitrite, ammonium, and silicate) were measured at the Nutrient Analytical Facility at Woods Hole Oceanographic Institute, Woods Hole, MA, using a SEAL AA3 four-channel segmented flow analyzer. Some additional silicate concentrations were measured by ICP-MS at the University of South Florida, St. Petersburg, FL. Measured pH and TA were used as pairs for input to CO2calc v 1.2.8 [Robbins et al., 2010] for carbonate system calculations based on the availability of measurements. The calculations were performed on the total pH scale using the carbonate dissociation constants (K\textsubscript{1} and K\textsubscript{2}) of Lueker et al. [2000]. The HSO\textsubscript{4}\textsuperscript{-} dissociation constant was taken from Dickson [1990a], and the B/S ratio was taken from Uppstrom [1974]. The dissociation constant of Lueker et al. [2000] was chosen based on “best practices” of Dickson et al. [2007] and the suggestion of Orr et al. [2015].
calculated data using dissociation constants characterized for low temperatures [Goyet and Poisson, 1989; Roy et al., 1993] found no significant difference \( p < 0.05 \) when using either of these constants. Uncertainty of \( \Omega_{\text{arag}} \) based on propagated uncertainties from replicate TA and pH measurements was calculated to be at most 0.02.

### 2.3. Water Source Mixing Model

We used conservative tracers and a mixing model to identify water sources, as has been done extensively in the Arctic Ocean [Tan and Strain, 1980; Østlund and Hut, 1984; Bauch et al., 1995, 2005; Yamamoto-Kawai et al., 2008, 2009a; Azetsu-Scott et al., 2012; Bauch et al., 2012; Lansard et al., 2012; Alkire et al., 2015]. The mixing model is used to quantify fractional contributions (\( f \)) of water from meteoric freshwater (MW), sea-ice melt freshwater (SIM), and seawater from Atlantic (ATW) and Pacific Inlet (PIW) sources. Each of these end-members has a distinct combination of the conservative constituents \( S \) and \( \delta^{18}O \), so large differences in their values of the freshwater sources versus seawater make this tracer useful to partition water sources into its constituent fractions. However, four end-members are not fully determined by a mixing model with only two parameters, so a third semiconservative tracer is often used to distinguish nutrient-rich Pacific-derived seawater from nutrient-poor Atlantic-derived seawater. A variety of methods have been used to estimate the role of Pacific Inlet Water into the Arctic Ocean including raw nutrient concentration maxima (\( \text{SiO}_4 \) maxima) [e.g., Anderson et al., 1994; Bauch et al., 1995; Jones et al., 1995; Wheeler et al., 1997; Swift et al., 1998; Schlosser et al., 1999], relationships of nutrient concentrations such as the Arctic N-P tracer (ANP) [Jones et al., 1998, 2003, 2008; Yamamoto-Kawai et al., 2008], and methods based on phosphate (\( \text{PO}_4^* \)) concentration modified with oxygen (\( O_2 \)) concentration to account for biological effects (\( \text{PO}_4^* \) developed by Broecker et al. [1985] and used by Ekwurzel et al. [2001], and in modified form, \( \text{PO}_4^* \), Newton et al. [2013]). All such nutrient-based tracers of water source are less than optimal because nutrient concentrations are modified by biological and physical processes, and thus less conservative than \( S \) and \( \delta^{18}O \). As a result, each semiconservative tracer of PIW has both advantages and disadvantages but results in some level of inaccuracy that varies under different conditions. For example, nutrient concentrations may be depleted in the highly productive upper water column and by contact with sediments at the seafloor [Jones and Anderson, 1986; Jones et al., 2008]. Meanwhile, while the \( \text{PO}_4^* \) tracer accounts for biological processes of production and mineralization, it can be modified by oxygen exchange with the atmosphere near the sea surface [Jones et al., 2008] and may also be subject to seasonal fluctuation in sources, otherwise assumed to be constant [Ekwurzel et al., 2001]. Likewise, the ANP tracer produces problematic results in surface waters with very low \( \text{NO}_3 \) with variable \( \text{PO}_4 \) concentrations, while nitrification/denitrification processes may affect the otherwise defined constant relationships for Atlantic-derived versus Pacific-derived seawater [Newton et al., 2013]. For these reasons, we investigated and compared several methods of resolving PIW from ATW (see supporting information for comparisons, following similar comparison of Alkire et al. [2015]). Based on this analysis, we resolved to use the simple \( \text{SiO}_4 \) nutrient maxima as a tracer of PIW, as in Bauch et al. [1995]. Our decision to use \( \text{SiO}_4 \) as the PIW tracer is based on several features of the 2010–2012 data set, which combines large numbers of samples of surface seawater where nutrient concentrations are very low, with relatively few samples collected from deep stations. The station data provide insufficient numbers of samples to define end-members based on relationships of nutrient concentrations. Concentrations of nitrate and phosphate for the surface data set are at or below detection limits, so the resulting analytical errors hinder the utility of the ANP tracer. Meanwhile oxygen exchange in near-surface water samples hinders the utility of the \( \text{PO}_4^* \) tracer in the bulk of the surface water data set. Nevertheless, our use of the \( \text{SiO}_4 \) maxima as a tracer recognizes the semiconservative nature of nutrient tracers, and the fact that this is especially problematic near the sea surface and seafloor. Thus, our use of a simple \( \text{SiO}_4 \)-maxima based method adds an additional step which attempts to explicitly account for biological uptake and remineralization by modification of raw fractions of PIW and ATW in low-salinity surface and high-salinity deep waters, as described below.

The mixing calculation begins with a model based on simple mass balance equations using three tracers:

\[
\begin{align*}
\text{f}_{\text{ATW}} + \text{f}_{\text{PIW}} + \text{f}_{\text{SIM}} + \text{f}_{\text{MW}} &= 1 \\
\text{f}_{\text{ATW}}(S_{\text{ATW}}) + \text{f}_{\text{PIW}}(S_{\text{PIW}}) + \text{f}_{\text{SIM}}(S_{\text{SIM}}) + \text{f}_{\text{MW}}(S_{\text{MW}}) &= S_{\text{observed}} \\
\text{f}_{\text{ATW}}(\delta^{18}O_{\text{ATW}}) + \text{f}_{\text{PIW}}(\delta^{18}O_{\text{PIW}}) + \text{f}_{\text{SIM}}(\delta^{18}O_{\text{SIM}}) + \text{f}_{\text{MW}}(\delta^{18}O_{\text{MW}}) &= \delta^{18}O_{\text{observed}} \\
\text{f}_{\text{ATW}}(S_{\text{ATW}}) + \text{f}_{\text{PIW}}(S_{\text{PIW}}) + \text{f}_{\text{SIM}}(S_{\text{SIM}}) + \text{f}_{\text{MW}}(S_{\text{MW}}) &= S_{\text{observed}} \\
\text{f}_{\text{ATW}}(\delta^{18}O_{\text{ATW}}) + \text{f}_{\text{PIW}}(\delta^{18}O_{\text{PIW}}) + \text{f}_{\text{SIM}}(\delta^{18}O_{\text{SIM}}) + \text{f}_{\text{MW}}(\delta^{18}O_{\text{MW}}) &= \delta^{18}O_{\text{observed}} \\
\end{align*}
\]

\( S \) and \( \delta^{18}O \) values used for SIM, ATW, PIW, and MW end-members follow closely Yamamoto-Kawai et al. [2008] and are similar to those in Robbins et al. [2013a]: MW: \( S = 0 \), \( \delta^{18}O = -20^{\circ} \); SIM: \( S = 4 \), \( \delta^{18}O = \ldots \)
$\delta^{18}$O_{surf} + 2.6\%o; ATW: $S = 34.87$, $\delta^{18}$O = 0.3\%o; PIW: $S = 32.5$, $\delta^{18}$O = −0.8\%o). The use of a variable $\delta^{18}$O value of SIM accounts for the fact as surface water freezes and remelts, it may already contain some inherited SIM [Bauch et al., 1995]. Hence, at a specific station the end-member $\delta^{18}$O is set by adding the sea-ice to water fractionation factor +2.6\%o [Melling and Moore, 1995] to the observed surface water value. The dissolved silicate concentration (Si) used for the four end-members follows directly from [Bauch et al., 1995]. The value used for PIW (40 $\mu$mol kg$^{-1}$) approximates maxima from profiles in the Bering Sea [Cooper et al., 1997], elsewhere in the Arctic [Jones and Anderson, 1986] as well as maxima from the data set described here. The value used for ATW (6 $\mu$mol kg$^{-1}$) is similar to the value used for Atlantic Water in the eastern Arctic Ocean [Dittmar et al., 2001] (5.6 $\mu$mol kg$^{-1}$) and is approximately equal to nutrient minima within the Atlantic layer of this data set. The silicate concentration used for the MW fraction (10 $\mu$mol kg$^{-1}$) follows directly that used by Bauch et al. [1995] and is supported by data from shelf waters off the Mackenzie Delta [Emmerton et al., 2008]. Although higher concentrations have been observed in freshwater runoff measured in Arctic rivers [Le Fouset et al., 2013], runoff is only a part of the MW fraction which also includes direct precipitation with negligible nutrient concentration, reducing the effective nutrient concentration in the MW fraction. In addition, runoff waters are extensively modified before reaching the shelf [Emmerton et al., 2008; Le Fouset et al., 2013], reducing the effective silicate concentration in the MW fraction of open ocean. Finally, the silicate concentration used for SIM was assumed to be 1 $\mu$mol kg$^{-1}$ [Macdonald and Carmack, 1991b; Bauch et al., 1995], which may be a representative mean value although more variable concentrations have been measured directly from sea-ice [Fransson et al., 2013].

A complete analysis of the sensitivity of model estimates of $f_{MW}$, $f_{SIM}$, $f_{ATW}$, $f_{PIW}$ to analytical and model uncertainty is provided in supporting information. Errors in calculated water source fractions introduced by analytical errors in measurements are small compared to errors introduced by inaccuracies in estimates of end-members. Model estimates are most sensitive to errors in the assumptions regarding end-members with similar compositions—i.e., the two seawater end-members (PIW and ATW). However, both errors from analytical uncertainty and model assumptions are relatively small compared to two potential inaccuracies introduced by semiconservative behavior of nutrient concentrations and the assumption that nutrient concentrations of end-members are static. First, biological removal of nutrients in surface waters is likely to produce too low estimates of PIW, despite the clear source of surface seawater from the Bering and Chukchi Seas through much of the western Arctic [Aagaard et al., 1981; Killworth and Smith, 1984]. Second, calculated PIW fractions are likely too high in the deep Canada and Makarov Basin due to elevated silicate concentration produced by biological remineralization [Jones and Anderson, 1986; Jones et al., 2008]. In order to correct for nonconservative behaviors such as uptake and remineralization of silicate, we follow an approach similar to Yamamoto-Kawai et al. [2008] and Newton et al. [2013], which explicitly modifies the method of calculating the fractions of PIW and ATW in low-salinity surface waters and high-salinity deep waters. In our modified $\text{SiO}_4$ maxima method, we stipulate in the model calculations that waters with $S < 33$ cannot be derived from the Atlantic deep water inflow to the Arctic. Hence, for waters above the halocline with $S < 33$, we reassign any calculated ATW fraction (resulting from too low silicate concentrations) to PIW. Similarly, we assume that despite relatively elevated silicate concentrations, saline waters of the deep Canada and Makarov Basin below the HL cannot be derived from the Pacific Inlet, except in part through brine rejected from sea-ice near the surface (although the origins of waters in the deep basins are somewhat enigmatic) [Jones et al., 1995; Timmermans and Garrett, 2006]. Therefore, for deep waters with $S > 34.75$, we reassign any calculated PIW fraction (resulting from excess silicate concentrations) to ATW. Hence, our calculations assume that for waters with salinities $33 < S < 34.75$, the four-component mixing model works as a near conservative tracer, and adequately distinguishes the two saline end-members (PIW and ATW) in addition to the freshwater end-members (SIM and MW). Nonetheless, outside of these limits, nonconservative behavior of nutrients leads to failure to distinguish ATW from PIW. Accordingly, for these waters, we revert to a two-component mass balance tracer ($S$ and $\delta^{18}$O) with a single seawater end-member, assigning this seawater to either a Pacific ($S < 33$) or Atlantic ($S > 34.75$) source.

### 2.4. Statistics

Pearson statistical correlations were used in Minitab 17 to evaluate linear correlation between variables $\text{PO}_4$, $\text{O}_2$, $\text{NO}_3 + \text{NO}_2$, $\text{Si}$, $\Omega_{at}$, $\text{pCO}_2$, $T$, $S$, $f_{MW}$, $f_{SIM}$, $f_{ATW}$ and $f_{PIW}$.
3. Results

3.1. Atmosphere and Ocean Circulation

Atmospheric and oceanic circulation in the Arctic (Figure 2a) oscillates between two modes of the Arctic Oscillation (AO). The +AO is characterized by a weak sea level pressure (SLP) gradient from the Western Arctic toward the Icelandic Low, while the −AO is characterized by a strong pressure gradient [Hurrell et al., 2003]. The Beaufort Gyre (BG, anticyclonic circulation of Canada Basin surface waters) and its associated Ekman-convergence driven accumulation of freshwater, are forced by this atmospheric circulation associated with high pressure over the Beaufort Sea [Proshutinsky et al., 2002]. Strong −AO conditions lead to a deflection of the Transpolar Drift (TD) toward Siberia, and a strengthened BG (TD−BG in Figure 2) [Mysak, 2001; Steele et al., 2004]. Meanwhile the +AO mode leads to a relatively strong TD and weakened BG (TD+BG in Figure 2). Because the annual AO pattern can be characterized by subannual variability, we analyzed the SLP and surface wind velocity during the summer months of 2005 and 2010–2013 (Figure 2b). A significant −AO event is evident during 2010, culminating in an overall trend since 1995 toward increased SLP over the Beaufort Sea and increased wind-driven spin-up of the Beaufort Gyre [Giles et al., 2012; Krishfield et al., 2014]. Thus, during the summer of the AOS05 cruise (2005) and the HLY1002 cruise (2010), the Arctic High SLP and Beaufort Gyre were particularly strong, although the SLP gradient toward the Icelandic Low was highly divergent between these two summers (high in 2005 low in 2010). From summer 2011, the −AO began to diminish, along with the associated wind field conditions driving freshwater accumulation in

Figure 2. Sea level pressure (SLP) and surface wind velocity averaged during summer months (June, July, August, September). (a) Long-term mean for 1948–2013, (b) individual years of data discussed here: 2005 (year of AOS05 cruise), and 2010–2012 (years of HLY1002, HLY1102, HLY1202 cruises). Data are from US National Center for Environmental Prediction (NCEP) and published by the Earth System Research Lab (http://www.esrl.noaa.gov).
end-member in the Canada Basin is largely derived from the Pacific Ocean via the Pacific Inlet (PIW, from direct precipitation and terrestrial runoff) and sea-ice meltwater (SIM; \cite{Swift et al., 1998}). The PML (depth 3.2.1. Polar Mixed Layer

aragonite saturation state (PML, HL, BHW).

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and lower parts of the HL as HL-u and HL-l. Following a brief review of the relevant water masses below, we discuss aragonite undersaturation in each water mass, and then use conservative tracers to quantify the fraction derived from four distinct sources (MW, SIM, PIW, and ATW) contributing to stratification of the water column aragonite saturation state (PML, HL, BHW).

3.2.1. Polar Mixed Layer

The PML (depth < ~90 m) includes both fresh and saline end-members, resulting in relatively low salinity (S < 33). The freshwater end-members involved in this mixing derive from both meteoric water (MW; S = 0 from direct precipitation and terrestrial runoff) and sea-ice meltwater (SIM; S = 4). Meanwhile, the saline end-member in the Canada Basin is largely derived from the Pacific Ocean via the Pacific Inlet (PIW, S = ~33) as well as from warmer Atlantic-derived waters (S = ~35) below the HL, with the latter being especially significant in the Makarov Basin \cite{Rudels et al., 1996, 2004}. During summer, PIW is modified on the shallow Bering, Chukchi and East Siberian Seas where highly coupled processes of pelagic productivity and sedimentation of organic matter producing water undersaturated with respect to CO$_2$ and relatively low in nutrients \cite{Cota et al., 1996; Cooper et al., 1997; Jones et al., 1998; Hill and Cota, 2005; Grebmeier et al., 2006}. The pCO$_2$ of the PML is often further reduced by cooling of the northward flowing water and typically has not had enough time to equilibrate with the atmosphere before being covered by sea-ice \cite{Anderson and Kaltin, 2001; Bates et al., 2006; Fransson et al., 2009}, resulting in relatively higher Q$_a$ values in the Bering Strait summer waters.

3.2.2. Halocline (Upper and Lower)

Below the PML, waters of the HL (from 90 to 220 m) are characterized by increasing S with depth. These HL waters are introduced to the Canada Basin from the shallow shelves of the Pacific Inlet (Bering, Chukchi, and East Siberian Seas) at a halocline centered around a salinity of ~33. The upper HL waters have elevated

the BG. In fact, SLP was relatively low in the Beaufort Sea during summer 2012, potentially resulting in spin-down of the BG in subsequent years \cite{Krishfield et al., 2014}.

3.2. Water Mass Definitions

We use variations in conservative water mass properties (potential temperature, \theta, S) to define the unique stratified water masses following similar work in the Arctic \cite{Aagaard et al., 1981, 1985; Aagaard and Carmack, 1989; Rudels et al., 1991, 1996; Swift et al., 1998}. Based on \theta–S profile data, we distinguish three water masses for the purpose of this study: The Polar Mixed Layer (PML), the Halocline Layer (HL), and the Below Halocline Waters (BHW; Figure 3). Although some studies distinguish an upper and lower halocline layer based differences in nutrient concentrations \cite{Jones and Anderson, 1986}, for the purposes of our analysis we consider a simple composite HL, with recognition that a gradient of properties often occurs within the HL. Where a distinction is needed, we refer to upper

and lower parts of the HL as HL-u and HL-l. Following a brief review of the relevant water masses below, we discuss aragonite undersaturation in each water mass, and then use conservative tracers to quantify the fraction derived from four distinct sources (MW, SIM, PIW, and ATW) contributing to stratification of the water column aragonite saturation state (PML, HL, BHW).

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3.2.2. Halocline (Upper and Lower)

Below the PML, waters of the HL (from 90 to 220 m) are characterized by increasing S with depth. These HL waters are introduced to the Canada Basin from the shallow shelves of the Pacific Inlet (Bering, Chukchi, and East Siberian Seas) at a halocline centered around a salinity of ~33. The upper HL waters have elevated


\textbf{Figure 3.} Potential temperature (\theta) versus salinity (S) plots from conductivity-temperature-depth (CTD) casts through the Canada and Makarov Basins from 3 years cruises (HLY1002, HLY1102, and HLY1202). PML-u = upper Polar Mixed Layer (0–30 m); PML-l = lower Polar Mixed Layer (30–90 m); HL = Halocline Layer (HL-u = upper part, HL-l = lower part); BHW = Below Halocline Waters. Data are separated into four regions with distinct patterns: (a) Southern Canada Basin shows a broad HL-u generally overlapping with PML; (b) Beaufort Sea shows a sharp HL-u and distinct PML; (c) Northern Canada Basin shows weakly developed HL-u and PML; (d) Makarov Basin showing a halocline lacking warm HL-u waters that are pronounced in more southern regions.
nutrient concentrations from remineralization of organic matter at the surface of the shelf sediments [Cooper et al., 1997, 1999, 2005; Grebmeier et al., 2006]. This source can be traced into and through the Arctic Ocean, and further into the Atlantic [Jones and Anderson, 1986; Jones et al., 2003; Carmack and McLaughlin, 2011; Anderson et al., 2013]. At the base the HL, a second halocline (referred to as the Lower Halocline Layer, LHL) may be present, with lower nutrient concentrations suggesting a distinct water mass source. Irrespective, below the HL is the transition to predominantly Atlantic derived water, classically defined by having $T > 0^\circC$ [Nansen, 1902].

3.2.3. Below Halocline Waters
Below the HL, waters are denser than the Pacific source ($S > 33$), and must therefore be of Atlantic origin (ATW), although the deep Canada and Makarov Basin waters likely have a small contribution of waters derived from the surrounding shelves [Jones et al., 1995; Timmermans and Garrett, 2006]. For the purposes of our study, we attribute all waters below the HL to have Atlantic origin, but recognizing that the poorly ventilated waters below $\sim 1500$ m are often distinguished as Canada Basin Deep Waters [Macdonald and Carmack, 1991a].

3.3. Water Masses and Undersaturated Zones: Aragonite Saturation State and Carbon Parameter Variations
Seawater aragonite saturation state ($Q_a$) varied significantly between the water masses outlined above (Figure 4a), with as many as three aragonite undersaturation zones ($Q_a < 1$) observed through the water profile. First, within the PML, a thin surficial lens (0–30 m depth) of aragonite undersaturated waters is found through much of the southern Canada Basin, where it covered greater than 20% of the surface in 2010–2011 [Robbins et al., 2013a]. In the lower PML ($\sim 30$–$90$ m), waters are generally supersaturated with respect to aragonite. Within the HL (from $\sim 90$ to $220$ m depth) a second aragonite undersaturation zone occurs throughout most of the Canada Basin and extends northward to the Alpha Ridge. North of the Alpha Ridge in the Makarov Basin, the physical and chemical features of the HL are still evident, but $Q_a > 1$ and thus, the entire PML and HL water column above 2000 m depth was still aragonite supersaturated in this basin when sampled in 2011. The third, and deepest, aragonite undersaturation zone in the BHW is at a relatively consistent depth of $\sim 2000$ m where comparatively warm waters predominantly derive from the Atlantic Ocean and are aragonite undersaturated to the bottom at $\sim 3800$ m depth. The lateral distribution of the PML, HL, and BHW aragonite undersaturation zones are distinct, with water columns showing between one and three aragonite undersaturation zones. In the southern Canada Basin ($\sim 75^\circN$), there are three aragonite undersaturation zones (the BHW, HL, and PML; Figure 4g), in the northern Canada Basin ($\sim 82^\circN$) there are two (the BHW and HL; Figure 4f), while there is a single aragonite saturation horizon in the Makarov Basin ($\sim 87.5^\circN$) with aragonite undersaturated waters in the BHW aragonite undersaturation zone (Figure 4e; the BHW aragonite undersaturation zone is only shown in section a of Figure 4 as the other sections focuses on the top 500 m to better illustrate the variability of these waters).

Both TA and TCO$_2$ concentrations largely are a function of salinity and consequently show a high degree of correlation when plotted versus each other (Figure 5). As salinity is low at the surface and increases with depth, the samples within the water masses of the Canada and Makarov Basins (PML, HL, and BHW) plot within distinct regions; each region contains samples that are undersaturated with respect to aragonite. Shallow samples ($< 50$ m) from the PML are relatively dilute in both parameters ($TA < 2200$ mmol kg$^{-1}_{SW}$; $TCO_2 < 2100$ mmol kg$^{-1}_{SW}$) and show strong correlation between TCO$_2$ and TA with a relatively consistent slope. Samples from the HL generally depart from the TCO$_2$–TA slope of the PML, and show relatively high TCO$_2$ values; i.e., these samples represent disproportionately high pCO$_2$, and are a typically undersaturated with respect to aragonite. Samples of the BHW cluster tightly with relatively high and linearly correlated TCO$_2$ and TA concentrations.

3.4. Water Source and Carbonate Chemical Composition
In a previous study, Robbins et al. [2013a] used $S$ and $\delta^{18}O$ data from HLY1012 and HLY1102 to estimate the proportions of sea-ice meltwater and meteoric freshwater in surface waters of the Canada and Makarov Basins. Here we use nutrient concentrations to deconvolve the seawater sources, and add data from HLY1202 to the surface water data set of [Robbins et al., 2013a]. Figure 6 shows sections of the calculated water sources ($f_{PIW}$, $f_{SMW}$, $f_{AWW}$) along a generalized south-north section from the Beaufort Sea to the North Pole using this four-component mass balance model. Figure 7a shows the distribution of calculated
freshwater sources ($f_{\text{MW}}$, $f_{\text{PIW}}$, and $f_{\text{SIM}}$) during 2010–2012 on TA-TCO$_2$ plots (as in Figure 5). The 2010–2012 data are compared to similarly analyzed station data from the AOS05 (2005) cruise [Anderson et al., 2010] shown in Figure 7b. Combining the water source data with aragonite saturation data shows that the three
undersaturated zones described in section 3.3 parse out into distinct water sources in each of the three water masses (PML, HL, and BHW). First, large fractions of SIM and MW are associated with low TA-TCO$_2$ values in the upper PML. Here $\Omega_a$ shows very strong correlations ($p < 0.001$) with $f_{\text{SIM}}$, $f_{\text{MW}}$, $S$, and $p$CO$_2$ ($R$ values of $-0.774$, $-0.531$, $0.778$, and $-0.666$, respectively). Second, large fractions of PIW are associated with relatively low slopes of the TA-TCO$_2$ relationship within the HL (i.e., relatively larger TCO$_2$ values near the high end of the TA-TCO$_2$ range). This is supported by highly significant ($p < 0.001$) correlation of $\Omega_a$ with pCO$_2$, Si, PO$_4$, NO$_2$ + NO$_3$ fATW, and fPIW (R = $-0.935$, $-0.911$, $-0.747$, $-0.914$, $0.914$, and $-0.921$, respectively) in the HL (Table 1). And third, at depths below ~2000 m, relatively high TA and TCO$_2$ values characterize these poorly ventilated aragonite-undersaturated waters of the lower BHW. Here $\Omega_a$ shows a tight negative correlation with depth and temperature ($R = -0.964$ and $R = -0.971$, respectively).

Figure 8 illustrates these relationships of $\Omega_a$ to the fraction of PIW and fresh water sources with $\Omega_a$ f$_{\text{PPW}}$ scatter plots of depth, $f_{\text{SIM}}$ and $f_{\text{MW}}$. Throughout the region sampled, waters of the PML and HL (90–220 m) show distinct correlations of $\Omega_a$ and $f_{\text{PPW}}$. A number of samples from the upper PML (<~50 m) show aragonite undersaturation ($\Omega_a < 1$). Figure 8c shows that high values of $f_{\text{SIM}}$ are largely associated with these aragonite-undersaturated shallow samples in the PML. Figure 8b shows that high values of $f_{\text{MW}}$ are largely found in both the PML and HL, where $\Omega_a$ frequently reaches undersaturated values. Similarly, high values of $f_{\text{MW}}$ are found in the PML-u, and associated with low $\Omega_a$ values. In the BHW, $\Omega_a$ varies from ~1.5 to values lower than 1, independent of SIM, MW, and PIW (Table 1 and Figure 9).

4. Discussion

4.1. Water Sources

Figure 6c shows that SIM is largely confined to the upper ~30 m of the PML, with little mixing of this freshwater into the HL or deeper horizons. Meteoric water from terrestrial runoff and direct precipitation (MW) is also abundant in the upper ~50 m of the PML, and is distributed throughout the Canada and Makarov Basins (Figure 6b). Pacific Inlet-derived water (PIW, intermediate $S$, and $\delta^{18}O$) is abundant throughout the HL (up to 220 m depth) of the southern Canada Basin and northward to the Alpha Ridge. Slightly negative values of $f_{\text{SIM}}$ occur within the HL. Negative values are meaningful in the calculations using the water source mixing model described above, because they indicate sea-ice production and brine rejection as opposed to melting. The fact that negative $f_{\text{SIM}}$ value are represented in the HL (Figure 6c) suggests that these waters are produced by sea-ice freezing in shallow open water conditions on the shelves after which the relatively dense brines mix into the bottom waters where they inherit the high-nutrient signature and
pCO₂ from remineralization of organic matter [Jones and Anderson, 1986; Jones et al., 2008; Fransson et al., 2013].

### 4.2. Multibathyal Aragonite Undersaturation Zones and Controlling Processes

One approach to distinguish the mechanisms behind changes in aragonite saturation has been to examine trends in TA-TCO₂ scatter plots [cf. Cai et al., 2010; Bates et al., 2013]. Figures 5a and 5b show TA-TCO₂ scatter plots of data from this study, while Figure 5c presents model predicted trends for water source mixing, and CO₂ addition. For example, addition of CO₂ by remineralization of organic carbon or invasion of CO₂ from the atmosphere increases the TCO₂:TA ratio, with pronounced effect of lowering Ωₐ values (gray arrows in Figure 5c). Primary productivity or brine pumping of CO₂ from surface waters to the subsurface would have the opposite effect of decreasing TCO₂:TA ratios, and increasing Ωₐ values.

Comparison of the data in Figure 5b suggests that mechanisms that increase the TCO₂:TA ratio (CO₂ addition, remineralization) appropriately account for low Ωₐ values from waters of the HL in which PIW is modified by coupled processes of primary productivity and respiration on shallow shelves of the Bering, Chukchi, and East Siberian Seas, thus importing additional remineralized CO₂ to the HL. Comparison of the data in Figure 5b to the model predictions in Figure 5c also illustrates closed-system dilution of ATW with three
relatively fresh water sources (PIW, SIM, and MW). Both mixing of SIM and MW produce strong dilution effects on $\text{TA}$ and $\text{T}_\text{CO}_2$ concentrations (illustrated by thin black arrows in Figure 5c). However, this closed-system mixing calculation does not account for $\text{CO}_2$ invasion at the surface and is not sufficient to account

Figure 7. Scatter plots of calculated water source superimposed on TA versus $\text{T}_\text{CO}_2$ (see data in Figure 5 for similar scatter plots of depth and $\Omega_2$). A. Oden AOSOS cruise data (2005) through the Canada and Makarov Basins; B. Healy cruises (HLY1002, HLY1102, and HLY1202) through the Canada and Makarov Basins reported here. Dashed outlines indicate regions of 2010–2012 samples from the BHW-u to BHW-l trend, the HL-u to HL-l trend, and the PML.
for changes in $\Omega_a$ in the open system of surface waters (Figure 5c; the effects of freshening and CO$_2$ invasion are presented in model by Bates et al. [2013]). Thick gray lines in Figure 5c illustrate conditions for the summer PML in which freshwater dilution occurs at the surface, combined with the net invasion of atmospheric CO$_2$ that would typify summer ice-free conditions, even if surface waters do not reach full equilibrium as found by Fransson et al. [2009]. In this scenario, the “net” combined effect of dilution and air-sea invasion reduce the buffering capacity and pH of waters diluted with MW or SIM (as observed by the lower Revelle factor of the Makarov Basin relative to that of the southern Canada Basin, ~14 versus ~18, respectively). Figure 5c shows that under such conditions, surface water of the PML is likely to reach aragonite undersaturation with as little as 30% freshwater addition in open-system CO$_2$ invasion from the atmosphere (gray line in Figure 5c). Thus the net effect is more substantial than that modeled assuming closed system assumptions (black arrows shown in Figure 5c, and in Bates et al. [2013]). Thus, the combined effects of sea-ice retreat, freshening of surface water and invasion of atmospheric CO$_2$, provides a mechanism that accounts for both the reduced $\Omega_a$ values and associated TA-TCO$_2$ trends observed throughout the PML.

The three mechanisms responsible for reduced $\Omega_a$ values throughout the Canada and Makarov Basins can also be understood in terms of $\Omega_a$-f$_{SAV}$ scatter plots (Figure 8). The first mechanism, dilution with freshwater from SIM and MW, is illustrated by surface waters of the upper PML (PML-u field in Figure 8). When exposed to atmospheric CO$_2$, these waters show decreased $\Omega_a$ values corresponding to high f$_{SAV}$ and/or f$_{SAW}$ values. The second mechanism is illustrated along the trend of the halocline (HL-I to HL-u fields in Figure 8) and within the lower PML (PML-I field in Figure 8). Along the trend of the halocline, the calculated f$_{SAW}$ values show strong negative correlation to $\Omega_a$ (HL-I to HL-u) with a return to high $\Omega_a$ values in the lower PML (notably in the Makarov Basin, PML-I). Here, addition of PIW to the HL has a relatively small dilution effect on TA and TCO$_2$ concentrations, although TCO$_2$/TA is increased due to remineralized organic carbon derived from the productive shelf seas. The third mechanism occurs only in Atlantic derived waters (BH-W fields in Figure 8). Here at increasing depth within the BH-W, $\Omega_a$ values are subject to T-driven and P-driven effects independent of $f_{SAV}$, $f_{SAW}$, and $f_{SAU}$.

The aragonite undersaturation zones of the PML, HL, and BH-W each show correlation to tracers of dominant processes: sea-ice melt, terrestrial runoff, remineralization of organic carbon, and physical consequences of temperature and pressure in deep waters. Each is reviewed in terms of these dominant processes below.

**PML**. The role of dilution with MW and SIM in driving aragonite undersaturation is evident in the uppermost PML where surface waters were largely aragonite undersaturated throughout the southern Canada Basin in 2010–2012 (south of ~80°N, Figures 4 and 6). Although meteoric freshwater is relatively abundant and homogeneous throughout the PML (~10–20% to depths of ~200 m), the fraction of sea-ice melt is more variable, reaching ~5–15% in this uppermost ~8 m in areas of reduced sea-ice coverage [Robbins et al., 2013a] (Figure 6). The role of dilution with SIM and invasion of atmospheric CO$_2$ in the upper PML are manifest statistically with high negative correlation of $\Omega_a$ values with $f_{SAW}$ and pCO$_2$ ($R = -0.774$ and ~0.666, respectively, Table 1). Previous work focused on high-resolution surface water data from HLY1002 and HLY1102 similarly showed sea-ice melt was most significantly correlated to aragonite saturation state ($R = -0.866$), with secondary and regional correlation with other indicators of biological processes (chlorophyll-a and

### Table 1. Pearson Statistics (R and p Values) for Correlation of $\Omega_a$ With Depth, Si, PO$_4$, NO$_2$, O$_2$, f$_{SAV}$, f$_{SAW}$, f$_{SAU}$, T, S, and pCO$_2$

<table>
<thead>
<tr>
<th>Water Mass</th>
<th>$z$</th>
<th>Si</th>
<th>PO$_4$</th>
<th>NO$_2$ + NO$_x$</th>
<th>O$_2$</th>
<th>f$_{SAV}$</th>
<th>f$_{SAW}$</th>
<th>f$_{SAU}$</th>
<th>T</th>
<th>S</th>
<th>pCO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PML-u $\Omega_a$</td>
<td>0.277</td>
<td>-0.16</td>
<td>0.344</td>
<td>0.277</td>
<td>0.092</td>
<td>-0.531</td>
<td>-0.774</td>
<td>0.450</td>
<td>-0.264</td>
<td>0.778</td>
<td>-0.666</td>
</tr>
<tr>
<td>PML-I $\Omega_a$</td>
<td>0.390</td>
<td>-0.775</td>
<td>-0.625</td>
<td>0.083</td>
<td>0.620</td>
<td>0.544</td>
<td>-0.143</td>
<td>0.748</td>
<td>-0.774</td>
<td>0.131</td>
<td>-0.302</td>
</tr>
<tr>
<td>HL $\Omega_a$</td>
<td>0.040</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>BHW-u $\Omega_a$</td>
<td>0.112</td>
<td>-0.111</td>
<td>-0.746</td>
<td>0.348</td>
<td>-0.188</td>
<td>0.183</td>
<td>0.914</td>
<td>-0.921</td>
<td>0.238</td>
<td>-0.109</td>
<td>-0.112</td>
</tr>
<tr>
<td>BHW-I $\Omega_a$</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.018</td>
<td>0.316</td>
<td>0.187</td>
<td>-0.085</td>
<td>-0.971</td>
<td>-0.222</td>
<td>-0.048</td>
<td>-0.012</td>
</tr>
<tr>
<td>NS</td>
<td>0.012</td>
<td>0.012</td>
<td>0.012</td>
<td>0.012</td>
<td>0.012</td>
<td>0.012</td>
<td>0.012</td>
<td>0.012</td>
<td>0.012</td>
<td>0.012</td>
<td>0.012</td>
</tr>
</tbody>
</table>

*PML-u: Polar Mixed Layer-upper (0–30 m); PML-I: Polar Mixed Layer-lower (30–90 m); HL: Halocline Layer, including HL-u and HL-l (90–220 m); BHW-u: Below Halocline Waters-upper (220–2000 m); BHL-l: Below Halocline Waters-lower (2000–4000 m).

**NS** = not significant.
Figure 8. Scatter plots of depth and calculated water source (MW, SIM) superimposed on $\Omega_a$ versus $f_{PIW}$ from 2010 to 2012 cruises in the Canada and Makarov Basins (HLY1002, HLY1102, and HLY1202). PML-u = upper Polar Mixed Layer (0–30 m); PML-l = lower Polar Mixed Layer (30–90 m); HL = Halocline Layer (HL-u = upper part, HL-l = lower part); BHW = Below Halocline Waters. (a) Depth, (b) $f_{MW}$, (c) $f_{SIM}$. Dashed outlines indicate fields of 2010–2012 samples from the BHW-u to BHW-l trend, the HL-u to HL-l trend, and the upper and lower PML (PML-u and PML-l).
bacterial productivity, $-0.493$ and $0.504$, respectively; Table 4 of Robbins et al. [2013a]). The role of biological processes are manifest in the lower PML with significant correlation with nutrients and $O_2$ (Table 1, $R = -0.775, -0.625, -0.830$ for Si, PO$_4$ and NO$_2$ + NO$_3$, respectively, and $R = 0.620$ for O$_2$).

**HL.** The role of remineralized organic carbon in driving aragonite undersaturation is most evident in the HL, with clearly distinct processes from those represented in the upper PML. In the HL, a continuous lens of aragonite undersaturation extends from the shelf northward to the Alpha Ridge (Figure 5). This role is further supported by a strong negative correlation of $\Omega_a$ values to $f_{CO_2}$ ($R = -0.921$) and to pCO$_2$ ($R = -0.935$) as well as strong negative correlations to nutrient concentrations such as Si ($R = -0.911$) and NO$_2$ + NO$_3$ ($R = -0.746$) and PO$_4$ ($R = -0.747$; Table 1).

**BHW.** The third aragonite undersaturation zone is evident below $\sim 2000$ m, in deep, largely Atlantic-derived water of the lower BHW. This horizon has drivers similar to those of the ACD found in all deep ocean basins, with significant correlation of $\Omega_a$ with depth (i.e., pressure; $R = -0.964$) and $T$ ($R = -0.971$; Table 1).

### 4.3. Decadal Changes in Mechanisms Driving Aragonite Undersaturation

In addition to documenting the distribution of the three western Arctic aragonite undersaturation zones, it is crucial to understand the decadal-scale stability of processes driving changes in each zone. While decadal shoaling of the aragonite saturation horizon in the Pacific Ocean has been documented [Feely et al., 2012], the complex nature of the multibathyal aragonite saturation state in the Arctic Ocean requires an understanding of the underlying mechanisms driving changes in the Arctic in order to better inform predictive regional models [Popova et al., 2014]. Comparing the 2010–2012 data to similar data from the same region in 2005 (Figures 7 and 8) shows no change in the properties of the observed aragonite saturation horizon within the deep BHW, as well as minimal change in distribution of the undersaturated high pCO$_2$ waters of the HL. However, the increased proportion of SiM in the upper PML is clearly evident in this comparison, where freshwater dilution and contact with increased atmospheric CO$_2$ in ice-free summer conditions have a profound effect on lowering of $\Omega_a$ values (Figure 7a). Due to relatively slow turnover of CO$_2$ in the deep BHW aragonite saturation horizon (>100 yr) [Jones, 2001; Tanhua et al., 2009] and stability of the variables involved ($P$, $T$), this horizon is likely stable at decadal time scales. However, the undersaturated conditions of the HL and PML are driven by processes such as the shelf-basin CO$_2$ and biological pump [Bates et al., 2009; Chierici and Fransson, 2009; Anderson et al., 2010; Chierici et al., 2011], air-sea CO$_2$ equilibration [Anderson and Kaltin, 2001; Bates et al., 2006], sea-ice meltwater [Chierici and Fransson, 2009; Yamamoto-Kawai et al., 2009a; Robbins et al., 2013a], and terrestrial runoff [Chierici and Fransson, 2009; Mathis et al., 2011], all of which are relatively responsive to anthropogenic and climatic perturbations at short time scales [Bates and Mathis, 2009].

In order to assess recent changes in the PML and HL aragonite undersaturation, Figure 9 compares south-north transects of distribution of aragonite undersaturated waters between the Oden (2005) and Healy (2010–2012) data sets. The primary change over this interval is the expansion of the PML aragonite undersaturation zone in the Canada Basin (depths < 50 m) from isolated areas freshwater-influenced shelves near the outlet of the Mackenzie River in 2005 [Chierici and Fransson, 2009], to vast areas of the open Canada Basin in 2010–2012. This expansion of aragonite undersaturated waters is one of the most profound recent changes in the western Arctic Ocean [Yamamoto-Kawai et al., 2009b; Cai et al., 2010; Chierici et al., 2011].
extending to a large area of the basin south of ∼80°N in 2010–2012 [Robbins et al., 2013a] (Figure 9). The northern extent of aragonite-undersaturated waters of the HL was similar in 2010–2012 to the situation in 2005, although there is historical evidence in variability of the spatial extent of the HL waters [Moore et al., 1983; Steele and Boyd, 1998; Bourgain and Gassard, 2011]. However, the upper, and in part (north of 76°N) the lower bounding surfaces of the HL aragonite undersaturation zone in the central Canada Basin were deeper in 2010–2011 as compared to 2005, suggesting a depression of this zone under a thicker PML (Figure 9). This may be due to increased stratification brought about by greater Ekman convergence driven by the Beaufort Gyre [Proshutinsky et al., 2002], as discussed in section 3.1. This observation is also supported by the south–north gradient in the depth of the HL aragonite undersaturation zone from >200 m depth near 75°N to <200 m depth beyond ∼80°N (Figure 9). This gradient coincides with the gradient in the depth of the PIW lens of the HL (Figure 6). The large-scale stability is likely controlled by the position of the barrier imposed by the Alpha Ridge, while variation may be driven by changes in the long-term wind field (Figure 2). Although SLP and anticyclonic wind velocities in the western Arctic were high in 2005 (Figure 2), the ensuing accumulation of freshwater in the BG didn’t reach its maximum until 2010, under relatively consistent −AO conditions [Giles et al., 2012]. The several year lag between atmospheric circulation patterns (oscillation of AO index, SLP & wind velocity) and the freshwater accumulation and depression of the HL aragonite undersaturation zone may be attributed to the several years it takes for sea-ice and PIW surface waters to be transported from source regions, and to accumulate in the BG under strengthened −AO conditions [Anderson et al., 2004; Steele et al., 2004].

4.4. Implications for Model Projections
Recent global climate system models have projected large-scale aragonite undersaturation in the surface waters of the Arctic Ocean during the 21st century, largely driven by the effects of increased freshening and CO2 uptake due to sea-ice melting [Steinacher et al., 2009]. Deal et al. [2013] cite projections of reduced $\Omega_a$ values by about 0.8–1.0 in much of the Pacific-Arctic Region (Bering and Chukchi Seas and adjacent Arctic seas), while CanESM1.5 [Arora et al., 2011] and Steinacher et al. [2009] have independently projected surface pH to decrease to ∼7.9 by midcentury and below 7.7 by end of the century. However, these most recent global models project less pronounced effects in the pelagic regions of the Canada Basin, while over $3.7 \times 10^7$ km$^2$ of surface waters have already become undersaturated in this region during the summer sea-ice minima of 2010–2011 [Robbins et al., 2013a]. Model comparisons with recent data provide the opportunity to refine our understanding of the processes controlling $\Omega_a$ and the spatial variability of the relevant processes.

Ocean acidification models focused specifically on the Arctic Ocean highlight the importance of spatial and temporal variability of fundamental controlling processes $\Omega_a$ [Popova et al., 2014]. Given such variability of multiple independent and coupled processes and the interplay between drivers of aragonite undersaturation throughout the water column, we will require further mechanistic understanding of the respective roles of relevant processes in order to make accurate projections of future trends. Such spatial variability is evident in patchiness of the marine biological pump and its effect on aragonite saturation, both in terms of seasonal and vertical variation of halocline source waters on the shallow shelves of the Bering, Chukchi and East Siberian Seas [Bates et al., 2006, 2009; Pipko et al., 2011; Cross et al., 2012]. The low pH and high TCO$_2$:TA ratio attributed to remineralization on the shallow shelf waters is observed in the HL undersaturated layer throughout the Pacific sector of the Arctic Ocean. This natural phenomenon is driven by nutrient and CO2 flux from the PIW and its vulnerability to additional acidification has been widely recognized [AMAP, 2013]. In areas of increased primary productivity and remineralization as a result of climate change, it is likely that aragonite undersaturation of the HL will intensify.

Aragonite-undersaturated waters of the HL are spatially distinct from those of the PML, having a saturated lens ($\Omega_a \sim 1.4$) separating the two zones (30–90 m depth). Shoaling of the aragonite undersaturation zones will likely continue throughout this century as seen in other basins [Feely and Chen, 1982; Feely et al., 2002; Sabine et al., 2002; Sarma et al., 2002]. In addition, it has been suggested that enhanced upwelling of HL waters may result from declines in summer sea-ice extent in coastal regions of the Beaufort Sea [Mathis et al., 2012; Thomson and Rogers, 2014], although increased sea-ice meltwater and enhanced stratification may hamper such mixing. These processes may ultimately merge the two upper zones into a single ∼250 m thick aragonite undersaturation zone.
In addition to spatial and temporal variability of biological processes in shelf waters, aragonite saturation in surface waters of the PML is largely driven by warming and enhanced melting sea-ice, and particularly of multiyear ice, combined with uptake of atmospheric CO$_2$. Because waters of the PML mix relatively rapidly, the PML aragonite undersaturation zone is relatively ephemeral, and is subject to rapid changes in the Arctic ocean-atmosphere system occurring on time scales faster than residence time of surface waters. For example, if the pack of multiyear sea-ice completely melts during summer, as is projected by at least the end of this century ([Overland and Wang, 2013]), meltwater dilution of the PML will continue to reduce buffering capacity. Moreover, if summer sea-ice cover continues to retreat, enhanced CO$_2$ invasion from the atmosphere is likely to continue at the surface, lowering pH ([Yamamoto-Kawai et al., 2009b; Robbins et al., 2013a]). However, the SIM fraction of the PML aragonite undersaturation zone will ultimately reach a maximum and begin to diminish due to outflow to the Atlantic Ocean (i.e., over decadal time scales of cyclicity inherent to the Beaufort Gyre) ([Proshutinsky et al., 2009]). Some projections of PML aragonite saturation conditions emphasize the additional role of enhanced biological fixation on the shelves, increasing total CO$_2$ uptake ([Bates and Mathis, 2009]). However, recent evidence suggests biological fixation throughout much of the pelagic Canada Basin has remained relatively constant after the sea-ice retreat of the last decade, and it is thereby projected that CO$_2$ uptake will diminish once air-sea equilibrium is reached ([Cai et al., 2010]). The data from the undersaturated surface waters of the PML during 2010–2012 presented in this study are more consistent with the latter interpretation, emphasizing the present roles of freshening by sea-ice melt combined with air-sea invasion rather than enhanced biological productivity over most of the Canada Basin.

In summary, this study complements previous work elucidating the roles of relevant processes ([Bates et al., 2009; Chierici and Fransson, 2009; Yamamoto-Kawai et al., 2009b; Cai et al., 2010; Chierici et al., 2011; Robbins et al., 2013a]) by differentiating the relative significance of key processes at work in the various stratified water bodies of the western Arctic Ocean. The three undersaturated zones described here represent the dominant influence of three separate processes, each having very different effective time scales.


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