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Assessing Ocean Acidification Variability in the Pacific-Arctic Region

as Part of the Russian-American Long-term Census of the Arctic

By Nicholas R. Bates

Launch of rosette from Russian research vessel *Professor Khromov* during a 2009 RUSALCA expedition. *Photo credit: Aleksey Ostrovskiy*

ABSTRACT. The Russian-American Long-term Census of the Arctic (RUSALCA) project provides a rare opportunity to study the Russian sector of the Pacific Arctic Region (PAR), which includes the Chukchi and East Siberian Seas. RUSALCA data from 2009 and 2012 allow fuller understanding of changes in ocean chemistry across this the region and, in particular, provide perspectives on the ocean carbon cycle, air-sea CO_2 gas exchange, and ocean acidification variability. Summertime surface waters of the western Chukchi Sea and East Siberian Sea mostly exhibited low pCO_2 (<100 to 400 µatm) and high pH (8.0 to 8.4) conditions during sea ice retreat. As earlier studies of the adjacent eastern Chukchi Sea show, this area of the PAR had a strong potential for ocean uptake of atmospheric CO_2, with saturation states for calcium carbonate ($CaCO_3$) minerals such as calcite and aragonite ($\Omega_{calcite}$ and $\Omega_{aragonite}$, respectively) having values generally greater than two, thereby facilitating $CaCO_3$ production. In contrast, fresher surface waters flowing into the Chukchi Sea from the East Siberian Sea and bottom waters on the PAR shelves exhibited high pCO_2 and low pH, $\Omega_{calcite}$, and $\Omega_{aragonite}$ conditions. Low Ω surface waters near the Russian coast and nearly 70% of waters next to the seafloor were corrosive to $CaCO_3$ minerals such as aragonite, with this change seemingly occurring at a more rapid rate than typical global open-ocean changes in ocean chemistry. The exposure of subsurface benthic communities and nearshore ecosystems near the Russian coast to potentially corrosive water is likely exacerbated by the ocean uptake of anthropogenic CO_2 and gradual ocean acidification. The RUSALCA project also highlights the complexities and uncertainties in the physical and biogeochemical drivers of the ocean carbon cycle and ocean chemistry in this region of the Arctic.

INTRODUCTION

During the last several decades, Arctic climate conditions have changed rapidly, resulting in complex regional and global environmental impacts. Major changes in the physical domain of the region, such as decreased summer sea ice cover and increasing air temperature, are well documented (e.g., Perovich et al., 2007; Stroeve et al., 2007, 2014; Markus et al., 2009; Perovich and Richter-Menge, 2009; Wang and Overland, 2009; Overland and Wang, 2013; Screen et al., 2013; Simmonds and Goverkar, 2014). However, large uncertainties remain in observed and anticipated responses in the biology and biogeochemistry of the Arctic Ocean (e.g., Grebmeier et al., 2010; Wassmann et al., 2011). For example, increased ice-free area and warmer temperatures may have caused changes in rates of primary production in the deep Arctic (e.g., Arrigo et al., 2008, 2014; Arrigo and van Dijken, 2011) and associated shelves (e.g., Ardyna et al., 2014), timing of the annual phytoplankton bloom (e.g., Kahru et al., 2010), composition of phytoplankton (e.g., Li et al., 2009), and functioning of the biological pump (e.g., Nishino et al., 2011), as well as enhanced export of carbon to the deep ocean (Lalande et al., 2009, 2014) and ultimately ocean carbon dioxide (CO_2) uptake resulting in ocean acidification (OA) in the region (e.g., Bates and Mathis, 2009; Steinacher et al., 2009).

The issues and uncertainties about the marine carbon cycle and ocean acidification in the Arctic Ocean are complex and unresolved. This paper focuses on a descriptive assessment of seawater CO_2-carbonate chemistry and OA variability in the Pacific Arctic Region (PAR), an area that includes the shallow shelves of the Chukchi and East Siberian Seas and the periphery of the deep Canada Basin (Figure 1). Compared to many other open-ocean and coastal environments, relatively few studies of seawater CO_2-carbonate chemistry and marine carbon cycle dynamics and assessments of air-sea CO_2 exchange rates and ocean acidification impacts have been conducted in the shelf seas and deep basin of the Arctic Ocean. This is due in part to the harsh polar climate and resulting difficulty in providing logistical support that have limited most research opportunities to icebreaker surveys conducted on the Arctic shelves during the summertime sea ice retreat. In recent years, increased international efforts have focused on the region in response to rapid changes in the ocean environment (e.g., sea ice loss, warming).

As a contribution to the efforts to understand environmental change in the Arctic, seawater CO_2-carbonate chemistry observations were collected as part of the Russian-American Long-term Census of the Arctic (RUSALCA) project. The primary goal of RUSALCA is to collect long-term, multidisciplinary, ocean-climate-relevant physical, biological, and biogeochemical data in the PAR, especially in the Russian sector of the Chukchi and East Siberian Seas. As such, RUSALCA focuses on improving scientific understanding of the region's ocean dynamics and feedbacks and identifying changes in key pelagic and benthic marine ecosystems. This paper describes RUSALCA's contribution to a fuller understanding of the physical and biogeochemical variability and drivers of the ocean carbon cycle and ocean chemistry in this region of the Arctic.

THE ARCTIC OCEAN CARBON CYCLE AND OCEAN ACIDIFICATION

The polar and subpolar regions of both hemispheres have large impacts on the exchange of CO_2 between atmosphere and ocean, and particularly on the global ocean uptake of anthropogenic CO_2. Low temperatures and the low buffering capacity of these waters facilitate ocean uptake of CO_2 from the atmosphere (Bates, 2006). In the high latitudes, ocean CO_2 sinks represent a significant contribution to the global ocean sink of ~1.4 Pg C yr^{-1} (Pg C = 10^{15} g C); perhaps 5–10% of global ocean CO_2 uptake occurs in the Arctic Ocean (e.g., Bates and Mathis, 2009; Takahashi et al., 2009; Schuster et al., 2013; Manizza et al., 2013; MacGilchrist et al., 2014). Quantifying and understanding the dynamics of ocean-atmosphere exchanges of CO_2 in permanently and seasonally ice-covered regions has been

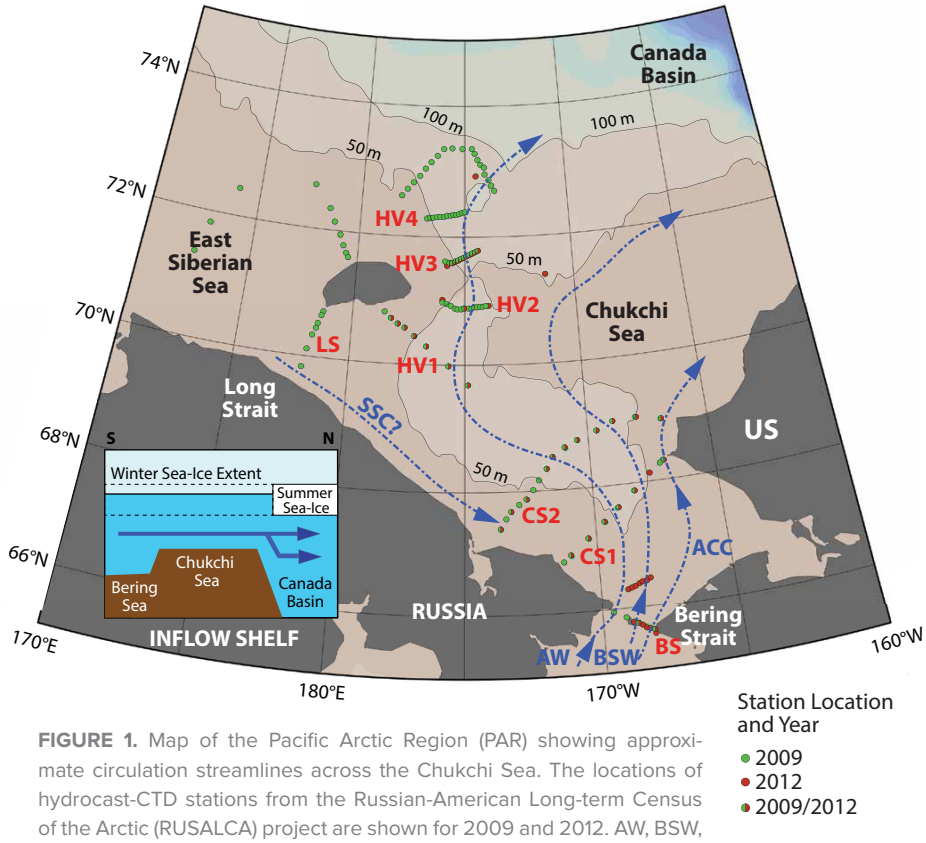

FIGURE 1. Map of the Pacific Arctic Region (PAR) showing approximate circulation streamlines across the Chukchi Sea. The locations of hydrocast-CTD stations from the Russian-American Long-term Census of the Arctic (RUSALCA) project are shown for 2009 and 2012. AW, BSW, and ACC refer to Anadyr Water, Bering Shelf Water, and Alaskan Coastal Current water, respectively. The hydrographic sections in the southern Chukchi Sea are denoted as BS (Bering Strait), CS1, and CS2. Sections across Herald Valley are denoted as HV1, HV2, HV3, and HV4. A section across Long Strait is denoted by LS. Anadyr Water flows northward from Bering Strait and out through Herald Valley. The Siberian Sea Current (SSC) is an intermittent summertime current that brings surface waters from the East Siberian Sea into the Chukchi Sea (Weingartner et al., 1999). INSET: Schematic of the "inflow" shelf (sensu Carmack and Wassmann, 2006) for the Chukchi Sea.

difficult to assess owing to lack of data (e.g., Bates and Mathis, 2009). It has also been difficult to predict future exchange dynamics due to rapid sea ice loss, particularly in the Arctic Ocean.

The release of anthropogenic CO_2 to the atmosphere and its uptake by the global ocean has significant implications for ocean chemistry and marine organisms and ecosystems. Over the last several decades, substantial increases in ocean CO_2 content have been observed (e.g., Takahashi et al., 2002, 2009; Bates et al., 2012, 2014a; Rhein et al., 2013). While the global ocean remains generally mildly alkaline at present, the uptake of anthropogenic CO_2 from the atmosphere into the ocean changes the chemical balance and equilibria of the seawater CO_2-carbonate system, resulting in gradual acidification of seawater (Caldeira and Wickett, 2003, 2005; Orr et al., 2005; Doney et al., 2009; Feely et al., 2009).

The Arctic Ocean, and in particular the western Arctic (Chukchi Sea, East Siberian Sea, and Canada Basin; Figure 1), shows clear evidence of warming (e.g., Stroeve et al., 2014), enhanced sea ice melt (Frey et al., 2014), and changes in ocean ecology (e.g., Arrigo et al., 2014). The Arctic Ocean carbon cycle and CO_2 exchanges among the components of the ocean-ice-atmosphere system are highly dynamic, especially in the PAR (Bates et al., 2006; Bates and Mathis, 2009; Schuster et al., 2013; Evans et al., 2015), and they are influenced by rapid change in the Arctic and complex feedbacks between remaining sea ice (Bates et al., 2014b), the water column, and the benthos (e.g., Mathis et al., 2014; Cai et al., 2014). Vulnerabilities of the Arctic marine carbon cycle relate to such factors as sea ice loss, warming, and other physical changes, biological and ecosystem changes, and changes in regional hydrology and freshwater input to the Arctic Ocean. Ocean acidification impacts have already been observed in the western Arctic Ocean (e.g., Chukchi Sea, Bates et al., 2009, 2013; East Siberian Sea, Semiletov et al., 2004, 2007; Anderson et al., 2009, 2011; I.P. Semiletov, University of Alaska, *pers. comm.*, March 2015) and Bering Sea (Bates et al., 2011; Mathis et al., 2011a,b; Cross et al., 2013, 2014).

THE GEOGRAPHIC SETTING OF THE PACIFIC ARCTIC REGION

The physical and biogeochemical properties of various PAR marine settings are highly influenced by seasonal ice cover and retreat, complex physical circulation and mixing of seawater, freshwater and sea ice melt source waters, and marine biogeochemical variability. The "inflow" shelf (sensu Carmack and Wassmann, 2006) of the broad and shallow (<70 m) Chukchi Sea (Figure 1 inset) is highly influenced by the Pacific inflow through Bering Strait of three nutrient-rich water masses (e.g., Anadyr Water [AW], Bering Shelf Water [BSW], and Alaskan Coastal Current water [ACC]) and outflow to the deep Canada Basin through submarine canyons such as Herald Valley and Barrow Canyon. Such northward supply of Pacific water supports high rates of open water and below-ice water column phytoplankton blooms during summertime sea ice retreat (e.g., Hill and Cota, 2005; Arrigo et al., 2012; Codispoti et al., 2013) and a dense seafloor benthic community (Grebmeier et al., 2008, 2010; Mathis et al., 2014). The less productive "interior" shelf of the East Siberian Sea has biogeochemical dynamics that are highly influenced by Siberian river freshwater inputs and shelf processes (e.g., Semiletov et al., 2004, 2007; Anderson et al., 2009, 2011), with

outflow of surface waters to the Chukchi Sea by way of the Siberian Sea Current (Weingartner et al., 1999). Adjacent to these shallow shelves are the oligotrophic mixed layer/euphotic zone waters of the deep Canada Basin (CB).

The physical and biogeochemical dynamics, feedbacks, and changes occurring in the PAR are complex and include, for example: (a) warming and sea ice changes; (b) Pacific and Atlantic water influences on shelf and deep basin waters; (c) Arctic river and hydrological cycle changes; and (d) shelf sediment and benthos coupling to water column processes and shelf-basin exchanges. This complexity reflects the underlying nature of different marine settings of the region.

SAMPLING AND METHODS

Water Column Sampling

The hydrography and biogeochemistry of the PAR was sampled in 2009 and 2012 during two late summer RUSALCA cruises aboard the Russian research vessel *Professor Khromov* that took place during the periods of maximum sea ice retreat. One hundred and fourteen hydrocast-CTD stations were occupied in 2009 (September 4–29), while 62 hydrocast-CTD stations were occupied in 2012 (August 30 to September 15). Water-column sampling was mainly conducted on the shallow shelves (< 100 m depth) of the Chukchi and East Siberia Seas. Core hydrography samples (e.g., salinity, temperature, inorganic nutrients) were collected as well as dissolved inorganic carbon (DIC) and total alkalinity (TA) samples (collected in ~300 ml Pyrex bottles that were poisoned with 100 µl Hg_2Cl, sealed, and stored in the dark before analysis).

RUSALCA samples were collected during several repeat sections across the region, shown in Figure 1. In the southern Chukchi Sea, these include sections at Bering Strait (BS) and from the Russian coast to the US coast of Alaska (CS1 and CS2). Further north in the western Chukchi Sea, five sections across the submarine canyon Herald Valley were occupied (HV1, HV2, HV3, HV4, and HV5). In 2009, a section was made across Long Strait (LS) between Wrangel Island and Siberia, and select hydrocast-CTD stations were occupied in the East Siberian Sea.

Seawater CO_2-Carbonate Chemistry Considerations

The terms and equations governing seawater CO_2-carbonate chemistry are as follows. DIC is the sum of bicarbonate ($[HCO_3^-]$), carbonate ($[CO_3^{2-}]$), and CO_2 in natural waters (Dickson et al., 2007) and thus defined as

$$DIC = [HCO_3^-] + [CO_3^{2-}] + [CO_2^*] \quad (1)$$

where $[CO_2^*]$ is equivalent to $[CO_2]_{aq}$ + $[H_2CO_3]$. Total alkalinity (TA) can be defined as

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^-] + \ldots \quad (2)$$

where $[B(OH)_4^-]$ is total borate concentration in seawater and "…" reflects other minor contributors to alkalinity. Fuller descriptions of TA and CO_2-carbonate chemistry may be found elsewhere (e.g., Stumm and Morgan, 1981; Butler, 1991; Dickson et al., 2007; Zeebe and Wolf-Gladrow, 2001). All components of the seawater CO_2-carbonate system, including $[HCO_3^-]$, $[CO_3^{2-}]$, and saturation states for $CaCO_3$ minerals such as calcite ($\Omega_{calcite}$) and aragonite ($\Omega_{aragonite}$), can be computed from two observed parameters such as DIC and TA. Values of <1 for $\Omega_{calcite}$ and $\Omega_{aragonite}$ indicate that seawater is potentially corrosive to $CaCO_3$ and promoting dissolution for carbonate minerals such as calcite and aragonite.

Relative to the issue of ocean acidification in the PAR, it is useful to state that physico-biogeochemical processes such as ocean release of CO_2 by air-sea gas exchange or marine ecosystem production act to decrease DIC and pCO_2 and increase pH, $\Omega_{calcite}$, and $\Omega_{aragonite}$ (e.g., Zeebe and Wolf-Gladrow, 2001). In contrast, ocean uptake of CO_2 and marine ecosystem respiration act oppositely (increasing DIC and pCO_2 and decreasing pH, $\Omega_{calcite}$, and $\Omega_{aragonite}$), while TA remains unchanged (except for minor changes associated with nitrate uptake or release; Brewer and Goldman, 1976; Dickson et al., 2007). Calcification/$CaCO_3$ precipitation decreases TA, while $CaCO_3$ dissolution increases TA.

Sampling and Chemical Analyses

Samples from the two RUSALCA cruises were analyzed at the Bermuda Institute of Ocean Sciences (BIOS). DIC was determined using a highly precise (0.03% CV; ~0.6 µmol kg^{-1}) coulometric-based analyzer (VINDTA 3C from the Marianda Co., Germany; Bates et al., 2012) used for high-quality open-ocean seawater CO_2-carbonate system studies (e.g., Bates, 2007; Bates et al., 2005, 2014a). TA was determined by a high-precision (<0.05% CV; ~1 µmol kg^{-1}) potentiometric technique using a Marianda VINDTA 2S. Multiple replicate samples were analyzed and analytical imprecision was less than 0.1% (~2 µmol kg^{-1}). DIC and TA analyses were routinely calibrated using seawater Certified Reference Material (CRM) from A.G. Dickson, Scripps Institute of Oceanography, and the accuracy of samples compared to the CRMs was less than 0.1% (~2 µmol kg^{-1}).

Data Computations and Visualization

Seawater CO_2-carbonate system parameters such as pCO_2 (µatm), pH (total scale), $\Omega_{aragonite}$, and $\Omega_{calcite}$ were computed from salinity (S), temperature (T, °C), TA, and DIC data with the Robbins et al. (2010) CO2calc software program. The carbonic acid dissociation constants pK_1 and pK_2 (Mehrbach et al., 1973, as refit by Dickson and Millero, 1987) were chosen to account for cold seawater temperatures (–1.6°C to ~6°C) observed in the PAR. We estimated the calculation error range for pCO_2, pH, and $\Omega_{aragonite}$ and $\Omega_{calcite}$ to be ±5 µatm, ±0.004, and ±0.007 (assuming analytical imprecision for DIC at ±0.5 µmol kg^{-1} and for TA at 2 µmol kg^{-1}), respectively. Ocean Data View 4 (Schlitzer, 2011) software was used to visualize the data.

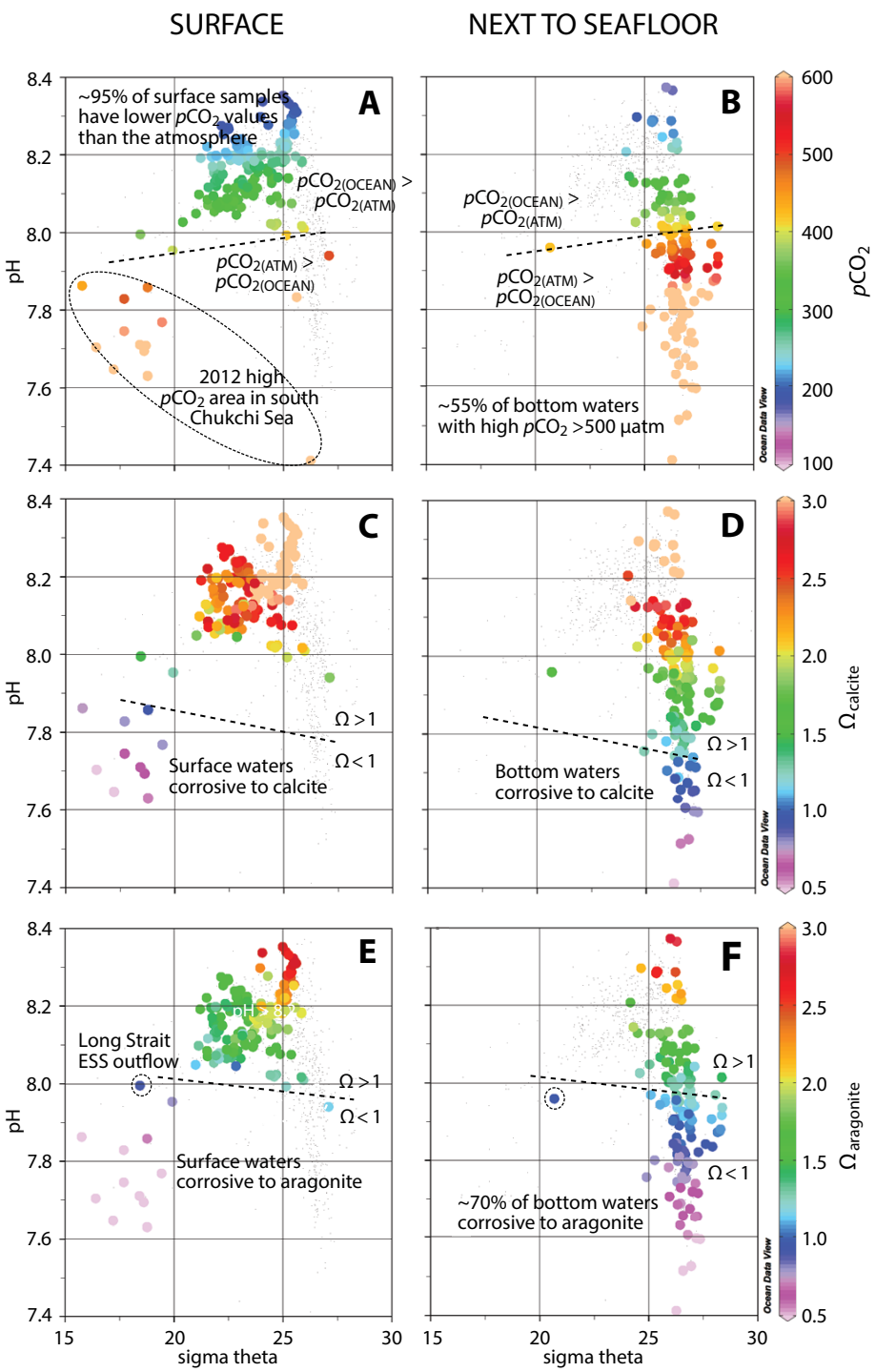

FIGURE 2. Seawater CO_2-carbonate chemistry variables plotted against sigma theta (density) in surface and next-to-seafloor waters of the PAR. In these plots, sigma theta is used to differentiate the fresher, sea ice melt influenced water masses from water masses that are predominantly seawater. (A) pH and pCO_2 (µatm) against sigma theta in surface waters. (B) pH and pCO_2 (µatm) against sigma theta in next-to-seafloor waters. The dashed line in the two upper plots differentiates waters with pCO_2 lower or higher than the atmosphere. (C) pH and $\Omega_{calcite}$ against sigma theta in surface waters. (D) pH and $\Omega_{calcite}$ against sigma theta in next-to-seafloor waters. (E) pH and $\Omega_{aragonite}$ against sigma theta in surface waters. (F) pH and $\Omega_{aragonite}$ against sigma theta in next-to-seafloor waters. The dashed lines in panels C, D, E, and F differentiate waters that have $\Omega_{aragonite}$ values higher than one or lower than one (i.e., corrosive to $CaCO_3$).

RESULTS AND DISCUSSION

This paper focuses on the water-column distribution and variability of ocean acidification indicators such as pCO_2, pH, and saturation states for $CaCO_3$ minerals such as calcite ($\Omega_{calcite}$) and aragonite ($\Omega_{aragonite}$), rather than that of DIC and TA (see Bates et al., 2013, for water-column distributions from the RUSALCA project). This treatment focuses first on surface waters, then bottom waters, and finally on the issue of year-to-year variability that may confound simple assessment of threshold conditions of existing and future vulnerability of the region to ocean acidification. Its geographic focus is on the rarely studied area of the western Chukchi Sea and East Siberian Sea within the Economic Exclusion Zone (EEZ) of Russia. Other studies of seawater CO_2-carbonate chemistry have focused on the eastern Chukchi Sea in the US sector of its EEZ (e.g., Pipko et al., 2002; Murata and Takizawa, 2003; Bates et al., 2009, 2013).

Surface Seawater CO_2-Carbonate Chemistry in the PAR

Although not shown here, in 2009 and 2012, surface water temperatures varied from ~ –1.6°C to ~ 7°C and salinities from 26 to 33.5. In Figure 2, sigma theta is plotted against pCO_2, pH, $\Omega_{calcite}$, and $\Omega_{aragonite}$ to illustrate the large variability in physical and seawater CO_2-carbonate chemistry properties. Sigma theta, as a measure of density, is helpful in showing the wide range of water masses present in the PAR. The surface waters have a large range in sigma theta from ~ 15 to 26, illustrating mixing between Pacific Ocean-derived seawater and sea ice melt (Figure 2A). The deeper, next-to-seafloor waters exhibit a much-reduced range in density (~ 24–26; cold and saline water; Figure 2B), likely reflecting the presence of winter water observed in the PAR in 2009, 2012, and other years (e.g., Lowry et al., 2015).

Surface CO_2 Variability. Surface pCO_2 was highly variable (~ 100 to 600 µatm) against a large range of sigma theta

(~15 to 26; Figure 2A). Approximately 95% of hydrocast-CTD stations have surface pCO_2 values lower than atmospheric pCO_2 values of ~395 to 400 µatm. The western Chukchi Sea east of Wrangel Island above Herald Valley exhibited much lower pCO_2 (<220 µatm) than the atmosphere, and this area was likely to be a strong summertime sink for atmospheric CO_2 (Figure 3A) while other areas were moderate ocean sinks for CO_2. Such low pCO_2 values in the western Chukchi Sea were not unexpected because similar observations have been reported previously for the eastern Chukchi Sea (e.g., Pipko et al., 2002; Murata and Takizawa, 2003; Bates, 2006; Bates et al., 2013). In these areas, high rates of summertime shelf pelagic primary production (e.g., Hill and Cota, 2005; Arrigo et al., 2012, 2014; Codispoti et al., 2013) and net community production (NCP) during sea ice retreat result in low DIC and pCO_2 conditions (e.g., Bates et al., 2005, 2014b; Mathis et al., 2009).

Surface pH and Ω Variability. In the areas of low pCO_2, the majority of surface pH values ranged from 8.0 to 8.4 (Figures 2A and 3C) while $\Omega_{calcite}$ and $\Omega_{aragonite}$ were mostly in the range of >1.5 to 3.5 (Figures 2C,E and 3E). As expected from seawater CO_2-carbonate equilibria (e.g., Zeebe and Wolf-Gladrow, 2001), the highest pH (>8.3) and Ω values (>2.5) were associated with the lowest pCO_2 (<250 µatm). Similar summertime conditions have been observed elsewhere on the Chukchi (Bates et al., 2009, 2013) and Bering Sea shelves (Mathis et al., 2011a,b; Cross et al., 2013), where mixed-layer/euphotic zone primary production seasonally increases pH and Ω values through changes in seawater CO_2-carbonate chemistry (Bates et al., 2009). The implication for the RUSALCA project from studies in adjacent areas is that surface pH, $\Omega_{calcite}$, and $\Omega_{aragonite}$ in the western Chukchi Sea were enhanced in summertime due to high rates of NCP.

Highly Modified East Siberian Sea Influenced Surface Waters. The exception to the above findings was the occurrence of a feature with high pCO_2 (~>500 µatm; Figures 2A and 3A) and low pH (7.6 to 7.9; Figures 2A and 3C), $\Omega_{calcite}$ (<0.6 to <1.1; Figure 2C), and $\Omega_{aragonite}$ (<0.5 to <1.0; Figures 2E and 3E) in the fresh, low sigma theta surface water found in the southern Chukchi Sea in 2012. The implication of these observations is that there may have been highly undersaturated waters corrosive to $CaCO_3$ during 2012 along the Russian coastline. It is unclear how frequent this feature is year to year, but it likely represents the outflow of East Siberian Sea surface waters through Long Strait into the Chukchi Sea by way of the Siberian Sea Current (Weingartner et al., 1999). While the cause of this feature is inferential at best because there was little supporting evidence regarding East Siberian Sea seawater CO_2-carbonate chemistry, in 2009, surface water sampled at the station nearest to the shore in Long Strait also had high pCO_2 and very low pH, $\Omega_{calcite}$, and $\Omega_{aragonite}$. Earlier and subsequent observations in the East Siberian Sea also show very high summertime pCO_2 and low pH, $\Omega_{calcite}$, and $\Omega_{aragonite}$ conditions across its shelf and in nearshore environments such as Tiksi Bay (e.g., Semiletov et al., 2004, 2007; Anderson et al., 2009, 2011) and thus were very similar to RUSALCA

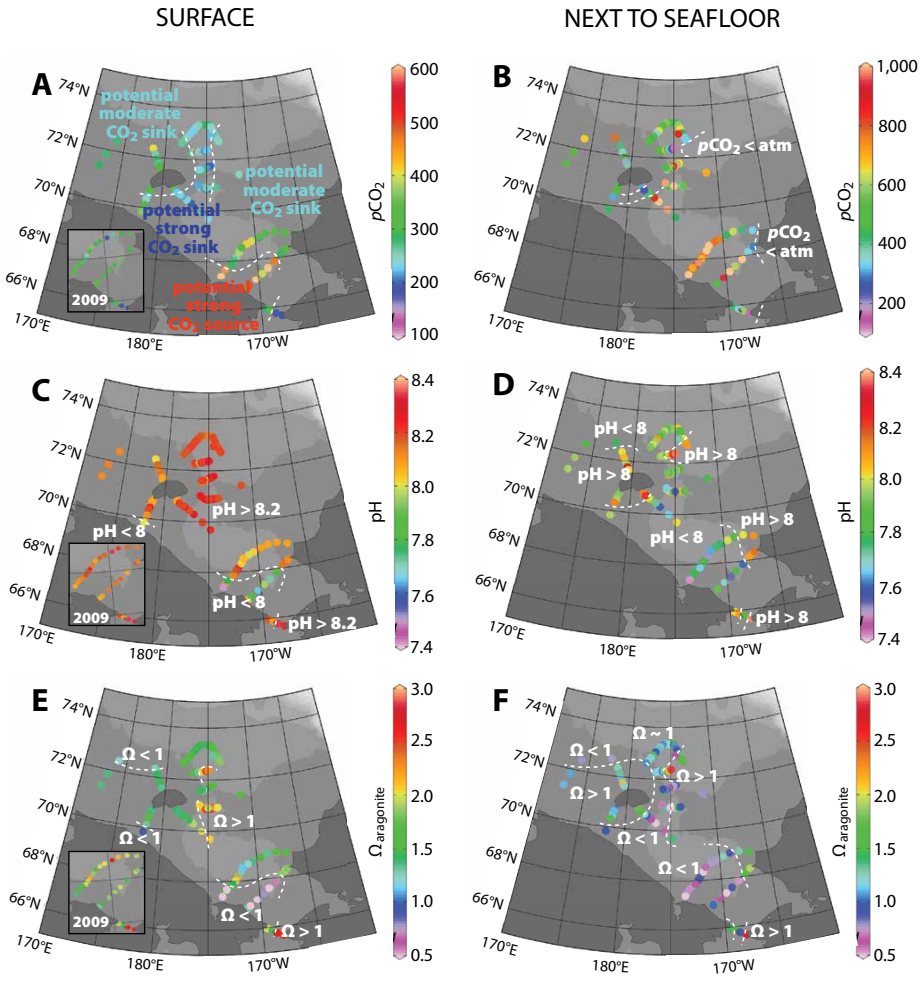

FIGURE 3. Surface seawater CO_2-carbonate chemistry maps of the PAR. (A) Surface water pCO_2 (µatm). Inset shows 2009 data. (B) Next-to-seafloor water pCO_2 (µatm). (C) Surface water pH. (D) Next-to-seafloor pH. (E) Surface water $\Omega_{aragonite}$. (F) Next-to-surface water $\Omega_{aragonite}$. The white dashed lines in the panels aim to highlight different surface and next-to-seafloor water chemistry (i.e., pCO_2, pH, and $\Omega_{aragonite}$) across the PAR. For example, the low pH East Siberian Sea waters present in the Southern Chukchi Sea can be observed in panels C and D.

observations in 2012.

The persistent calcite and aragonite undersaturation observed across much of the East Siberian Sea may be due to recent increased freshwater inputs to the Siberian shelves (I.P. Semiletov, University of Alaska, *pers. comm.*, March 2015). In the absence of oxygen isotope and other data, it is difficult to confirm this supposition because the inorganic carbon end member values for Siberian rivers, sea ice melt, and East Siberian Sea seawater are not well constrained. The physical and biological drivers for such changes in the East Siberian Sea and Siberian Sea Current remain uncertain, but this biogeochemical change appears to be exerting its influence on the Chukchi Sea through exchanges across Long Strait. As discussed later, the $\Omega_{calcite}$ and $\Omega_{aragonite}$ conditions of the three water masses inflowing through Bering Strait (e.g., AW, BSW, and ACC) have values higher than 1.5 (Figure 4). This result suggests that Pacific Ocean waters entering the Arctic through Bering Strait were not likely to have contributed to the low Ω feature in the southern Chukchi Sea.

Next-to-Seafloor Seawater CO_2-Carbonate Chemistry in the PAR

The CO_2-carbonate chemistry of nearest-to-seafloor or bottom waters was markedly different from surface waters in the PAR. The cold and saline bottom waters on the shelves of the Chukchi and East Siberian Seas had higher sigma theta values (25–27; Figure 2B), and at least 55% of next-to-seafloor water had pCO_2 values greater than 500 µatm and pH less than 8.0 (Figure 2B). In the southern Chukchi Sea and along the bottom of Herald Valley, pCO_2 reached as high as 1,000 µatm and pH was as low as 7.4 (Figure 3B,D). With respect to calcite and aragonite, at least 15% and 75% of bottom waters were undersaturated (Ω < 1), respectively (Figures 2D,F and 3F), and thus were corrosive to $CaCO_3$ minerals. Even in other areas of the eastern Chukchi Sea and East Siberian Sea, $\Omega_{aragonite}$ values did not exceed a value of 2. In previous studies, the majority of bottom waters in the Chukchi Sea were undersaturated with respect to $CaCO_3$ (i.e., Bates et al., 2009, 2013) during summertime. This finding appears broadly characteristic of the PAR and Bering Sea shelves (e.g., Mathis et al., 2011a,b; Cross et al., 2013) and, as others have suggested, results from respiration of organic matter in subsurface waters and benthic communities (Bates et al., 2009; Mathis et al., 2014).

The implications of undersaturated (Ω < 1) bottom water conditions for the benthic community and in particular shelly fauna is difficult to assess without long-term time series of seawater chemistry and benthic surveys. However, anthropogenic CO_2 uptake by the oceans (and in particular the North Pacific Ocean source waters for the PAR) will have reduced $\Omega_{aragonite}$ values by 0.5 and 0.3 for calcite and aragonite, respectively (Bates

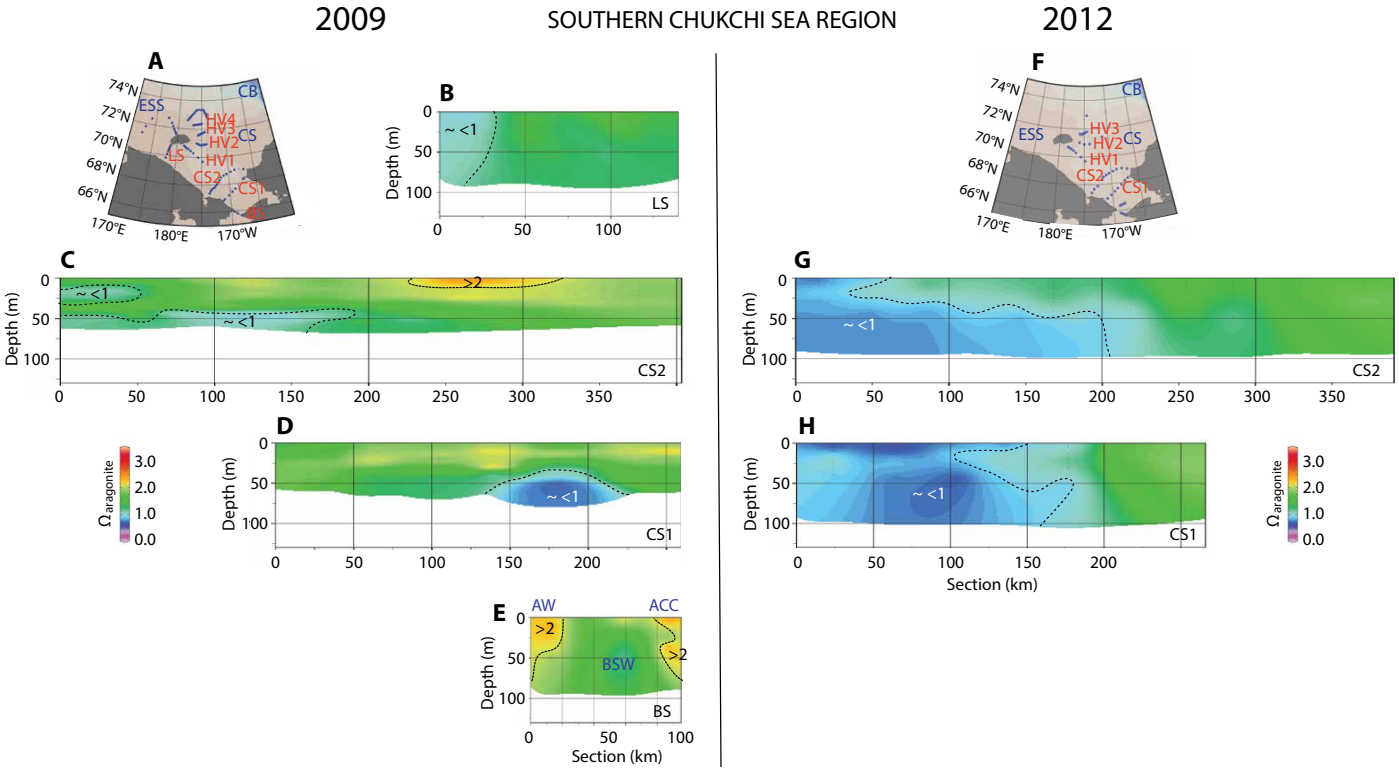

FIGURE 4. Repeat sections of $\Omega_{aragonite}$ in the southern Chukchi Sea at LS, BS, CS1, and CS2 in 2009 and 2012. In the left-hand part of the figure, panel A shows the sampling map for the 2009 RUSALCA cruise, while panels B, C, D, and E show sections for LS, BS, CS1, and CS2, respectively. In the right-hand part of the figure, panel F shows the sampling map for the 2012 RUSALCA cruise, while panels G and H show sections for CS1 and CS2, respectively. All of these sections have identical horizontal distance scales, and the sections are arranged from south to north.

et al., 2013), which is perhaps two to three times the range of changes observed in the open ocean (Bates et al., 2014a). Thus, the emplacement of summertime undersaturated bottom waters may be a feature of the Anthropocene (sensu Lewis and Maslin, 2015), or at least an expanded feature with an ocean acidification imprint. But, it should be remembered that complex interaction of changes in circulation, freshwater inputs, sea ice melt, seasonal timing, and biological community and net ecosystem metabolism processes will also have imparted their influence on seawater CO_2-carbonate chemistry in the PAR.

Spatial and Between Year Variability of Seawater CO_2-Carbonate Chemistry in the PAR

The RUSALCA project was fortunate to be able to repeat five sections of hydrography and seawater CO_2-carbonate chemistry in 2009 and 2012 (CS1, CS2, HV1, HV2, and HV3; Figures 4 and 5). These sections provide evidence of year-to-year variability in the PAR as hinted above. The high pCO_2 and low pH, $\Omega_{calcite}$, and $\Omega_{aragonite}$ conditions in subsurface waters were observed in Bering Shelf Water at Bering Strait and northward across the Chukchi Sea (Figure 4; only $\Omega_{aragonite}$ shown) to the outflow along Herald Valley (Figure 5; only $\Omega_{aragonite}$ shown), following the northward current movement. The low subsurface feature was more strongly pronounced in 2012 than in 2009, with a difference in Ω of ~0.5. The variability in the low pCO_2 and high pH, $\Omega_{calcite}$, and $\Omega_{aragonite}$ conditions in surface waters across the PAR was also pronounced. For example, surface $\Omega_{aragonite}$ values were higher by at least 0.8 to 1.2 in 2009 compared to 2012 (Figure 5). In other oceans, the changes in $\Omega_{aragonite}$, for example, range from a decrease of 0.02 to 0.1 per decade based on sustained time series of ocean chemistry (Bates et al., 2014a).

The large year-to-year variability in the PAR likely reflects complex physical

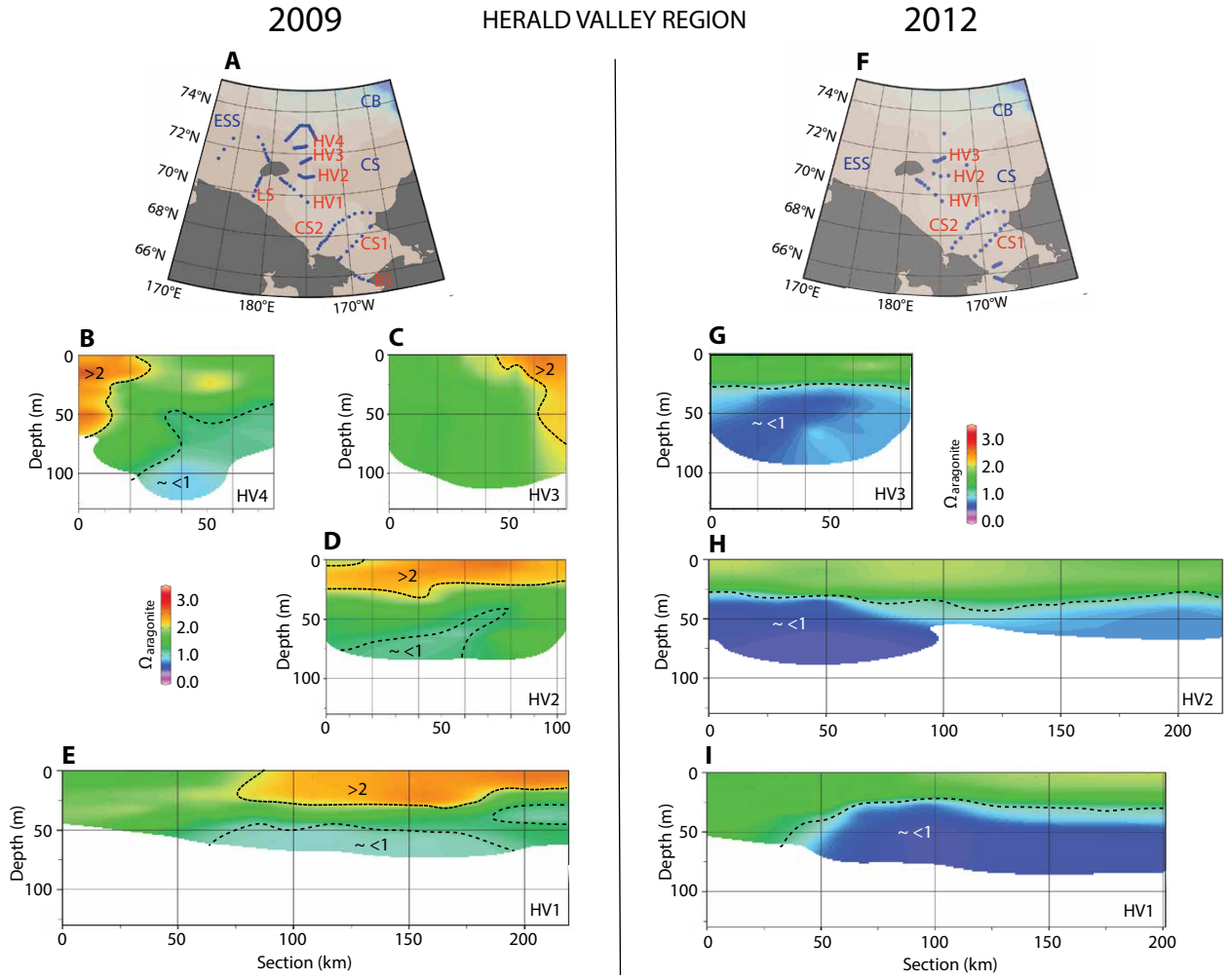

FIGURE 5. Repeat sections of $\Omega_{aragonite}$ across Herald Valley in the Northeast Chukchi Sea at HV1, HV2, HV3, and HV4 in 2009 and 2012. In the left-hand part of the figure, panel A shows the sampling map for the 2009 RUSALCA cruise, while panels B, C, D, and E, show sections for HV4, HV3, HV2, and HV1, respectively. In the right-hand part of the figure, panel F shows the sampling map for the 2012 RUSALCA cruise, while panels G, H, and I show sections for HV3, HV2, and HV1, respectively. All of these sections have identical horizontal distance scales, and the sections are arranged from south to north.

and biogeochemical processes, including changes in seasonal timing; circulation; freshwater inputs; sea ice melt, retreat, and freeze-up; and net ecosystem metabolism (including primary production and respiration as well as $CaCO_3$ precipitation and dissolution). Such year-to-year variability will also make it difficult to predict future thresholds (e.g., $\Omega < 1$) for when the shelves of the PAR transition into a condition where $CaCO_3$ dissolution is a normal occurrence. These predictions require longer-term assessment and understanding of seawater chemistry changes and interactions with other changing physical and biogeochemical phenologies.

CONCLUSIONS

RUSALCA sampling and analysis of ocean chemistry have reinforced the evidence that low pH and $\Omega_{aragonite}$ values for $CaCO_3$ minerals are seasonally present across the eastern Chukchi Sea as well as other areas of the Chukchi Sea (Bates et al., 2009, 2013), East Siberian Sea (Semiletov et al., 2004, 2007; Anderson et al., 2009, 2011), and Bering Sea shelf waters (e.g., Mathis et al., 2011a,b; Cross et al., 2013). At present, the ecosystem component of the benthos that produces $CaCO_3$ (i.e., shelly fauna) appears to be exposed to potentially corrosive seawater conditions during summertime sea ice retreat.

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