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Ocean acidification from 1997 to 2011 in the subarctic western North Pacific Ocean

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Abstract

Rising atmospheric CO_2 contents have led to greater CO_2 uptake by the oceans, lowering both pH due to increasing hydrogen ions and $CaCO_3$ saturation states due to declining carbonate ion (CO_3^{2-}). Here, we used previously compiled data sets and new data collected in 2010 and 2011 to investigate ocean acidification of the North Pacific western subarctic gyre. In winter, the western subarctic gyre is a source of CO_2 to the atmosphere because of convective mixing of deep waters rich in dissolved inorganic carbon (DIC). We calculated pH in winter mixed layer from DIC and total alkalinity (TA), and found that it decreased at the rate of $-0.0011 \pm 0.0004\,\mathrm{yr}^{-1}$ from 1997 to 2011. This decrease rate is slower than that expected under condition of seawater/atmosphere equilibration, and it is also slower than the rate in the subtropical regions ($-0.002\,\mathrm{yr}^{-1}$). The slow rate is caused by a reduction of CO_2 emission in winter due to an increase in TA. Below the mixed layer, the calcite saturation horizon ($\sim 185\,\mathrm{m}$ depth) shoaled at the rate of $2.9 \pm 0.9\,\mathrm{m\,yr}^{-1}$ as the result of the declining CO_3^{2-} concentration ($-0.03 \pm 0.01\,\mu\mathrm{mol\,kg}^{-1}\,\mathrm{yr}^{-1}$). Between 200 m and 300 m depth, pH decline during the study period ($-0.0051 \pm 0.0010\,\mathrm{yr}^{-1}$) was larger than ever reported in the open North Pacific. This enhanced acidification rate below the calcite saturation horizon reflected not only the uptake of anthropogenic CO_2 but also the increase in the decomposition of organic matter evaluated from the increase in AOU, which suggests that the dissolution of $CaCO_3$ particles increased.

1 Introduction

Globally, anthropogenic CO_2 was taken up by the oceans at a rate of $2.2 \pm 0.4\,\mathrm{Pg\,C\,yr}^{-1}$ during the 1990s (Bindoff et al., 2007). This CO_2 uptake by the oceans has increased the hydrogen ion (H^+) concentration (i.e., lowered the pH) and lowered the $CaCO_3$ saturation state (Ω), by decreasing the carbonate ion (CO_3^{2-}) concentration, thereby leading to bicarbonate ion (HCO_3^-) formation. These changes in carbonate system affect marine organisms and ecosystems throughout the world's oceans (Doney et al., 2009).

Ocean acidification of surface and subsurface waters of the North Pacific Ocean has been clearly documented in time-series and repeat hydrography data (direct basinwide observations) over the past two decades (e.g., Dore et al., 2009; Byrne et al., 2010; Midorikawa et al., 2010; Ishii et al., 2011; Feely et al., 2004, 2012; Murata and Saito, 2012). The observed pH changes in the surface ocean are consistent with those predicted based on equilibration of atmospheric CO_2 with the seawater (about $-0.002\,yr^{-1}$) (Dore et al., 2009; Byrne et al., 2010; Midorikawa et al., 2010; Ishii et al., 2011). In subsurface water, pH decreases ($-0.003\,yr^{-1}$ at Station ALOHA (22.75° N, 158° W), Dore et al., 2009; $-0.004\,yr^{-1}$ in North Pacific Intermediate Water, Byrne et al., 2010) have been enhanced by the accumulation of anthropogenic CO_2 and by natural variability related to temporal changes in physical and biogeochemical processes such as ocean ventilation, and remineralization of organic matter related to apparent oxygen utilization (AOU). The downward transport of anthropogenic CO_2 taken up by the oceans since the preindustrial era has caused shoaling of the $CaCO_3$ saturation horizons of both aragonite and calcite in the North Pacific (Feely and Chen, 1982; Feely et al., 2004, 2012; Murata and Saito, 2012). These results are caused by an increase of H^+ (i.e., a decrease of pH) and a concurrent decrease of CO_3^{2-} concentration, and will impact many marine calcifying species in surface and subsurface water of North Pacific (e.g., coccolithophores, foraminifera, and pteropods). Furthermore, the observed increase in total alkalinity (TA) at the depth of the aragonite saturation horizon between 1970 and 1990 is consistent with the calculated increase in $CaCO_3$ dissolution caused by the shoaling of the horizon (Sarma et al., 2002), although the uncertainty is large (Bindoff et al., 2007).

Projections of the $CaCO_3$ saturation horizon of aragonite based on the Intergovernmental Panel on Climate Change (IPCC) IS92a scenario (an atmospheric CO_2 concentration of 788 ppmv in 2100) for future emissions of anthropogenic CO_2 indicate that the surface mixed layer (0–100 m) in the Southern Ocean, and the subarctic Pacific

Ocean will become undersaturated with respect to aragonite around 2020–2040 (Orr et al., 2005; Guinotte et al., 2006). For this reason, seawater at the high latitudes has high Revelle factor and is characterized by low concentrations of CO_3^{2-} and shallow of $CaCO_3$ saturation horizon (Takahashi et al., 2006; Feely et al., 2004). Thus, even if a smaller change in Ω accompanies future increases in atmospheric CO_2, the surface waters in these regions will be the first to switch from being supersaturated to being undersaturated with respect to $CaCO_3$. In particular, models project that the first region to become undersaturated will be the western subarctic North Pacific (Fig. 1) during winter (Orr et al., 2005; Guinotte et al., 2006), because wintertime surface waters in this region have lower Ω content and shallower $CaCO_3$ saturation horizon (Fig. 2) than the open Pacific Ocean and Southern Ocean (Feely et al., 2004, 2012). The lower Ω in the winter is caused by the convective mixing of deep waters rich in dissolved inorganic carbon (DIC), accompanying with a strong CO_2 source (e.g., Tsurushima et al., 2002; Wakita et al., 2010a) (Fig. 2). These results mean that in this region, ocean acidification in winter is affected not only by increases in atmospheric CO_2 but also by decadal variations of CO_2 emissions. Therefore, assessment of the present progression of acidification in winter in the western subarctic gyre of the North Pacific from field observations is an urgent task.

In this study, we are aimed at clarifying progression of ocean acidification in the in the western subarctic gyre by examining the temporal changes of pH and $CaCO_3$ saturation horizon, which are indicators of ocean acidification, and related chemical properties (dissolved inorganic carbon (DIC), TA, and oceanic CO_2) below the winter mixed layer at two time-series stations (K2 and KNOT) during 1997–2011 (Fig. 1).

2 Data and analyses

From January 2010 to July 2011, we conducted hydrographic observations at stations K2 and KNOT during five cruises (MR10-01, January to February 2010; MR10-06, October 2010; MR11-02, February to March 2011; MR11-03, April 2011, and MR11-05, July 2011) of the R/V *Mirai* of the Japan Agency for Marine–Earth Science and Technology. These observations comprised 20 CTD casts at K2, and in four CTD casts at KNOT. DIC and TA were measured by using coulometrical and potentiometrical techniques, respectively. Those values were calibrated against certified reference material provided by Prof. A. G. Dickson (Scripps Institution of Oceanography). The precision of both DIC and TA was ±0.1 %. Dissolved oxygen (DO) and nutrients (silicate, phosphate, and nitrate) concentrations were measured with an automatic photometric titrator and a continuous flow analyzer, respectively. Data sets collected at K2 and KNOT from 2010 to 2011 will be opened to publish on the JAMSTEC data web site (http://ebcrpa.jamstec.go.jp/k2s1/en/index.html) and the Carbon Dioxide Information and Analysis Center web site (http://cdiac.ornl.gov/oceans/Moorings/K2.html). We also merged compiled data sets from KNOT and K2 for 1997–2008, in which the systematic errors were corrected (Wakita et al., 2010b,c). In addition, we used oceanic physical and chemical data collected at KNOT and K2 during WOCE-P1 (2007) (Fukasawa et al., 2008).

K2 and KNOT are both located in the western subarctic gyre (Fig. 1). We obtained a decadal time-series by combining data from the two stations, because the duration of sampling at each individual station data was not sufficient. Typically, in this region the minimum temperature (T_{min}) in the water column is associated the remnant of the mixed layer water in the preceding winter and occurs at about 26.5σ_θ (~ 100 m), and the maximum temperature occurs at about 27.1σ_θ (~ 370 m) (e.g., Wakita et al., 2010a). Each year, the surface mixed layer reached its maximum depth from mid-March to early April (Fig. 2a) and the coldest mixed-layer temperatures were observed in early April (Fig. 2b). Because spring to fall surface mixed layer temperatures did not influence T_{min} (Wakita et al., 2010a), we identify the T_{min} layer as the remnant of the winter (early April) mixed-layer water. But, station KNOT is just north of the subarctic front (Fig. 1), so occasionally no T_{min} water is observed because of the northward migration of subtropical water (Tsurushima et al., 2002). In our analysis we did not use observation data if no T_{min} layer could be identified.

DIC, TA, phosphate, silicate and AOU in the winter mixed layer (i.e., $\mathrm{DIC_{win}}$, $\mathrm{TA_{win}}$, $\mathrm{PO_{4win}}$, $\mathrm{Si_{win}}$, $\mathrm{AOU_{win}}$) are obtained from in the corresponding values in the T_{min} layer ($\mathrm{DIC}_{T\mathrm{min}}$, $\mathrm{TA}_{T\mathrm{min}}$, $\mathrm{PO}_{4T\mathrm{min}}$, $\mathrm{Si}_{T\mathrm{min}}$ and $\mathrm{AOU}_{T\mathrm{min}}$) following Wakita et al. (2010a). $\mathrm{DIC}_{T\mathrm{min}}$, $\mathrm{AOU}_{T\mathrm{min}}$, $\mathrm{PO}_{4T\mathrm{min}}$, and $\mathrm{Si}_{T\mathrm{min}}$ varied seasonally, reaching minima in winter, but $\mathrm{TA}_{T\mathrm{min}}$ showed no distinct seasonal variation (Wakita et al., 2010a). In spring, observed values of $\mathrm{DIC}_{T\mathrm{min}}$, $\mathrm{AOU}_{T\mathrm{min}}$, $\mathrm{PO}_{4T\mathrm{min}}$, and $\mathrm{Si}_{T\mathrm{min}}$ increased compared with those of the previous winter because of the decomposition of organic matter. We calculated AOU by subtracting the observed DO concentration from the saturated concentration calculated from temperature and salinity using the equation of Weiss (1970). We assumed that DO in the winter mixed layer was homogeneously saturated (i.e., AOU = 0) because of strong vertical mixing and air–sea exchange. We calculated $\mathrm{DIC_{win}}$, $\mathrm{PO_{4win}}$, and $\mathrm{Si_{win}}$ from observed $\mathrm{DIC}_{T\mathrm{min}}$, $\mathrm{PO}_{4T\mathrm{min}}$, and $\mathrm{Si}_{T\mathrm{min}}$, and stoichiometric ratios of decomposition with the following equations:

$$\mathrm{DIC_{win}} = \mathrm{DIC}_{T\mathrm{min}} - \mathrm{C}/-\mathrm{O_2} \times \mathrm{AOU}_{T\mathrm{min}} \tag{1}$$

$$\mathrm{PO_{4win}} = \mathrm{PO}_{4T\mathrm{min}} - \mathrm{P}/-\mathrm{O_2} \times \mathrm{AOU}_{T\mathrm{min}} \tag{2}$$

$$\mathrm{Si_{win}} = \mathrm{Si}_{T\mathrm{min}} - \mathrm{Si}/-\mathrm{O_2} \times \mathrm{AOU}_{T\mathrm{min}} \tag{3}$$

where $\mathrm{C}/-\mathrm{O_2}$ (117/170) and $\mathrm{P}/-\mathrm{O_2}$ (1/170) are the stoichiometric ratios of carbon and phosphorus to oxygen during the decomposition of organic matter (Anderson and Sarmiento, 1994). We used $\mathrm{Si}/-\mathrm{O_2}$ of 0.18 because $\mathrm{Si}_{T\mathrm{min}}$ was positively correlated with $\mathrm{AOU}_{T\mathrm{win}}$ ($r = 0.76$, $p < 0.001$).

After the values of T_{min} (depth, temperature, salinity, and σ_θ) were determined from continuous CTD data (1 db resolution), we obtained DO, DIC, TA, and nutrients concentrations at the isopycnal surface where T_{min} occurred by linear interpolation of discrete bottle-sampling data. Note that the values of depth, salinity and σ_θ in the T_{min} layer from continuous CTD data are not necessarily identical to those from discrete bottle sampling. For the isopycnal analysis, the values of DO, DIC, TA, and nutrients on each isopycnal surface from $26.7\sigma_\theta$ to $27.0\sigma_\theta$ were also obtained by linear interpolation of discrete bottle sampling data.

Using CO2SYS software (Pierrot et al., 2006), we calculated the mixing ratio of CO_2 by volume in dry air ($x\mathrm{CO_2}$), pH (total scale) at the in situ temperature ($\mathrm{pH}_T^{\text{in situ}}$) and at 25 °C ($\mathrm{pH}_T^{25}$), the carbonate ion concentration ($\mathrm{CO_3^{2-}}$), and Ω from measured DIC, TA, phosphate, and silicate values. The carbonate dissociation constants required for the calculation are Mehrbach et al. (1973) as refitted by Dickson and Millero (1987), by using potential temperature, salinity and 0 db pressure in the winter mixed layer ($T_{\min}$ layer), and the in situ temperature, salinity and in situ pressure in subsurface waters. We also calculated Ω with respect to the two minerals forms of $\mathrm{CaCO_3}$, aragonite ($\Omega_{\text{aragonite}}$) and calcite ($\Omega_{\text{calcite}}$), as the ion product of calcium ion ($\mathrm{Ca^{2+}}$) and $\mathrm{CO_3^{2-}}$ ions:

$$\Omega = [\mathrm{Ca^{2+}}][\mathrm{CO_3^{2-}}]/K'_{\mathrm{sp}} \tag{4}$$

where the square brackets indicate the concentrations of the enclosed species, and K'_{sp} is the thermodynamic solubility product constant for aragonite or calcite (Mucci, 1983). We estimated $[\mathrm{Ca^{2+}}]$ by assuming the following linear relationship with salinity (S): $[\mathrm{Ca^{2+}}] = 0.01028 \times S/35$ (Millero, 1982).

3 Results and discussion

3.1 Acidification in the winter mixed layer

During the study period, $\mathrm{pH}_T^{\text{in situ}}$ and pH_T^{25} in the winter mixed layer significantly decreased at rate of $-0.0011 \pm 0.0004\,\mathrm{yr}^{-1}$ ($p < 0.01$) and $-0.0010 \pm 0.0004\,\mathrm{yr}^{-1}$ ($p < 0.05$) respectively (Fig. 3), whereas $\Omega_{\text{aragonite}}$ Ω_{calcite} and $\mathrm{CO_3^{2-}}$ did not decrease significantly ($p > 0.08$) (not shown). We estimated $\mathrm{pH}_T^{\text{in situ}}$, $\Omega_{\text{aragonite}}$, Ω_{calcite}, and $x\mathrm{CO_2}$ in the winter mixed layer from DIC, TA, phosphate and silicate as described in Sect. 2.

In the winter mixed layer, pH decreased more slowly than predicted from oceanic equilibration with the increasing atmospheric CO_2 ($-0.002\,\mathrm{pH}_T^{\text{in situ}}\,\mathrm{yr}^{-1}$), when it was calculated by using the increase in atmospheric CO_2 (2.1 ppm yr^{-1}) in late winter (the beginning of April) from 1997 to 2011 at 44.4° N (Conway et al., 2012) and constant TA_{win}. In addition, the pH decreasing rate was slower than the rates, which determined in the central North Pacific near Hawaii ($-0.0019 \pm 0.0002\,pH_T^{in\,situ}\,yr^{-1}$, Dore et al., 2009), the subtropical western North Pacific along 137° E in winter ($-0.0015 \pm 0.0002\,pH_T^{in\,situ}\,yr^{-1}$ to $-0.0021 \pm 0.0002\,pH_T^{in\,situ}\,yr^{-1}$, Midorikawa et al., 2010), off the south coast of Honshu, Japan ($-0.0020 \pm 0.0007\,pH_T^{in\,situ}\,yr^{-1}$, Ishii et al., 2011) and along 152° W between Hawaii and Alaska ($-0.0017\,pH_T^{25}\,yr^{-1}$, Byrne et al., 2010).

Because the western subarctic gyre is a source of CO_2 to the atmosphere in winter, owing to strong vertical mixing of deep waters rich in DIC, TA and nutrients (e.g., Takahashi et al., 2006), this slower pH decrease resulted from the combination of the increase of anthropogenic atmospheric CO_2, and the wintertime variation in the CO_2 emissions caused by the strong vertical mixing. We evaluated the CO_2 emission in winter from the difference between atmospheric and oceanic xCO$_2$. The increase of atmospheric xCO$_2$ from 1997 to 2011 (2.1 ± 0.0 ppm yr^{-1}) in winter is significantly higher than that of oceanic xCO$_2$ (1.2 ± 0.4 ppm yr^{-1}, $p < 0.005$), calculated from DIC_{win} and TA_{win}, both of which increased significantly during that period ($0.9 \pm 0.2\,\mu mol\,kg^{-1}\,yr^{-1}$, $p < 0.001$, and $0.5 \pm 0.2\,\mu mol\,kg^{-1}\,yr^{-1}$, $p < 0.01$, respectively) (Fig. 3). These results support the suggestion by Wakita et al. (2010a) that the decadal reduction in CO_2 emission in winter is due to the increase of TA.

In CO_2 system calculations based on DIC changes at constant TA in the seawater, the oceanic xCO$_2$ increase and the pH decrease are proportional to the DIC increase. If TA in seawater is increasing over time, however, then the oceanic xCO$_2$ increasing trend and pH decreasing rate must be slower than those calculated from the increase of DIC at constant TA. By applying this theoretical framework to the study region and assuming increasing DIC_{win} and constant TA_{win} ($2230\,\mu mol\,kg^{-1}$ in 1997), we estimate an oceanic xCO$_2$ increase and pH decrease of 2.6 ppm yr^{-1} and $-0.0026\,pH_T^{in\,situ}\,yr^{-1}$, respectively (Fig. 3). However, these rates are twice the actual oceanic xCO$_2$ increase and pH decrease rates in the winter mixed layer. Thus, the increasing trend of TA_{win} inhibits 50 % of CO_2 emission and acidification in winter by increasing DIC_{win} and favors the uptake of CO_2 in the winter mixed layer of western subarctic gyre.

Although the depth of winter mixed layer (T_{min} layer) remained unchanged during the study period (Fig. 3), the variation of TA_{win} was moderately but significantly correlated with that of the winter mixed layer depth ($r = 0.37$). The variation of the winter mixed layer is considered to be linked to atmospheric forcing such as wind stress, which are likely to be greatly affected by climate variation. Thus, CO_2 emission and acidification in winter should be affected by climate variation. Further investigation of the climate variations are needed to predict how ocean CO_2 emissions and acidification will evolve in this region in the future.

In addition to the increase in DIC_{win} and TA_{win}, PO_{4win} and Si_{win} also significantly increased during 1997–2011 ($0.012 \pm 0.002\,\mu\text{mol}\,\text{kg}^{-1}\,\text{yr}^{-1}$, $p < 0.001$, and $0.28 \pm 0.09\,\mu\text{mol}\,\text{kg}^{-1}\,\text{yr}^{-1}$, $p < 0.05$, respectively), whereas the density of the winter mixed layer (T_{min} layer) significantly decreased ($-0.003 \pm 0.002\,\text{kg}\,\text{m}^{-3}\,\text{yr}^{-1}$, $p < 0.05$). These results differ from those of Ono et al. (2001, 2002), who reported linear decreasing trends in physical and chemical properties such as salinity, and phosphate in the winter mixed layer in the Oyashio region and the subarctic western North Pacific from 1968 to 1998 as a result of occurrence of surface stratification. More accurate data and longer time series are required to determine the reason for this discrepancy.

3.2 Acidification around the $CaCO_3$ saturation horizons

Below the mixed layer in the western subarctic region, the calcite saturation horizon ($\Omega_{calcite} = 1$, ~ 185 m) has significantly shoaled at the rate of $2.9 \pm 0.9\,\text{m}\,\text{yr}^{-1}$ ($p < 0.001$), whereas the aragonite saturation horizon ($\Omega_{aragonite} = 1$) has remained constant at about 120 m depth (Fig. 4). This shoaling rate of $\Omega_{calcite} = 1$ is nearly three times higher than that in the Alaskan gyre between 40° N and 50° N from 1991 to 2006 (~ $1\,\text{m}\,\text{yr}^{-1}$) (Feely et al., 2012). One cause of upwards migration of the saturation horizon is the decrease of CO_3^{2-} concentration, because oceanic CO_2 uptake lowers Ω due to declining CO_3^{2-}. At the depth where $\Omega_{calcite} = 1$, a significant decrease in CO_3^{2-} at a rate of $-0.03 \pm 0.01\,\mu mol\,kg^{-1}\,yr^{-1}$ ($p < 0.005$) (Fig. 4) has thus caused shoaling of $\Omega_{calcite} = 1$.

Between $26.7\sigma_\theta$ and $27.0\sigma_\theta$, that is, around the depth where $\Omega_{aragonite} = 1$ ($\sim 26.8\sigma_\theta$), pH declined from 1997 to 2011 (Fig. 5, Table 1). The pH decrease rate in the 26.7–27.0σ_θ layer (-0.003 to $-0.005\,yr^{-1}$) was faster than the acidification rate expected from equilibration with the atmosphere ($-0.002\,yr^{-1}$). The elevated acidification rate at $26.9\sigma_\theta$ (Table 1) is higher than previous observed rate in the open North Pacific (at 250 m depth at Station ALOHA, $-0.003\,pH_T^{in\,situ}\,yr^{-1}$, Dore et al., 2009, and in the upper 500 m along 152° W between Hawaii and Alaska, $-0.004\,pH_T^{25}\,yr^{-1}$, Byrne et al., 2010), which include both anthropogenic and natural variations.

In addition, $\Omega_{aragonite}$ and $\Omega_{calcite}$ in the 26.8–27.0σ_θ layer significantly decreased at rates of -0.004 to $-0.005\,yr^{-1}$ and -0.006 to $-0.008\,yr^{-1}$, respectively, during our study period (Fig. 5, Table 1). These subsurface rates are slower than rates in subtropical mode water ($-0.034\Omega_{aragonite}\,yr^{-1}$) or in subsurface waters of the subarctic region (north of 40° N) along 179° E and 152° W (about $-0.007\,\Omega_{aragonite}\,yr^{-1}$ and $-0.010\,\Omega_{calcite}\,yr^{-1}$, Murata and Saito, 2012; Feely et al., 2012). In the western subarctic gyre, the significant increase in TA at a rate of $0.5 \pm 0.1\,\mu mol\,kg^{-1}\,yr^{-1}$ on the $26.9\sigma_\theta$ surface (Table 2) can account for the slower decline in Ω and CO_3^{2-} concentration in subsurface waters. In fact, the observed decrease rate of CO_3^{2-} on the $26.9\sigma_\theta$ surface ($-0.36\,\mu mol\,kg^{-1}\,yr^{-1}$) is slower than the rate calculated by using increasing DIC and constant TA ($-0.49\,\mu mol\,kg^{-1}\,yr^{-1}$); this calculated rate predicts a faster decline of Ω ($-0.007\,\Omega_{aragonite}\,yr^{-1}$, $-0.010\,\Omega_{calcite}\,yr^{-1}$) than the observed declines, which is in good agreement with rates in the subarctic region along 179° E and 152° W (Murata and Saito, 2012; Feely et al., 2012). Because one component of TA and DIC is CO_3^{2-}, increases in TA slow the decrease rates of $\Omega_{aragonite}$ and $\Omega_{calcite}$ in intermediate waters.

3.3 Impact of other properties on the pH decrease rate on the $26.9\sigma_\theta$ surface

Because we found that the pH decrease rate was enhanced between $26.8\sigma_\theta$ and $27.0\sigma_\theta$, we focus on the factors controlling the largest pH decrease rate, on $26.9\sigma_\theta$ ($-0.0051\,\text{pH}_T^{\text{in situ}}\,\text{yr}^{-1}$, Table 1), which was at the depth of the temperature maximum (e.g., Wakita et al., 2010a). In this study, we calculated $\text{pH}_T^{\text{in situ}}$ from pressure, temperature, salinity, phosphate, silicate, DIC, and TA; so, the pH decrease reflects significant temporal changes in these properties on $26.9\sigma_\theta$ from 1997 to 2011 (Table 2). Therefore, to investigate which properties dominantly controlled pH changes, we expressed the pH change (decrease) from 1997 to 2011 (ΔpH) as the sum of the change in each property, as follows:

$$\begin{aligned}\Delta\text{pH} =&(\partial\text{pH}/\partial\text{Press})\Delta\text{Press} + (\partial\text{pH}/\partial T)\Delta T + (\partial\text{pH}/\partial S)\Delta S + (\partial\text{pH}/\partial\text{PO}_4)\Delta\text{PO}_4\\ &+ (\partial\text{pH}/\partial\text{Si})\Delta\text{Si} + (\partial\text{pH}/\partial\text{DIC})\Delta\text{DIC} + (\partial\text{pH}/\partial\text{TA})\Delta\text{TA}\end{aligned} \tag{5}$$

where Press, T, and S are pressure (unit: db), temperature (unit: °C), and salinity, respectively. ΔPress, ΔT, ΔS, ΔPO_4, ΔSi, ΔDIC, and ΔTA show the changes in Press, T, S, PO_4, Si, DIC, and TA, respectively. In the actual calculation, we evaluated the rate of pH change by allowing one parameter to vary while using mean values for the other parameters. For example, we estimated the contribution of ΔDIC to ΔpH ($(\partial\text{pH}/\partial\text{DIC})\Delta\text{DIC}$) by calculating ΔpH using the increasing values of DIC from 1997 to 2011 and mean values for the other parameters ($-0.0064 \pm 0.0010\,\text{pH}_T^{\text{in situ}}\,\text{yr}^{-1}$, $p < 0.001$) and then computed the impact of ΔDIC on ΔpH to be 127 % by dividing the ΔDIC contribution by the rate of pH decline on $26.9\sigma_\theta$ ($-0.0064/-0.0051 \times 100$) (Fig. 6).

The results of these calculations show that ΔDIC had the largest negative impact on ΔpH (127 ± 32 %) and ΔTA had the largest positive impact (−34 ± 8 %) (Fig. 6). The increases in DIC and in temperature (ΔT impact, 8±2 %) over time enhanced the rate of acidification. The contribution of ΔT ($-0.0004 \pm 0.0001\,\text{pH}_T^{\text{in situ}}\,\text{yr}^{-1}$) was equivalent to the difference between the in situ and fixed temperature pH trends (Table 1). ΔTA and shoaling of the $26.9\sigma_\theta$ isopycnal surface (ΔPress, −2 ± 1 %) inhibited the pH decrease.

The impacts of ΔS, ΔPO_4, and ΔSi were negligibly small ($\sim 0\%$). The lack of a ΔS contribution means that the influence of local changes evaporation and precipitation was very low; therefore, there is no need to use salinity-normalized values of DIC, TA, and nutrients to correct for such an effect.

3.4 Contribution of the DIC increase to enhanced acidification

As shown in Sect. 3.3, ΔDIC dominantly accounted for the faster pH decline on $26.9\sigma_\theta$. We investigated factors affecting the DIC increase rate at this depth ($2.0 \pm 0.3\,\mu\mathrm{mol\,kg^{-1}\,yr^{-1}}$, $p < 0.001$) (Fig. 7, Table 2).

Changes of DIC in subsurface water are controlled by the gas exchange of CO_2 at the air–sea interface ($\mathrm{DIC_{air\text{-}sea}}$), the decomposition of organic matter ($\mathrm{DIC_{org}}$) and the dissolution of calcium carbonate ($\mathrm{DIC_{CaCO_3}}$). We can express the observed DIC change ($\Delta\mathrm{DIC_{obs}}$), as follows (e.g., Sabine et al., 2002):

$$\Delta\mathrm{DIC_{obs}} = \Delta\mathrm{DIC_{air\text{-}sea}} + \Delta\mathrm{DIC_{org}} + \Delta\mathrm{DIC_{CaCO_3}} \tag{6}$$

$\Delta\mathrm{DIC_{org}}$ is calculated as following,

$$\Delta\mathrm{DIC_{org}} = (\mathrm{C_{org}}/-\mathrm{O_2})\Delta\mathrm{AOU_{obs}} \tag{7}$$

where $\Delta\mathrm{AOU_{obs}}$ is the observed rate of the AOU change. AOU significantly increased at a rate of $1.8 \pm 0.4\,\mu\mathrm{mol\,kg^{-1}\,yr^{-1}}$ ($p < 0.0001$) (Fig. 7). $\Delta\mathrm{DIC_{org}}$ was calculated to be $1.2 \pm 0.3\,\mu\mathrm{mol\,kg^{-1}\,yr^{-1}}$.

The dissolution of $CaCO_3$ neutralizes CO_2 taken up by seawater and increases TA via the reaction ($CaCO_3 + CO_2 + H_2O \rightarrow 2HCO_3^- + Ca^{2+}$). We evaluated $\Delta\mathrm{DIC_{CaCO_3}}$ as $\Delta CaCO_3$ (Feely et al., 2004):

$$\Delta\mathrm{DIC_{CaCO_3}} = \Delta CaCO_3 = 0.5(\mathrm{TA} - \mathrm{TA}^\circ) + 0.63(16/170\mathrm{AOU}) \tag{8}$$

where TA° is preformed TA, calculated by using the equation of Sabine et al. (2002). $\Delta\mathrm{DIC_{CaCO_3}}$ significantly increased at a rate of $0.3 \pm 0.1\,\mu\mathrm{mol\,kg^{-1}\,yr^{-1}}$ ($p < 0.0001$)

(Fig. 7). This result, which is consistent with the 50 % increase of TA on the same isopycnal surface (Table 2), suggests that the dissolution of $CaCO_3$ particles increased as a result of the enhanced acidification caused by anthropogenic CO_2 and the AOU increase below the depth of $\Omega = 1$ (120–200 m); these saturation depths are shallower than the saturation depth in the open North Pacific (Feely et al., 2004).

By subtracting ΔDIC_{org} and ΔDIC_{CaCO_3} from ΔDIC_{obs} according to Eq. (6), we estimated $\Delta DIC_{air-sea}$ to be $0.5 \pm 0.4\,\mu mol\,kg^{-1}\,yr^{-1}$. This rate is indistinguishable from that expected under condition of seawater/atmosphere equilibration ($0.7\,\mu mol\,kg^{-1}\,yr^{-1}$), when calculated from the increase of atmospheric CO_2 ($2.1\,ppm\,yr^{-1}$) from 1997 to 2011 at 44.4° N (Conway et al., 2012) and constant TA_{win}. We assumed that $\Delta DIC_{air-sea}$ indicates the DIC increase due to the uptake of anthropogenic CO_2 (ΔDIC_{anth}). $DIC_{air-sea}$ includes the DIC content of waters in equilibrium with pre-industrial atmospheric CO_2 (280 µatm) (DIC_{eq280}) and the DIC content due to the of air–sea disequilibrium CO_2 effect (DIC_{diseq}). DIC_{eq280} remains constant over time and its trend can be cancelled out. We also can neglecte temporal change of DIC_{diseq} on $26.9\sigma_\theta$, i.e., $\Delta DIC_{diseq} = 0$, because $\Delta DIC_{air-sea}$ on $26.9\sigma_\theta$ ($0.5\,\mu mol\,kg^{-1}\,yr^{-1}$) was lower than the DIC_{win} increase ($0.9\,\mu mol\,kg^{-1}\,yr^{-1}$) which affected by the increase of anthropogenic CO_2 and the reduction of CO_2 emission in winter (Wakita et al., 2010a).

The contribution of ΔDIC ($2.0 \pm 0.3\,\mu mol\,kg^{-1}\,yr^{-1}$) is thus accounted for by ΔDIC_{org} (60 ± 17 %), ΔDIC_{anth} (25 ± 22 %) and ΔDIC_{CaCO_3} (15 ± 5 %). Acidification of intermediate water in the western subarctic gyre ($-0.0051 \pm 0.0010\,pH_T^{in\ situ}\,yr^{-1}$) was enhanced by increases in the decomposition of organic matter (75 ± 29 %) and, in the anthropogenic CO_2 uptake (31 ± 29 %), by the increased dissolution of $CaCO_3$ particles (19 ± 8 %) and by water temperature warming (8 ± 2 %), and it was inhibited by the TA increase (−34 ± 8 %) and the shoaling of the isopycnal surface (−2 ± 1 %). Because the ΔDIC_{CaCO_3} is equivalent to ∼ 50 % increase of TA, the enhanced contribution of the increased dissolution of $CaCO_3$ particles to faster pH decline could offset the inhibited contribution of TA increase. Non-anthropogenic CO_2 factor corresponds to ΔDIC_{org}

evaluated from AOU increase and must also contribute the pH decrease, independently of the uptake of anthropogenic CO_2. The non-anthropogenic CO_2 contribution dominantly accounted for the enhanced acidification of intermediate water rather than anthropogenic CO_2 uptake, but our value might be an overestimate. This is because the long-term trends and bi-decadal oscillations of AOU in subsurface waters in the northwestern subarctic Pacific Ocean have been reported (ex., Ono et al., 2001; Osafune and Yasuda, 2006; Watanabe et al., 2008; Takatani et al., 2012). In our data, collected during 1997–2011, AOU varies on a shorter than bi-decadal cycle and the AOU increase on $26.9\sigma_\theta$ ($1.8 \pm 0.4\,\mu\text{mol}\,\text{kg}^{-1}\,\text{yr}^{-1}$) was twice that from 1968 to 1998 in the Oyashio region near the western subarctic gyre ($0.8 \pm 0.3\,\mu\text{mol}\,\text{kg}^{-1}\,\text{yr}^{-1}$) (Ono et al., 2001). Considering this context and the stoichiometric ratio of carbon to oxygen from organic matter decomposition, the minimum possible contribution of non-anthropogenic CO_2 ($0.8 \times 117/170 = 0.55\,\mu\text{mol}\,\text{kg}^{-1}\,\text{yr}^{-1}$) is the same as the anthropogenic CO_2 uptake ($0.5 \pm 0.4\,\mu\text{mol}\,\text{kg}^{-1}\,\text{yr}^{-1}$) in the western subarctic gyre, which is the same the uptake rate in intermediate water along 152° W during 1991–2006 (Byrne et al., 2010) and 179° E during 1993–2007 (Murata and Saito, 2011). Thus, the enhanced acidification (pH decrease) between 200 and 300 m depth in this region reflects both anthropogenic CO_2 and non-anthropogenic CO_2 contribution, which will not affect the spatial distributions of acidification rates (Murata and Saito, 2011).

Temporal changes of AOU in the subsurface waters thus reflect those of both physical processes such as ocean circulation and ventilation and biological processes such as the production and remineralization of organic matter. The changes of physical processes will be dominant in causing the AOU changes (e.g., Deutsch et al., 2005; Mecking et al., 2008). The temporal variations of AOU in the $26.7–27.2\sigma_\theta$ layer in the Oyashio region and a wintertime wind stress curl anomaly in this region are negatively and positively correlated, respectively, with the bi-decadal component of the North Pacific Index (Ono et al., 2001; Ishi and Hanawa, 2005). Because AOU was positively correlated with DIC in the subsurface waters of the western subarctic gyre ($r = 0.99$) due to the decomposition of organic matter, DIC might also exhibit a bi-decadal oscillation. In addition, in this region, the weakening of the overturning circulation due to reduced winds since the 1970's causes DIC increase by AOU increase rather than anthropogenic CO_2 uptake (Feely et al., 2012). Considering that minimum estimates of anthropogenic CO_2 and non-anthropogenic CO_2 contributions are of similar magnitude, at least half of the pH decrease rate in the intermediate waters may be related to atmospheric forcing change related with the climate variations.

4 Conclusions

Anthropogenic CO_2 uptake and natural variability due to temporal changes in physical and biogeochemical processes affect acidifications in the both the winter mixed layer and intermediate waters in the western subarctic gyre. In the winter mixed layer, pH decreased at $-0.0011 \pm 0.0004\,\mathrm{pH}_T^{\text{in situ}}\,\mathrm{yr}^{-1}$ from 1997 to 2011, whereas $\Omega_{\text{aragonite}}$, Ω_{calcite}, and CO_3^{2-} remained unchanged. This decreasing trend of pH was slower than that predicted based on equilibration of atmospheric CO_2 with the seawater ($-0.002\,\mathrm{pH}_T^{\text{in situ}}\,\mathrm{yr}^{-1}$) and slower than decrease rates in other regions (Dore et al., 2009; Midorikawa et al., 2010; Ishii et al., 2011; Byrne et al., 2010). We attribute this lower rate to a reduction of CO_2 emission in winter caused by increased TA_{win}. Although the correlation of TA_{win} with the depth of the winter mixed layer ($r = 0.37$) is quite small, it is significant.

Below the mixed layer, the calcite saturation horizon ($\Omega_{\text{calcite}} = 1$) has shoaled at $2.9 \pm 0.9\,\mathrm{m\,yr}^{-1}$ because of declines in CO_3^{2-} ($-0.03 \pm 0.01\,\mu\mathrm{mol\,kg}^{-1}\,\mathrm{yr}^{-1}$), and the acidification rate at ~ 200 m depth ($-0.0051 \pm 0.0010\,\mathrm{pH}_T^{\text{in situ}}\,\mathrm{yr}^{-1}$) was larger than ever reported in the open North Pacific during the study period (e.g., Dore et al., 2009; Byrne et al., 2010). The enhanced pH decline reflected not only the uptake of anthropogenic CO_2 but also natural variability evaluated from the increase in AOU, which suggests that the dissolution of $CaCO_3$ particles increased. The TA increase due to this increase of $CaCO_3$ dissolution inhibited the decrease rate of $\Omega_{\text{aragonite}}$ and Ω_{calcite} in the intermediate water (-0.004 to $-0.005\,\text{yr}^{-1}$ and -0.006 to $-0.008\,\text{yr}^{-1}$).

The acidification observed at K2 and KNOT will affect carbonate forming biota in the surface and subsurface waters of the western subarctic region. However, our detection of the pH decrease in the winter mixed layer is not enough to clarify the impact of acidification on biological production and ecosystems in the entire western subarctic gyre. Therefore, the temporal variation of the pH in the mixed layer needs to be evaluated by using more accurate data from a longer time-series. Moreover, the CO_2 efflux from the winter mixed layer and the enhanced pH decrease in the subsurface waters must be related to changes in atmospheric forcing as well as the anthropogenic increase in atmospheric CO_2. Additional time-series data are required to investigate the relationships among temporal variability of pH, oceanic physical processes, and atmospheric forcing/climate index.

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Table 1. Rates of decrease of pH (total scale) at the in situ temperature ($\mathrm{pH}_T^{\text{in situ}}$) and at 25 °C ($\mathrm{pH}_T^{25}$), and Ω in the western subarctic gyre from 1997 to 2011. Error values are the standard error of the slope of the linear regression.

Layer	Depth [m][a]	$\mathrm{pH}_T^{\text{in situ}}$ [yr^{-1}]	pH_T^{25} [yr^{-1}]	$\Omega_{\text{Aragonite}}$ [yr^{-1}]	Ω_{calcite} [yr^{-1}]
$26.7\sigma_\theta$	144.0 ± 13.9	−0.0022 ± 0.0010 ($p < 0.05$)	−0.0019 ± 0.0009 ($p < 0.05$)	–	–
$26.8\sigma_\theta$	172.4 ± 19.1	−0.0036 ± 0.0009 ($p < 0.001$)	−0.0030 ± 0.0008 ($p < 0.001$)	−0.0040 ± 0.0012 ($p < 0.001$)	−0.0064 ± 0.0020 ($p < 0.001$)
$26.9\sigma_\theta$	215.3 ± 27.9	−0.0051 ± 0.0010 ($p < 0.001$)	−0.0042 ± 0.0009 ($p < 0.001$)	−0.0048 ± 0.0011 ($p < 0.001$)	−0.0077 ± 0.0018 ($p < 0.001$)
$27.0\sigma_\theta$	279.8 ± 33.3	−0.0039 ± 0.0009 ($p < 0.0001$)	−0.0032 ± 0.0008 ($p < 0.001$)	−0.0035 ± 0.0009 ($p < 0.001$)	−0.0055 ± 0.0015 ($p < 0.001$)

[a] Averages and standard deviations at the isopycnal surfaces.

Table 2. Rates of change in DIC and other parameters on the $26.9\sigma_\theta$ surface in the western subarctic gyre. Error values are the standard error of the slope of the linear regression.

Parameters	Rates	[units]	p value
Pressure	-1.72 ± 0.58	[db yr^{-1}]	< 0.005
Temperature	0.025 ± 0.005	[°C yr^{-1}]	< 0.001
Salinity	0.0027 ± 0.0006	[yr^{-1}]	< 0.001
Phosphate	0.011 ± 0.002	[µmol kg^{-1} yr^{-1}]	< 0.001
Silicate	0.23 ± 0.06	[µmol kg^{-1} yr^{-1}]	< 0.001
TA	0.5 ± 0.1	[µmol kg^{-1} yr^{-1}]	< 0.001
DIC	2.0 ± 0.3	[µmol kg^{-1} yr^{-1}]	< 0.001

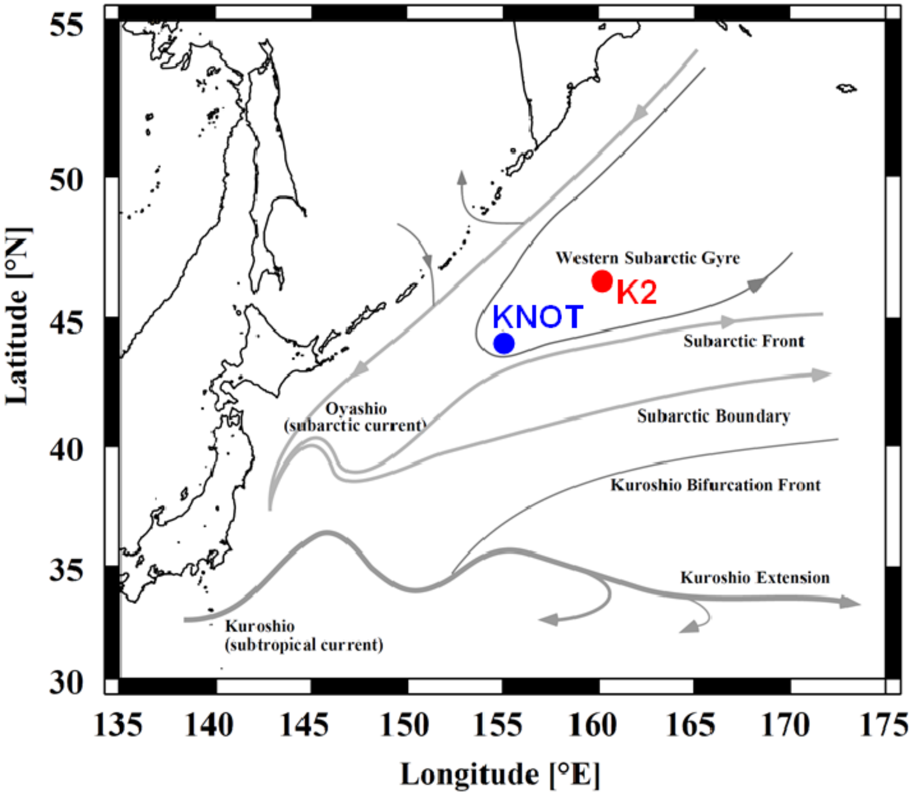

Fig. 1. Time-series stations and the main ocean currents in the western North Pacific.

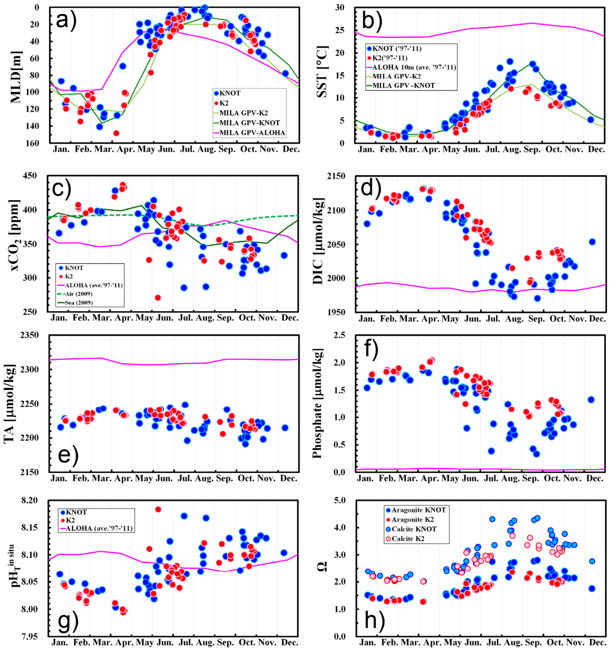

Fig. 2. Seasonal variations of **(a)** the maximum mixed layer depth (MLD), **(b)** sea surface temperature (SST), **(c)** oceanic and atmospheric $x\mathrm{CO}_2$, **(d)** DIC, **(e)** TA, **(f)** phosphate, **(g)** pH (total scale) at the in situ temperature ($\mathrm{pH}_T^{\text{in situ}}$), and **(h)** CaCO_3 saturation states (Ω) with respect to aragonite and calcite in the surface mixed layer at KNOT (blue circles) and K2 (red circles). These figures were plotted using all data from 1997 to 2011 in order to examine typical seasonal variations and for comparison with the climatological monthly means of MIxed Layer data set of Argo, Grid Point Value (MILA GPV) (Hosoda et al., 2010) **(a, b)**, data from Station ALOHA (Dore et al., 2010) **(b–g)**, and Takahashi et al. (2009) **(c)**. Values of oceanic $x\mathrm{CO}_2$ **(c)**, $\mathrm{pH}_T^{\text{in situ}}$ **(g)** and Ω **(h)** were calculated from TA and DIC. The density criterion in the surface mixed layer was smaller than 0.125 kg m^{-3} (de Boyer Montégut et al., 2004).

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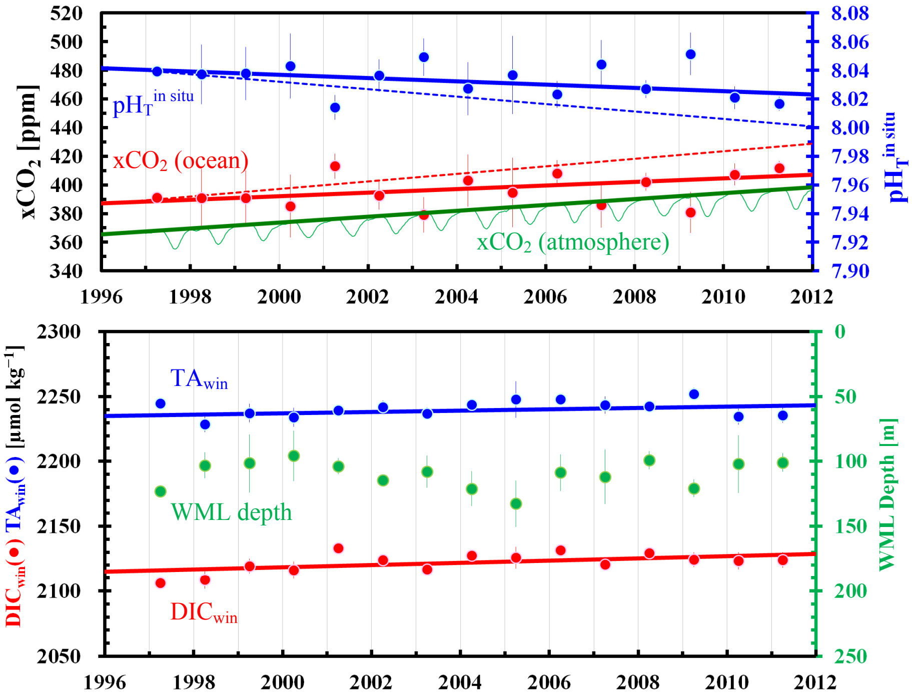

Fig. 3. Time-series of $pH_T^{\text{in situ}}$ (blue circles) and $x\text{CO}_2$ in the ocean (red circles) and the atmosphere (light green curve) at 44.4° N (Conway et al., 2012) (upper panel), and DIC, TA, and depth in the winter mixed layer (DIC_{win}, TA_{win}, WML depth) (lower panel). Regression lines for 1997 to 2011 are shown for $pH_T^{\text{in situ}}$ (blue line, $-0.0011 \pm 0.0004\,\text{yr}^{-1}$, $p < 0.01$); oceanic $x\text{CO}_2$ in winter (red line, $1.2 \pm 0.4\,\text{ppm}\,\text{yr}^{-1}$, $p < 0.005$); atmospheric $x\text{CO}_2$ in winter (green line, $2.1 \pm 0.0\,\text{ppm}\,\text{yr}^{-1}$, $p < 0.001$); TA_{win} (blue line, $0.5 \pm 0.2\,\mu\text{mol}\,\text{kg}^{-1}\,\text{yr}^{-1}$, $p < 0.01$); and DIC_{win} (red line, $0.9 \pm 0.2\,\mu\text{mol}\,\text{kg}^{-1}\,\text{yr}^{-1}$, $p < 0.001$). Regression lines shown for the theoretical $pH_T^{\text{in situ}}$ (blue dashed line, $-0.0026\,\text{yr}^{-1}$) and $x\text{CO}_2$ in the ocean (red dashed line, $2.6\,\text{ppm}\,\text{yr}^{-1}$) were calculated by using increasing values of DIC and constant TA ($2240\,\mu\text{mol}\,\text{kg}^{-1}$).

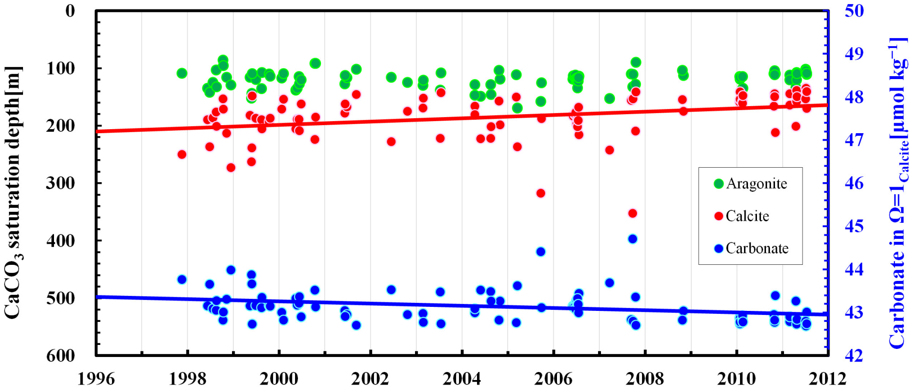

Fig. 4. Time-series of the depth of the saturation state of seawater with respect to aragonite (green circles) and calcite ($\Omega_{\text{calcite}=1}$; red circles) (left axis), and the concentration of carbonate where $\Omega_{\text{calcite}=1}$ (blue circles) in the western subarctic gyre (right axis). Regression lines for 1997 to 2011 are shown for $\Omega_{\text{calcite}=1}$ (red line, $-2.9 \pm 0.9\,\text{m}\,\text{yr}^{-1}$, $p < 0.001$) and carbonate where $\Omega_{\text{calcite}=1}$ (blue line, $-0.03 \pm 0.01\,\mu\text{mol}\,\text{kg}^{-1}\,\text{yr}^{-1}$, $p < 0.005$).

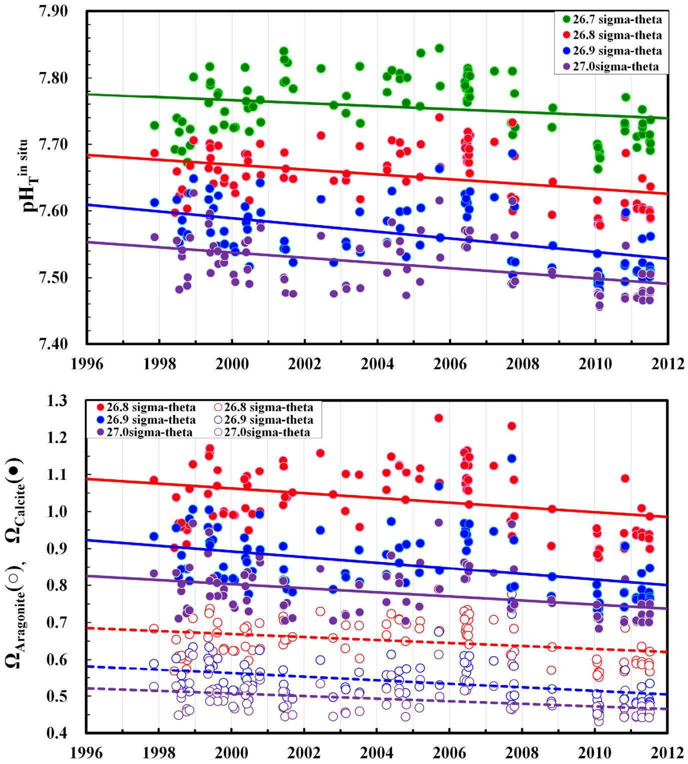

Fig. 5. Time-series of $pH_T^{\text{in situ}}$ (upper panel), and the saturation state of seawater with respect to aragonite ($\Omega_{\text{Aragonite}}$, open circles) and calcite (Ω_{Calcite}, closed circles) (lower panel) in the $26.7\sigma_\theta$–$27.0\sigma_\theta$ layer. The regression lines for $pH_T^{\text{in situ}}$, $\Omega_{\text{Aragonite}}$, and $\Omega_{\text{calcite}=1}$ decrease significantly from 1997 to 2011 (see Table 1).

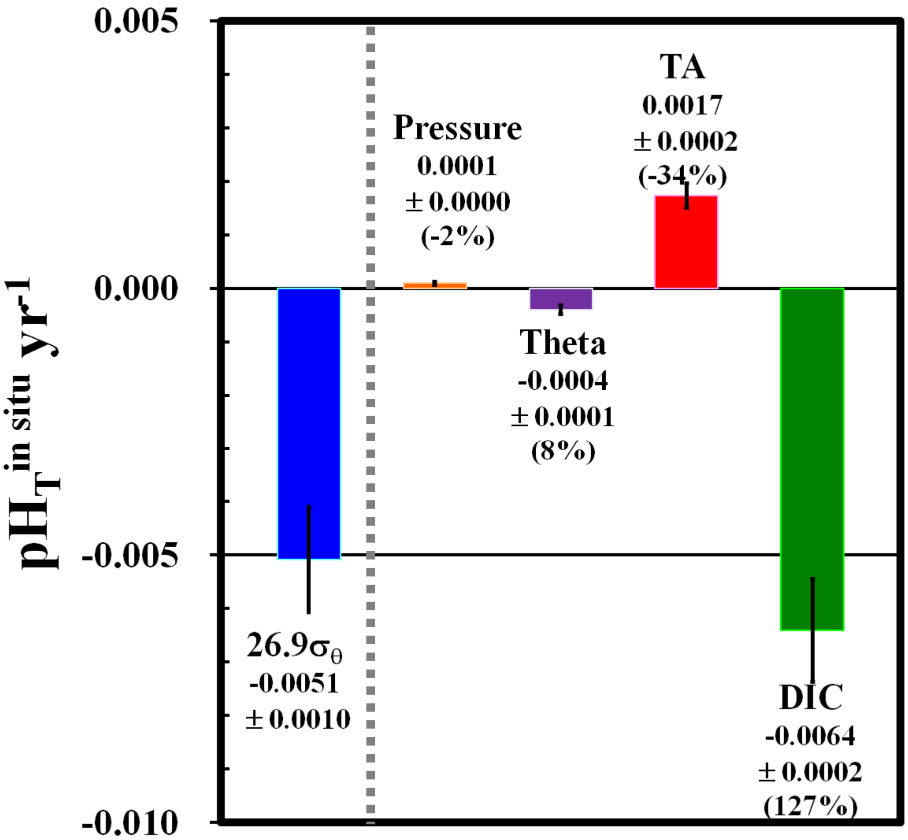

Fig. 6. Contributions of various parameters to the pH decrease on the $26.9\sigma_\theta$ surface. The percentages in parentheses indicate the relative contribution of each parameter to the pH decrease ($-0.0051 \pm 0.0010\,pH_T^{in\ situ}\,yr^{-1}$).

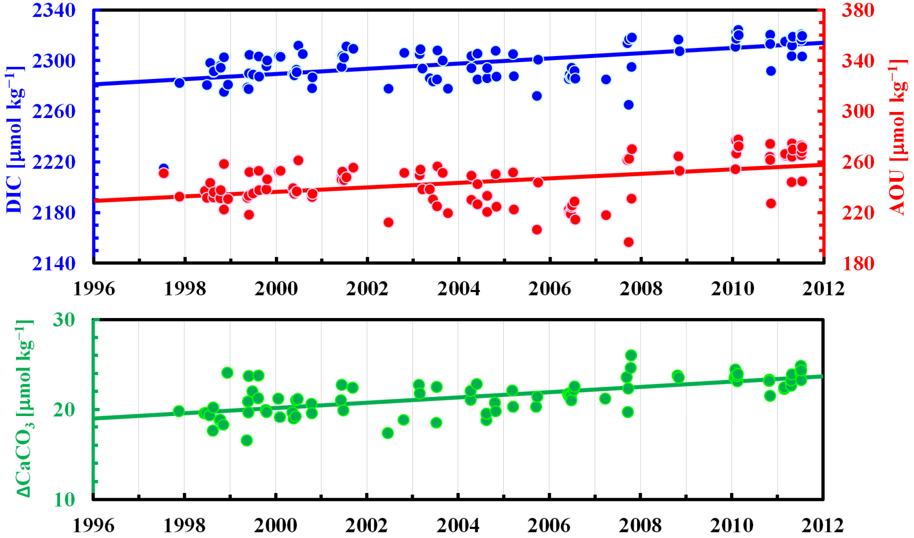

Fig. 7. Time-series of DIC (blue circles) and AOU (red circles) (upper panel) and $\Delta CaCO_3$ (green circles) (lower panel) on the $26.9\sigma_\theta$ surface. Regression lines for 1997 to 2011 are shown for DIC (blue line, $2.0 \pm 0.3\,\mu mol\,kg^{-1}\,yr^{-1}$, $p < 0.001$), AOU (red line, $1.8 \pm 0.4\,\mu mol\,kg^{-1}\,yr^{-1}$, $p < 0.001$) and $\Delta CaCO_3$ (green line, $0.3 \pm 0.1\,\mu mol\,kg^{-1}\,yr^{-1}$, $p < 0.001$).