Reply to comments of Reviewer #1, Professor Lee Cooper

We would like to thank Professor Lee Cooper for a thorough review of this paper. We have addressed all comments and suggestions. Please find our responses below

I have more misgivings about the extension of using the moored data and apparent correlations developed between AOU and ocean acidification to estimate undersaturation of calcite minerals over the course of the year. While I am not surprised that undersaturation is probably common due to mineralization and high productivity, the conclusions are based upon the assumption that oxygen utilization continues at fairly constant rates over the winter, and I think the small published set of sediment oxygen utilization measurements available from arctic shelves does not strongly support this assumption. Only one study (Devol et al. 1997) is cited to support this assumption, and it sampled in the winter in unproductive waters much different from the moored site.

--We agree that we need to discuss more about the winter AOU and its correlation to our reconstruction of $CaCO_3$ saturation state. A relatively constant positive AOU (~50 μmol kg^{-1}) was observed over the winter for two years. As mentioned in the text, same level of AOU was also found in the hypersaline water that is formed in contact with atmosphere. This suggests that positive AOU in winter bottom water is not due to insufficient gas exchange but oxygen consumption. Although there is no year-round observation of sediment oxygen uptake in southern Chukchi Sea, it is known that oxygen uptake rate has a seasonal variation and is low in winter prior to initiation of biological production in spring. Previous studies in other Arctic waters have observed that sediment oxygen uptake rate in winter is not zero but is about half of that in summer in 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 Canadian high Arctic (Welch et al., 1997). Winter AOU observed by moored sensor in our study was about 1/3 ~ 1/2 of autumn AOU. Therefore, we presume that the positive AOU in bottom water during winter can be explained by continued sediment oxygen uptake. Discussions on this have been included in the revised text as follows:

(p7, line 2-) "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 a l., 1998; Grant et al., 2002; Clough et al., 2005). Accordingly, 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, winter sediment oxygen uptake rate is not zero but is about half of that in summer in 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 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.

(p9, line 14-)" 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 remineralization quotient of DO and DIC is held relatively constant over the course of the year as observed in Young Sound (ΔDIC/ΔDO = 0.8~1.1, Rysgaard et al., 1998), the summer/autumn relationship between DIC (and TA) and T, S, 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."

The moored data used (Nishino et al. 2016) also had to be managed—corrections undertaken for AOU data that were corrected because of apparent issues with the data that are mentioned in Nishino et al. 2016.

--We have carefully checked data and calculations and found that there was a mistake in unit conversion (from saturation % to μmol/kg) in Nishino et al. (2016) for the 3rd set of mooring data. This was the cause of the large difference of 69 μmol/kg between bottle and sensor measurements mentioned in their paper. With correct unit conversion, the difference was only 4 μmol/kg. In our original manuscript, we did not use calculations by Nishino et al. (2016) and used data correctly converted from original sensor output. Therefore, this mistake does not affect our results. This issue is now mentioned in the text to not cause same concern to readers:

(p4, line 17-) "Note that a correction of -69 μmol 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 μmol kg^{-1}. With correct conversion, the difference between sensor data and bottle data obtained on 1 September 2013 was reduced from 69 μmol kg^{-1} to 4 μmol kg^{-1}. Accordingly, we did not apply any correction to DO sensor data in the present paper."

Finally, the use of this correlation method for estimating calcium carbonate dissolution potential was initially demonstrated in California and Oregon, so it really hasn't been confirmed to work in the Arctic where there are much more extreme seasonal changes in biological activity.

--Our study is the first attempt to use this method to highly productive Arctic shelf sea. We agree that this should be confirmed in the future by using direct observations of carbonate parameters throughout the year. We have noted this in the revised text to read:

(p11, line 30-) "We should note that this study is the first attempt to reconstruct 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 sampler is desired to confirm our results.

The authors defend their approach by stating that their shipboard sampling bracketed both high productivity in July and high oxygen utilization in October although my examination of the Nishino et al 2016 results suggest that sampling in July may have missed the highest primary productivity.

--We agree that the maximum chlorophyll a was observed in May/June. However, our two shipboard samplings were made in two different period with high and low DO conditions. To be more accurate, text has been modified from "ship-based observations captured both higher and lower ends of seasonal variation in DO" to (p6, line 14-) "ship-based observations were made when DO was at higher and lower parts of seasonal variation", from "our ship-based observations in autumn 2012 and summer 2013 have captured the lowest and the highest Ω periods, respectively." to (p9, line 7-) "our ship-based observations in autumn 2012 and summer 2013 have captured low and high Ω periods, respectively."

I don't think this is necessarily a flawed paper because the available evidence suggests that widespread undersaturation with respect to carbonate minerals on productive arctic shelves is probably correct, but I don't think the evidence provided here is strongly convincing either.

--We have revised the manuscript to describe results in an honest manner. Sentences have been changed to be more exact and fair, for example, "bottom water was kept at aragonite undersaturation for most of the winter" was changed to "Ω in bottom water was kept low during winter" and "intermittent undersaturation was found" was changed to "intermittent undersaturation was suggested".

The title was also change from "prolonged undersaturation…" to "Seasonal variation of $CaCO_3$ saturation state in bottom water of a biological hotspot in the Chukchi Sea, Arctic Ocean".

We hope the revised manuscript will meet the requirements for publication.

The manuscript is also unevenly written, and would benefit from efforts of a native English language editor. A number of mistakes in spelling, in the references, and even in the spelling of the author names suggest a hasty assembly of the manuscript. I have provided some editing suggestions below and posed a few additional questions and concerns, but this is not a comprehensive editing effort.

--We are sorry that we have submitted the manuscript with many typographical errors and really appreciate your kind editing. We will ask an English Language Service to edit our revised manuscript when it is accepted for publication.

Page 2: Line 25. I don't follow why the reference to Talmange and Gobler, 2009 needs to be made here. This reference has already been made (prior page, Line 29) to document larval stage vulnerability, although that reference is about non-polar invertebrates. The statement and reference repeated here is redundant

--The reference has been removed. The sentence has been modified to read (p2, line 10-) "Because many benthic organisms have planktonic larval stages, timing and duration of $CaCO_3$ can be critical for their growth and populations".

Page 5: Line 27-30. Most of the published data for sediment oxygen utilization rates for the northern Bering and Chukchi seas indicates that there is significant seasonal variation and it is lower in the late winter prior to initiation of the sea ice edge bloom. I think the Devol et al. paper is dubious to cite here because the winter sampling was done in nutrient-poor, near-shore waters that do not have high AOU at any time of year.

--See response to the first comment above.

Page 8. Line 16. This really isn't a complete sentence.

--The text has been changed as follows:

(p 10, line 9-) "In order to roughly quantify the effect of anthropogenic CO2 on timing and duration of CaCO3 undersaturation in our 2-year time series of Ω, we have estimated Ω in two cases: 1) preindustrial period case with atmospheric partial pressure of CO2 (pCO2) of 280ppm, and 2) future case with pCO2 of 650 ppm. Following previous studies (Gruber et al., 1996; Sabine et al., 1999; Yamamoto-Kawai et al., 2013; 2015), DIC concentration in year t is expressed as: DICt = DICEQt-0 + (Δdiseq + Δbio), where…".

Page 9. Line 6-7. The sentence is not grammatically correct and I am not sure what the authors are trying to say.

--The sentence has been deleted.

Page 9. Line 25. Change "to" to "from"

--We could not find "to" in this line and are not sure where the reviewer found this error. This will be corrected when we have the professional English editing.

Page 9. Lines 27-29. The Nishino et al. 2016 paper appears to show that the maximum chlorophyll a bloom can occur prior to July, so the early summer sampling may not have successfully sampled the most productive period.

--We agree that chlorophyll a was highest in June, though it is still high in July. The text has been changed from "under photosynthesis in early summer 2013" to (p11, line 19-) "under an influence of photosynthesis".

All of following have been changed as suggested.

Page 1: Line 3. I think Dr. Nishino's name is misspelled.

Page 1: Line 26. Change "to affect" to "which affects"

Page 2: Line 3. Salisbury et al. reference misspelled.

Page 2: Line 7. Change "Nutrients. . ..is carried" to "Nutrients. . ..are carried"

Page 2: Line 8. Change "making the sea to have very high primary productivity" to "promoting very high primary productivity"

Page 2: Line 9. Add the article "A" before "proportion"

Page 2: Line 14. Change spices to species

Page 2: Line 22. Lower case 3 needed for calcium carbonate molecular symbol.

Page 2: Line 24. Change "difficulties in" to "the lack of"

Page 3: line 2. Change was to were

Page 3: line 15. "the" before maintenance not necessary

Page 3: line 27. Delete "that" and change "is" to "as"

Page 3: Line 29. Insert a "the" before "two visits"

Page 4: Line 10. Change "kept at near" to "remained at a near"

Page 5: Line 23. Change kept to remained

Page 5: Line 31. Change captured to sampled

Page 6: Line 26. Change "in" to "to a"

Page 7: Line 15. Remove "of" The sentence would also read better if it starts with the article "the"

Page 7: Line 25. Suggest should be suggests.

Page 7: Line 28. Devol reference should be 1997, not 1996.

Page 7: Line 30 persisted should be persistent.

Page 8. Line 31. Change "process" to "processes" and "is" to "are"

Page 9. Line 1. Change is to are

Page 9. Line 2. Add "the" between that and primary production.

Page 9. Line 3. There is a Grebmeier, 2012 reference in the literature cited, but not a Grebmeier et al. 2012.

Page 9. Line 9. Change "even with half productivity than today" to "even with half the productivity occurring today"

Page 9. Line 15. Change "it is indicated" to "it suggests"

Page 9. Line 16. Change "occupation" to "the proportion of"

Page 9. Line 17. Change "occupies" to "increases to"

Page 9. Line 18. Change These to This and indicate to indicates; add the article "a" has and significant.

Page 9. Line 22. I suggest changing Horizontal to Spatial

Page 9. Line 26. The mooring observations are presented in Nishino et al. 2016, so I think it is more accurate to state that the authors used the data from Nishino et al. 2016 to estimate calcium carbonate undersaturation.

Page 9. Line 33. Change "Occupation of calcite" to "The period of calcite"

Page 10, Line 2. Insert "subject to" between "been" and "aragonite"

Page 10. Line 5. Change two-hold to two-fold; change "occupation" to "the period of"

Page 10. Line 6. Change "year-long occupation under highly stratified condition.

Occupation. . .” to “year-round periods under highly stratified conditions. Periods of”

Page 10. Line 8. I suggest changing “surely” to “clearly”. It is less colloquial and more specific

Page 10. Line 10. Kroeker’s name is misspelled.

Page 10. Line 12. Change “may be conflicting the fact” to “is not consistent with the fact”

Page 10. Line 29. Since there was no formal presentation of oxygen isotope data, I don’t think an acknowledgement is necessary.

Page 12. Line 17. Global Change Boil should be Global Change Biol

Page 13, line 25. Raven reference is not in alphabetical order.

Figure 1. The arrows identifying the mooring sites are not clear.

Figure 8 caption. Corrected should be collected. Also trawl is misspelled.

~~Prolonged aragonite undersaturation~~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 ~~bottom waters of~~ 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 were 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 factor controlling 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 two-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. ~~Results showed prolonged undersaturation for both aragonite~~Estimated Ω was high in spring and ~~calcite even during~~ early summer, decreased in later summer, and remained relatively low in winter~~ period, not only in 2012 but also in 2013.~~. Calculations ~~also suggest~~indicated a possibility that bottom water~~ in the hotspot~~ 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 two~~ or three~~-fold longer by now.~~ When atmospheric pCO_2 increases to 650 ppm, occupation of aragonite and calcite undersaturation can be as long as two third and one third of a year, respectively. Anthropogenic CO_2 has significant impact on duration of $CaCO_3$ undersaturation in the bottom water of the Chukchi Sea, even though horizontal and seasonal variability in Ω is controlled by biological processes.~~

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., ~~The Royal Society,~~Raven et al., 2005; Orr et al., 2005). Increasing acidity and consequent changes in seawater chemistry are expected to impact marine ecosystem and may threaten some organisms (e.g., Gattuso and Hansson 2011; Branch et al. 2013). Of particular concern is the impact ~~of ocean acidification~~ on calcifying organisms, such as coralline algae, pteropods, bivalves, corals etc., because acidification lowers the saturation state (Ω) of calcium carbonate ($CaCO_3$) in seawater ~~to affect~~which affects the ability of these organisms to produce and maintain their shells or skeletons~~ (e.g., Kroeker~~

~~et al. 2013 and references therein).~~. In fact, a decrease in Ω of ~~bottom~~ 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 (~~Sulisbury~~Salisbury, 2008; Yamamoto-Kawai et al., 2011), and respiration at the bottom of 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 exhibits 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.

~~The Chukchi Sea is a vast and shallow shelf sea north of the Bering Strait. Nutrients upwelled onto the Bering shelf is carried by northward flowing Pacific-origin water to the Chukchi Sea, making the sea to have very high primary productivity (e.g., Springer and McRoy, 1993). Large proportion of produced organic matter is directly delivered to the seabed, due to shallow bottom depth and mismatch between seasonal dynamics of phytoplankton and zooplankton (e.g., Grebmeier et al., 2006). Exported organic matter is remineralized back to CO_2 at depth and lowers Ω of bottom water (e.g., Bates et al., 2009). At the same time, high export rate of organic matter supports very high benthic biomass that are prey for higher trophic levels such as diving ducks, seals, whales and walruses (Grebmeier et al., 2006; Fabry et al., 2009). Because calcifying bivalves, amphipods, brittle stars and crabs are dominant spices in benthic community of the Chukchi Sea (Fabry et al.,2009; Blanchard et al., 2013), they are key component of the ecosystem. Ocean acidification, therefore, could have considerable impacts on the ecosystem and biogeochemical cycles of the Chukchi Sea. In addition, because of shallow bottom depth of ~50 m, anthropogenic CO_2 can immediately penetrate into bottom water to which benthos are exposed.~~

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 ~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 communities in large areas of this shelf sea has 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 ~~difficulties in~~the lack of shipboard observations during ice-covered months. Because many ~~organisms may be more vulnerable during early development stages and many~~ benthic organisms have planktonic larval stages ~~(e.g., Talmange and Gobler, 2009),~~, timing and duration of $CaCO_3$ can be critical for their growth and populations.

In the present paper, we show ~~distribution of Ω in bottom water of the Chukchi Sea~~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% in the end of May and ~~discuss factors~~ to <30% in the beginning of June. Therefore, observations were carried out about 3 months and 1 months 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 ~~observations~~results, we attempt to reconstruct seasonal variations of Ω in the bottom water in the southern Chukchi Sea by using data from a two-year-round mooring observation between July 2012 and July 2014~~ in Hope Valley,~~.

2 Study Area

The Chukchi Sea is a ~~biological "hotspot" in the southern Chukchi Sea (~~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 a year. Pacific-origin water enters through the Bering Strait and distributes 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 whole water column and modifies the water to be "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 are 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 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 the result, high export rate of organic matter supports very high benthic biomass that are prey for higher trophic levels such as diving ducks, seals, whales and walruses (Grebmeier et al., 2006; Fabry et al., 2009).~~; Nishino et al., 2016)~~.

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., 2009). ~~Because c~~Calcifying bivalves (Fig. 1), amphipods, brittle stars and crabs are dominant spices in benthic community of the Chukchi Sea (Fabry et al.,2009; Blanchard et al., 2013) and are key component of the ecosystem. Ocean acidification, therefore, could have considerable impacts on the ecosystem and biogeochemical cycles of the Chukchi Sea. ~~2~~In addition, because of 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 Marin-Earth Science and Technology (JAMSTEC) from 13 September to 4 October in 2012 (Kikuchi et al., 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 bottom depth shallower than 70 m. During both cruises, hydrographic casts ~~was~~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 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-Maru. ~~DIC from both cruises were analyzed~~Intercomparison of two method in a previous study (Li et al., 2013) showed good agreement of 0.88±2.03 μmol kg^{-1}. Also, S-TA relationship between two cruises did not show any obvious offset (Fig. 2). DIC from both cruises were analysed using a coulometer system. Measurements of TA and DIC were calibrated against a certified reference material distributed by A. G. Dickson at Scripps Institute of Oceanography, USA, or General Environmental Technos Co~~.~~., Japan. The pooled standard deviation (Sp) for duplicate samples was < 2.2 μmol kg^{-1} and < 5.5 μmol kg^{-1} for TA and DIC, respectively. Observations of TA, DIC, nutrients, T, S and pressure were used to calculate Ω for aragonite (Ωar) or calcite (Ωca) and ~~pCO_2 (partial pressure~~fCO_2 (fugacity of CO_2) by using the CO2sys program (Lewis and Wallace, 1998) with constants of ~~Lucker~~Mehrbach et al. ~~(2000~~(1973) refit by Dickson and Millero (1987) for K1 and K2 and Dickson (1990) for KSO_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 K1 and K2 constants will give lower Ω than using other constants. The maximum difference of 0.07 in Ωar was estimated in their study in the Canadian Arctic Archipelago and in 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 set of K1 and K2 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 μmol kg^{-1}. Nutrient samples were analysed according to the GO-SHIP Repeat Hydrography Manual (Hydes et al., 2010) with precision of <0.1 μmol kg^{-1} for nitrate, nitrite and phosphate, <0.6 μmol kg^{-1} for silicate, and <0.4 μmol kg^{-1} for ammonium. Cumulative analytical errors in TA, DIC, phosphate and silicate can cause a maximum error of 0.08 in Ωar and 0.13 in Ωca.

A mooring system was deployed in Hope Valley from 16 July 2012 to 19 July 2014. The system was first deployed at 67º 42'N, 168º 50'W from 16 July 2012 to 2 October 2012, and then moved slightly to the north at 68º 02'N, 168º 50'W on 3 October 2012. On 20 July 2013, the system was recovered for ~~the~~ 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 from the bottom. Data were recorded every hour. ~~Details of~~T and S data were acquired using a MicroCAT C-T recorder, SBE 37-SM (Sea-Bird Electronics, USA). Maximum drift in sensors over 1 year were 0.002 ºC for T and 0.01 for S in pre- and post-calibration comparisons (Nishino et al., 2016). 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 μmol 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 μmol kg^{-1}. With correct conversion, the difference between sensor data and bottle data obtained on 1 September 2013 was reduced from 69 μmol kg^{-1} to 4 μmol 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).

34 Results and discussions

34.1 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 (Ωar < 1; black circles in Fig. 1) was observed at stations off Pt. Barrow, in Hope Valley, in Bering Strait, and near the northern continental slope. The lowest Ωar was observed on 3 October 2012 in Hope Valley at 68ºN, in the dome-like structure of bottom water with low T, high S and low DO (Fig. 2; Nishino et al., 2016).) with high TA, high DIC and high fCO_2 (Fig. 3). Calcite undersaturation was also found in this dome in Hope Valley (Figs. 1b1 and 23). Nishino et al. (2016) describe that the dome-like structure isas 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 difference 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 summer 2013,2013, Ω in bottom water was 1.1~2.8 for aragonite and 1.7~4.4 for calcite: all of observed waters were oversaturated with respect to aragonite and calcite (Figs. 1c1 and 1c4). Although stations in Hope Valley again showed thea dome-like feature with lowin T and low, DO, and fCO_2, they were not as prominent as in 2012 (Fig. 24). Ω in bottom waters at these stations were slightly lower than stations north or south but still well oversaturated with respect to $CaCO_3$ (Ωar =1.7 ~1.9; Ωca =2.8 ~3.0). Waters with lower Ωar of 1.1~1.2 and Ωca of 1.8 ~1.9 were found in northern stations at around 71ºN where T and DO were also lower and fCO_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. Figure 3 shows Relationships between Ωar and T, S or apparent oxygen utilization (AOU; difference between saturation and observed concentrations of DO).) are shown in Fig. 5. Ωar showed the highest correlation with AOU and data from two cruises were distributed on a line in the Ωar-AOU diagram (Fig. 35). AOU is a measure of how much oxygen has been consumed by respiration and decomposition of organic matter in the water column. Accordingly, high AOU corresponds to high $pCO_2$$fCO_2$ (Fig. 6) and therefore low Ω. (Fig. 5). Negative AOU value is a sign of photosynthesis which produces DO and, consumes CO_2 toand increases Ω. As shown in Fig. 6, biogeochemical conditions between two ship-based observations were different: autumn 2012 was under very strong influence of remineralization whereas summer 2013 was influenced of photosynthesis in early summer 2013.

Ωar increased with increasing T and ~~regression~~ their relationships~~lines~~ for two cruises were similar in slope but different in intercept (Fig. ~~3~~5). Ωar also increased with decreasing S in bottom waters, whereas Ωar decreased with decreasing S in upper waters (Fig. ~~3~~5). The latter is explained by mixing with freshwater, which lowers calcium ion concentration and alkalinity to decrease Ωar as indicated by previous studies (Salisbury et al., 2008; Yamamoto-Kawai et al., 2009). In fact, aragonite undersaturation were observed in very low S surface waters in 2012 (Fig. ~~3~~5). The opposite relationship in bottom waters is probably because higher bottom S creates stronger stratification of water column that prevent release of CO_2 produced by respiration at depth. These results show that variations in Ω in the Chukchi Sea bottom water is controlled largely by organic matter remineralization with minor contributions of T and S. ~~This is consistent with previous studies that have pointed out the importance of high primary production and remineralization of exported organic matter to induce undersaturation of $CaCO_3$ in bottom waters of the Chukchi Sea (Bates et al., 2009; 2013; Bates, 2015).~~ 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, 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. ~~2~~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 unusual year with strong stratification, due to an input of sea ice meltwater, and with remarkably low DO concentration at depth. ~~Stronger~~Strong stratification ~~should prevent~~prevents ventilation and ~~accumulate~~accumulates more CO_2 in the bottom water. This explains high AOU, high fCO_2 and low Ω in bottom water in autumn 2012 (Fig. ~~2~~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. ~~3~~5) might be due to low photosynthetic activity associated with stronger stratification and to mixing with sea ice meltwater (~~Nishion~~Nishino et al., 2016). In addition, input of sea ice meltwater itself lowered Ω in surface waters in 2012 as evident in Fig. ~~3b~~5. The fact that ranges of T and S for bottom waters were not significantly different between two cruises (Fig. ~~3~~5) indicates that the accumulation of more CO_2 produced by respiration was the major cause of the much lower Ωar in autumn 2012 than summer 2013.

~~3~~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. ~~4~~7). Ship-based observations were made near the mooring site (~68ºN) on 14 September 2012, 3 October 2012 and 16 July 2013 and ~~agreed well~~a comparison with sensor data~~.~~ is summarized in Table 1, together with observations on 1 September 2013 by Nishino et al. (2016). 24-hr 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 of relatively large differences found in all T, S and DO data on 15 July 2013 when ship-based observation was made 31 km away from the mooring site. Other than this, two observations agreed within 0.2 °C in T, 0.15 in S and 11 μmol kg^{-1} in DO.

T, S and DO (AOU) ranged from -1.92 to 2.~~-~~73 °C, 30.41 to 35.49, and 62.~~66~~ 7 to 416.~~39~~ 4 (-32.~~66~~ 7 to 294.9~~2),~~) μmol kg^{-1}, respectively. Note that ship-based observations ~~captured~~were made when DO was at ~~both~~ higher and lower ~~ends~~parts of seasonal variation~~ in DO~~. During summer/autumn months, T, S and DO showed large ~~and high frequent variability~~fluctuations. Because all three parameters changed simultaneously, this is likely due to changes in 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 summer/autumn months, decreased from October to December due to atmospheric cooling, and ~~kept~~remained at a near freezing temperature (~ -1.8 °C) from January to May. Summer/autumn T was lower in 2012 than in 2013. Stronger stratification of 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. 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 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 water mass from active ice formation area, such as coastal polynya region where brine rejection from freezing seawater increases S of bottom water to form “hypersaline water” (Weingartner et al., 1998). Such event was not observed in the following winter.

DO increased and reached supersaturation (negative AOU) in May and June (Fig. ~~4~~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 μmol kg^{-1} in July to ~125 μmol kg^{-1} in September 2012 and to ~225 μmol kg^{-1} in September 2013 (Fig. ~~4~~7). DO was ~~kept~~remained low until the onset of winter convection in October/November. As mentioned in the previous section, DO in bottom water was unusually low in autumn 2012, due to strong stratification that prevented ventilation of bottom water. During winter, DO was relatively stable at ~325 μmol kg^{-1}. This concentration corresponds to ~~~50~~60 μmol kg^{-1} in AOU and ~85 % in saturation level~~, indicating undersaturation of DO during winter~~ even in the hypersaline water that is formed in contact with atmosphere. This suggests that positive AOU (DO undersaturation) in winter ~~bottom water~~ is not due to insufficient gas exchange~~, but to continued consumption of~~. Continued sediment oxygen ~~by benthic organisms during winter. In fact, Devol et al. (1997) reported~~uptake is a possible reason for the undersaturation. Previous studies in shallow Arctic seas have found that ~~benthic~~sediment oxygen ~~consumption~~uptake rate ~~in winter was~~ is regulated by the availability of organic matter and macrofaunal biomass (Grebmeier and McRoy, 1989; Rysgaard et a l., 1998; Grant et al., 2002; Clough et al., 2005). Accordingly, 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, winter sediment oxygen uptake rate is not zero but is about half of ~~or comparable to~~ that in summer in 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 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~~s~~ in summer 2013 ~~captured~~sampled bottom water that was under ~~the~~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~~ar~~ in bottom water between two ship-based observations in September/October 2012 and July 2013.

~~3~~4.3 Regression analysis

Based on ship-based and mooring observations, we try to reconstruct 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 (Juranek 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-time scales (Juranek 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 cruses 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 solubility of $CaCO_3$ (Mucci, 1983; Millero 1995).

DIC is controlled by physical (solubility and gas exchange) and biological processes (photosynthesis and respiration) and therefore is 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 increase both S and TA of the underlying water). A bloom of calcifying primary producer can cause a drawdown of TA (Murata and Takizawa, 2002). However, neither bloom of calcifies nor TA drawdown in S-TA diagram was observed during our observations (Fig. 2). Mixing between sea water 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 ~~(not shown)~~ but only in surface waters with S < 31~~.~~ (Fig. 2). Accordingly, we used T, S and AOU to estimate DIC (DICest) and S to estimate TA (TAest) only for waters with S>31.

~~The best predictions~~ Regression equations obtained for DIC and TA ~~(DICest and TAest) were obtained when all three parameters were used:~~ are:

DICest = 1.06 × AOU - 17.03 × T + 41.54 × S + 743.94 (r^2=0.96, RMSE=24.46, n=184) ~~and TAest = 0.04 × AOU − 4.24 × T + 45.34 × S + 760.35 (r^2=0.85, RMSE=13.13, n=184). However, because warming or cooling do not directly alter TA, observed correlation between TA and T should reflect characteristics of different water masses. Thus this relationship may not hold for other seasons in this shallow shelf sea where cooling or warming can significantly change T in the bottom water without changing TA. For estimation of TA, therefore, we decided to use a regression equation only with S:~~ (1)

and

TAest = 59.23 × S + 370.34 (r^2=0.83, RMSE=14.03, n=184~~).~~) (2).

Although biological activities can change TA ~~in~~to a small extent by adding or removing nitrate or ammonium, the inclusion of AOU did not ~~significantly~~ improve the regression model (r^2=0.83, 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 5a~~Fig.8a shows a ~~good~~ linear correlation between observations (Ωobs) and estimations (Ωest) with r^2 =0.94 for aragonite (r^2 =0.94 calcite, not shown). Larger differences between two values were found in surface waters with Ωest values higher than 2.5 for aragonite and 4.0 for calcite~~.~~ (Fig. 8a) and with high temperature (>6°C). This might be due to rapid warming at the surface that could cause temporal decoupling of oxygen and carbon because of differences in temperature dependence of solubility and in gas exchange rate. Including these samples, RMSE was 0.17 for Ωar and 0.~~28~~27 for Ωca (n = 184)(Figure 8a).

In order to evaluate ~~obtained~~the regression equations~~,~~ (1) and (2), we have applied ~~the same equations~~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 Japan Agency for Marine-Earth science and Technology (JAMSTEC). These cruise observations were carried out in August, September or October. ~~Total 127 samples with S > 31 and with observations of DIC and TA were found in the~~In our study area (latitude> 66°N, bottom depth < 70 m~~).~~), total 127 set of discrete bottle sample data of DIC, TA and DO, together with sensor data of T and S (>31)were found. For each dataset, we have calculated DICest and TAest from T, S and AOU using the equations (1) and (2). AOU was calculated from discrete bottle DO data. DICest and TAest agreed with observed bottle data of DIC and TA with r^2=0.96 and 0.83, respectively. Ω calculated from DICest and TAest (Ωest) was ~~well~~ correlated with observed Ω (Ωobs) with a regression equation of Ωarest = 1.15 × Ωarobs - 0.~~04~~06 (r^2 = 0.~~77~~78, RMSE=0.36, Fig. ~~5b~~8b) and Ωcaest = 1.14 × Ωcaobs - 0.06 (r^2 = 0.~~77~~78, RMSE=0.57). ~~These RMSE values were regarded as~~ We regard RMSEs estimated in this evaluation represent cumulative errors in ~~reconstructed Ω~~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 K1and K2 constants as mentioned in section 3 should be considered. Therefore, we present Ωest with a range of ±RMSE+0.09 for aragonite and ±RMSE+0.14 for calcite in the following section~~.~~ (-0.36 to +0.45 for Ωarest and -0.57 to +0.71 for Ωcaest).

Cross et al. (2013) pointed out the possibility of shallow-water $CaCO_3$ mineral dissolution, which could cause an increase in TA by 36 umol 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 ratio of water ($\delta^{18}O$) 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 $\delta^{18}O$ as shown in Yamamoto-Kawai et al. (2005), rather than with Ω of the water. Therefore, we consider that effect of mineral dissolution is insignificant in waters discussed in our analysis.

~~3~~

4.4 Seasonal variation of Ω in Hope Valley bottom water

Based on the analysis in the section 4.3~~.3.,~~, the regression equations ~~for DIC and TA~~ were applied to the mooring data in Hope Valley~~, a biological hotspot in the Chukchi Sea. Waters~~ (excluding data with S < 31 ~~were~~observed intermittently ~~observed~~ between 8 and 21 November 2013~~ and excluded from the analysis. Reconstructed variation of~~).

The reconstructed Ω is shown in Fig. ~~6~~9 with ~~±~~range of -0.36 and +0.45 for aragonite, and ~~±~~ -0.57 and +0.71 for calcite. For the whole period, Ωest ranged from 0.2 to 2.1 for aragonite and from 0.3 to 3.4 for calcite (Fig. ~~6~~9). It was shown that our ship-based observations in autumn 2012 and summer 2013 have captured ~~the lowest~~low and ~~the highest~~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 ~~autumn 2012,~~ the unusually stratified ~~year~~autumn 2012, bottom water Ω was ~0.3 for aragonite and ~0.5 for calcite. ~~The lowest value of 0.2 and 0.3, respectively, was found on 27 November. In autumn~~In 2013, Ω ~~was higher than in 2012 but was still below 1 for~~decreased after our ship-based observation in July, and intermittent aragonite ~~for most of the days~~undersaturation was predicted in August, September and October~~.~~, although Ω was higher than in same months in 2012. At the beginning of cooling and convection period in November/December 2012 and October/November 2013, ventilation of bottom water increased DO and Ω. Then, ~~bottom water was kept at aragonite undersaturation for most of the winter until the start of photosynthesis in May. Even during spring and early summer months, intermittent undersaturation was found, showing~~Ω in bottom water was 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 remineralization quotient of DO and DIC is held relatively constant over the course of the year as observed in Young Sound (ΔDIC/ΔDO = 0.8~1.1, Rysgaard et al., 1998), the summer/autumn relationship between DIC (and TA) and T, S, 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 ~~suggest~~suggests that ~~undersaturation occurs not only at the mooring site in~~ low Ω is a ~~hotspot but also in surrounding areas~~widespread feature during winter. ~~Relatively low Ω in winter is likely due to continued respiration and organic matter decomposition by benthic organisms during winter (Devol et al., 1996) as suggested by positive AOU.~~ An exception is the hypersaline water that could have high calcium ion ~~concentrations~~concentration and 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.

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

reported ~~persisted~~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 of 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 Ωar and reported that bottom water became partially undersaturated in September and broadly undersaturated in October in 2010, with a lowest Ωar 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, ~~total hours~~integrated period of aragonite undersaturation was counted to be ~~6258 hours and 5320 hours, respectively. These corresponds to 261 days, 8.5~~ 8.6 months ~~or 71 % of a year~~ for the first year, and ~~221 days,~~ 7.5~~3~~ months ~~or 61 % of a year~~ for the second year. For calcite, undersaturation was not as frequent as aragonite (Fig. ~~6~~9) but ~~found~~suggested not only for ~~the unusual~~ autumn 2012 but also in 2013 on an intermittent basis. ~~Total hours~~Integrated period of calcite undersaturation was ~~2252 hours (94 days, 3~~3.1 months and 0.8 months~~, 26 % of a year) and 545 hours (23 days, 0.7 month and 6 % of a year)~~ for 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 ~~2~~3), total ~~hours~~time of undersaturation estimated here is likely at a maximum within the Chukchi Sea.

~~3~~4.5 Anthropogenic impact on Ω

In order to roughly quantify the effect of anthropogenic CO_2 on timing and duration of $CaCO_3$ undersaturation in our 2-year time series of Ω, we have ~~followed~~estimated Ω in two cases: 1) preindustrial period case with atmospheric partial pressure of CO_2 (pCO_2) of 280 ppm, and 2) future case with pCO_2 of 650 ppm. Following previous studies (Gruber et al., 1996; Sabine et al., 1999; Yamamoto-Kawai et al., 2013; 2015~~).~~), DIC concentration ~~observed~~ in a year t~~-obs can be~~ is expressed as:

DICt~~-obs~~ = DICEQt-0 + (Δdiseq + Δbio~~)~~),

where DICEQt-0 is DIC of seawater in equilibrium with the atmospheric CO_2 in the year t-0 when the water parcel was last in contact with the atmosphere, Δdiseq and Δbio represents air-sea equilibrium at the surface and change in DIC due to biological activity. In case of the shallow Chukchi Sea shelf, t-0 can be assumed to be the observed year (t-obs) and therefore the sum of the last two terms can be calculated by comparing ~~observed~~ DIC and DICEQ for the year t-obs. In ~~calculating~~this study, we used DICest calculated using equation (1) with mooring data as DIC in the year t-obs. For calculation of DICEQt-0, we have used pCO_2 of 380 ppm, with TAest, T and S from mooring data. Then, assuming that Δdiseq and Δbio do not change with time, DIC in any year t can be estimated by using atmospheric pCO_2 at the year t. We have estimated Ω with DICt for the pre-industrial period when pCO_2 was 280 ppm, and for ~~the year 2066, 50 years after the present~~future when pCO_2 reaches 650 ppm (50 years later in the high CO_2 emission scenario (RCP8.5~~, Riahi et al., 2011~~), and end of the century in a moderate scenario (RCP6) (IPCC, 2013).

~~Figure 7~~Fig. 10 shows time-series of Ω for ~~the case of pre-industrial period and that of 50 years later at the mooring site.~~two cases. For the ~~former~~preindustrial case, Ω ranged from 0.2 to 2.6 for aragonite and from 0.4 to 4.1 for calcite. For the ~~latter~~future

case, Ω ranged from 0.2 to 1.5 for aragonite and from 0.2 to 2.4 for calcite. Caveat here is that our calculation is based on an assumption that terms Δdiseq and Δbio have not changed since pre-industrial period~~.~~, and therefore provides only very rough estimates. As biological ~~process is~~processes are the major factor changing DIC in bottom water, changes in Δbio can cause significant error in estimated Ω for the past and the future. For example, if biological production and subsequent remineralization at depth is lower in the past or in the future, Ω should be higher than shown in Fig. ~~7~~10. At the moment, unfortunately, trends in productivity in the southern Chukchi Sea ~~is~~are still under debate. Lee et al. (2007) and Yun et al.~~,~~ (2014) show that the primary production rate in recent years are lower than previous estimates made in 1990s. From chlorophyll a analysis, Grebmeier ~~et al.~~ (2012) and Arrigo and van Dijken (2011) have suggested an increase in primary productivity in 2000s in the Chukchi Sea. Grebmeier et al. (2015) also showed an increase in benthic biomass from 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 pre-industrial case with (Δdiseq + Δbio) term half of that at present. ~~Because Δdiseq should be much smaller than Δbio in our highly productive study area, this is considered to represent half productivity and half respiration than today. With half biological activity, Ω is~~With half (Δdiseq + Δbio), Ω was estimated to range from 0.6 to 2.2 for aragonite and from 1.0 to 3.5 for calcite in pre-industrial case. This means that $CaCO_3$ undersaturation ~~of bottom water of biological hotspot~~ might have occurred, at least for aragonite, even with ~~half~~the productivity much lower than that occurring today and without perturbation by anthropogenic CO_2. This may be the case ~~only in hotspots or~~ 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 CO_2 (Bates et al., 2009; 2013; Mathis and Questel, 2013).

In terms of duration, period of aragonite (~~and~~ calcite) undersaturation was estimated to be 3.9 (2.6) and 1.7 (0.3) months~~occupies 33 % (22 %) and 16 % (3 %) of~~ in the first and second year, respectively, in the ~~case of~~ pre-industrial period case ~~with no change in productivity~~. By comparing with original estimate of 7.5-8.6 months, ~~for 2012 and 2013,~~ it ~~is~~ was ~~indicated~~ suggested that the period of aragonite undersaturation has been significantly extended by an input of ~~that~~ anthropogenic CO_2 ~~has largely increased the period of aragonite undersaturation~~by now ~~in the study site from 33 % to 71% and from 16 % to 61 %~~. ~~In the future case with atmospheric pCO_2 of 650 ppm, occupation of aragonite undersaturation increases to 99 % and 66 % for the first and second year, respectively. Calcite undersaturation occupies 75 % and 38 % of the first and second year, respectively. These analysis indicate that anthropogenic CO_2 has~~In the future case with atmospheric pCO_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 CO_2 has a significant impact on duration of ~~saturation condition of~~ $CaCO_3$ undersaturation in the bottom water even though seasonal and interannual variations of Ω is mainly controlled by biological processes.

~~4~~5 Summary and conclusions

~~Horizontal~~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 ~~controlling~~to lower Ω of bottom water in the Chukchi Sea, with minor but significant control of T and S.

~~We also performed mooring observation~~ Mooring observations of AOU, T and S for two years in Hope Valley~~, a biological hotspot, where lowest Ω was observed in cruise observations in 2012. Mooring data revealed~~ (Nishino et al., 2016) showed that our ship-based observations captured conditions ~~at both ends of seasonal and interannual variations in biological processes:~~ under very strong influence of remineralization in autumn 2012, and under ~~the~~ an influence of photosynthesis in early summer 2013. This explains large difference in Ω between 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 ~~of this biological hotspot showed prolonged~~suggested frequent undersaturation for both aragonite and calcite, not only in 2012 but also in 2013. The period of aragonite undersaturation ~~occupied~~could be more than 7.5 month (60 ~~%~~%) of a year. ~~Occupation of calcite undersaturation was 26 % for highly stratified first year and 6 % in second year.~~ Such ~~prolonged~~frequent aragonite undersaturation may be harmful for benthic calcifiers who rely on a 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 CO_2 has significantly extended the period aragonite undersaturation to more than two~~ or three~~-fold longer by now. ~~Calcite undersaturation period was also extended to about two-hold longer than pre-industrial period.~~ With increased atmospheric pCO_2~~ of 650 ppm~~, ~~occupation~~the period of aragonite undersaturation ~~should~~ will extend further~~increase to more than two third of a year, with possibility of almost year-long occupation under highly stratified condition~~. ~~Occupation of calcite undersaturation will also increase to more than one third of a year. Surely~~Clearly, anthropogenic CO_2 has significant impact on duration of $CaCO_3$ undersaturation in the bottom water even though seasonal and interannual variations in Ω is controlled by biological processes. We should note that this study is the first attempt to reconstruct 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 sampler is desired to confirm our results.

It has been revealed that $CaCO_3$ undersaturation has negative impacts on calcifying organisms (e.g., ~~Kroeder~~Kroeker et al., 2013). Therefore, continuous occurrence of undersaturation since pre-industrial period in ~~a biological hotspot in~~ the southern Chukchi Sea ~~may be conflicting~~is not consistent with the fact that bivalves are dominant in benthic community in this area (Grebmeier, 2012; Grebmeier et al., ~~2012;~~ 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 Hope Valley hot-spot area, both well-grown adults and small young individuals (Fig. ~~8~~1). This may suggest tolerance of these bivalves to $CaCO_3$ undersaturation with protection

mechanisms such as external organic layer (Ries et al., 2009), companion of 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 $CaCO_3$ undersaturation in surrounding water. With rapidly increasing anthropogenic CO_2 in recent and future years, quantification of the responses of local calcifying organisms to low Ω is an urgent issue for the future study. ~~A biological hotspot of~~ The Chukchi Sea, ~~with~~ already ~~prolonged~~undergoing $CaCO_3$ 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.

~~**References**~~

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Table 1. Comparison of 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 24-hours mean with standard deviation (S.D.). Distances between mooring site and ship-based sampling site are also indicated in km.

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

Figure captions

Figure 1.~~—~~ Distribution of Ωar (a and c) and Ωca (b and d) in bottom water in September/October 2012 (a and b) and July 2013 (c and d). Circled stations were undersaturated with $CaCO_3$ minerals. Stations in red polygon were used in Fig. ~~2. Red~~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.

Figure 2.~~—~~ Relationship between salinity and total alkalinity (TA, μmol kg^{-1}) observed during cruises in 2012 and 2013.

Figure 3. Vertical sections of (a) salinity, (b) temperature~~ (°C),~~, (c) dissolved oxygen (~~μmol kg^{-1}~~DO), (d) Dissolved Inorganic Carbon (DIC), (e) Total Alkalinity (TA), (f) fCO_2, (g) Ωar and (e) Ωca~~. Left panels are for 2012 and right panels are for 2013.~~ in September/October 2012. See Fig. 1 for locations.

~~**Figure 3**~~

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

Figure 5. Relationships between (a) Ωar and temperature, (b) Ωar and salinity, and (c) Ωar and apparent oxygen utilization (AOU~~(~~, μmol kg^{-1}). ~~Blue and red dots are for 2012 and 2013, respectively. Black circles indicate bottom water samples.~~

Figure ~~4.~~ 6. Relationships between AOU (μmol kg-1) and fCO_2 (μatm).

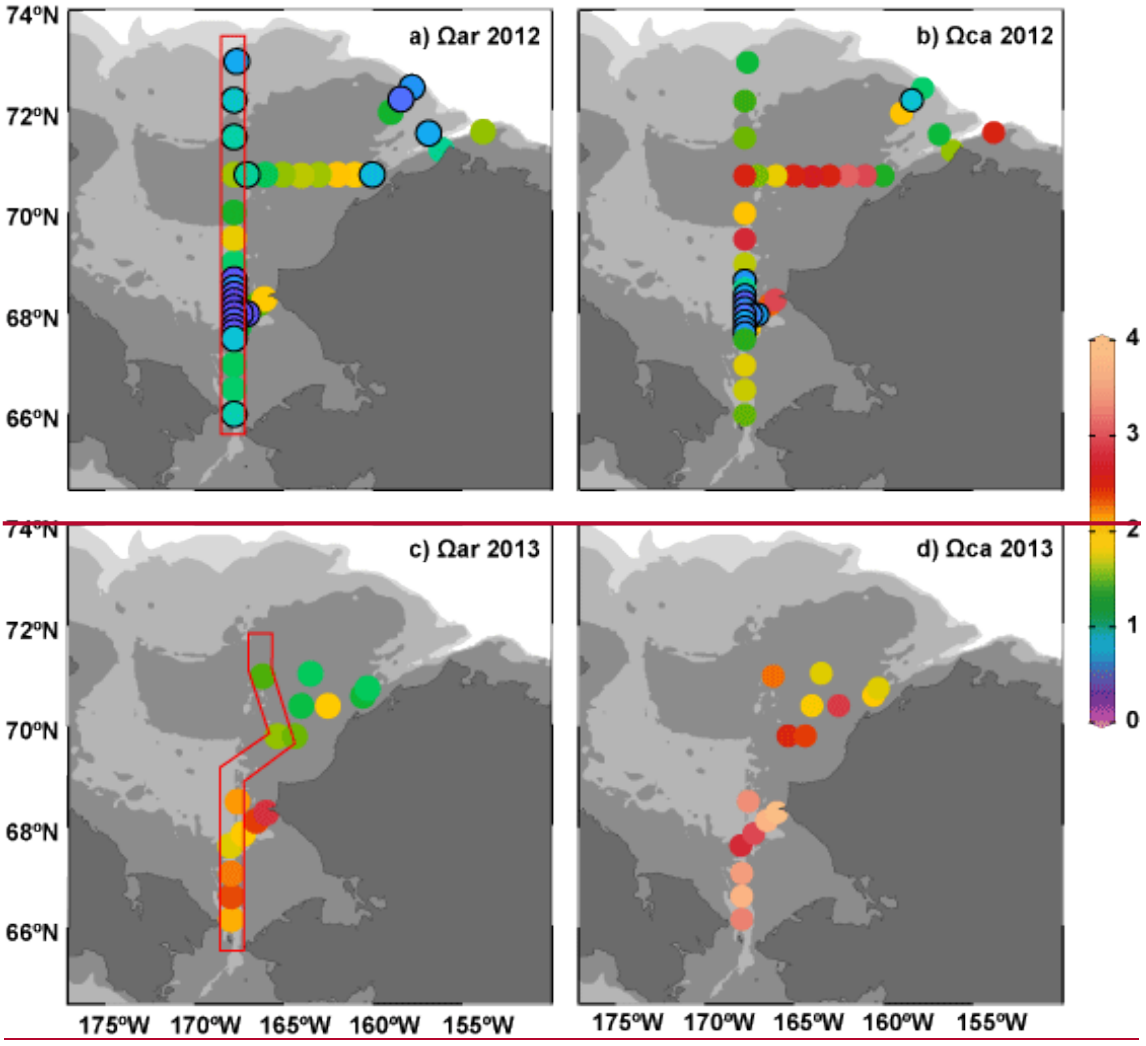
Figure 7. Time series of salinity (top), temperature (middle; ~~℃~~°C), and dissolved oxygen and AOU (bottom; μmol kg-1). Red symbols indicate ship-based observations. In the bottom panel, dots and squares are ship-based data of dissolved oxygen and AOU, respectively.

Figure ~~5.~~ 8. Comparison between Ωar estimated from T, S, and AOU~~,~~ data using equation (1) and (2) (Ωar ~~observed during~~(est)), and Ωar estimated from bottle DIC and TA (Ωar (obs)) for ship-based-cruises (a) in 2012 and 2013, and (b) in 2000, 2002, 2006, 2009 and 2010.

Figure ~~6~~9. Time series of Ωar (top) and Ωca (bottom) reconstructed from mooring data of T, S and AOU (a black line). Red symbols indicate ship-based observations. ~~Black and g~~Gray lines~~ are Ω and Ω±RMSE (0.36 for aragonite and 0.57 for calcite)~~indicate range of -0.36 to +0.45 for Ωar and -0.57 to +0.71 for Ωca (see text).

Figrue ~~7.~~ 10. Time series of Ωar (top) and Ωca (bottom) for cases when atmospheric CO_2 concentration was 280 ppm (blue; pre-industrial period) or 650 ppm (red~~; 50 years later~~). See text for details.

~~**Figure 8.** Photo of bivalves corrected by a dredge taw near the mooring location during T/S Oshoro-Maru cruise in 2013.~~


a) Ωar 2012
b) Ωca 2012
c) Ωar 2013
d) Ωca 2013
74°N
72°N
70°N
68°N
66°N
175°W
170°W
165°W
160°W
155°W
4
3
2
1
0

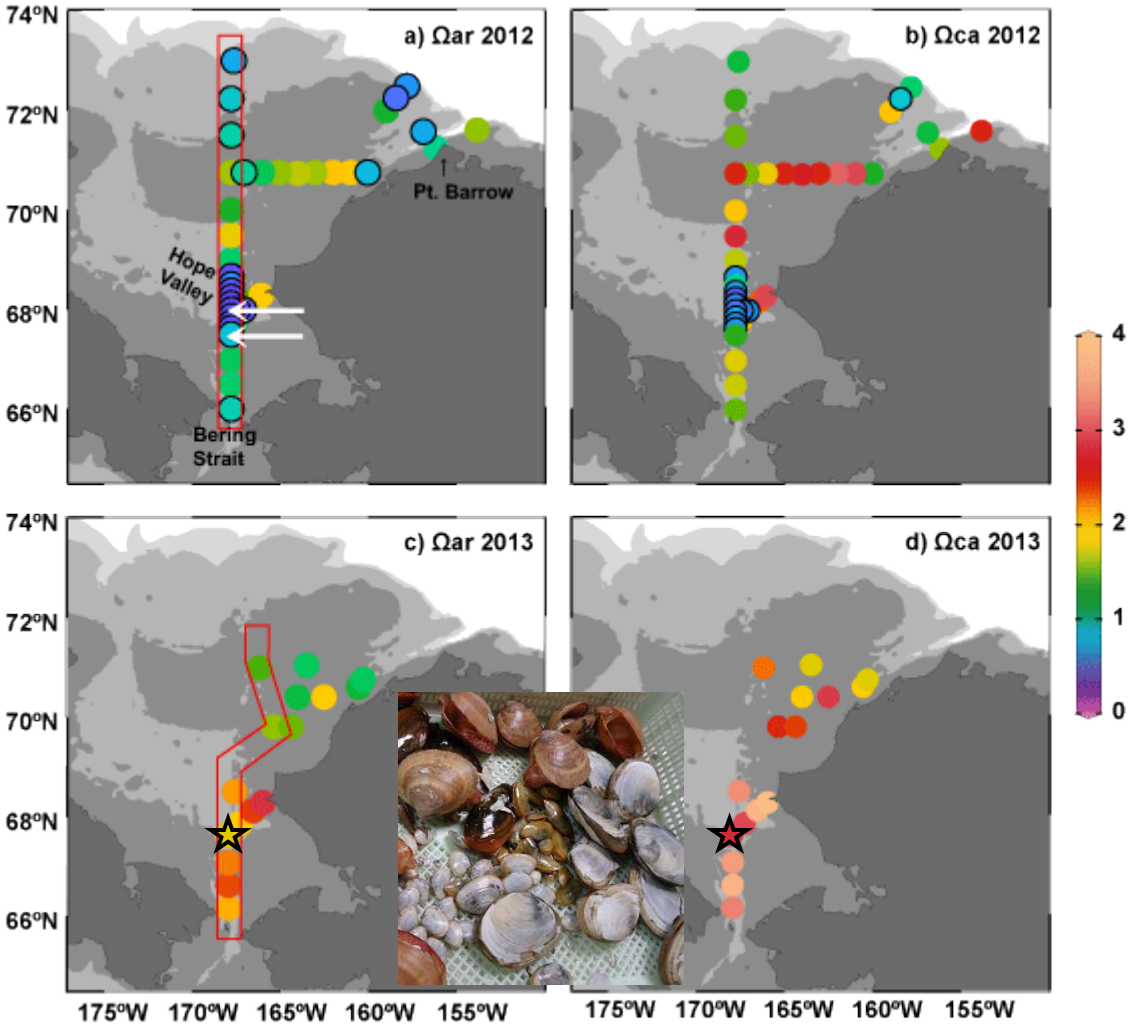
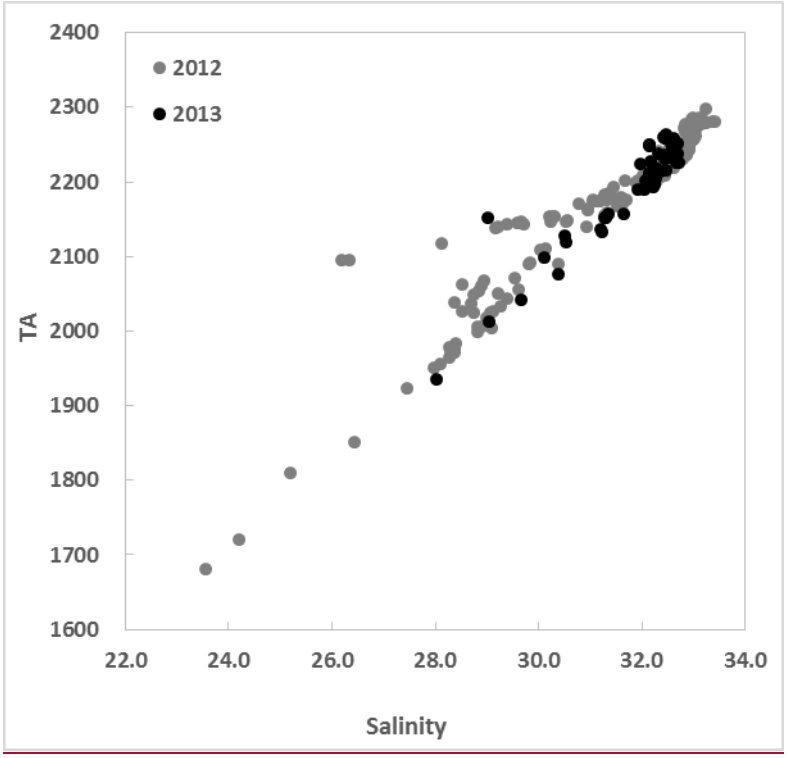


Fig. 1: Distribution of Ωar (a and c) and Ωca (b and d) in bottom water in September/October 2012 (a and b) and July 2013 (c and d). Circled stations were undersaturated with $CaCO_3$ minerals. Stations in red polygon were used in Fig. 2. ~~Red~~White arrows indicate mooring sites. An insert photo shows bivalves collected by a dredge trawl at a station marked with a star in July 2013.


2012
2013
TA
Salinity
2400
2300
2200
2100
2000
1900
1800
1700
1600
22.0
24.0
26.0
28.0
30.0
32.0
34.0

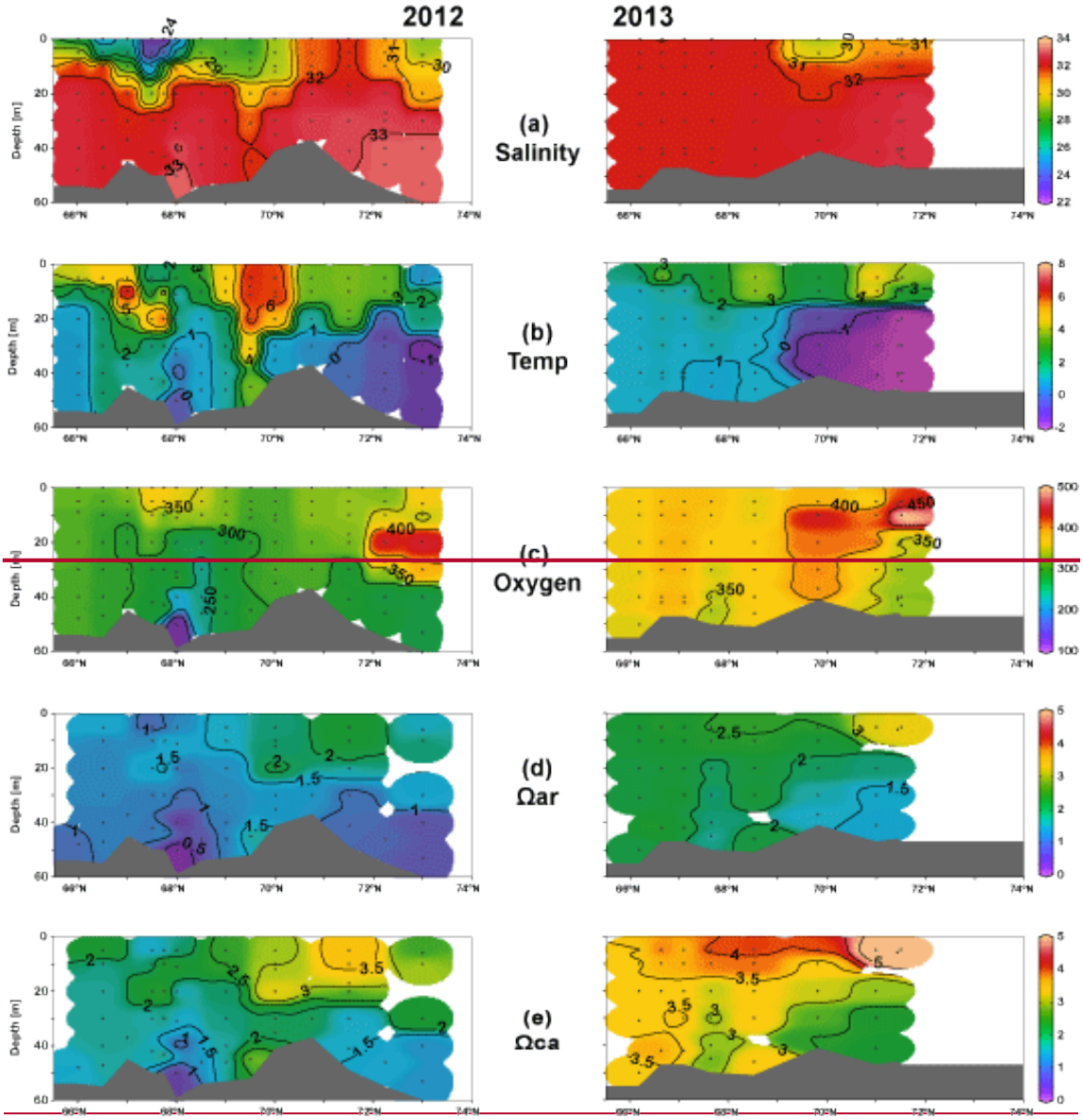


Fig. ~~2~~2: Relationship between salinity and total alkalinity (TA, µmol kg^{-1}) observed during cruises in 2012 and 2013.

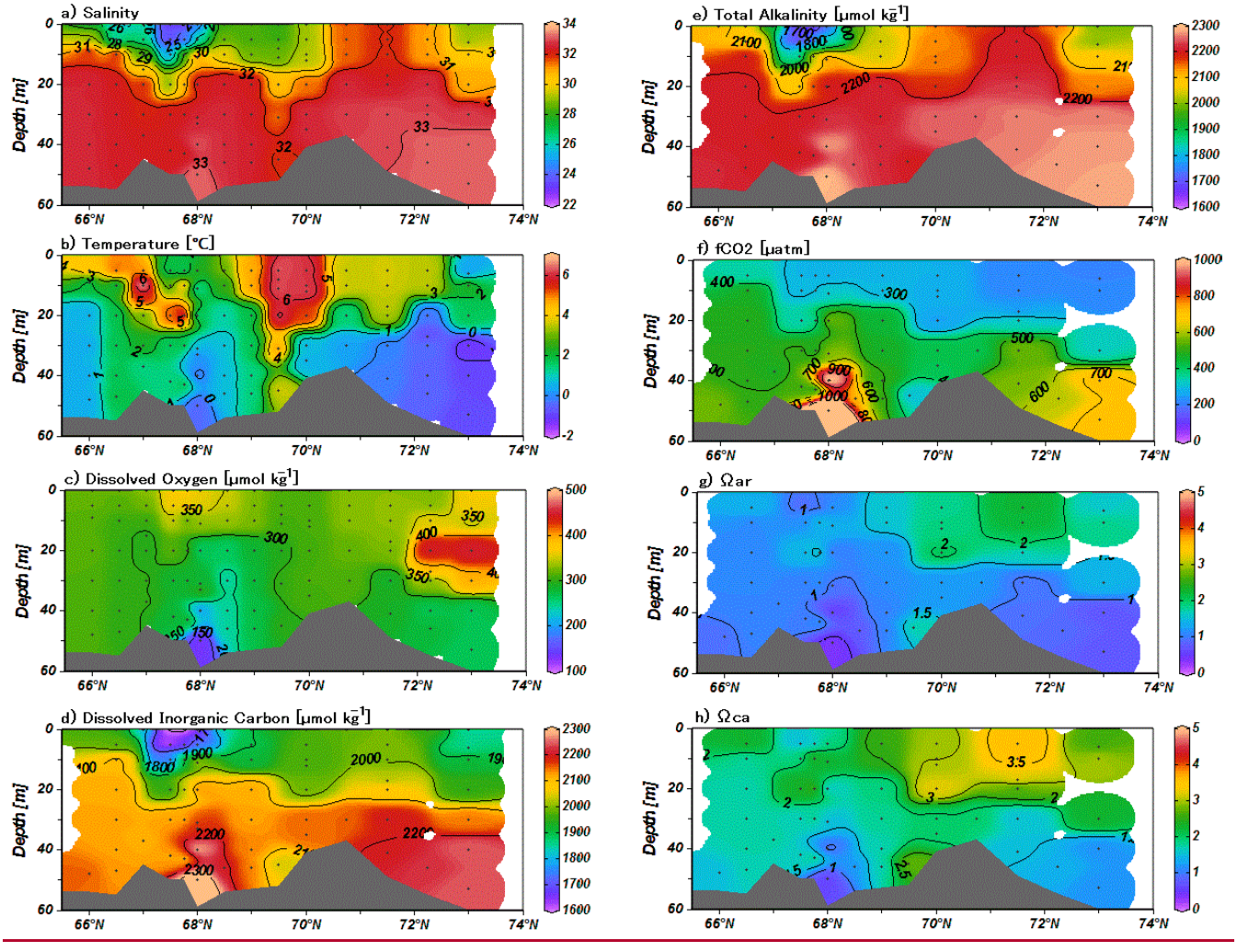
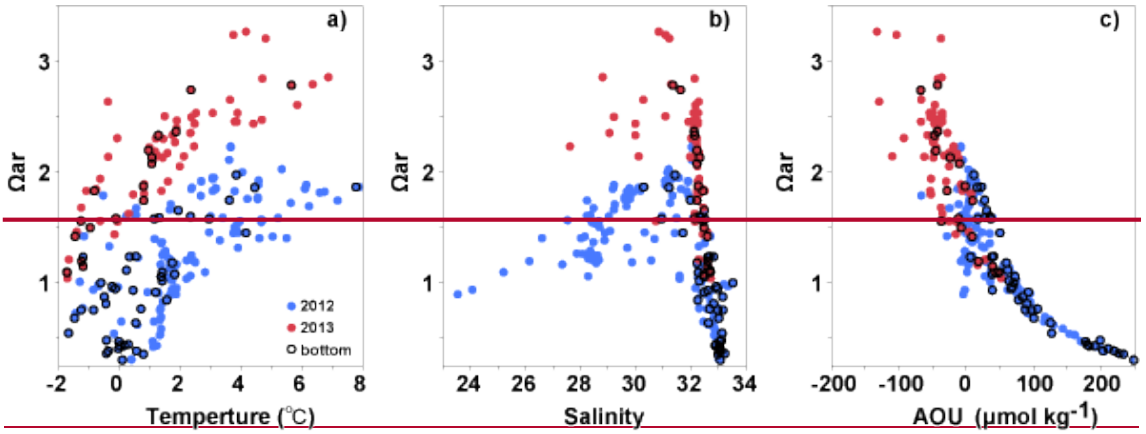


Fig. 3: Vertical sections of (a) salinity, (b) temperature ~~(°C),~~, (c) dissolved oxygen (~~μmol kg^{-1}~~DO), (d) Dissolved Inorganic Carbon (DIC), (e) Total Alkalinity (TA), (f) fCO_2, (g) Ωar and (e) Ωca~~. Left panels are for 2012 and right panels are for 2013.~~ in September/October 2012. See Fig. 1 for locations.



~~Fig. 3: Relationships between (a) Ωar and temperature, (b) Ωar and salinity, and (c) Ωar and AOU (μmol kg-1). Blue and red dots are for 2012 and 2013, respectively. Black circles indicate bottom water samples.~~

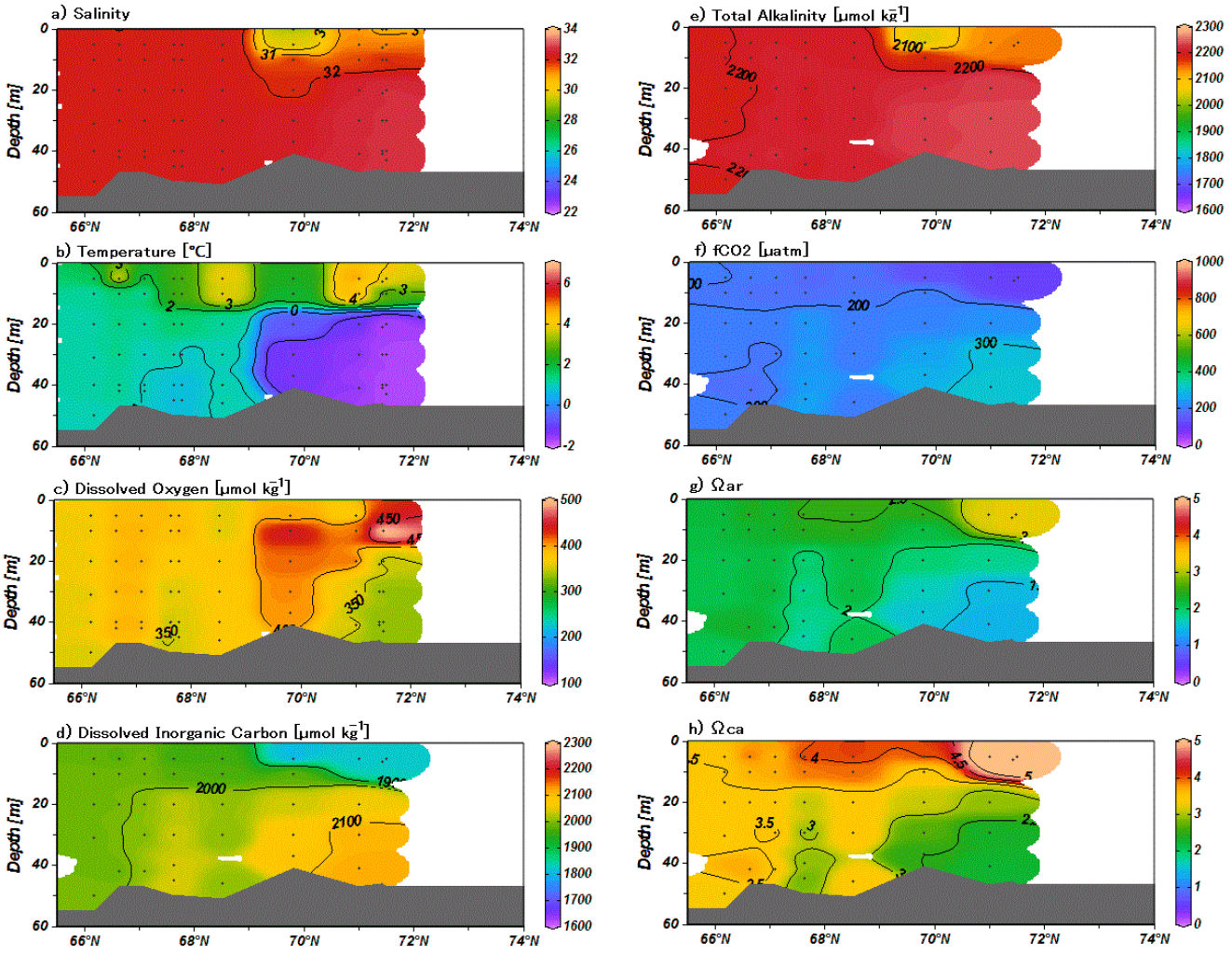
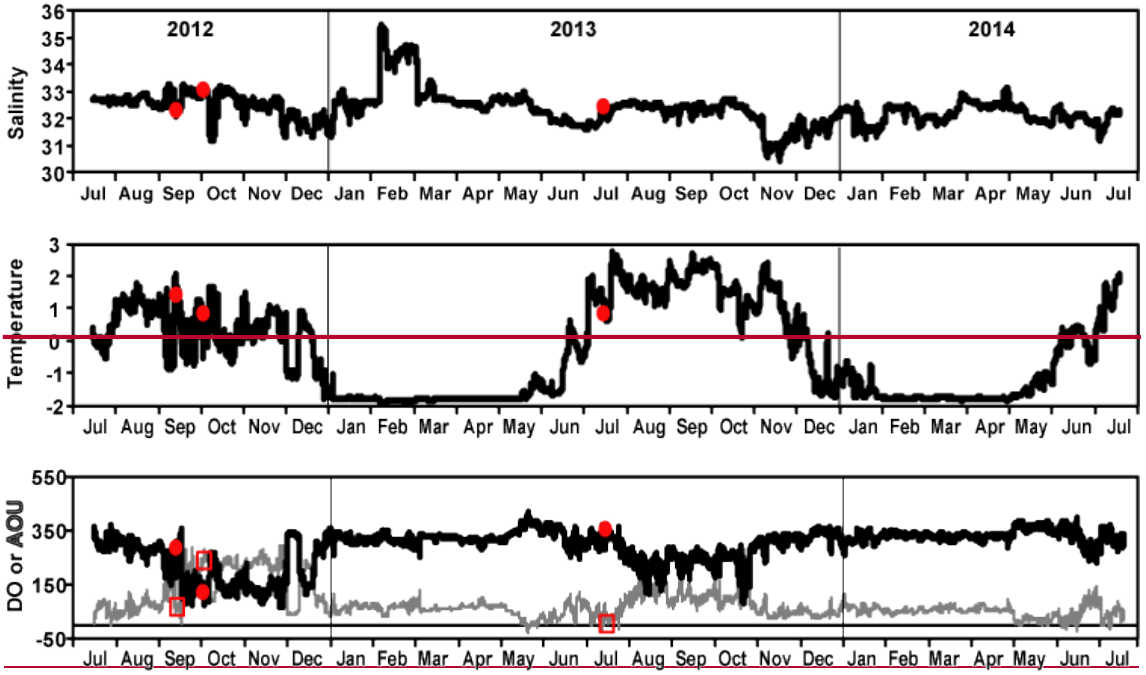


Fig. 4: Same as Figure 4 but in July 2013. See Fig. 1 for locations.


2012
2013
2014
Salinity
36
35
34
33
32
31
30
Temperature
3
2
1
0
-1
-2
DO or AOU
550
350
150
-50
Jul Aug Sep Oct Nov Dec Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec Jan Feb Mar Apr May Jun Jul

~~Fig. 4~~

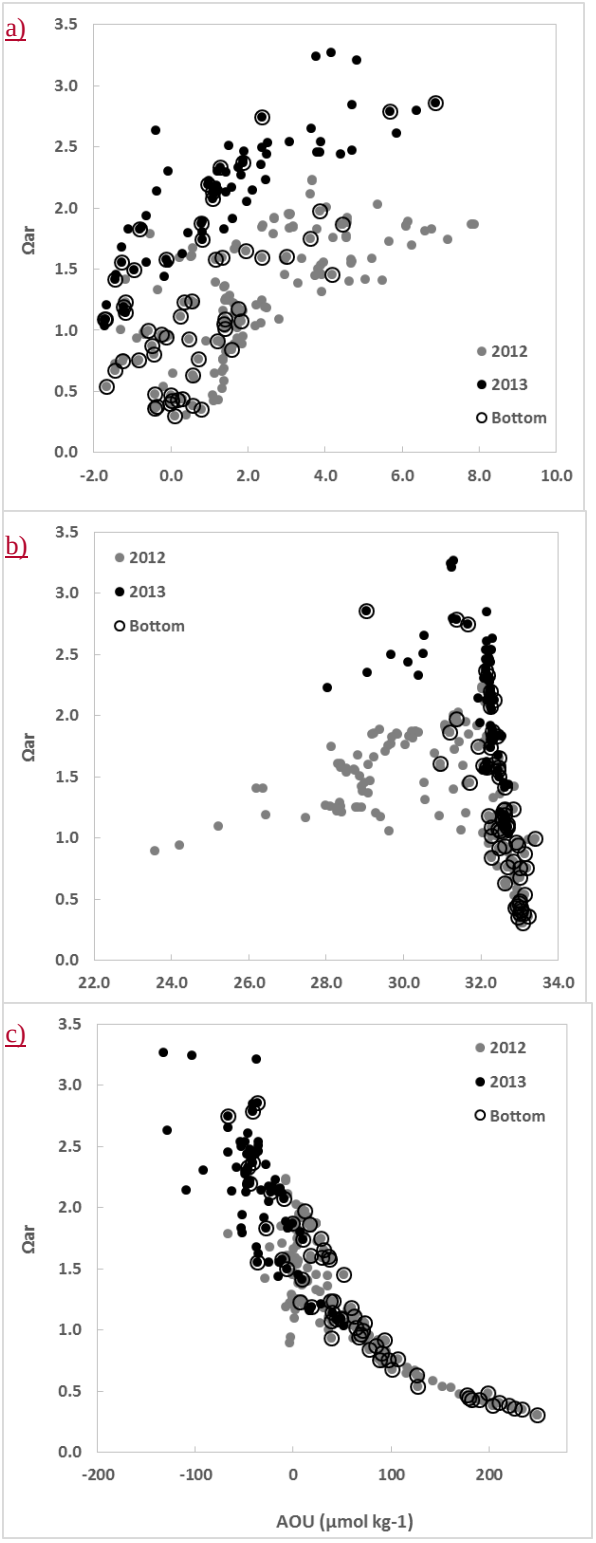


Fig. 5: Relationships between (a) Ωar and temperature, (b) Ωar and salinity, and (c) Ωar and apparent oxygen utilization (AOU, µmol kg^{-1}).

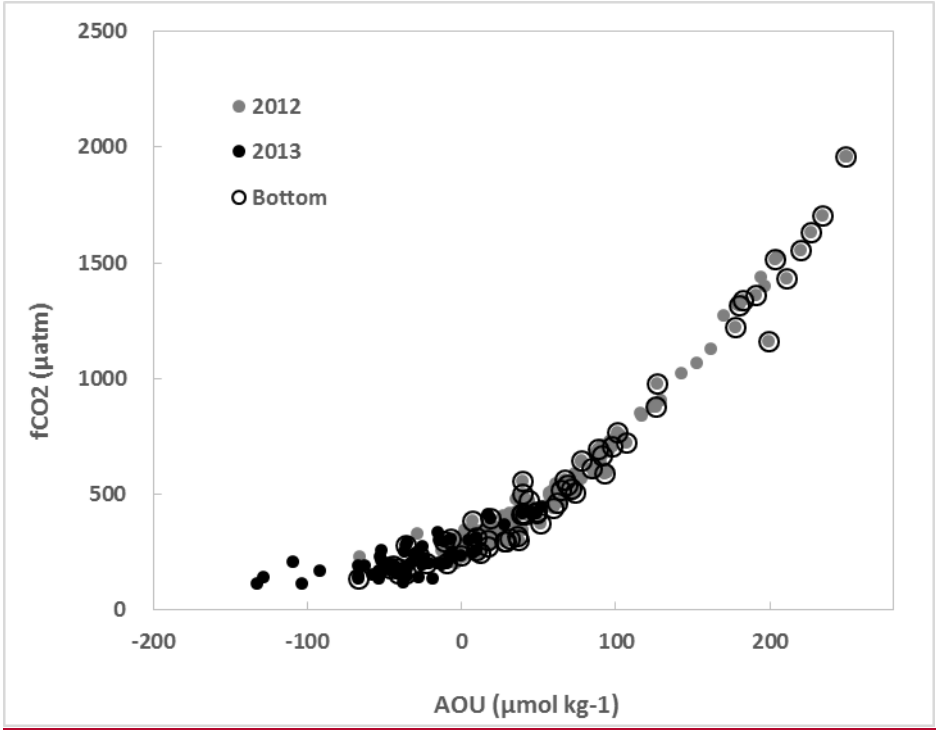


Fig. 6. Relationships between AOU (µmol kg^{-1}) and fCO_2 (µatm).

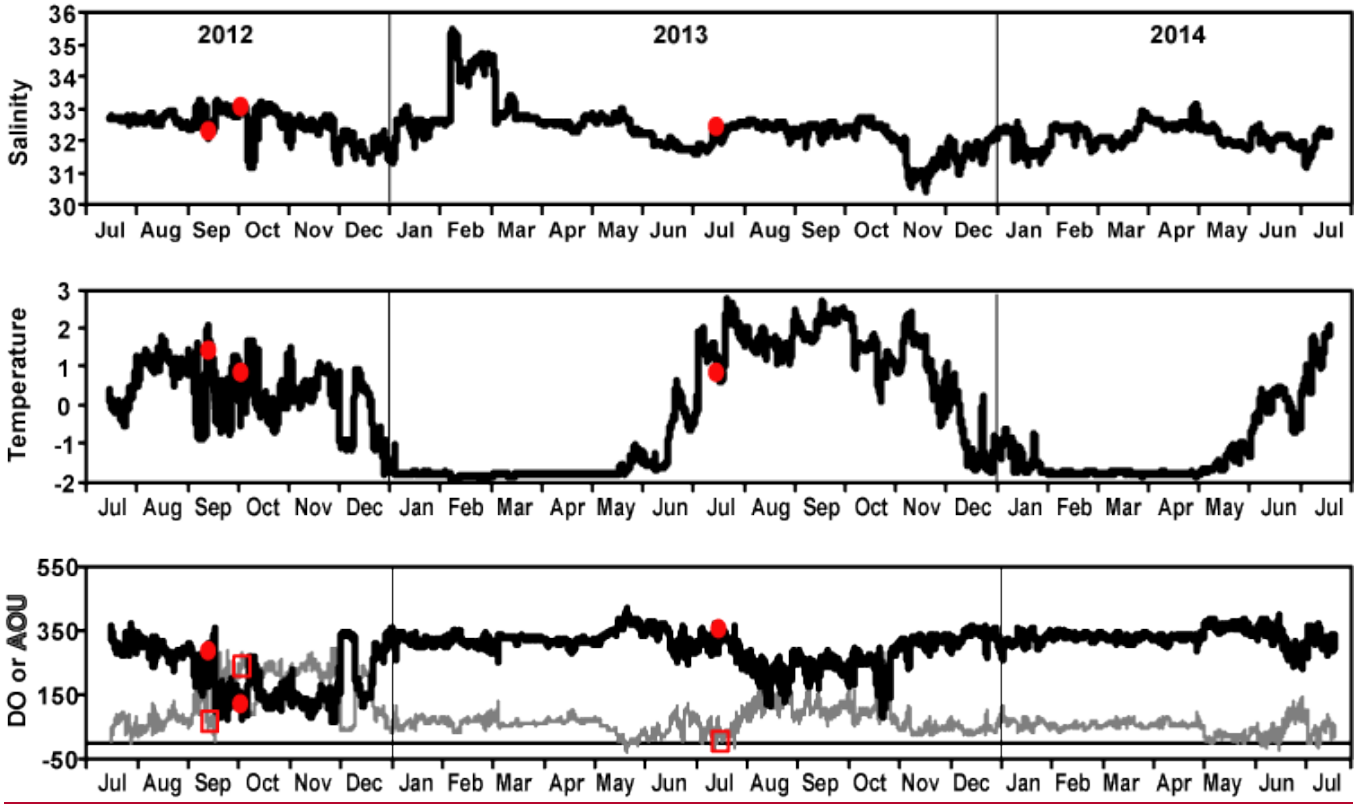
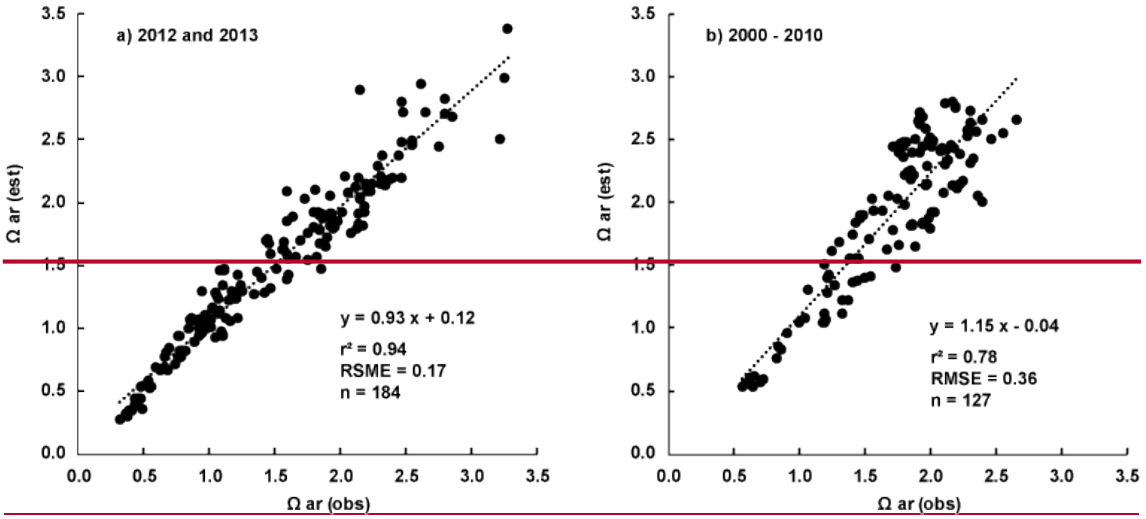


Fig. 7: Time series of salinity (top), temperature (middle; ℃), and dissolved oxygen and AOU (bottom; μmol kg^{-1}). Red symbols indicate ship-based observations. In the bottom panel, dots and squares are ship-based data of dissolved oxygen and AOU, respectively.



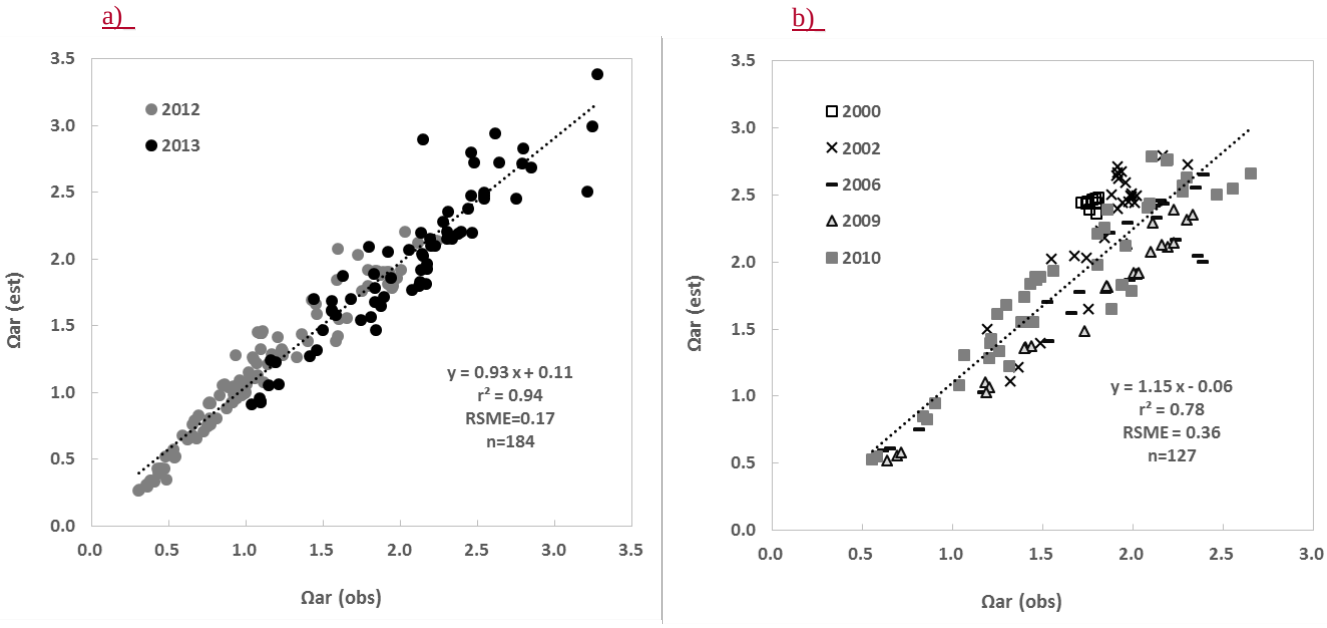
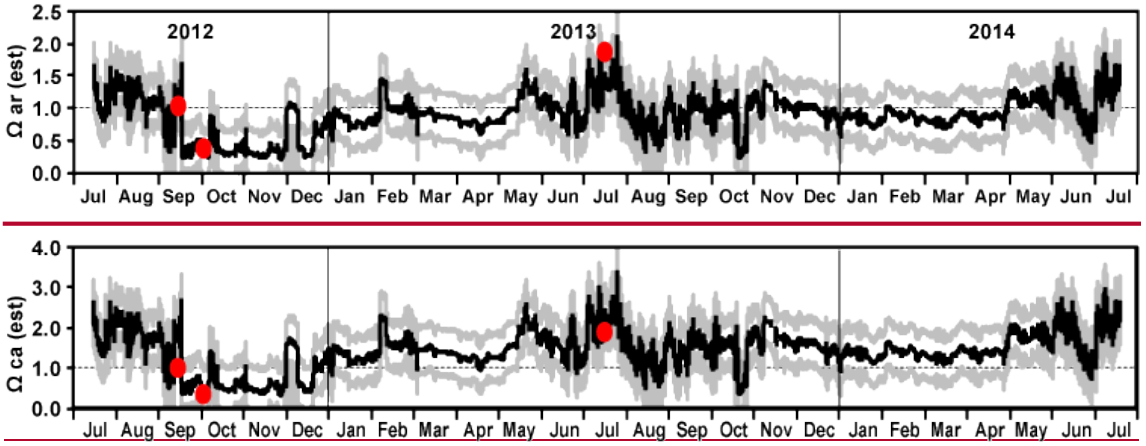
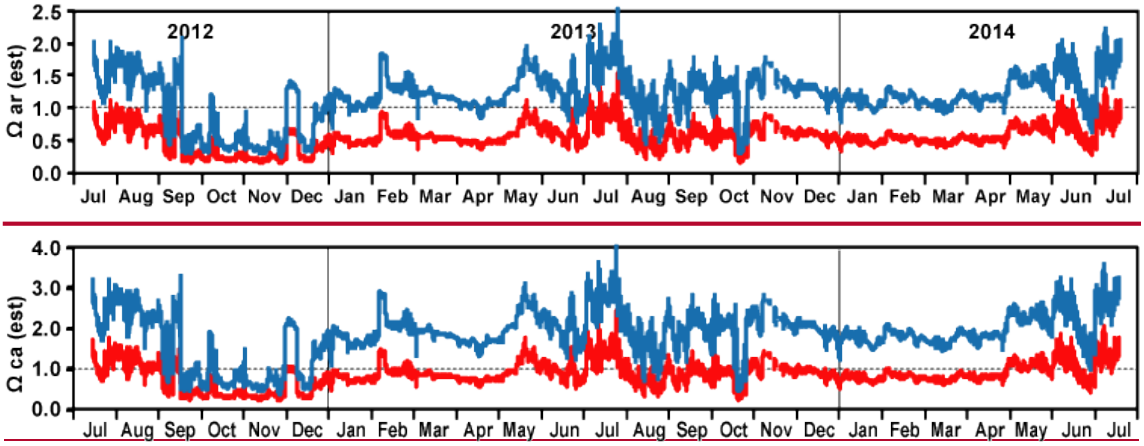


Fig. ~~5~~8: Comparison between Ωar estimated from T, S, and AOU~~,~~ data using equation (1) and (2) (Ωar ~~observed during~~(est)), and Ωar estimated from bottle DIC and TA (Ωar (obs)) for ship-based-cruises (a) in 2012 and 2013, and (b) in 2000, 2002, 2006, 2009 and 2010.



~~Fig. 6:~~ Time series of Ωar (top) and Ωca (bottom) reconstructed from mooring data of T, S and AOU (black line). Red symbols indicate ship-based observations. ~~Black and g~~Gray lines indicate a range of -0.36 to +0.45 for Ωar and -0.57 to +0.71 for Ωca (see text) ~~are Ω and Ω±RMSE (0.36 for aragonite and 0.57 for calcite).~~.



~~Fig. 7~~

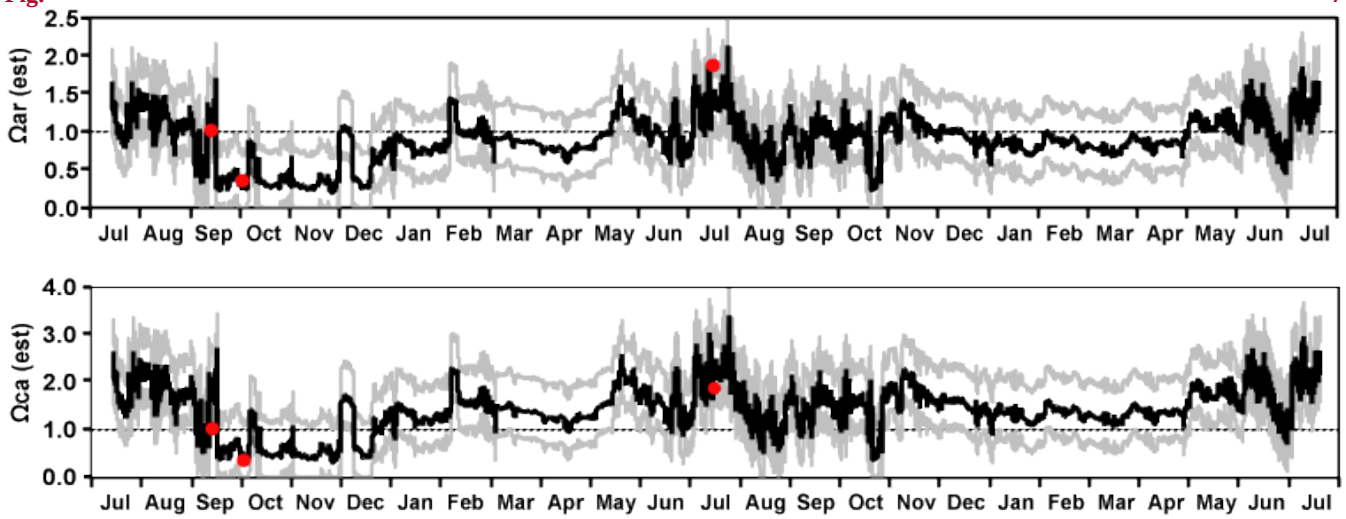


Fig. 9: Time series of Ωar (top) and Ωca (bottom) reconstructed from mooring data of T, S and AOU. Ω values (black line) are shown with range of uncertainty (grey lines).

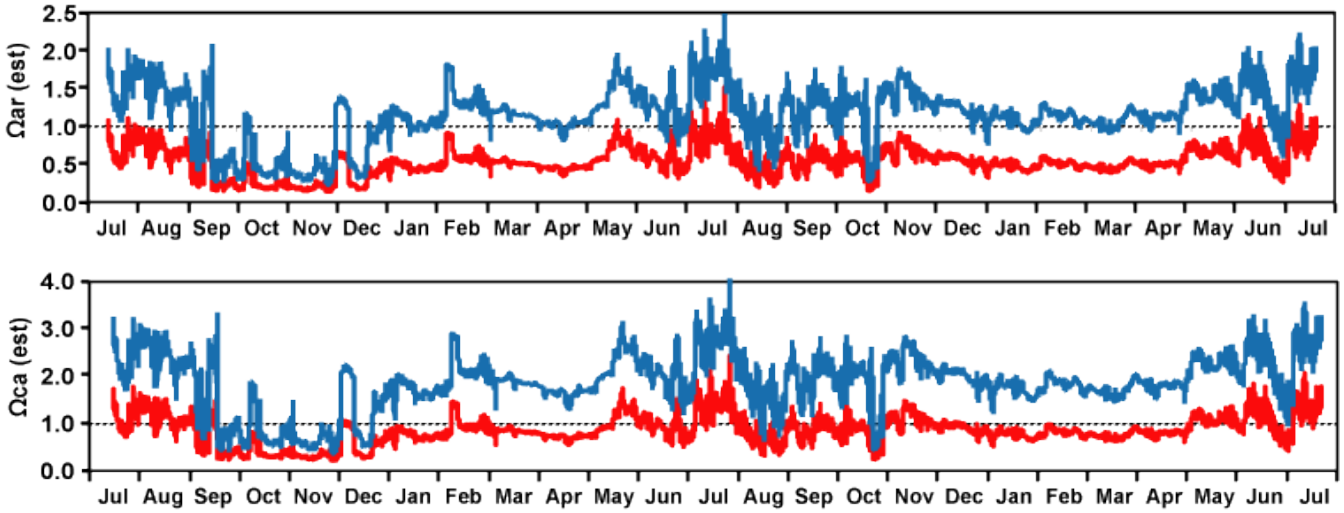


Fig. 10: Time series of Ωar (top) and Ωca (bottom) for cases when atmospheric CO_2 concentration was 280 ppm (blue; pre-industrial period) or 650 ppm (red~~; 50 years later~~). See text for details.

~~**Fig. 8: Photo of bivalves corrected by a dredge taw near the mooring location during T/S Oshoro-Maru cruise in 2013.**~~