



Seasonal variation of CaCO_3 saturation state in bottom water of a biological hotspot in the Chukchi Sea, Arctic Ocean

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Abstract. Distribution of calcium carbonate saturation state (Ω) was observed in the Chukchi Sea in autumn 2012 and early summer 2013. Ω in bottom water ranged from 0.3 to 2.0 for aragonite and from 0.5 to 3.2 for calcite in 2012. In 2013, Ω in bottom water was 1.1–2.8 for aragonite and 1.7–4.4 for calcite. Aragonite and calcite undersaturation was found in high productivity regions in autumn 2012 but not in early summer 2013. Comparison with other parameters has indicated that biological processes – respiration and photosynthesis – are major factors controlling the regional and temporal variability of Ω . From these ship-based observations, we have obtained empirical equations to reconstruct Ω from temperature, salinity and apparent oxygen utilization. Using 2-year-round mooring data and these equations, we have reconstructed seasonal variation of Ω in bottom water in Hope Valley, a biological hotspot in the southern Chukchi Sea. Estimated Ω was high in spring and early summer, decreased in later summer, and remained relatively low in winter. Calculations indicated a possibility that bottom water could have been undersaturated for aragonite on an intermittent basis even in the pre-industrial period, and that anthropogenic CO_2 has extended the period of aragonite undersaturation to more than 2-fold longer by now.

tem and may threaten some organisms (e.g., Gattuso and Hansson, 2011; Branch et al., 2013). Of particular concern is the impact on calcifying organisms, such as coralline algae, pteropods, bivalves, and corals, because acidification lowers the saturation state (Ω) of calcium carbonate (CaCO_3) in seawater, which affects the ability of these organisms to produce and maintain their shells or skeletons. In fact, a decrease in Ω of water can cause enhanced mortality of juvenile shellfish (Green et al., 2009; Talmage and Gobler, 2009) and decreased calcification, growth, development and abundance of calcifiers (Kroeker et al., 2013, and references therein).

The shallow shelf seas of the Arctic Ocean are known to be especially vulnerable to ocean acidification. Cold water dissolves more CO_2 , large freshwater inputs from rivers and sea ice melt reduce calcium ion concentrations and alkalinity, the buffering capacity of seawater to added CO_2 (Salisbury, 2008; Yamamoto-Kawai et al., 2011), and respiration at the bottom of a salt stratified water column accumulates CO_2 in bottom water (Bates et al., 2009). Because of these characteristics, both surface and bottom waters of Arctic shelf seas exhibit naturally low Ω compared to other ocean waters (e.g., Fabry et al., 2009; Mathis et al., 2015; Yamamoto-Kawai et al., 2013). The Chukchi Sea is one of these seas.

Recent studies have found bottom waters already undersaturated with respect to aragonite-type CaCO_3 in the Chukchi Sea during summer and autumn (Bates et al., 2009, 2013; Bates, 2015; Mathis et al., 2014). Bates et al. (2013) reported that $\sim 40\%$ of sampled bottom waters during summertime cruises between 2009 and 2011 were aragonite-undersaturated. Some bottom waters were also undersaturated with respect to calcite, a less soluble form of CaCO_3 than aragonite. These studies indicate that benthic commu-

1 Introduction

During the last decade, ocean acidification due to uptake of anthropogenic carbon dioxide (CO_2) has emerged as an urgent issue in ocean research (e.g., Raven et al., 2005; Orr et al., 2005). Increasing acidity and consequent changes in seawater chemistry are expected to impact the marine ecosys-

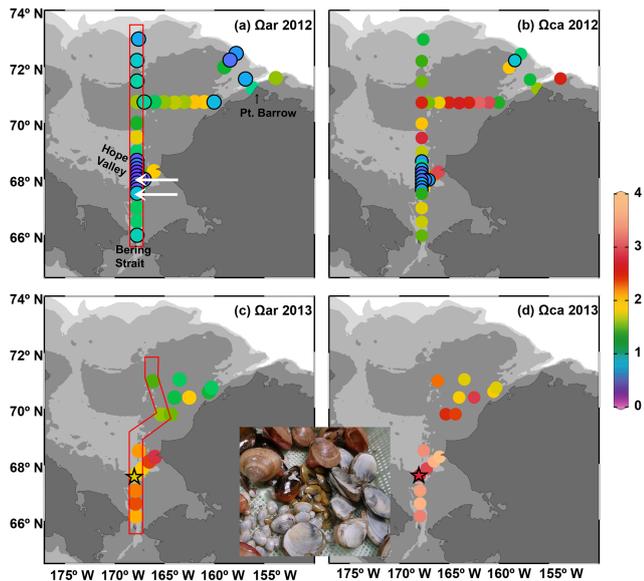


Figure 1. Distribution of Ω_{ar} (a, c) and Ω_{ca} (b, d) in bottom water in September–October 2012 (a, b) and July 2013 (c, d). Circled stations were undersaturated with CaCO_3 minerals. Stations in red polygon were used in Fig. 3. White arrows indicate mooring sites. An insert photo shows bivalves collected by a dredge trawl at a station marked with a star in July 2013.

nities in large areas of this shelf sea have been exposed to bottom waters that are corrosive for their CaCO_3 shells and skeletons, at least seasonally. However, full seasonal variation of Ω is still unrevealed due to the lack of shipboard observations during ice-covered months. Because many benthic organisms have planktonic larval stages, timing and duration of CaCO_3 undersaturation in bottom water can be critical for their growth and populations.

In the present paper, we show results of ship-based observations in September–October of 2012 and early July of 2013 in the Chukchi Sea. In both years, sea ice concentration decreased to $< 80\%$ at the end of May and to $< 30\%$ at the beginning of June. Therefore, observations were carried out about 3 months and 1 month after the ice retreat in 2012 and 2013, respectively. Because of the difference in season as well as interannual variability in hydrographic conditions, distribution of Ω was largely different between two observations. By comparing with distributions of physical and biogeochemical parameters, factors controlling Ω will be discussed. Based on these results, we attempt to reconstruct seasonal variations of Ω in the bottom water in the southern Chukchi Sea by using data from a 2-year-round mooring observation between July 2012 and July 2014.

2 Study area

The Chukchi Sea is a vast and shallow (~ 50 m) shelf sea north of the Bering Strait (Fig. 1) and is covered by ice for 7

or 8 months of the year. Pacific-origin water enters through the Bering Strait and spreads across the Chukchi Sea. The Pacific water transports heat and freshwater to the Arctic Ocean during summer months. In winter, atmospheric cooling and brine injection from growing sea ice mixes the whole water column and modifies the water to form “Pacific winter water”, which is characterized by low temperature and relatively high salinity (~ 33). In coastal polynyas, hypersaline winter water ($S > 34$) occasionally forms. Even in summertime, the remnant Pacific winter water is often observed at the bottom of the shelf beneath the warm and fresh upper layer.

The Pacific water also transports nutrients to the Chukchi Sea. Nutrient-rich water upwelled onto the Bering shelf is carried northward, promoting very high primary productivity in the sea (e.g., Springer and McRoy, 1993). Using the nutrients, spring phytoplankton bloom occurs immediately after the sea ice retreat or even under sea ice (Fujiwara et al., 2016; Lowry et al., 2014). Relatively high primary production continues to autumn (Wang et al., 2005). Because of the shallow bottom depth and the mismatch between seasonal dynamics of phytoplankton and zooplankton, a large proportion of produced organic matter is directly delivered to the seabed (e.g., Grebmeier et al., 2006). As a result, the high export rate of organic matter supports very high benthic biomass that is prey for higher trophic levels such as diving ducks, seals, whales and walrus (Grebmeier et al., 2006; Fabry et al., 2009).

Exported organic matter is remineralized back to nutrients and CO_2 in shelf bottom water and sediments. This accumulates CO_2 in bottom water and lowers Ω , to the level of CaCO_3 undersaturation in summer/autumn (e.g., Bates et al., 2009). Calcifying bivalves (Fig. 1), amphipods, brittle stars and crabs are dominant species in the benthic community of the Chukchi Sea (Fabry et al., 2009; Blanchard et al., 2013) and are key components of the ecosystem. Ocean acidification, therefore, could have considerable impacts on the ecosystem and biogeochemical cycles of the Chukchi Sea. In addition, because of the shallow bottom depth of ~ 50 m, vertical mixing induced by wind, tide or atmospheric cooling can bring anthropogenic CO_2 into bottom water to which benthos are exposed.

3 Observation and analysis

Hydrographic data were collected in the Chukchi and Bering seas during the cruises of R/V *Mirai* of the Japan Agency for Marine–Earth Science and Technology (JAMSTEC) from 13 September to 4 October in 2012 (Kikuchi, 2012) and T/S *Oshoro-Maru* of Hokkaido University from 3 July to 18 July in 2013 (Hirawake et al., 2013). In the present paper, we use data from stations north of 66°N with a bottom depth shallower than 70 m. During both cruises, hydrographic casts were performed using a Sea-Bird 9plus CTD to which a carousel water sampler with Niskin bottles was mounted. Seawater samples were collected for total alkalinity (TA) and

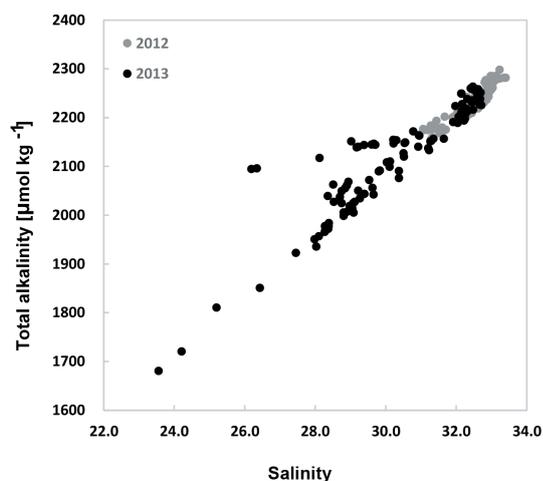


Figure 2. Relationship between salinity and total alkalinity (TA, $\mu\text{mol kg}^{-1}$) observed during cruises in 2012 and 2013.

dissolved inorganic carbon (DIC) as well as complementary data (S : salinity; T : temperature; DO: dissolved oxygen; and nutrients). Samples for TA and DIC were collected according to Dickson et al. (2007). TA was measured using a spectrophotometric system (Yao and Byrne, 1998) for samples from *Mirai* and an open cell titration system (Dickson et al., 2007) for samples from *Oshoro-Marui*. Intercomparison of two methods in a previous study (Li et al., 2013) showed good agreement of $0.88 \pm 2.03 \mu\text{mol kg}^{-1}$. Also, the S –TA relationship between two cruises did not show any obvious offset (Fig. 2). DIC from both cruises was analyzed using a coulometer system. Measurements of TA and DIC were calibrated against a certified reference material distributed by A. G. Dickson at the Scripps Institute of Oceanography, USA, or General Environmental Technos Co., Japan. The pooled standard deviation (S_p) for duplicate samples was <2.2 and $<5.5 \mu\text{mol kg}^{-1}$ for TA and DIC, respectively. Observations of TA, DIC, nutrients, T , S and pressure were used to calculate Ω for aragonite (Ω_{ar}) or calcite (Ω_{ca}) and $f\text{CO}_2$ (fugacity of CO_2) by using the CO2sys program (Lewis and Wallace, 1998) with constants of Mehrbach et al. (1973) re-fit by Dickson and Millero (1987) for K_1 and K_2 and Dickson (1990) for K_{SO_4} . We have chosen these constants following previous studies in the Arctic Ocean (e.g., Azetsu-Scott et al., 2010; Bates et al., 2009, 2015). However, as evaluated by Azetsu-Scott et al. (2010), the use of these K_1 and K_2 constants will give lower Ω than using other constants. The maximum difference of 0.07 in Ω_{ar} was estimated in their study in the Canadian Arctic Archipelago and in the Labrador Sea. In the case of our dataset, Ω will be higher by up to 0.09 for aragonite and 0.14 for calcite when other sets of K_1 and K_2 listed in Azetsu-Scott et al. (2010) are used. This will be included in error estimates for reconstruction of seasonal variation in Ω .

Bottle DO was determined by Winkler titration following World Ocean Circulation Experiment Hydrographic Program operations and methods (Dickson, 1996) with precision of $0.12 \mu\text{mol kg}^{-1}$. Nutrient samples were analyzed according to the GO-SHIP Repeat Hydrography Manual (Hydes et al., 2010) with a precision of $<0.1 \mu\text{mol kg}^{-1}$ for nitrate, nitrite and phosphate, $<0.6 \mu\text{mol kg}^{-1}$ for silicate, and $<0.4 \mu\text{mol kg}^{-1}$ for ammonium. Cumulative analytical errors in TA, DIC, phosphate and silicate can cause a maximum error of 0.08 in Ω_{ar} and 0.13 in Ω_{ca} .

A mooring system was deployed in Hope Valley from 16 July 2012 to 19 July 2014. The system was first deployed at $67^\circ 42' \text{N}$, $168^\circ 50' \text{W}$ from 16 July 2012 to 2 October 2012, and then moved slightly to the north at $68^\circ 02' 4 \text{N}$, $168^\circ 50' \text{W}$ on 3 October 2012. On 20 July 2013, the system was recovered for maintenance and redeployed at the latter location until 19 July 2014. Bottom depth was 52, 59 and 60 m, respectively, for each deployment. Sensors for T , S , DO, chlorophyll a and turbidity were equipped on the mooring at 7 m above the bottom. Data were recorded every hour. T and S data were acquired using a MicroCAT C-T recorder, SBE 37-SM (Sea-Bird Electronics, USA). The maximum drifts in sensors over 1 year were 0.002°C for T and 0.01 for S in pre- and post-calibration comparisons (Nishino et al., 2016). The DO sensor used for mooring observation was an AROW-USB phosphorescent DO sensor (JFE Advantech Co., Ltd., Japan). The sensor was calibrated using oxygen-saturated and anoxic water to determine the linear relationship between them with 2% accuracy (Nishino et al., 2016). Note that a correction of $-69 \mu\text{mol kg}^{-1}$ applied for the third mooring data in Nishino et al. (2016) was found to be due to an artificial error in conversion of original sensor output to concentration in $\mu\text{mol kg}^{-1}$. With correct conversion, the difference between sensor data and bottle data obtained on 1 September 2013 was reduced from 69 to $4 \mu\text{mol kg}^{-1}$. Accordingly, we did not apply any correction to DO sensor data in the present paper. Details of other sensor and mooring observations are described in Nishino et al. (2016).

4 Results and discussions

4.1 Ship-based observations

Distributions of Ω in bottom waters of the Chukchi Sea (Fig. 1) were significantly different between September–October 2012 (hereafter autumn 2012) and July 2013 (hereafter summer 2013). In autumn 2012, Ω in bottom water ranged from 0.3 to 2.0 for aragonite and from 0.5 to 3.2 for calcite. Aragonite undersaturation ($\Omega_{\text{ar}} < 1$; black circles in Fig. 1) was observed at stations off Pt. Barrow, in Hope Valley, in the Bering Strait, and near the northern continental slope. The lowest Ω_{ar} was observed on 3 October 2012 in Hope Valley at 68°N , in the dome-like structure of bottom water with low T , high S and low DO (Nishino et al., 2016)

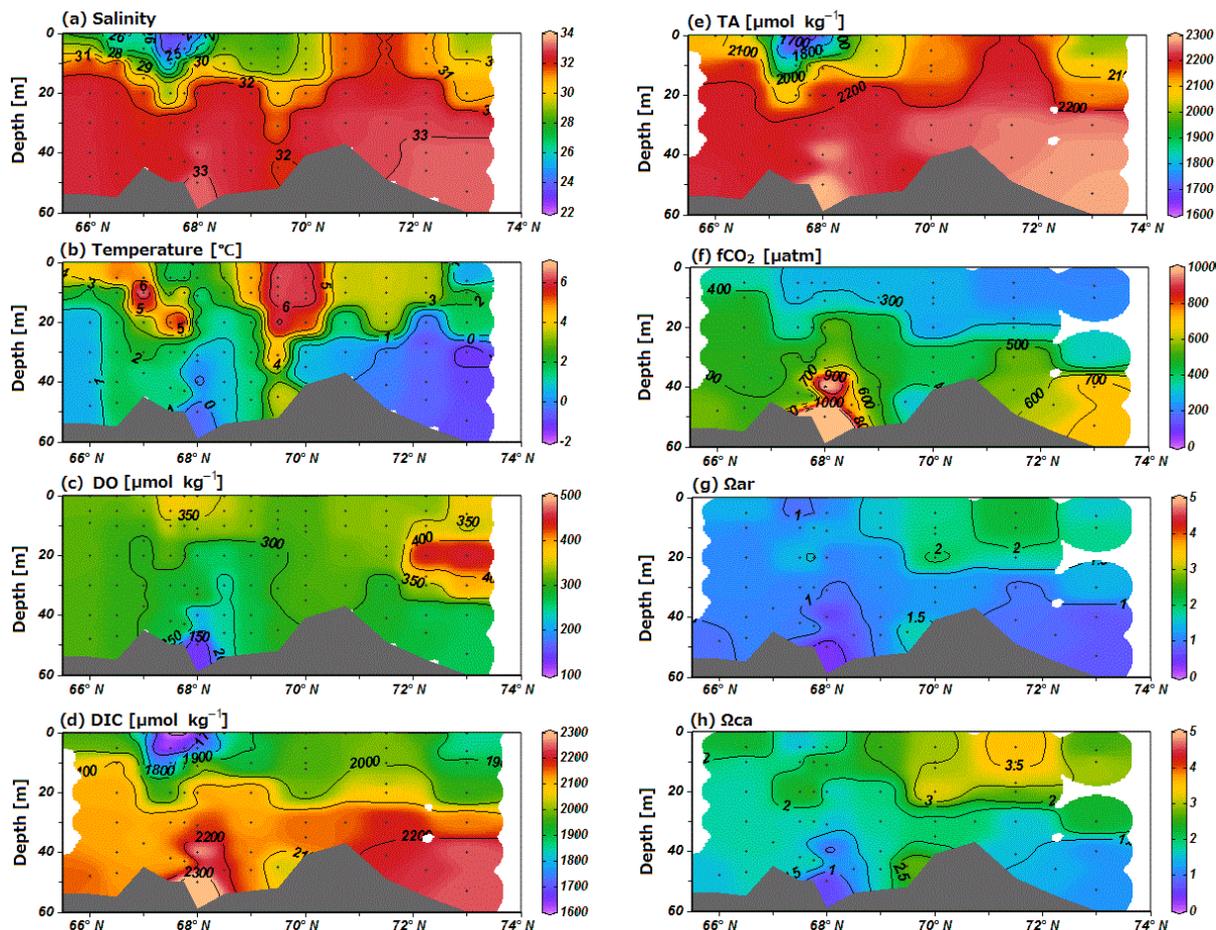


Figure 3. Vertical sections of (a) salinity, (b) temperature, (c) dissolved oxygen (DO), (d) dissolved inorganic carbon (DIC), (e) total alkalinity (TA), (f) $f\text{CO}_2$, (g) Ω_{ar} and (h) Ω_{ca} in September–October 2012. See Fig. 1 for locations.

with high TA, high DIC and high $f\text{CO}_2$ (Fig. 3). Calcite undersaturation was also found in this dome (Figs. 1 and 3). Nishino et al. (2016) describe the dome-like structure as a common feature found in this region associated with Hope Valley topographic depression, although water properties can differ between years and seasons. Note that stations along 168° W in Hope Valley were visited twice on 13–17 September and 3–4 October in 2012 and the differences in Ω values of bottom water between the two visits (<0.2) were smaller than differences between stations inside and outside of the dome-like structure (~ 0.7).

In 2013, Ω in bottom water was 1.1–2.8 for aragonite and 1.7–4.4 for calcite: all of the observed waters were oversaturated with respect to aragonite and calcite (Figs. 1 and 4). Although stations in Hope Valley again showed a dome-like feature in T , DO, and $f\text{CO}_2$, they were not as prominent as in 2012 (Fig. 4). Ω in bottom waters at these stations was slightly lower than stations north or south but still very oversaturated with respect to CaCO₃ ($\Omega_{\text{ar}} = 1.7$ – 1.9 ; $\Omega_{\text{ca}} = 2.8$ – 3.0). Waters with lower Ω_{ar} of 1.1–1.2 and Ω_{ca} of 1.8–1.9

were found in northern stations at around 71° N where T and DO were lower and $f\text{CO}_2$ was higher than in the south.

In both years, low Ω was observed in bottom waters with low T , low DO and high S . Relationships between Ω_{ar} and T , S or apparent oxygen utilization (AOU, the difference between saturation and observed concentrations of DO) are shown in Fig. 5. Ω_{ar} showed the highest correlation with AOU and data from two cruises were distributed on a line in the Ω_{ar} –AOU diagram (Fig. 5). AOU is a measure of how much oxygen has been consumed by respiration and decomposition of organic matter. Accordingly, high AOU corresponds to high $f\text{CO}_2$ (Fig. 6) and therefore low Ω (Fig. 5). A negative AOU value is a sign of photosynthesis that produces DO, consumes CO₂ and increases Ω . As shown in Fig. 6, biogeochemical conditions between two ship-based observations were different: autumn 2012 was under a very strong influence of remineralization, whereas summer 2013 was influenced by photosynthesis in early summer 2013.

Ω_{ar} increased with increasing T and their relationships for two cruises were similar in slope but different in intercept (Fig. 5). Ω_{ar} also increased with decreasing S in bottom wa-

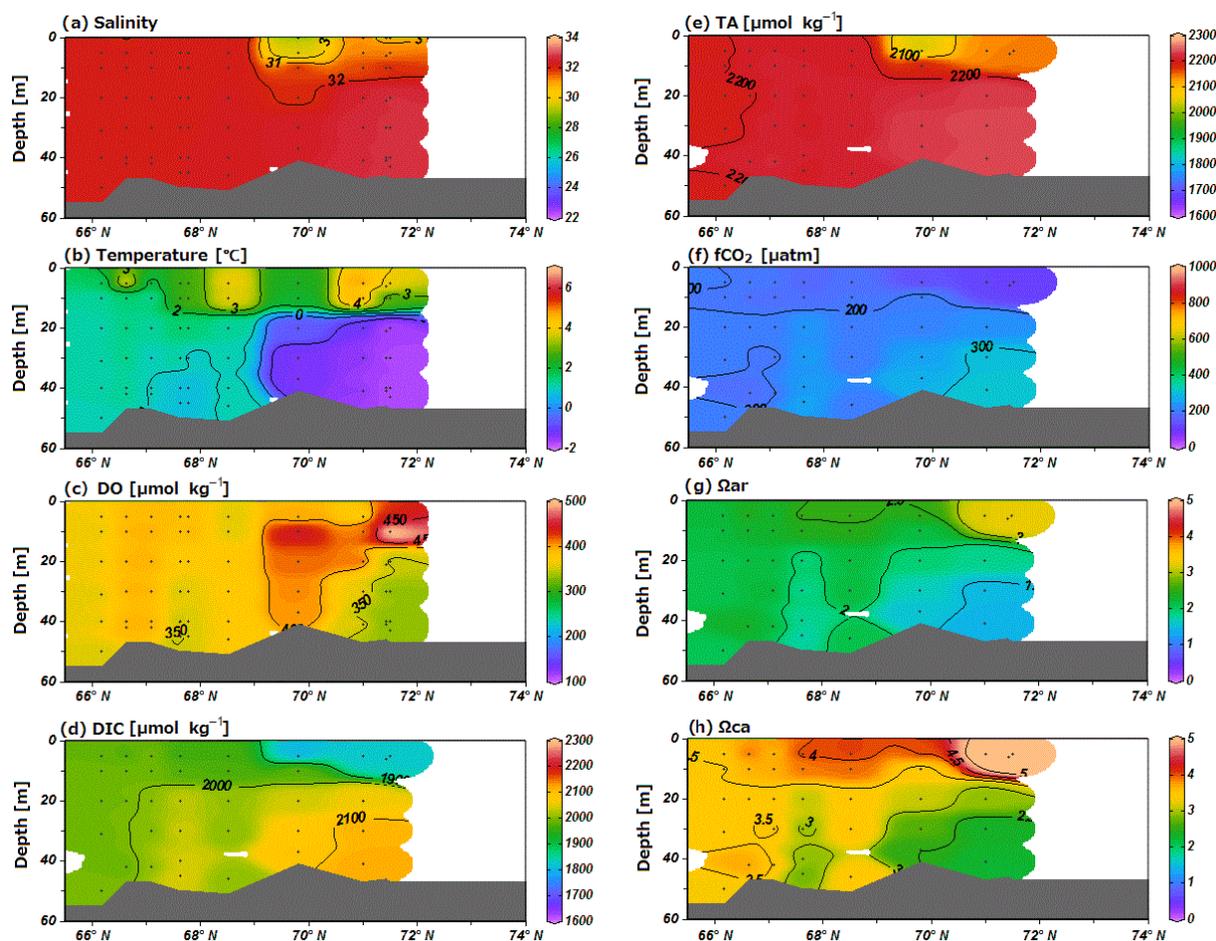


Figure 4. Same as Fig. 4 but in July 2013. See Fig. 1 for locations.

ters, whereas Ω_{ar} decreased with decreasing S in upper waters (Fig. 5). The latter is explained by mixing with freshwater, which lowers calcium ion concentration and alkalinity to decrease Ω_{ar} , as indicated by previous studies (Salisbury et al., 2008; Yamamoto-Kawai et al., 2009). In fact, aragonite undersaturation was observed in very low S surface waters in 2012 (Fig. 5). The opposite relationship in bottom waters is probably because higher bottom S creates stronger stratification of the water column that prevents release of CO₂ produced by respiration at depth. These results show that variations in Ω in the Chukchi Sea bottom water are controlled largely by organic matter remineralization with minor contributions of T and S . In fact, low Ω waters were observed in regions off Pt. Barrow and Hope Valley, known as biological “hotspots” in the Chukchi Sea, characterized by high primary productivity, high export flux of organic matter to depth, a high respiration rate in sediment community, and high benthic biomass (Grebmeier et al., 2006; Nishino et al., 2016).

In autumn 2012, Ω was much lower than in summer 2013, not only in bottom water but for the whole water column

(Fig. 3). Nishino et al. (2016) compared hydrographic conditions in this area in late summer of 2004, 2008, 2010, 2012 and 2013, and found that 2012 was an unusual year with strong stratification, due to an input of sea ice meltwater, and with remarkably low DO concentration at depth. Strong stratification prevents ventilation and accumulates more CO₂ in the bottom water. This explains high AOU, high $f\text{CO}_2$ and low Ω in bottom water in autumn 2012 (Fig. 3). Seasonal variation in Ω should also be a cause of the difference between two observations as described in the following sections. In upper layers of the water column, lower Ω in 2012 relative to S and T than in 2013 (Fig. 5) might be due to low photosynthetic activity associated with stronger stratification and to mixing with sea ice meltwater (Nishino et al., 2016). In addition, input of sea ice meltwater itself lowered Ω in surface waters in 2012, as is evident in Fig. 5. The fact that ranges of T and S for bottom waters were not significantly different between two cruises (Fig. 5) indicates that the accumulation of more CO₂ produced by respiration was the major cause of the much lower Ω_{ar} in autumn 2012 than summer 2013.

Table 1. Comparison of depth (D), temperature (T), salinity (S) and dissolved oxygen (DO) between mooring and ship-based observations collected at the nearest location and time to the mooring data acquisition. Mooring data are the 24 h mean with standard deviation (SD). Distances between the mooring site and the ship-based sampling site are also indicated in kilometers.

Date and site distance	Parameter	Mooring		Ship-based	difference
		24 h mean	SD		
09/14/2012 23 km	D (m)	44.56	±0.08	41.80	−2.76
	T (°C)	1.59	±0.03	1.40	−0.19
	S	32.22	±0.01	32.26	0.05
	DO ($\mu\text{mol kg}^{-1}$)	284.76	±2.50	279.80	−4.96
10/03/2012 5 km	D (m)	54.03	±0.04	51.50	−2.53
	T (°C)	0.69	±0.13	0.80	0.11
	S	33.01	±0.02	32.96	−0.05
	DO ($\mu\text{mol kg}^{-1}$)	102.89	±4.40	113.65	10.76
07/16/2013 31 km	D (m)	53.99	±0.03	51.53	−2.46
	T (°C)	1.14	±0.08	0.79	−0.35
	S	32.08	±0.03	32.28	0.20
	DO ($\mu\text{mol kg}^{-1}$)	316.32	±7.28	350.40	34.07
09/01/2013 4 km	D (m)	52.78	±0.05	52.50	−0.28
	T (°C)	2.31	±0.10	2.29	−0.03
	S	32.26	±0.05	32.41	0.15
	DO ($\mu\text{mol kg}^{-1}$)	267.23	±8.20	270.92	3.69

4.2 Mooring observations

Mooring data revealed seasonal variation in T , S , DO and AOU in bottom water in Hope Valley where aragonite and calcite undersaturations were observed in autumn 2012 (Fig. 7). Ship-based observations were made near the mooring site ($\sim 68^\circ\text{N}$) on 14 September 2012, 3 October 2012 and 16 July 2013, and a comparison with sensor data is summarized in Table 1, together with observations on 1 September 2013 by Nishino et al. (2016). The 24 h mean data are shown in Table 1 for sensor data with standard deviations. Differences in Table 1 reflect not only instrumental errors but also inhomogeneity of water properties at the observation sites. This is likely a reason for relatively large differences found in all T , S and DO data on 16 July 2013 when a ship-based observation was made 31 km away from the mooring site. Other than this, two observations agreed to within 0.2°C in T , 0.15 in S and $11 \mu\text{mol kg}^{-1}$ in DO.

T , S and DO (AOU) ranged from -1.92 to 2.73°C , 30.41 to 35.49 , and 62.7 to 416.4 (-32.7 to 294.9) $\mu\text{mol kg}^{-1}$, respectively. Note that ship-based observations were made when DO was at higher and lower parts of seasonal variation. During summer/autumn months, T , S and DO showed large fluctuations. Because all three parameters changed simultaneously, this is likely due to changes in the water current, which carries water masses with different characteristics from surrounding areas. This also indicates horizontal inhomogeneity of bottom water properties during summer/autumn.

T was high in the summer/autumn months, decreased from October to December due to atmospheric cooling, and remained at a near freezing temperature ($\sim -1.8^\circ\text{C}$) from January to May. Summer/autumn T was lower in 2012 than in 2013. Stronger stratification of the water column due to a meltwater input in 2012 (Nishino et al., 2016) may be the cause of this difference. This is also consistent with higher S in bottom water in 2012 than in 2013. The mean S for the whole observation period was 32.4 . In both years, freshening was observed at the beginning of the cooling period, because of mixing of low- S upper waters into the bottom layer by vertical convection (Woodgate et al., 2005). Another freshening was also found at the beginning of warming periods due to melting of sea ice (Woodgate et al., 2005). In the winter of 2013, S increased rapidly in February to as high as 35.49 and then decreased sharply in March. This suggests an advection of a water mass from an active ice formation area, such as a coastal polynya region where brine rejection from freezing seawater increases the S of bottom water to form “hyper-saline water” (Weingartner et al., 1998). Such an event was not observed in the following winter.

DO increased and reached supersaturation (negative AOU) in May and June (Fig. 7), accompanied by a sharp increase in chlorophyll a concentration (Nishino et al., 2016), indicating effects of oxygen production by photosynthesis even in the bottom water. DO then decreased from ~ 300 in July to $\sim 125 \mu\text{mol kg}^{-1}$ in September 2012 and to $\sim 225 \mu\text{mol kg}^{-1}$ in September 2013 (Fig. 7). DO remained low until the onset of winter convection in October–November. As mentioned in the previous section, DO in bottom water was unusually low

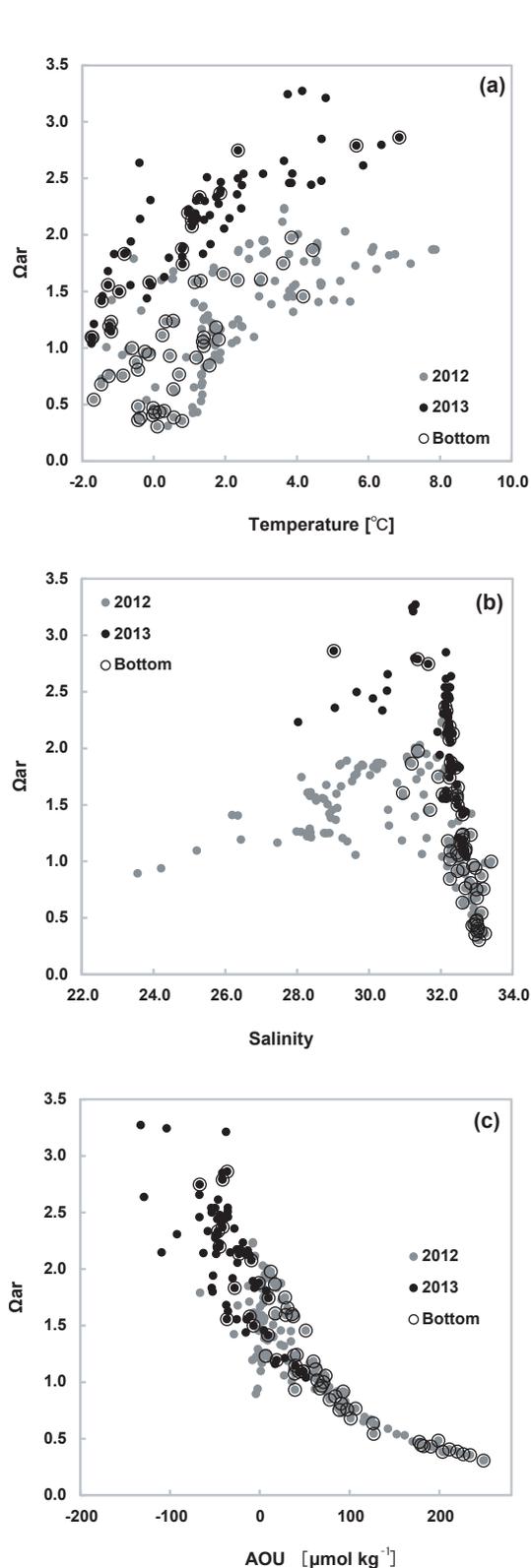


Figure 5. Relationships between (a) Ω_{ar} and temperature, (b) Ω_{ar} and salinity, and (c) Ω_{ar} and apparent oxygen utilization (AOU, $\mu\text{mol kg}^{-1}$).

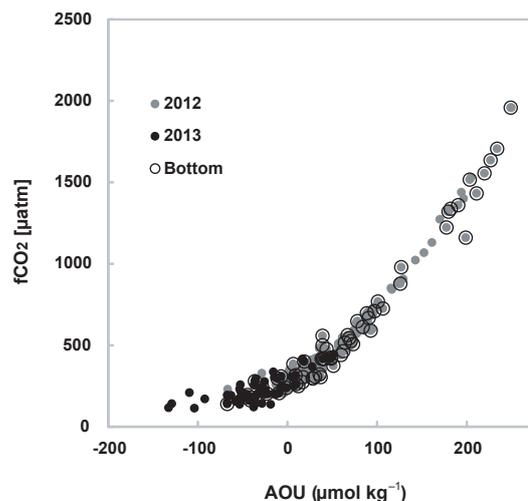


Figure 6. Relationships between AOU ($\mu\text{mol kg}^{-1}$) and $f\text{CO}_2$ (μatm).

in autumn 2012, due to strong stratification that prevented ventilation of bottom water. During winter, DO was relatively stable, at $\sim 325 \mu\text{mol kg}^{-1}$. This concentration corresponds to $\sim 60 \mu\text{mol kg}^{-1}$ in AOU and $\sim 85\%$ in saturation level even in the hypersaline water that is formed in contact with the atmosphere. This suggests that positive AOU (DO undersaturation) in winter is not due to insufficient gas exchange. Continued sediment oxygen uptake is a possible reason for the undersaturation. Previous studies in shallow Arctic seas have found that sediment oxygen uptake rate is regulated by the availability of organic matter and macrofaunal biomass (Grebmeier and McRoy, 1989; Rysgaard et al., 1998; Grant et al., 2002; Clough et al., 2005). Accordingly, the oxygen uptake rate has a seasonal variation and is low in winter prior to initiation of biological production in spring (Cooper et al., 2002; Grant et al., 2002). Nevertheless, the winter sediment oxygen uptake rate is not zero, but is about half of that in summer in the coastal area north of Pt. Barrow, Alaska (Devol et al., 1997), in Young Sound in Northeast Greenland (Rysgaard et al., 1998) and in Resolute Bay in the Canadian high Arctic (Welch et al., 1997). In our observations, mean AOU in mid-winter (February to April) was 1/3–1/2 of that in October. Therefore we consider that positive AOU was maintained by benthic respiration during winter.

The analysis of mooring data indicates that our ship-based observation in summer 2013 sampled bottom water that was under an influence of photosynthesis. In autumn 2012, on the other hand, we have observed bottom water that was largely affected by organic matter decomposition. This explains the differences in AOU and Ω in bottom water between two ship-based observations in September–October 2012 and July 2013.

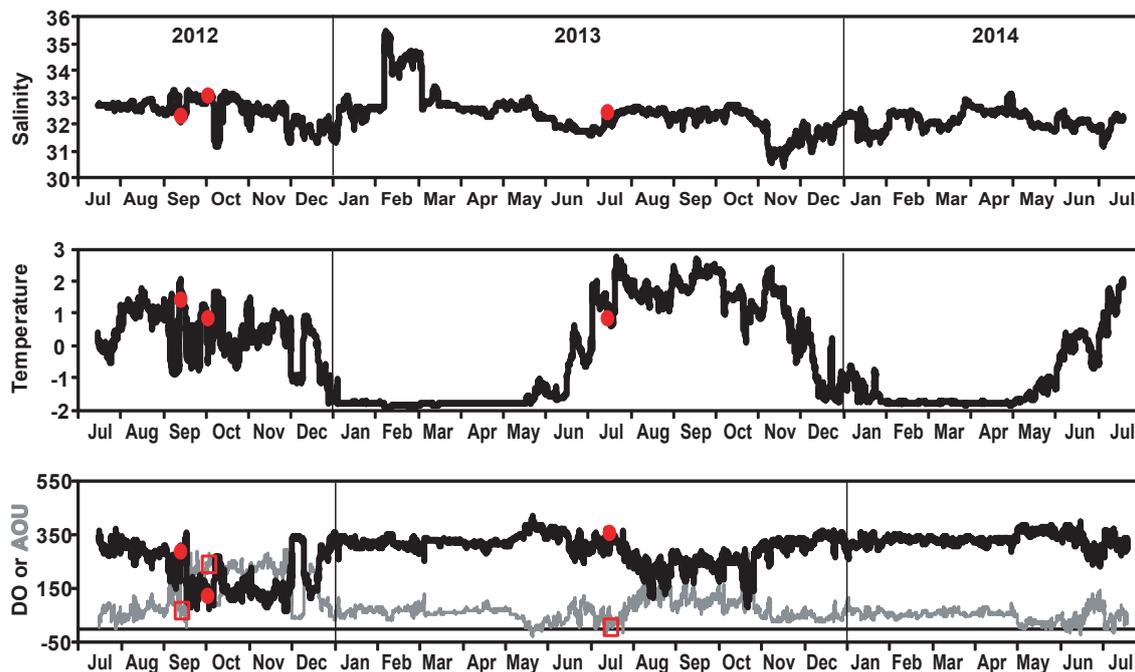


Figure 7. Time series of salinity (top), temperature (middle; °C), and dissolved oxygen and AOU (bottom; $\mu\text{mol kg}^{-1}$). Red symbols indicate ship-based observations. In the bottom panel, dots and squares are ship-based data of dissolved oxygen and AOU, respectively.

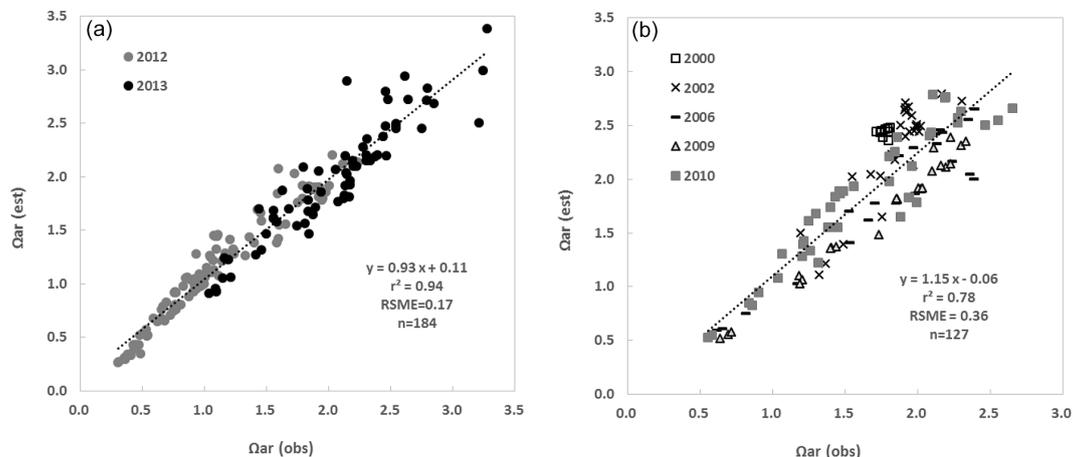


Figure 8. Comparison between Ω_{ar} estimated from T , S , and AOU data using Eqs. (1) and (2) (Ω_{ar} (est)), and Ω_{ar} estimated from bottle DIC and TA (Ω_{ar} (obs)) for ship-based cruises (a) in 2012 and 2013, and (b) in 2000, 2002, 2006, 2009 and 2010.

4.3 Regression analysis

Based on ship-based and mooring observations, we try to reconstruct the seasonal evolution of Ω in the bottom water of Hope Valley. Previous studies have used multiple linear regression models to robustly determine carbonate parameters such as DIC, TA, Ω , and pH from observations of T , S , DO or nutrients (Juraneck et al., 2009; Alin et al., 2012). These empirical equations were successfully used to reconstruct seasonal and interannual cycles, as well as high-frequency variability in short timescales (Juraneck et al., 2009; Alin et

al., 2012; Leinweber and Gruber, 2013; Evans et al., 2013). In the present study, we employ a similar approach to estimate Ω . We use observations from two cruises to determine regression equations for DIC and TA using T , S and AOU as input parameters. The goodness of the fit was assessed by correlation coefficients (r^2) and root mean square error (RMSE). AOU, not DO itself, is used as a measure of biological process because DO concentration changes with T and S . We then calculate Ω from estimated TA and DIC with observed T , S and pressure, rather than directly estimate Ω from input parameters. In this way, we can take into account

the effects of T , S and pressure on the solubility of CaCO₃ (Mucci, 1983; Millero, 1995).

DIC is controlled by physical (solubility and gas exchange) and biological processes (photosynthesis and respiration) and therefore can be expressed as a function of T , S and AOU. TA in the study area is a function of S , as it is determined by mixing of Pacific-origin seawater with freshwater and formation of sea ice (brine rejection increases both the S and TA of the underlying water). A bloom of a calcifying primary producer can cause a drawdown of TA (Murata and Takizawa, 2002). However, neither bloom of calcifiers Ω_{ar} nor TA drawdown in the S -TA diagram was observed during our observations (Fig. 2). Mixing between seawater and freshwater sources with different TA (high in river and low in sea ice meltwater and precipitation; Yamamoto-Kawai et al., 2005) is evident in the S -TA diagram, but only in surface waters with $S < 31$ (Fig. 2). Accordingly, we used T , S and AOU to estimate DIC (DIC_{est}) and S to estimate TA (TA_{est}) only for waters with $S > 31$.

Regression equations obtained for DIC and TA are

$$\text{DIC}_{\text{est}} = 1.06 \times \text{AOU} - 17.03 \times T + 41.54 \times S + 743.94$$

$$(r^2 = 0.96, \text{RMSE} = 24.46, n = 184) \quad (1)$$

and

$$\text{TA}_{\text{est}} = 59.23 \times S + 370.34$$

$$(r^2 = 0.83, \text{RMSE} = 14.03, n = 184). \quad (2)$$

Although biological activities can change TA to a small extent by adding or removing nitrate or ammonium, the inclusion of AOU did not improve the regression model ($r^2 = 0.83$, $\text{RMSE} = 14.06$). Inclusion or replacement of proxies of other biological processes, such as nutrients or chlorophyll a concentration, did not significantly improve the estimate of DIC and TA.

Figure 8a shows a linear correlation between observations (Ω_{obs}) and estimations (Ω_{est}), with $r^2 = 0.94$ for aragonite ($r^2 = 0.94$ calcite, not shown). Larger differences between the two values were found in surface waters, with Ω_{est} values higher than 2.5 for aragonite and 4.0 for calcite (Fig. 8a) and with high temperature ($> 6^\circ\text{C}$). This might be due to rapid warming at the surface that could cause temporal decoupling of oxygen and carbon because of differences in the temperature dependence of solubility and in the gas exchange rate. Including these samples, RMSE was 0.17 for Ω_{ar} and 0.27 for Ω_{ca} ($n = 184$; Fig. 8a).

In order to evaluate the regression Eqs. (1) and (2), we have applied these to independent data from R/V *Mirai* cruises in the Chukchi Sea in 2000, 2002, 2006, 2009 and 2010, downloaded from the website of the Japan Agency for Marine-Earth Science and Technology (JAMSTEC). These cruise observations were carried out in August, September or October. In our study area (latitude $> 66^\circ\text{N}$, bottom depth $< 70\text{m}$), the total 127 set of discrete bottle

sample data of DIC, TA and DO, together with sensor data of T and S (> 31), was found. For each dataset, we have calculated DIC_{est} and TA_{est} from T , S and AOU using Eqs. (1) and (2). AOU was calculated from discrete bottle DO data. DIC_{est} and TA_{est} agreed with observed bottle data of DIC and TA with $r^2 = 0.96$ and 0.83, respectively. Ω calculated from DIC_{est} and TA_{est} (Ω_{est}) was correlated with observed Ω (Ω_{obs}) with a regression equation of $\Omega_{\text{arest}} = 1.15 \times \Omega_{\text{arobs}} - 0.06$ ($r^2 = 0.78$, $\text{RMSE} = 0.36$, Fig. 8b) and $\Omega_{\text{caest}} = 1.14 \times \Omega_{\text{caobs}} - 0.06$ ($r^2 = 0.78$, $\text{RMSE} = 0.57$). We consider RMSEs estimated in this evaluation to represent cumulative errors in sampling, sample analysis, regression analysis, and application of equations to other years with different hydrographic and biogeochemical conditions. In addition to this, a possible systematic error caused by the choice of K_1 and K_2 constants as mentioned in Sect. 3 should be considered. Therefore, we present Ω_{est} with a range of $\pm\text{RMSE} + 0.09$ for aragonite and $\pm\text{RMSE} + 0.14$ for calcite in the following section (-0.36 to $+0.45$ for Ω_{arest} and -0.57 to $+0.71$ for Ω_{caest}).

Cross et al. (2013) pointed out the possibility of shallow-water CaCO₃ mineral dissolution, which could cause an increase in TA by $36 \mu\text{mol kg}^{-1}$ in the northern Bering Sea where aragonite undersaturation lasts for 5 months from spring to autumn. In our study area, an increase in TA was also found in some bottom waters. However, this was likely due to brine injection rather than mineral dissolution. This was suggested by a comparison of S , TA and oxygen isotope ratios of water ($\delta^{18}\text{O}$) observed in cruises of R/V *Mirai* in 2000, 2002, 2009, 2010 and 2012 in the Chukchi Sea. The increase in TA was correlated with brine content, estimated from $\delta^{18}\text{O}$ as shown in Yamamoto-Kawai et al. (2005), rather than with the Ω of the water. Therefore, we consider that the effect of mineral dissolution is insignificant in waters discussed in our analysis.

4.4 Seasonal variation of Ω in Hope Valley bottom water

Based on the analysis in Sect. 4.3, the regression equations were applied to the mooring data in Hope Valley (excluding data with $S < 31$ observed intermittently between 8 and 21 November 2013).

The reconstructed Ω is shown in Fig. 9 with a range of -0.36 and $+0.45$ for aragonite, and -0.57 and $+0.71$ for calcite. For the whole period, Ω_{est} ranged from 0.2 to 2.1 for aragonite and from 0.3 to 3.4 for calcite (Fig. 9). It was shown that our ship-based observations in autumn 2012 and summer 2013 captured low and high Ω periods, respectively. Seasonal variation of Ω mirrors that of DO, low in autumn due to stratification and respiration and high in spring and early summer due to photosynthesis. In the unusually stratified autumn 2012, bottom water Ω was ~ 0.3 for aragonite and ~ 0.5 for calcite. In 2013, Ω decreased after our ship-based observation in July, and intermittent aragonite undersaturation

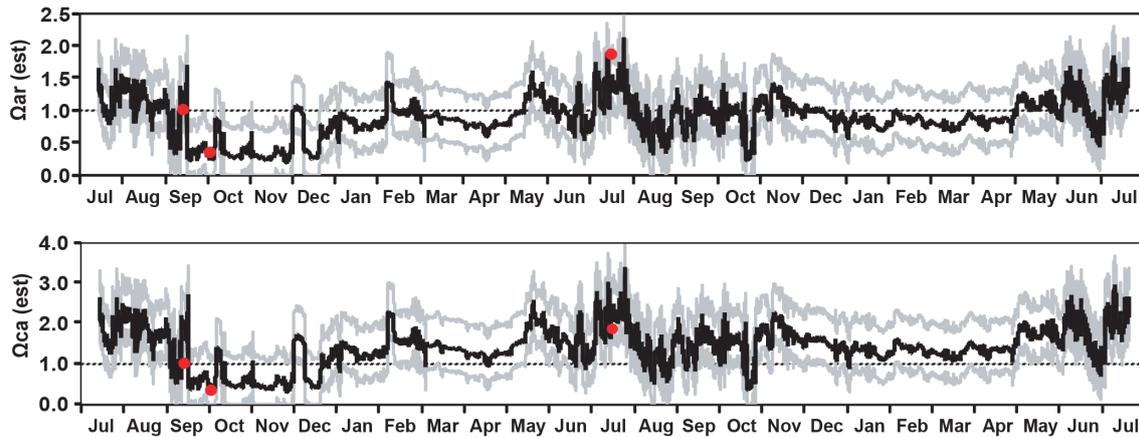


Figure 9. Time series of Ω_{ar} (top) and Ω_{ca} (bottom) reconstructed from mooring data of T , S and AOU (a black line). Red symbols indicate ship-based observations. Gray lines indicate ranges of -0.36 to $+0.45$ for Ω_{ar} and -0.57 to $+0.71$ for Ω_{ca} (see text).

was predicted in August, September and October, although Ω was higher than in the same months in 2012. At the beginning of the cooling and convection periods in November–December 2012 and October–November 2013, ventilation of bottom water increased DO and Ω . Then, Ω in bottom water remained low during winter until the initiation of photosynthesis in May. Low Ω in winter is likely due to continued respiration by benthic organisms, as suggested by positive AOU. Although equations obtained from summer/autumn data were used to estimate winter Ω , we presume this is acceptable because summer/autumn bottom water is a remnant of winter water that was modified by remineralization of organic matter after spring. If the remineralization quotient of DO and DIC is held relatively constant over the course of the year as observed in Young Sound ($\Delta\text{DIC}/\Delta\text{DO} = 0.8$ – 1.1 , Rysgaard et al., 1998), the summer/autumn relationship between DIC (and TA) and T , S , and AOU could be applicable to winter data. This assumption should be verified by direct winter observation by ship-based sampling, chemical sensors, or automatic water samplers in the future.

From spring to autumn, predicted large temporal variation in Ω suggests inhomogeneous distribution of undersaturated waters during this period. In winter, in contrast, variability in Ω is relatively small. This suggests that low Ω is a widespread feature during winter. An exception is the hypersaline water that could have a high calcium ion concentration and an alkalinity concentration to result in high Ω . However, S of this water is out of the range of ship-based observations used for multiple linear regression analysis, and thus Ω of this water is not very reliable.

The reconstructed Ω suggests the frequent occurrence of aragonite undersaturation in the bottom water of the Chukchi Sea, not only in summer/autumn, but also in the winter months. In previous studies, continuous aragonite undersaturation has been observed in bottom waters in the Bering and Chukchi seas, but in limited seasons. Cross et al. (2013) re-

ported persistent aragonite undersaturation of bottom water of the northern Bering Sea shelf for at least 5 months from mid-April to early October in 2009. Mathis et al. (2014) indicated sustained bottom aragonite undersaturation on the southern Bering Sea shelf for at least 4 months from mid-June to early October in 2011. In the northern Chukchi Sea around 71.5°N and 165°W , Mathis and Questel (2013) observed seasonal changes in Ω_{ar} and reported that bottom water became partially undersaturated in September and broadly undersaturated in October in 2010, with a lowest Ω_{ar} value of ~ 0.7 . The present study is the first to estimate year-round variability of Ω in the bottom water of the Chukchi Sea. For the first (from 16 July 2012 to 16 July 2013) and second (from 16 July 2013 to 16 July 2014) full-year mooring observations, the integrated period of aragonite undersaturation was counted to be 8.6 months for the first year and 7.5 months for the second year. For calcite, undersaturation was not as frequent as aragonite (Fig. 9), but was suggested not only for autumn 2012 but also in 2013 on an intermittent basis. The integrated periods of calcite undersaturation were 3.1 months and 0.8 months for the first and second year, respectively. Considering that the mooring site is located in a biological hotspot where the lowest Ω was observed in autumn (Figs. 1 and 3), the total time of undersaturation estimated here is likely at a maximum within the Chukchi Sea.

4.5 Anthropogenic impact on Ω

In order to roughly quantify the effect of anthropogenic CO₂ on the timing and duration of CaCO₃ undersaturation in our 2-year time series of Ω , we have estimated Ω in two cases: (1) the preindustrial period case with an atmospheric partial pressure of CO₂ ($p\text{CO}_2$) of 280 ppm, and (2) the future case with $p\text{CO}_2$ of 650 ppm. Following previous studies (Gruber et al., 1996; Sabine et al., 1999; Yamamoto-Kawai et al.,

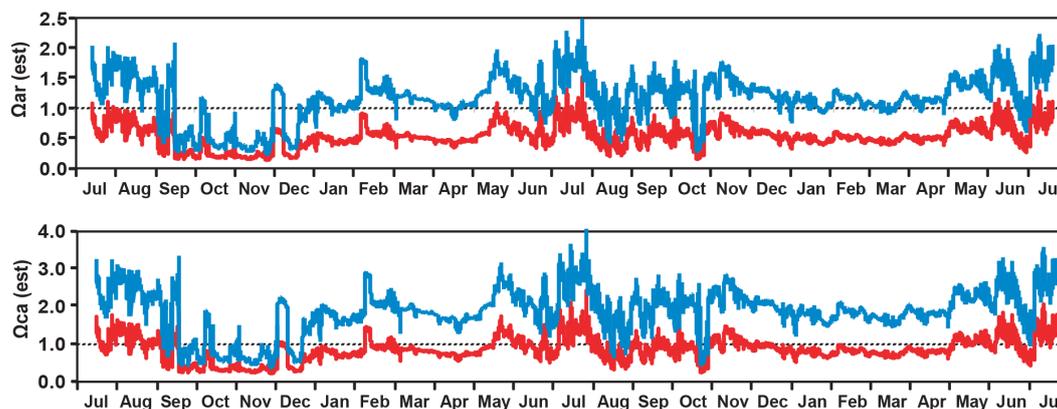


Figure 10. Time series of Ω_{ar} (top) and Ω_{ca} (bottom) for cases when atmospheric CO₂ concentration was 280 ppm (blue; pre-industrial period) or 650 ppm (red). See text for details.

2013, 2015), DIC concentration in a year t is expressed as

$$\text{DIC}_t = \text{DICEQ}_{t-0} + (\Delta_{\text{diseq}} + \Delta_{\text{bio}}), \quad (3)$$

where DICEQ_{t-0} is DIC of seawater in equilibrium with the atmospheric CO₂ in the year $t-0$ when the water parcel was last in contact with the atmosphere; Δ_{diseq} and Δ_{bio} represent the air–sea equilibrium at the surface and the change in DIC due to biological activity. In the case of the shallow Chukchi Sea shelf, $t-0$ can be assumed to be the observed year ($t\text{-obs}$), and therefore the sum of the last two terms can be calculated by comparing DIC and DICEQ for the year $t\text{-obs}$. In this study, we used DIC_{est} calculated using Eq. (1) with mooring data as DIC in the year $t\text{-obs}$. For calculation of DICEQ_{t-0} , we have used $p\text{CO}_2$ of 380 ppm, with TA_{est} , T and S from mooring data. Then, assuming that Δ_{diseq} and Δ_{bio} do not change with time, DIC in any year t can be estimated by using atmospheric $p\text{CO}_2$ at the year t . We have estimated Ω with DIC_t for the pre-industrial period when $p\text{CO}_2$ was 280 ppm, and for the future when $p\text{CO}_2$ reaches 650 ppm (50 years later in the high CO₂ emission scenario (RCP8.5), and the end of the century in a moderate scenario (RCP6; IPCC, 2013)).

Figure 10 shows time series of Ω for two cases. For the preindustrial case, Ω ranged from 0.2 to 2.6 for aragonite and from 0.4 to 4.1 for calcite. For the future case, Ω ranged from 0.2 to 1.5 for aragonite and from 0.2 to 2.4 for calcite. The caveat here is that our calculation is based on an assumption that terms Δ_{diseq} and Δ_{bio} have not changed since the pre-industrial period, and therefore provides only very rough estimates. As biological processes are the major factor changing DIC in bottom water, changes in Δ_{bio} can cause significant error in estimated Ω for the past and the future. For example, if biological production and subsequent remineralization at depth are lower in the past or in the future, Ω should be higher than shown in Fig. 10. At the moment, unfortunately, trends in productivity in the southern Chukchi Sea are still under debate. Lee et al. (2007) and Yun et al. (2014) show

that the primary production rates in recent years are lower than previous estimates made in the 1990s. From chlorophyll a analysis, Grebmeier (2012) and Arrigo and van Dijken (2011) have suggested an increase in primary productivity in the 2000s in the Chukchi Sea. Grebmeier et al. (2015) also showed an increase in benthic biomass from the 1970s to 2010 followed by a decline between 2010 and 2012 in our study area. To get a rough idea, we have calculated Ω for the pre-industrial case with the $(\Delta_{\text{diseq}} + \Delta_{\text{bio}})$ term half of that at present. With half $(\Delta_{\text{diseq}} + \Delta_{\text{bio}})$, Ω was estimated to range from 0.6 to 2.2 for aragonite and from 1.0 to 3.5 for calcite in the pre-industrial case. This means that CaCO₃ undersaturation might have occurred, at least for aragonite, even with the productivity much lower than that occurring today and without perturbation by anthropogenic CO₂. This may be the case only in our study site, because previous studies in the Chukchi Sea have suggested that undersaturation in bottom water is a recent phenomenon caused by anthropogenic CO₂ (Bates et al., 2009, 2013; Mathis and Questel, 2013).

In terms of duration, the period of aragonite (calcite) undersaturation was estimated to be 3.9 (2.6) and 1.7 (0.3) months in the first and second year, respectively, in the pre-industrial period case. By comparing with the original estimate of 7.5–8.6 months, it was suggested that the period of aragonite undersaturation has been significantly extended by an input of anthropogenic CO₂ by now. In the future case with an atmospheric $p\text{CO}_2$ of 650 ppm, the period of undersaturation is estimated to increase further to > 11 months for aragonite and half a year for calcite. This analysis indicates that anthropogenic CO₂ has a significant impact on the duration of CaCO₃ undersaturation in the bottom water even though seasonal and interannual variations of Ω are mainly controlled by biological processes.

5 Summary and conclusions

Spatial distribution of Ω in bottom water of the Chukchi Sea was observed in autumn 2012 and early summer 2013. Both aragonite and calcite undersaturation was observed in highly productive regions, including Hope Valley, but only in 2012. Comparison with AOU, T and S showed that organic matter remineralization is the major factor to lower Ω of bottom water in the Chukchi Sea, with minor but significant control of T and S .

Mooring observations of AOU, T and S for 2 years in Hope Valley (Nishino et al., 2016) showed that our ship-based observations captured conditions under the very strong influence of remineralization in autumn 2012, and under an influence of photosynthesis in early summer 2013. This explains the large difference in Ω between the two cruises.

Using cruise observations, we have obtained empirical equations to reconstruct Ω from data of T , S and AOU and applied them to 2-year-round mooring data in Hope Valley. Reconstructed variation of Ω in bottom water suggested frequent undersaturation for both aragonite and calcite, not only in 2012, but also in 2013. The period of aragonite undersaturation could be more than 7.5 months (60%) of a year. Such frequent aragonite undersaturation may be harmful for benthic calcifiers who rely on planktonic early life stages with shells composed of aragonite. Calculations suggest that bottom water in the biological hotspot could have been subject to aragonite undersaturation on an intermittent basis even in the pre-industrial period. It was also suggested that anthropogenic CO₂ has significantly extended the period of aragonite undersaturation to more than 2-fold longer by now. With increased atmospheric $p\text{CO}_2$, the period of aragonite undersaturation will extend further. Clearly, anthropogenic CO₂ has a significant impact on the duration of CaCO₃ undersaturation in the bottom water even though seasonal and interannual variations in Ω are controlled by biological processes. We should note that this study is the first attempt to reconstruct the seasonal variation of Ω using a method that has not been confirmed to work in Arctic shelf seas, where seasonal changes in biological activity are extremely large. Direct observation of carbonate parameters in winter by using sensors or water samplers is desired to confirm our results.

It has been revealed that CaCO₃ undersaturation has negative impacts on calcifying organisms (e.g., Kroeker et al., 2013). Therefore, continuous occurrence of undersaturation since the pre-industrial period in the southern Chukchi Sea is not consistent with the fact that bivalves are dominant in the benthic community in this area (Grebmeier, 2012; Grebmeier et al., 2015). In fact, when we collected benthic organisms by using a dredge during the cruise of T/S *Oshoro-maru* in 2013, many bivalves were found in the Hope Valley hotspot area, both well-grown adults and small young individuals (Fig. 1). This may suggest tolerance of these bivalves to CaCO₃ undersaturation with protection mechanisms such as an external organic layer (Ries et al., 2009), companion of the energetic

cost of calcification by abundant supply of food (Wood et al., 2008), migration, or mismatch in timing of their planktonic and settling stages and occurrence of CaCO₃ undersaturation in surrounding water. With rapidly increasing anthropogenic CO₂ in recent and future years, quantification of the responses of local calcifying organisms to low Ω is an urgent issue for future study. The Chukchi Sea, already undergoing CaCO₃ undersaturation, should provide a research field to assess vulnerability and resilience of organisms to ocean acidification, or to find direct evidence of consequences of ocean acidification in Arctic seas.

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