Recent change in the oceanic uptake rate of anthropogenic carbon in the North Pacific subpolar region determined by using a carbon-13 time series

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[1] Applying the δ^{13}C approach to time series of observations in the North Pacific subpolar region (Station KNOT; 44°00′N, 155°00′E), we demonstrated time series of vertical distributions of oceanic anthropogenic carbon. We found that the vertical distributions of oceanic anthropogenic carbon during 1999–2006 were almost consistent with those estimated by the other carbon-based quasi-conservative tracer approach (ΔC*). Comparing the oceanic anthropogenic carbon contents and the water-column inventories among 1999, 2000, and 2006, we found the recent oceanic uptake rate of anthropogenic carbon above 27.3 σ_θ to be 0.86 ± 0.12 μmol kg^{-1} yr^{-1}, which was 1.2 times higher than the expected value derived from oceanic equilibration with increasing atmospheric CO_2. Considering the strengthened ocean stratification with a bidecadal oscillation and the recent increase in alkalinity from the Sea of Okhotsk, it was possible to explain the difference in the recent oceanic uptake rate of anthropogenic carbon between our result and the expected one.

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1. Introduction

[2] Anthropogenic CO_2 emitted to the atmosphere is responsible for the observed global warming, strengthening of ocean stratification, decline in phytoplankton productivity, and ocean acidification over several decades [e.g., *Watanabe et al.*, 2001; *Chiba et al.*, 2004; *Feely et al.*, 2004; *IPCC*, 2007; *Sabine et al.*, 2008]. One possible consequence of the increased atmospheric anthropogenic CO_2 content is a decline in the efficiency of absorption of anthropogenic carbon by the ocean, which might have a positive feedback effect. When considering the present and future balance of anthropogenic carbon, it is necessary to determine how much anthropogenic carbon the ocean absorbs and where the carbon accumulates in the ocean.

[3] Several observational data-based approaches have been used to investigate anthropogenic carbon in the ocean, including the following approaches: (1) the dissolved inorganic carbon (DIC) time-series approach [e.g., *Wakita et al.*, 2005], (2) the noncarbon conservative tracer approach based on transient chemical tracers [e.g., *Watanabe et al.*, 2000; *McNeil et al.*, 2003], (3) the empirical hydrographic relationship approach with multiple linear regression of inorganic carbon versus other hydrographic parameters [e.g., *Brewer et al.*, 1995; *Sabine et al.*, 2008], and (iv) the carbon-based quasi-conservative tracer approach [e.g., *Quay et al.*, 2003; *Sabine et al.*, 2004a; *Sonnerup et al.*, 2007].

[4] *Sabine et al.* [2004b] reviewed these observational data-based approaches in detail to clarify the advantages and disadvantages of each.

[5] 1. The DIC time-series approach has the advantage that the increase in carbon is directly measured, but it is difficult for this approach to distinguish the anthropogenic uptake of carbon from the natural uptake. In particular, in relation to the decadal natural oscillation and the strengthening ocean stratification caused by global warming, it is hard to estimate only the anthropogenic carbon in the ocean without large uncertainties [e.g., *Wakita et al.*, 2005; *Sabine et al.*, 2008].

[6] 2. The noncarbon conservative tracer approach has the advantage that it uses transient chemical tracers not influenced by biological activity. This approach is a powerful tool for determining the spatiotemporal distribution of anthropogenic carbon in the ocean because many transient chemical tracer data are readily available. However, it is difficult to validate the reliability owing to the lack of direct measurements of carbon.

[7] 3. The empirical hydrographic relationship approach has the advantage that it uses strong correlations with hydrographic parameters not affected by anthropogenic CO_2 to correct the modest water mass variations that complicate the interpretation of results in the DIC time-series approach. Unfortunately, the measured values of each parameter used in the regression have uncertain larger systematic biases.

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Table 1. Estimations for Long-Term Trends of S-δ^{13}C and DIC, and Dynamic Constraint Ratio (D) in Sea Surface Water[a]

	Analytical Method	S-δ^{13}C (‰ δ^{13}C yr^{-1})	DIC (μmol kg^{-1} yr^{-1})	D (‰ (μmol kg^{-1})$^{-1}$)	References
Observational time-series data					
Subpolar region					
North Pacific, KNOT (44°00′N, 155°00′E)	TCM	−0.019 ± 0.002	1.62 ± 0.42	−0.012 ± 0.003	This study[b]
	FSEM	−0.012 ± 0.010	1.00 ± 0.90	−0.012 ± 0.015	*Tanaka et al.* [2003][c]
	ΔC*	-	1.4 ± 0.3	-	*Wakita et al.* [2010][d]
Subtropical region					
North Atlantic, BATS (31°50′N, 64°10′W)	TCM	−0.025 ± 0.002	1.32 ± 0.18	−0.019 ± 0.003	*Bacastow et al.* [1996] *Bates et al.* [2002]
North Pacific, HOT (22°45′N, 158°00′W)	TCM	−0.025 ± 0.002	1.00 ± 0.33	−0.025 ± 0.008	*Gruber et al.* [1999] *Winn et al.* [1998]
Model calculation					
Global mean				−0.016 to −0.019	*Keir et al.* [1999] *McNeil et al.* [2001]

[a]ΔC*, carbon-based quasi-conservative tracer approach; DIC, dissolved inorganic carbon; FSEM, Fourier sine expansion method; TCM, temperature correction method (see text for details). Mean ± standard error.
[b]Estimation based on the data set from 1997 to 2006.
[c]Estimation based on the data set from 1997 to 2002.
[d]Estimation based on the data set from 1997 to 2008 at ca. 100 m depth.

[8] 4. Therefore, the carbon-based quasi-conservative tracer approach has been widely used as a compromise between the DIC time-series approach and the noncarbon conservative tracer approach, which are as follows: (1) one approach involves the use of thermodynamic and stoichiometric relationships to derive the carbon-based quasi-conservative tracer, the ΔC* approach [*Gruber et al.*, 1996] and (2) the other is based on changes in δ^{13}C, the δ^{13}C approach [*Quay et al.*, 2003].

[9] The ΔC* approach is useful for determining the spatial distribution of anthropogenic carbon in the ocean given certain assumptions, while the ΔC* approach has the disadvantage that an air-sea disequilibrium can affect the estimate of anthropogenic carbon. Thus the ΔC* approach has been widely used in most estimations of oceanic anthropogenic carbon despite the disadvantage. In contrast, the δ^{13}C approach has advantages over both the DIC time-series approach and the ΔC* approach. The anthropogenic δ^{13}C signal in the ocean is generally large relative to the seasonal variability in δ^{13}C, in contrast to DIC or pCO$_2$ [*Quay et al.*, 2003]. For example, in the subtropical regions, *Gruber et al.* [2002] demonstrated that anthropogenic change in δ^{13}C decreases in the surface water by 0.25‰ per decade, which is of the same magnitude as the variation in its seasonal cycle, whereas the corresponding decadal increase in DIC corresponds to only 20% of its seasonal amplitude of variation. In subpolar regions, *Tanaka et al.* [2003] showed that the anthropogenic change in δ^{13}C relative to the amplitude of its seasonal variation (~10%) is also larger than the corresponding change in DIC in relation to its seasonal variation. Gas exchange between the atmosphere and the ocean causes this decrease in the δ^{13}C in DIC, which is recognized as the oceanic δ^{13}C Seuss effect (S-δ^{13}C).

[10] The accumulation rate of oceanic anthropogenic carbon was recently estimated using the oceanic S-δ^{13}C [*Quay et al.*, 1992; *Tans et al.*, 1993; *Bacastow et al.*, 1996; *Heimann and Maier-Reimer*, 1996; *Keir et al.*, 1998; *Gruber and Keeling*, 2001; *Körtzinger et al.*, 2003; *Quay et al.*, 2003, 2007; *Sonnerup et al.*, 2007]. The method used in most cases is to compare the δ^{13}C of DIC among several cruises, with sufficient time intervals separating the cruises to allow resolution of the relatively small decrease in long-term δ^{13}C. However, the seasonal variability of δ^{13}C in the ocean has hardly been considered in the estimation of S-δ^{13}C, and the lack of high-quality historical δ^{13}C data has also made it difficult to estimate S-δ^{13}C exactly.

[11] To overcome the problem, long-time-series observations have been carried out since the late 1980s at two stations in the subtropical region (Station BATS, 31°50′N, 64°10′W; and Station HOT, 22°45′N, 158°00′W) and since the late 1990s at one station in the North Pacific subpolar region (Station KNOT, 44°00′N, 155°00′E). The two subtropical stations and the one subpolar station are the only oceanic stations worldwide at which long-time-series observations of oceanic carbon species along with other hydrographic parameters have been carried out. A long time series of carbon species can allow consideration of the seasonal variability of δ^{13}C in the ocean. However, we can find another disadvantage in the δ^{13}C approach. The decrease in δ^{13}C and the increase in anthropogenic CO$_2$ are strongly correlated on a global scale with the use of fossil fuels (S-δ^{13}C) [e.g., *Friedli et al.*, 1986; *Takahashi et al.*, 2000; *Körtzinger et al.*, 2003]. Despite this fact, the ratio of the decreasing rate of δ^{13}C to the increasing rate of DIC in the ocean (the dynamic constraint ratio, D) varies significantly spatially because of variability in the surface residence time with respect to gas exchange and circulation. In fact, the δ^{13}C signal shows large differences between the subtropical and the subpolar regions [*McNeil et al.*, 2001; *Gruber et al.*, 2002; *Tanaka et al.*, 2003] (Table 1). In addition, the seasonal variability has been considered in the estimation of D only at the two stations in the subtropical regions of the North Atlantic and North Pacific [*Gruber et al.*, 1999] and the one station in the subpolar region of the North Pacific [*Tanaka et al.*, 2003]. Thus, to clarify the ocean uptake of anthropogenic CO$_2$ on a global scale, the δ^{13}C approach could not have been used.

[12] The Intergovernmental Panel on Climate Change [*IPCC*, 2007] reported that global warming has led to changes in the global ocean environment. In the North Pacific several studies have shown the same trends as observed globally as a result of the weakening of the

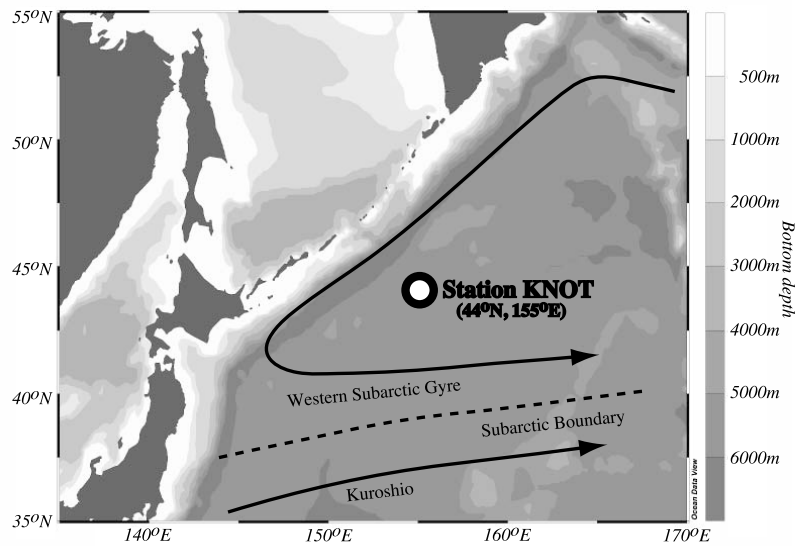

Figure 1. Sampling location in the North Pacific subpolar region, Station KNOT (44°00′N, 155°00′E).

formation and circulation of the North Pacific Intermediate Water (NPIW) [e.g., *Ono et al.*, 2001; *Watanabe et al.*, 2001; *Emerson et al.*, 2004; *Nakanowatari et al.*, 2007]. The NPIW is the only water mass produced in the North Pacific, and one of its origins is the western North Pacific subpolar region including the Okhotsk Sea [e.g., *Yasuda*, 1997]. It spreads throughout the North Pacific, affecting the climate there. Consequently, it is possible to reduce the efficiency of uptake of anthropogenic CO_2 in the North Pacific subpolar region.

[13] In this region, *D* has already been estimated, taking into account seasonal variability based on time-series observations at Station KNOT [*Tanaka et al.*, 2003], although the error was significant large. We focus here only on gyre-scale changes in the uptake of anthropogenic carbon by the ocean, rather than global scale, because the $\delta^{13}C$ signal of DIC is a powerful tool on this scale, and the time series of $\delta^{13}C$ has a potential to exactly estimate the oceanic uptake rate of anthropogenic CO_2 without it being necessary to distinguish between the anthropogenic effect and the decadal natural oscillation. Therefore, we tried to use the time-series data set of $\delta^{13}C$ at Station KNOT (Figures 1 and 2) to estimate the vertical profiles of oceanic anthropogenic CO_2 independently from the other approaches. In addition, we tried to derive the oceanic uptake rate of anthropogenic CO_2 and the recent changes in the efficiency of CO_2 uptake in the North Pacific subpolar region.

2. Data Set

[14] Time-series observations of hydrographic properties at Station KNOT were carried out from July 1997 to July 2004 and in May 2006, during cruises of T/S *Housei Maru*, T/S *Oshoro Maru*, R/V *Bousei Maru*, and R/V *Mirai*. Station KNOT is at 44°00′N, 155°00′E in the southwestern part of the North Pacific subpolar region (Figure 1). The vertical profiles of $\delta^{13}C$ were obtained for 0 to 3000 m depth during 11 cruises in 1999, 2000, and 2006. Seawater samples for $\delta^{13}C$ analysis were collected in 120 mL glass bottles, poisoned with a saturated solution of $HgCl_2$ immediately after sampling, and stored under refrigeration in the dark. In the laboratory the CO_2 gas samples for $\delta^{13}C$ were extracted from the seawater by a modification of the method of *Kroopnick* [1974] and measured using a mass spectrometer (Finnigan MAT, Delta S). $\delta^{13}C$ values are expressed as the per mil deviation of the ^{13}C-to-^{12}C isotopic ratio relative to the Peedee belemnite standard. The precision of $\delta^{13}C$ measurements determined by a replicate analysis was less than ±0.02‰ $\delta^{13}C$. The variation in $\delta^{13}C$ among the different cruises was 0.02‰ $\delta^{13}C$, for DIC from below a 2500 m water depth. The DIC content was determined according to the Department of Energy protocol [*Dickson and Goyet*, 1994]. We corrected the DIC content against certified reference materials provided by Professor A. G. Dickson (Scripps Institute of Oceanography) and estimated the variation in DIC to be 0.1%. We also compared DIC values below a 2500 m water depth among different cruises and found the variability of DIC to be 2.4 μmol kg^{-1}. In this study, therefore, we used these time -series of $\delta^{13}C$ and DIC data without making any correction for bias. In addition, dissolved oxygen (DO) was measured by the Winkler method, and the offset was less than 1 μmol kg^{-1}. We also used the DO data without making any correction for the offset. The foregoing data sets will be opened soon on the homepage of PACIFICA (Pacific Ocean Interior Carbon), followed in PICES (North Pacific Marine Science Organization; http:/cidiac.orml.gov/ocean/PACIFICA).

3. Methods

3.1. Concept for Estimating the Vertical Profile of Oceanic Anthropogenic Carbon

[15] The observed DIC (DIC_{obs}) and $\delta^{13}C$ of DIC ($\delta^{13}C_{obs}$) consist of three components: (1) the amounts of DIC and $\delta^{13}C$ derived from the exchange of CO_2 between the air and the sea (DIC_{as} and $\delta^{13}C_{as}$), (2) the changes in

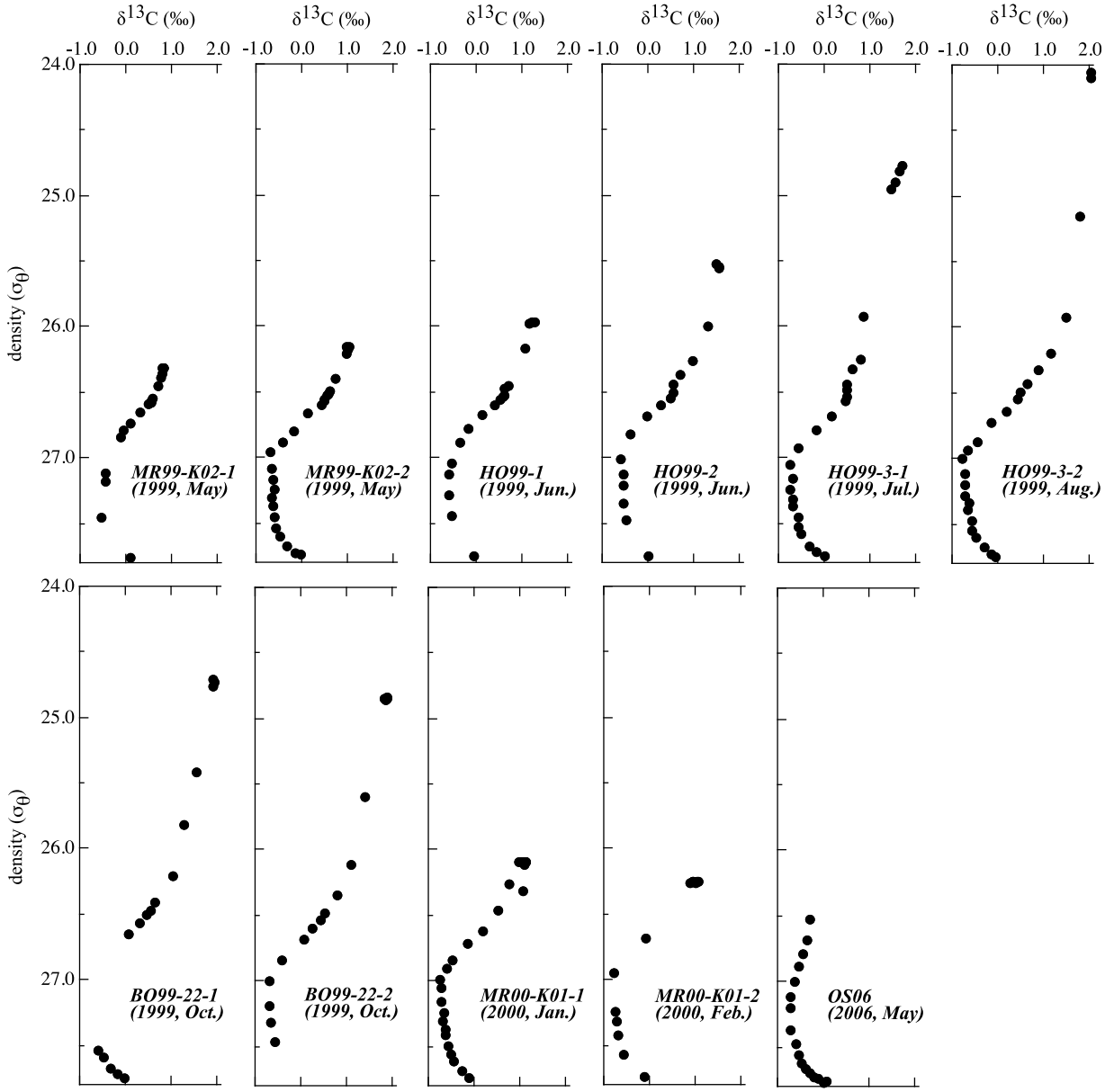

Figure 2. Time series of vertical profiles of δ^{13}C versus density during 1999, 2000, and 2006 at Station KNOT.

DIC and δ^{13}C due to the net production and remineralization of organic matter derived from phytoplankton (ΔDIC_{org} and $\delta^{13}C_{org}$), and (3) the changes in DIC and δ^{13}C due to the production and dissolution of $CaCO_3$ (ΔDIC_{CaCO_3} and $\delta^{13}C_{CaCO_3}$). The latter two components for both DIC and δ^{13}C can be replaced by the apparent oxygen utilization (AOU), the stoichiometric ratio of carbon remineralization to AOU ($R_{DIC/AOU}$), and the half of the change in alkalinity from the surface water (ΔAlk/2) as follows:

$$\begin{aligned} DIC_{obs} &= DIC_{as} + \Delta DIC_{org} + \Delta DIC_{CaCO_3} \\ &= DIC_{as} + R_{DIC/AOU}AOU + (\Delta Alk + \Delta DIN)/2 \\ &= DIC_{as} + R_{DIC/AOU}AOU + \left[(Alk_{obs} - Alk_0) + R_{DIN/AOU}AOU\right]/2, \end{aligned} \tag{1}$$

and

$$\begin{aligned} \delta^{13}C_{obs}DIC_{obs} &= \delta^{13}C_{as}DIC_{as} + \delta^{13}C_{org}\Delta DIC_{org} + \delta^{13}C_{CaCO_3}\Delta DIC_{CaCO_3} \\ &= \delta^{13}C_{as}DIC_{as} + \delta^{13}C_{org}R_{DIC/AOU}AOU \\ &\quad + \delta^{13}C_{CaCO_3}\left[(Alk_{obs} - Alk_0) + R_{DIN/AOU}AOU\right]/2, \end{aligned} \tag{2}$$

where Alk_{obs} and Alk_0 are the observed alkalinity and the preformed alkalinity, respectively. DIN and $R_{DIN/AOU}$ are the dissolved inorganic nitrogen and the stoichiometric ratio of oceanic fixed nitrogen remineralization to AOU, respectively.

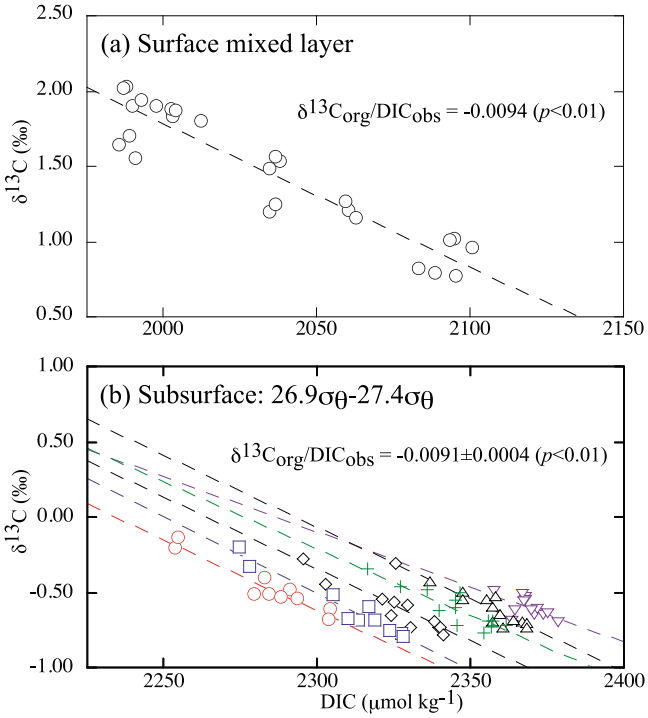

Figure 3. Relationship between $\delta^{13}C_{obs}$ and observed dissolved inorganic carbon (DIC_{obs}) in (a) surface water (0–10 m) and (b) subsurface waters below the winter mixed layer: red circles, 26.9 σ_θ; blue squares, 27.0 σ_θ; black diamonds, 27.1 σ_θ; green crosses, 27.2 σ_θ; black triangles, 27.3 σ_θ; purple inverted triangles, 27.4 σ_θ.

[16] Arranging equations (1) and (2) in terms of $\delta^{13}C_{as}$, we can obtain the following equation:

$$\delta^{13}C_{as} = \frac{\left\{\begin{array}{c}\delta^{13}C_{obs} - \left(\delta^{13}C_{org}/DIC_{obs}\right)R_{DIC/AOU}AOU \\ -\varepsilon_{CaCO_3}\left[\left(Alk_{obs} - Alk_0\right) + R_{DIN/AOU}AOU\right]/2DIC_{obs}\end{array}\right\}}{1 - R_{DIC/AOU}AOU\dfrac{AOU}{DIC_{obs}}}, \quad (3)$$

where ε_{CaCO_3} is the difference fractionation factor of ^{13}C in $CaCO_3$ produced at the sea surface ($\varepsilon_{CaCO_3} = \delta^{13}C_{CaCO_3} - \delta^{13}C_{as}$). $R_{DIC/AOU}$ is assumed to be an almost-constant value of 106/170 [*Anderson and Sarmiento*, 1994], because the influence of anthropogenic CO_2 on DIC_{obs} is expected to be only a few percent [e.g., *Sabine et al.*, 2004b]. Combining this equation with the dynamic constraint ratio corrected for the seasonal variability (D), we can estimate the amount of oceanic anthropogenic carbon (C_{ant}) accumulated from the preindustrial era (0) to an arbitrary time (t):

$$C_{ant(t)} = \frac{\delta^{13}C_{as(t)} - \delta^{13}C_{as(0)}}{D}, \quad (4)$$

In the case where $\delta^{13}C_{as(0)}$ cannot be clarified, it is difficult to estimate C_{ant}. In this case, focusing only on the rate of oceanic uptake of anthropogenic carbon during an arbitrary time interval (ΔC_{ant}) and not the increase over the entire time from the preindustrial period to the present, we can estimate ΔC_{ant} here as follows:

$$\Delta C_{ant} = \left(C_{ant(t+\Delta t)} - C_{ant(t)}\right)/\Delta t = \left(\frac{\delta^{13}C_{as(t+\Delta t)} - \delta^{13}C_{as(t)}}{D}\right)/\Delta t. \quad (5)$$

[17] At Station KNOT in the North Pacific subpolar region, D has already been estimated to be −0.012‰ (μmol kg^{-1})$^{-1}$ in the surface water [*Tanaka et al.*, 2003], although the error was significantly large. Considering ε_{CaCO_3} = +1‰ [*Romanek et al.*, 1992] and the expected value of ΔAlk_0 in the Pacific [*Sabine et al.*, 2002], we can neglect the second term in the numerator on the right-hand side of equation (3) as the change in alkalinity because it is much smaller than the estimated $\delta^{13}C_{as}$. To obtain the relationship of $\delta^{13}C_{org}/DIC_{obs}$ in equation (3), therefore, we can also use equation (5) to evaluate ΔC_{ant} for a specific period. These errors are discussed in detail in section 3.2.

3.2. Error Estimations

3.2.1. Sensitivity of $\delta^{13}C_{as}$ to a Change in Alkalinity

[18] Since it is actually difficult to obtain the value of Alk_0 from observational data, *Sabine et al.* [2002] proposed an empirical equation for Alk_0 in the Pacific that was expressed in terms of salinity, phosphate, DO, and potential temperature. In addition, *Romanek et al.* [1992] showed that ε_{CaCO_3} = +1‰ when calcite is formed in seawater. *Anderson and Sarmiento* [1994] also estimated $R_{DIN/AOU}$ to be 16/170. Using these relationships with our observations of DIC_{obs}, we estimated that the change in the second term of the numerator on the right-hand side of equation (3) was less than 0.01‰ in the North Pacific subpolar region, which was equivalent to being within 0.5% of all the numerators in equation (3) for the range of $\delta^{13}C_{obs}$ from −0.8‰ to 2.0‰ in our study (Figure 2). Therefore, it is possible to neglect the second term in the numerator on the right-hand side of equation (3) as the change in alkalinity.

3.2.2. Estimation of $\delta^{13}C_{org}/DIC_{obs}$

[19] Considering the difference in the fractionation factor of ^{13}C between phytoplankton and seawater ($\varepsilon_{org} = \delta^{13}C_{org} - \delta^{13}C_{as}$), and arranging equations (1)–(3) in terms of $\delta^{13}C_{obs}$, we obtain the following equation:

$$\begin{aligned}\delta^{13}C_{obs} &= \left(\delta^{13}C_{org}/DIC_{obs}\right)DIC_{obs} - \varepsilon_{org}\left(DIC_{as}/DIC_{obs}\right) \\ &\quad + \left(\varepsilon_{CaCO_3} - \varepsilon_{org}\right)\left[\left(Alk_{obs} - Alk_0\right) + R_{DIN/AOU}AOU\right]/2DIC_{obs} \\ &\approx \left(\delta^{13}C_{org}/DIC_{obs}\right)DIC_{obs} - \varepsilon_{org}\left(DIC_{as}/DIC_{obs}\right) \quad (6)\end{aligned}$$

$$= \delta^{13}C_{org} - \varepsilon_{org}\left(DIC_{as}/DIC_{obs}\right). \quad (6')$$

Equation (6) may allow us to evaluate $\delta^{13}C_{org}/DIC_{obs}$ as the slope of a line obtained by plotting the time-series data of $\delta^{13}C_{obs}$ against DIC_{obs} in the surface mixed layer and/or the subsurface isopycnal horizons at a fixed observation site. In the surface mixed layer and the six isopycnal horizons below the winter mixed layer (26.9 σ_θ, 27.0 σ_θ, 27.1 σ_θ,

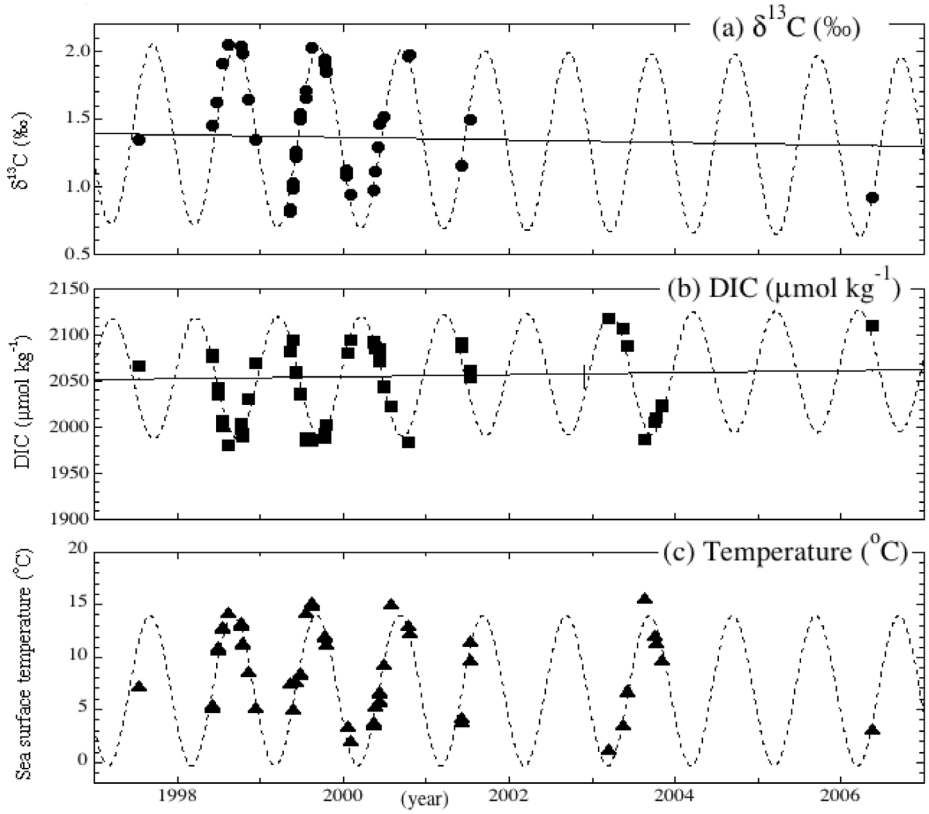

Figure 4. Time-series data for (a) $\delta^{13}C$, (b) DIC, and (c) water temperature in the surface mixed layer at Station KNOT from 1997 to 2006 according to the fitting curve method used by *Tanaka et al.* [2003]. Fitting curves obtained using the Fourier sine expansion were as follows: (a) $\delta^{13}C = -0.012y + 22 + 0.66 \sin[2\pi(y - 2030)/1.0]$ ($R = 0.97$, SE = 0.02‰ $\delta^{13}C$, $p < 0.10$); (b) DIC = $1.0y + 44 + 66 \sin[2\pi(y - 1999)/1.0]$ ($R = 0.96$, SE = 1.4 μmol C kg^{-1}, $p < 0.10$); (c) $T = -0.00y + 14 + 7.12 \sin[2\pi(y - 2011)/1.0]$ ($R = 0.96$, SE = 0.12°C, $p < 0.10$). Solid and dashed lines show the linear trend and fitted curve, respectively.

27.2 σ_θ, 27.3 σ_θ, and 27.4 σ_θ) at Station KNOT, we found that all values of $\delta^{13}C_{org}/DIC_{obs}$ were almost constant at -0.0092 ± 0.0003‰ (μmol kg^{-1})$^{-1}$ throughout the water column (Figure 3). However, equation (6) does not exactly include the processes of air-sea exchange, while the terms $\delta^{13}C_{org}/DIC_{obs}$ and DIC_{obs} on the right-hand side are not independent of each other. In addition, in the case of using equation (6'), unfortunately, there were few data sets for $\delta^{13}C_{org}$ at Station KNOT.

[20] *Rau et al.* [1989] demonstrated a relationship between $\delta^{13}C_{org}$ and aqueous CO_2 ($CO_{2\ (aq)}$) in sea surface water based on phytoplankton data in the South Atlantic and Southern oceans ($\delta^{13}C_{org} = -0.8[CO_{2\ (aq)}] - 12.6$) although the relationship had an error of about ±10% and there may be somewhat different plankton species between the South Atlantic and Southern sceans and the North Pacific. Using the equation of *Rau et al.* [1989] and the oceanic carbonate system calculation under the condition that the disequilibrium of CO_2 and $\delta^{13}C$ and Alk were constant over time, while atmospheric pCO_2 changed from 280 to 380 μatm [*Pierrot et al.*, 2006], we found the change in $\delta^{13}C_{org}/DIC$ from the preindustrial era to the present to be within the error of ±7%. Within this error of ±7% we can use the value of $\delta^{13}C_{org}/DIC$ as the slope of a line obtained by plotting the time-series data of $\delta^{13}C_{obs}$ against DIC_{obs} in the present seawater of Station KNOT (-0.0092‰ (μmol kg^{-1})$^{-1}$) (Figure 3), to estimate the relationship between $\delta^{13}C$ and DIC in the preindustrial era. Therefore, the DIC content during the preindustrial era can be estimated by assuming an atmospheric pCO_2 of 280 μatm under the condition that the disequilibrium of CO_2 and $\delta^{13}C$ and Alk were constant over time. Applying the estimated DIC to the relationship between DIC and $\delta^{13}C$ in the surface mixed layer with AOU = 0 (Figure 3a), we can estimate $\delta^{13}C_{as(0)}$ to be 1.29‰ in the surface mixed layer. If we know D has significantly smaller errors, independent of the other approaches, we can estimate both the amount of oceanic anthropogenic carbon (C_{ant}) and the rate of oceanic uptake of anthropogenic carbon during an arbitrary time interval (ΔC_{ant}) based on equations (4) and (5).

3.2.3. Application Range of *D* and Total Errors in C_{ant}

[21] After the industrial revolution, the contents of both $\delta^{13}C$ and CO_2 in the atmosphere have been changing globally because both are affected by the burning of fossil fuels [e.g., *Friedli et al.*, 1986]. In fact, the increase in atmospheric CO_2 and the decrease in atmospheric $\delta^{13}C$ over time show a strong linear correlation [e.g., *Körtzinger et al.*, 2003]. At Station KNOT, after correcting for the seasonal variation in $\delta^{13}C$ from 1997 to 2001, *Tanaka et al.* [2003] showed D to be -0.012‰ (μmol kg^{-1})$^{-1}$ by using the Fourier sine expansion method for the time series of DIC and $\delta^{13}C$, although the error of D was as great as 90%. If we

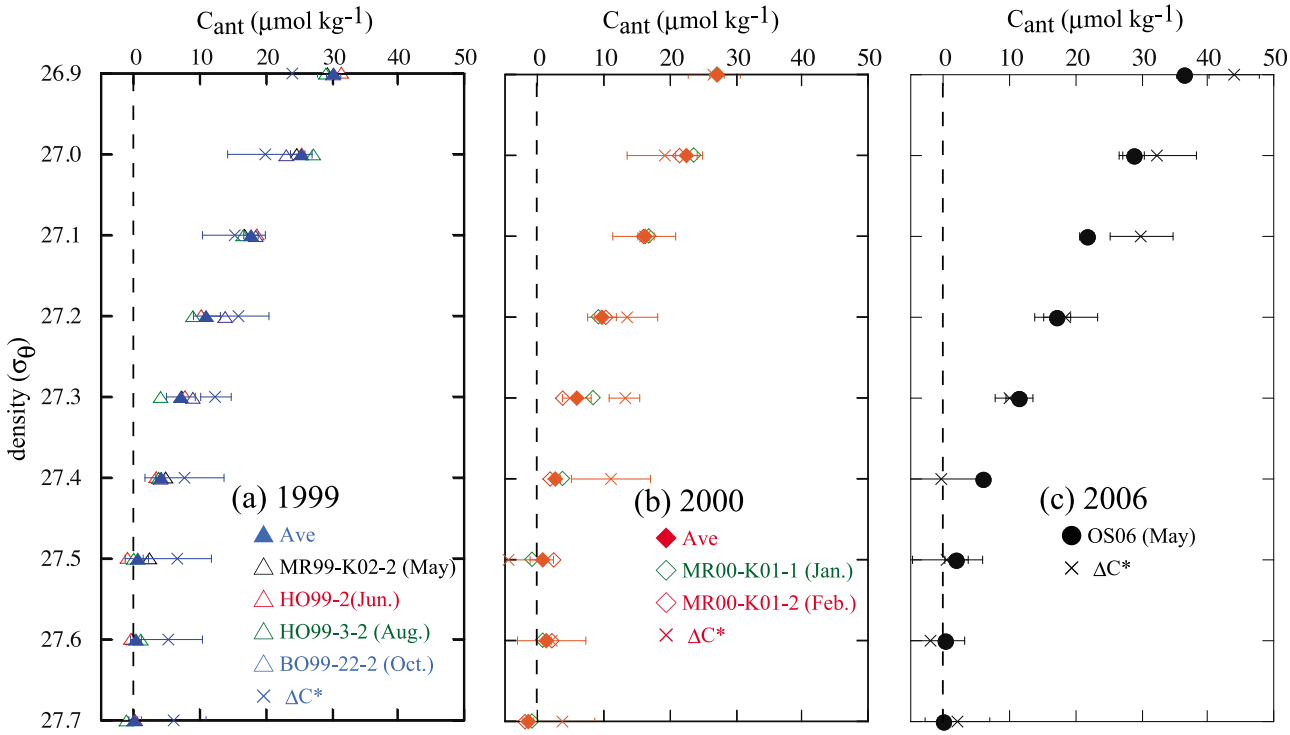

Figure 5. Vertical profiles of C_{ant} and ΔC^* at Station KNOT: (a) 1999, (b) 2000, and (c) 2006. Filled symbols show the average value of C_{ant} in each isopycnal horizon, with the standard error, and are the data from each cruise and the average value for each year, respectively. Error bars in 2006 are based on the average deviations between 1999 and 2000. Crosses show the estimated values of ΔC^*, according to *Sabine et al.* [2002]. Cruise hydrographic data for the high-salinity water mass derived from the subtropical region ($S > 33.2$) [*Tsurushima et al.*, 2002] are not shown, because we tried to compare C_{ant} in a single water mass in the subpolar region.

obtain D with significantly smaller errors than *Tanaka et al.* [2003] at Station KNOT, it is possible to estimate the content of anthropogenic carbon.

[22] *Bacastow et al.* [1996] reported that the $\delta^{13}C$ value fit a straight line in time (t) plus the sea surface temperature (T) spline. We apply this concept here to time series of $\delta^{13}C$ and DIC from 1997 to 2006 at Station KNOT (Figure 4) to obtain a more exact value of D compared to that of *Tanaka et al.* [2003] as follows:

$$X_{obs} = a + bt + cT(t), \tag{7}$$

where X_{obs} refers to one within $\delta^{13}C$ and DIC. a, b, and c are constants. Here b represents the long-term trend component. We obtained long-term trends of -0.0019 ± 0.002‰ yr^{-1} for $\delta^{13}C$ and 1.62 ± 0.42 μmol kg^{-1} yr^{-1} for DIC, respectively (Table 1). Our estimate for the increasing trend of DIC almost agreed with that of *Wakita et al.* [2010] during the same period at Station KNOT, while our estimate was somewhat larger than that of *Tanaka et al.* [2003], owing to the longer time-series data set compared to that of *Tanaka et al.* [2003]. As a result, the long-term trends of $\delta^{13}C$ and DIC in this study resulted in a D value of -0.012 ± 0.003‰ (μmol kg^{-1})$^{-1}$ (Table 1). The error in D in this study was estimated to be ±25%, which was significantly lower than that of *Tanaka et al.* [2003], while the value of D agreed with that of *Tanaka et al.* [2003], as D is probably constant over time. As mentioned, we already found the slope of $\delta^{13}C_{org}$/DIC to have an error of ±7% from the preindustrial era to the present. Upon adding up all the errors, the potential errors of $C_{ant(t)}$ and ΔC_{ant} were estimated to be about 30%. Considering the error, we can estimate both $C_{ant\ (t)}$ and ΔC_{ant} independently from the other approaches. *Sabine et al.* [2002] reported that the carbon-based quasi-conservative tracer approach (ΔC^*), which was widely used, had an error of ΔC^* for the entire Pacific of more than ±7.5 μmol kg^{-1} with the distributions. If there was 40 μmol kg^{-1} C_{ant} in the surface mixed layer in the middle 2000s, the error of the $\delta^{13}C$ approach in our study is almost the same as that of C*. In the case of deeper water, the $\delta^{13}C$ approach in our study could have a significant advantage owing to the error's potentially being smaller than that for ΔC^*.

4. Results and Discussion

4.1. Vertical Distribution of C_{ant}

[23] We have tried here to compare the vertical distributions of anthropogenic CO_2 between our $\delta^{13}C$ approach and ΔC^* at Station KNOT to clarify exactly both C_{ant} and ΔC_{ant} in the western North Pacific. To elucidate the distribution of C_{ant} in the same water mass in the subpolar region, we used only the cruise hydrographic data set except for the data

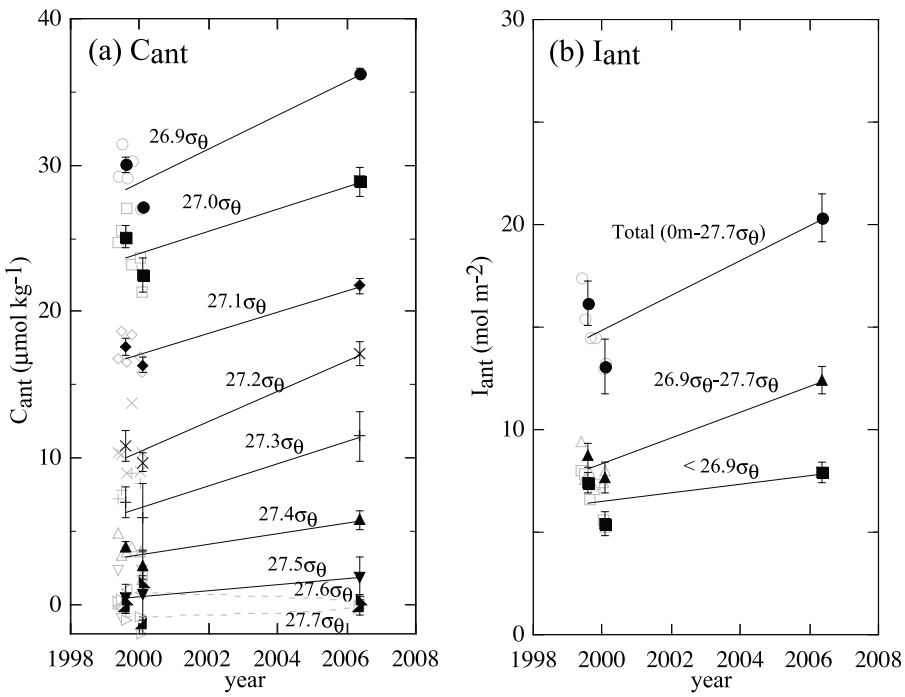

Figure 6. Temporal changes in C_{ant} and I_{ant} at Station KNOT. (a) C_{ant} in the isopycnal horizons from 26.9 σ_θ to 27.7 σ_θ. Significant linear trends of C_{ant} (ΔC_{ant}) with $p < 0.05$ are shown as solid lines: $\Delta C_{ant\ (26.9\sigma\theta)}$ = 1.1 μmol kg^{-1} yr^{-1}; $\Delta C_{ant\ (27.0\sigma\theta)}$ = 0.8 μmol kg^{-1} yr^{-1}; $\Delta C_{ant\ (27.1\sigma\theta)}$ = 0.7 μmol kg^{-1} yr^{-1}; $\Delta C_{ant\ (27.2\sigma\theta)}$ = 1.0 μmol kg^{-1} yr^{-1}; $\Delta C_{ant\ (27.3\sigma\theta)}$ = 0.8 μmol kg^{-1} yr^{-1}; $\Delta C_{ant\ (27.4\sigma\theta)}$ = 0.4 μmol kg^{-1} yr^{-1}; $\Delta C_{ant\ (27.5\sigma\theta)}$ = 0.2 μmol kg^{-1} yr^{-1}. (b) I_{ant} above 26.9 σ_θ, I_{ant} from 26.9 σ_θ to 27.7 σ_θ, and total I_{ant} from 0 m to 27.7 σ_θ. Significant linear trends of I_{ant} (ΔI_{ant}) with $p < 0.05$ are shown as solid lines: $\Delta I_{ant\ (0m-26.9\sigma\theta)}$ = 0.21 mol m^{-2} yr^{-1}; $\Delta I_{ant\ (26.9\sigma\theta-27.7\sigma\theta)}$ = 0.63 mol m^{-2} yr^{-1}; $\Delta I_{ant\ (0m-27.7\sigma\theta)}$ = 0.84 mol m^{-2} yr^{-1}. Light gray symbols and filled symbols are the data from each cruise and the average value for each year with the standard error, respectively. Error bars in 2006 are based on the average deviations between 1999 and 2000.

from a high-salinity water mass derived from the subtropical regions ($S > 33.2$) [*Tsurushima et al.*, 2002].

[24] Using the δ^{13}C approach, we obtained the vertical profiles of C_{ant} during 1999, 2000, and 2006 at Station KNOT along with those of ΔC^* calculated according to *Sabine et al.* [2002] (Figure 5). At Station KNOT, C_{ant} generally reached its maximum value at 26.9 σ_θ, just below the winter mixed layer and decreased with density. It approached 0 at 27.6 σ_θ, near the deeper part of the NPIW (around 1500 m). ΔC^* also decreased with density as well as C_{ant}. For the difference in C_{ant} between the two approaches, we found the relative average difference to be 2 μmol kg^{-1} (Σ ($\Delta C^* - C_{ant}$)/n, where n = the number of the data) and the absolute average difference to be 4 μmol kg^{-1} ($\Sigma|\Delta C^* - C_{ant}|/n$). These differences indicate that the two approaches for estimating the oceanic anthropogenic carbon were consistent with each other within these inherent uncertainties.

[25] In contrast, we found the change in vertical distribution of C_{ant} from 1999 to 2006 to be due to the atmospheric anthropogenic carbon invasion with time. C_{ant} near 26.9 σ_θ increased from 30 μmol kg^{-1} in 1999 to 40 μmol kg^{-1} in 2006, while C_{ant} around 27.6 σ_θ did not change around 0 μmol kg^{-1}, which is consistent with the ΔC^* within these inherent uncertainties. Therefore, these results show that our δ^{13}C approach has a significant potential for estimating the amount of oceanic anthropogenic carbon and for elucidating the detailed time evolution in the North Pacific subpolar region.

4.2. Temporal Change in C_{ant} Among 1999, 2000, and 2006

[26] The temporal change in C_{ant} from 1999 to 2006 showed a significant increasing trend (ΔC_{ant}), 0.2–1.1 μmol kg^{-1} yr^{-1} from 26.9 σ_θ to 27.5 σ_θ (Figure 6a). Assuming that C_{ant} from 0 m to 26.9 σ_θ was equal to that at 26.9 σ_θ, we found that the water-column inventory of C_{ant} (I_{ant}) from 0 m to 27.7 σ_θ increased from 16.2 to 20.4 mol m^{-2} during the period from 1999 to 2006 (Figure 6b). We also found that ΔC_{ant} above 27.3 σ_θ ranged from 0.7 to 1.1 μmol kg^{-1} yr^{-1} and had an average value of 0.86 ± 0.12 μmol kg^{-1} yr^{-1}. This value was higher by 20% than the expected value of 0.7 μmol kg^{-1} yr^{-1} based on oceanic equilibration with increasing atmospheric CO_2 between 1999 and 2006 [*Pierrot et al.*, 2006; *IPCC*, 2007].

[27] Recently, some studies have reported that ocean stratification has been progressing with a clear bidecadal oscillation of 18.6 years in the North Pacific [*Ono et al.*, 2001; *Watanabe et al.*, 2001, 2003; *Osafune and Yasuda*, 2006; *Yasuda et al.*, 2006; *Nakanowatari et al.*, 2007; *Watanabe et al.*, 2008; *Yasuda*, 2009]. It is possible that the efficiency of oceanic absorption of anthropogenic carbon declines and works as a positive feedback system for the

increasing atmospheric CO_2. Given the declining efficiency of CO_2 absorption in the ocean, what could have caused the recent significant increase in ΔC_{ant} in this region other than the expected value from the simple increasing atmospheric CO_2?

[28] At the end of the 1990s at Station KNOT, the 18.6 year oscillation caused the ocean stratification to strengthen compared to the average climatological hydrographic condition based on a time series of DO [*Watanabe et al.*, 2008]. This interannual variability derived from the 18.6 year oscillation may affect our ΔC_{ant} result because our estimation is essentially a linear rate calculation of C_{ant} between 1999 and 2006 owing to a nondetectable substantial change in C_{ant} between 1999 and 2000. On the basis of the 18.6 year oscillation of DO between 1999 and 2006, the strengthening of ocean stratification could cause a ΔC_{ant} larger by 7% than the simple average hydrographic condition. Thus, it is possible to explain about one third of the difference in ΔC_{ant} between our result and the expected one. Additionally, at Station KNOT, *Wakita et al.* [2010] found that the decadal time series of alkalinity below the winter mixed layer had a significant linear increasing trend of 0.7 ± 0.1 μmol kg^{-1} yr^{-1} with decreasing salinity of 0.002 ± 0.001 from 1998 to 2008 ($p < 0.05$). This corresponds to an increase in DIC of 0.35 μmol kg^{-1} yr^{-1}, which may explain partially our estimation of ΔC_{ant} that is higher than the expected one. However, it is difficult to explain this increasing trend of alkalinity solely by the dissolution of biological $CaCO_3$ derived from the anthropogenic CO_2 perturbation, because the saturation state depth of calcite was above 27.0 σ_θ, which suggests that the recent increase in alkalinity derived from a system outside of this region. *Watanabe et al.* [2009] reported a recent increase in alkalinity of 2.6 μmol kg^{-1} yr^{-1} over the Okhotsk Sea subsurface water, which was mainly derived from the increasing alkalinity efflux from the Amur River, whose catchment area is the tenth largest in the world. They suggested that the increase in alkalinity spread over the North Pacific with the decreasing salinity, which might have caused an increase of 20% in the oceanic absorption of anthropogenic CO_2 in the North Pacific subpolar region. This effect could explain the rest of the difference in ΔC_{ant} between our result and the expected one.

5. Concluding Remarks

[29] We used the $\delta^{13}C$ approach to estimate the oceanic anthropogenic carbon content (C_{ant}) and the oceanic uptake rate of anthropogenic carbon (ΔC_{ant}) at Station KNOT in the North Pacific subpolar region from 1999 to 2006. Considering the error of about 30% at this site, we found that the $\delta^{13}C$ approach has the potential to estimate both C_{ant} and ΔC_{ant} independently from other approaches for estimating the oceanic uptake of anthropogenic CO_2. In addition, we compared the C_{ant} between our approach and the ΔC^* approach to clarify exactly both C_{ant} and ΔC_{ant} in the western North Pacific. The vertical profiles of C_{ant} during this period were consistent with those of ΔC^* within the inherent uncertainties. We found that at Station KNOT, C_{ant} extended to 27.3 σ_θ in the deeper part of the NPIW. The maximum C_{ant} increased from 30 to 40 μmol kg^{-1} during this period, and the total water-column inventory of anthropogenic carbon also increased at a rate of 0.8 mol m^{-2} yr^{-1}, from 16 to 20 mol m^{-2}. The oceanic uptake rate of anthropogenic carbon (ΔC_{ant}) was 1.2 times higher than the expected rate for simple climatological carbon species. The difference in ΔC_{ant} between our result and the expected one can be explained by considering the strengthened ocean stratification with a bidecadal oscillation and the recent increase in alkalinity in the Sea of Okhotsk.

[30] Unfortunately, our approach for estimating the oceanic uptake of anthropogenic CO_2 still has a large uncertainty derived from the dynamic constraint ratio (D) and the $\delta^{13}C_{org}$ in planktons inhabiting Station KNOT. To obtain a more accurate value of the oceanic uptake of anthropogenic CO_2, it will be necessary to continue to observe detailed time series of DIC and of $\delta^{13}C$ of DIC with plankton $\delta^{13}C$ at Station KNOT in the future.

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