

Temporal Change of Dissolved Inorganic Carbon in the Subsurface Water at Station KNOT (44°N, 155°E) in the Western North Pacific Subpolar Region

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The dissolved inorganic carbon (DIC) and related chemical species have been measured from 1992 to 2001 at Station KNOT (44°N, 155°E) in the western North Pacific subpolar region. DIC (1.3~2.3 $\mu\text{mol/kg/yr}$) and apparent oxygen utilization (AOU, 0.7~1.8 $\mu\text{mol/kg/yr}$) have increased while total alkalinity remained constant in the intermediate water (26.9~27.3 σ_θ). The increases of DIC in the upper intermediate water (26.9~27.1 σ_θ) were higher than those in the lower one (27.2~27.3 σ_θ). The temporal change of DIC would be controlled by the increase of anthropogenic CO₂, the decomposition of organic matter and the non-anthropogenic CO₂ absorbed at the region of intermediate water formation. We estimated the increase of anthropogenic CO₂ to be only 0.5~0.7 $\mu\text{mol/kg/yr}$ under equilibrium with the atmospheric CO₂ content. The effect of decomposition was estimated to be $0.8 \pm 0.7 \mu\text{mol/kg/yr}$ from AOU increase. The remainder of non-anthropogenic CO₂ had increased by $0.6 \pm 1.1 \mu\text{mol/kg/yr}$. We suggest that the non-anthropogenic CO₂ increase is controlled by the accumulation of CO₂ liberated back to atmosphere at the region of intermediate water formation due to the decrease of difference between DIC in the winter mixed layer and DIC under equilibrium with the atmospheric CO₂ content, and the reduction of diapycnal vertical water exchange between mixed layer and pycnocline waters. In future, more accurate and longer time series data will be required to confirm our results.

Keywords:

- Dissolved inorganic carbon,
- temporal change,
- anthropogenic CO₂,
- western North Pacific subpolar region.

1. Introduction

The increase of atmospheric CO₂ concentration (e.g., Keeling and Whorf, 2002) has recently generated considerable interest in global carbon cycles. The oceans have taken up anthropogenic CO₂ of 1.6~2.0 Pg C/yr in the 1990s (e.g., McNeil *et al.*, 2003). High latitudinal oceans are especially important as a sink for anthropogenic CO₂ since they are the source of the intermediate and deep water masses, and a direct pathway for the transport of anthropogenic CO₂ into the ocean interior.

The uptake rate of anthropogenic CO₂ in the North Pacific was estimated in the 1990s to be 0.55 ± 0.09 Pg C/yr, which is about 32% of the total for the global

ocean (Watanabe *et al.*, 2000). Its subpolar region is the only area forming southward North Pacific Intermediate Water (NPIW), characterized by a salinity minimum centered at 26.8 σ_θ (e.g., Reid, 1965; Talley, 1991). The subpolar region is therefore an important area for transporting anthropogenic CO₂ into the ocean interior over the North Pacific (e.g., Tsunogai *et al.*, 1993).

The rate of increase of anthropogenic CO₂ and the dissolved inorganic carbon (DIC) inventory in the North Pacific has been estimated in several recent studies. Watanabe *et al.* (2000) indirectly estimated the rate of increase of anthropogenic CO₂ inventory with a tracer dating technique in the North Pacific. In the temperate North Pacific, Tsunogai *et al.* (1993), Slansky *et al.* (1997) and Ono *et al.* (1998) directly estimated the rate of increase of DIC inventory between the 1970s and the 1990s. Watanabe *et al.* (1996) and Takahashi *et al.* (1999) also

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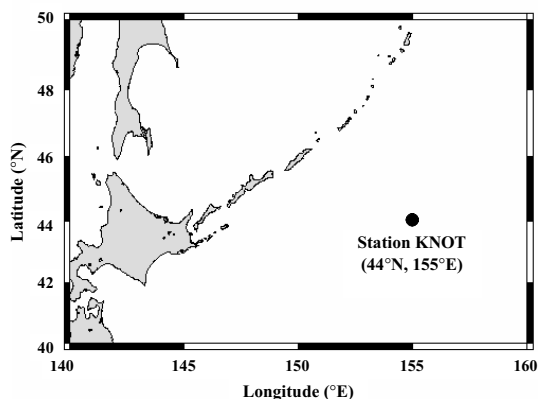


Fig. 1. Location of Station KNOT in the western North Pacific subpolar region.

found a significant increase of DIC inventory between 1973 and 1992 in the subpolar North Pacific. However, these analyses were based substantially on a single pair dataset, and included the potential uncertainty in the rate of DIC increase due to the choice of data sets (Ono *et al.*, 2000). Thus, the most fundamental and reliable approach to the direct estimation of the oceanic rate of anthropogenic CO₂ increase is to collect more accurate, longer time series observations of the oceanic CO₂ species.

We have observed the oceanic CO₂ species and its related hydrographic components (dissolved O₂, DO) from 1992 to 2001 at a station, 44°N, 155°E, in the western North Pacific subpolar region (Fig. 1). This station is named KNOT and has been a Japanese JGOFS time series station since 1998 (e.g. Tsurushima *et al.*, 2002). The purpose of this study is to estimate directly the oceanic rate of anthropogenic CO₂ increase at Station KNOT by using our decadal data of the oceanic CO₂ species in 1992~2001. Moreover, we examined the factors controlling the rate of increase of DIC in the intermediate water (26.9~27.3σ_θ) during the same period.

2. Methods

2.1 Sampling and shipboard measurements of chemical parameters

Station KNOT is located in the western subpolar gyre and just north of the Subpolar Front during the period from 1982 to 1995 (Isoda *et al.*, 2002). At Station KNOT, the seasonal amplitude of DIC in surface mixed layer was 107 μmol/kg in the 1999~2000 time series, which was larger than those at other pelagic ocean time series sites (Tsurushima *et al.*, 2002). This large variation is mainly due to biological production in spring to fall and strong vertical mixing in winter (Tsurushima *et al.*, 2002; Imai

et al., 2002).

On the T/S *Hokusei Maru*, Hokkaido University, CTD observations and water samplings were carried out at Station KNOT from 1993 to 2001 (Fig. 1 and Table 1). Seawater samples were collected from 13~16 layers from the surface to 1500 db in 1992~1997 and 25 layers from the surface to 3000 db in 1998~2001. We obtained samples by using 1.2-l Niskin bottles for the 1992~1997 observations and 10-l Niskin bottles for the 1998~2001 series, mounted on a CTD system. We measured temperature, salinity, DO, DIC and total alkalinity (TA). Temperature and salinity were measured with a Neil Brown (MARK IIIB) CTD system in 1992~1997 and a Seabird CTD system in 1998~2001. DO, DIC and TA were analyzed on board within 24 hours of sampling. Sampling, measurement and standardization of DO measurement in the seawater were carried out according to JGOFS protocols (Knap *et al.*, 1996). We analyzed DO with a piston burette (Metrohm Ltd.) in 1992~1997 and potentiometric titration with an autoburette (751 GPD Titrino, Metrohm Ltd.) in 1998~2001. The precision of DO analysis was estimated as < 0.7 μmol/kg, obtained from duplicate determinations. We calculated Apparent Oxygen Utilization (AOU) as the difference between observed concentration and equilibrium concentration with atmosphere (Weiss, 1970).

2.2 Measurements of DIC and TA

The methods by which DIC and TA were measured in this study are listed in detail in Table 1. A modified coulometric method of Johnson *et al.* (1985) was used for the determination of DIC. In 1992 and 1995, the sampling, measurement and standardization for DIC were carried out according to the method of Tsunogai *et al.* (1993). This method uses a calcium carbonate reagent of JIS K8617 special grade (purity 98.90%) as our reference material as well as a running substandard seawater sample. The coefficient of variation in DIC was ±0.2%. In 1997, 2000 (00/7) and 2001, the DIC contents were determined by the method described in Ono *et al.* (1998). We prepared and used a working standard of DIC on board the vessel according to the method described by Dickson *et al.* (2003). This working DIC standard was calibrated against sodium carbonate (Asahi Glass Co., Ltd., purity 99.97%) at least every half-year according to a DOE (1994). Since 2000, we calibrated our working standard once a year against a US certified reference material of DIC distributed by A. G. Dickson of Scripps Institution of Oceanography (SIO-CRM). The DIC content determined by our working standard agreed with that of SIO-CRM within about 2 μmol/kg (±0.1%) in 2000 (00/7) and 2001. The precision of DIC analysis was estimated as ±0.1% from duplicate determinations in 1997, 2000 (00/7) and 2001.

Table 1. Observations carried out from 1992 to 2001 at Station KNOT and methods of DO, DIC and TA analyses.

Code name ^(a)	Cruise name	Sampling date year/month/day	Depth ^(b) (m)	Layer ^(c)	Temp.	Salinity	DO	DIC	TA
92/6	HO92-2	1992/06/23	1500	16	Neil Brown		piston burette	Tsunogai <i>et al.</i> (1993)	×
95/6	HO95-2	1995/06/23	1500	13	Neil Brown		piston burette	Tsunogai <i>et al.</i> (1993)	×
97/7	HO97-3	1997/07/13	1500	13	Neil Brown		piston burette	Ono <i>et al.</i> (1998)	×
98/6-1	HO98-1	1998/06/04	3000	25	Seabird		autoburette	Tsurushima <i>et al.</i> (2002) ^(e)	Tsurushima <i>et al.</i> (2002) ^(f)
98/6-2	HO98-2	1998/06/26	3000	25	Seabird		autoburette	Tsurushima <i>et al.</i> (2002) ^(e)	Tsurushima <i>et al.</i> (2002) ^(f)
98/7	HO98-3-1	1998/07/21	3000	25	Seabird		autoburette	Tsurushima <i>et al.</i> (2002) ^(e)	Tsurushima <i>et al.</i> (2002) ^(f)
98/8	HO98-3-2	1998/08/13	3000	25	Seabird		autoburette	Tsurushima <i>et al.</i> (2002) ^(e)	Tsurushima <i>et al.</i> (2002) ^(f)
99/6-1	HO99-1	1999/06/05	3000	25	Seabird		autoburette	Tsurushima <i>et al.</i> (2002) ^(e)	Tsurushima <i>et al.</i> (2002) ^(f)
99/6-2	HO99-2	1999/06/27	3000	25	Seabird		autoburette	Tsurushima <i>et al.</i> (2002) ^(e)	Tsurushima <i>et al.</i> (2002) ^(f)
99/7	HO99-3-1	1999/07/22	3000	25	Seabird		autoburette	Tsurushima <i>et al.</i> (2002) ^(e)	Tsurushima <i>et al.</i> (2002) ^(f)
99/8	HO99-3-2	1999/08/14	3000	25	Seabird		autoburette	Tsurushima <i>et al.</i> (2002) ^(e)	Tsurushima <i>et al.</i> (2002) ^(f)
00/6-1	HO00-1	2000/06/09	3000	25	Seabird		autoburette	Tsurushima <i>et al.</i> (2002) ^(e)	Tsurushima <i>et al.</i> (2002) ^(f)
00/6-2	HO00-2	2000/06/25	3000	25	Seabird		autoburette	Tsurushima <i>et al.</i> (2002) ^(e)	Tsurushima <i>et al.</i> (2002) ^(f)
00/7	HO00-3B	2000/07/31	3000	25	Seabird		autoburette	Ono <i>et al.</i> (1998) ^(d)	Ono <i>et al.</i> (1998)
01/6	HO01-1	2001/06/04	3000	25	Seabird		autoburette	Ono <i>et al.</i> (1998) ^(d)	Ono <i>et al.</i> (1998)
01/7	HO01-3A	2001/07/12	3000	25	Seabird		autoburette	Ono <i>et al.</i> (1998) ^(d)	Ono <i>et al.</i> (1998)

^(a)Sampling year and month are given in the code name.

^(b)Maximum water depth of sampling.

^(c)Number of sampling layers.

^(d)DIC content determined by our working standard agreed well with that certified manometrically at SIO-CRM within 2 $\mu\text{mol/kg}$ ($\pm 0.1\%$) in 2000 and 2001.

^(e)DIC content of SIO-CRM we determined and that certified in SIO differed by 6.3 $\mu\text{mol/kg}$ in 1999, and showed good agreement within about 2 $\mu\text{mol/kg}$ in 2000.

^(f)TA contents in our working standards showed no significant difference from that of the SIO-CRM.

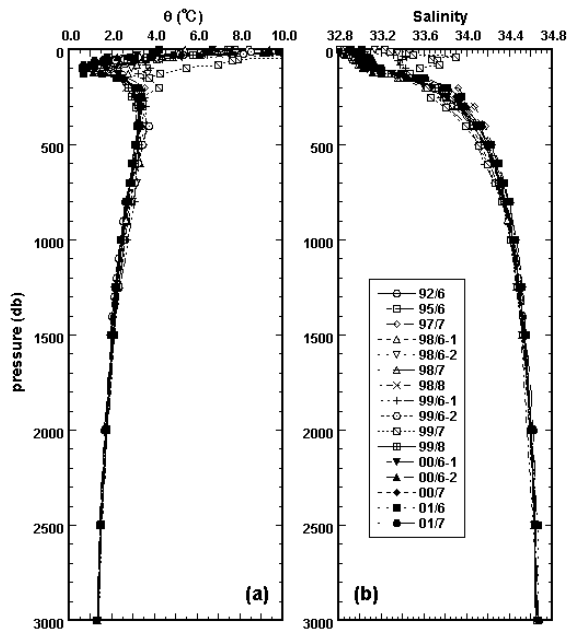


Fig. 2. Vertical profiles of (a) potential temperature (θ) and (b) salinity at Station KNOT from 1992 to 2001.

In 1998, 1999 and 2000 (00/6-1, 00/6-2), the sampling, measurement and standardization for DIC and TA were carried out according to the method described by Tsurushima *et al.* (2002). The working standards of DIC and TA were examined at the PICES (North Pacific Marine Science Organization) international intercalibration exercises in 1999 and 2000. The difference between DIC content of SIO-CRM we determined and that certified in SIO was $6.3 \mu\text{mol/kg}$ in 1999, and showed good agreement, less than about $2 \mu\text{mol/kg}$ ($\pm 0.1\%$) in 2000. At the PICES intercalibration in 2000, our TA contents showed no significant difference from the SIO-CRM. The precisions of DIC and TA analyses were estimated as $\pm 0.1\%$ from duplicate determinations in 1998, 1999 and 2000 (00/6-1, 00/6-2).

In 2000 (00/7) and 2001, TA was determined by the improved single point titration method described by Culbertson *et al.* (1970). We measured TA using a glass electrode standardized against Tris buffer (DOE, 1994), 2-aminopyridine buffer (DOE, 1994). Drift was corrected using a 0.03 M phthalic acid buffer of a seawater base. The precision of TA was determined as $\pm 0.2\%$ from duplicate determinations in 2000 (00/7) and 2001.

2.3 Correction of systematic errors among datasets

We eliminated the systematic errors of DO and DIC among each dataset, because the methods used for these determinations were slightly different from cruise to

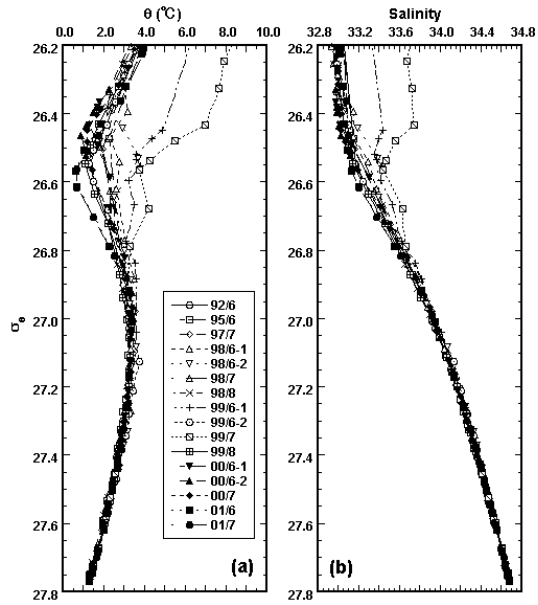


Fig. 3. Profiles of (a) potential temperature (θ) and (b) salinity against density (σ_θ) at Station KNOT from 1992 to 2001.

cruise. We corrected the DIC concentrations during the period from 98/6-1 to 01/7 to the certified SIO-CRM value, because we calibrated the working standard against SIO-CRM once a year from 1998 to 2001.

For the preceding periods, we corrected the systematic errors assuming that oceanic properties in the water mass deeper than $27.4\sigma_\theta$ (820 m) had been constant for the period from 1992 to 2001, because the water mass deeper than $27.4\sigma_\theta$ has not changed for the last ten years within the variations of potential temperature (θ) ($\pm 0.01 \sim \pm 0.02^\circ\text{C}$) and salinity ($\pm 0.001 \sim \pm 0.002$) (Figs. 2 and 3), and because AOU and CFC-11 deeper than $27.4\sigma_\theta$ in 1985 agreed with those in 1999 at Station KNOT (Watanabe *et al.*, 2001). We corrected the contents of DO and DIC in 92/6, 95/6 and 97/7 at the isopycnal surfaces of $27.4\sigma_\theta$, $27.5\sigma_\theta$ and $27.6\sigma_\theta$ to fit the mean observed value from 1998 to 2001 at the same isopycnal surfaces (Table 2). The values of DO and DIC at each isopycnal surface were obtained by linear interpolation. For contents of DO in 97/7, $-10 \mu\text{mol/kg}$ was added to original data. We added the DIC contents to $19 \mu\text{mol/kg}$ in 92/6, $10 \mu\text{mol/kg}$ in 95/6 and $10 \mu\text{mol/kg}$ in 97/7. These systematic errors probably derive from the standardization because of the absence of a common reference material (SIO-CRM). The above corrections of DIC and DO are listed in Table 3. After the corrections, the standard errors of DO ($\pm 0.8 \sim \pm 1.2 \mu\text{mol/kg}$) and DIC ($\pm 1 \mu\text{mol/kg}$) on $27.4\sigma_\theta$, $27.5\sigma_\theta$ and $27.6\sigma_\theta$ during last ten years agree

Table 2. Average concentrations of DO and DIC with their standard errors at each isopycnal surface at Station KNOT from 1998 to 2001.

σ_θ	Depth (ave.) (m)	DO ($\mu\text{mol/kg}$)	DIC ($\mu\text{mol/kg}$)
27.40	816	30.5 ± 1.4	2372 ± 1
27.50	1091	37.9 ± 0.6	2377 ± 1
27.60	1511	57.6 ± 1.2	2377 ± 1
27.70	2216	97.1 ± 1.1	2362 ± 1
27.73	2478	110.8 ± 1.1	2354 ± 1
27.75	2798	124.3 ± 1.2	2345 ± 1

Table 3. Values of the corrections of DO and DIC from 1992 to 2001 at Station KNOT.

Code name	DO ($\mu\text{mol/kg}$)	DIC ($\mu\text{mol/kg}$)
92/6	—	19
95/6	—	10
97/7	-10	10
98/6-1	—	6.3
98/6-2	—	6.3
98/7	—	6.3
98/8	—	6.3
99/6-1	—	6.3
99/6-2	—	6.3
99/7	—	6.3
99/8	—	6.3
00/6-1	—	—
00/6-2	—	—
00/7	—	2
01/6	—	2
01/7	—	2

with those in each isopycnal surface of $27.7\sigma_\theta$, $27.73\sigma_\theta$ and $27.75\sigma_\theta$ from 1998 to 2001 (Table 2), which suggests that these corrections are appropriate.

3. Results and Discussion

3.1 Decadal change of the structure of water mass

The vertical distributions of θ and salinity from 1992 to 2001 are shown in Figs. 2 and 3. The layer of minimum temperature that was the remnant of the winter mixed layer water usually existed at about $26.6\sigma_\theta$ (about 100 m) and the maximum temperature was observed between $27.0\sigma_\theta$ (about 300 m) and $27.1\sigma_\theta$ (about 390 m) in the last ten years. These observations indicate that Station KNOT was located in the western subpolar gyre from 1992 to 2001, according to Favorite *et al.* (1976) and Ueno and Yasuda (2000).

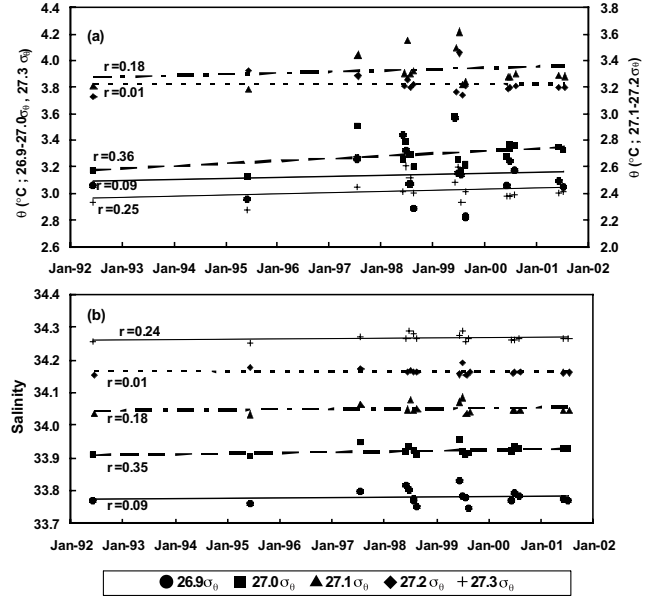


Fig. 4. (a) Potential temperature (θ) and (b) salinity on the isopycnal surface of $26.9\sigma_\theta$ (solid circles), $27.0\sigma_\theta$ (solid squares), $27.1\sigma_\theta$ (solid triangles), $27.2\sigma_\theta$ (solid diamonds), $27.3\sigma_\theta$ (plus) and $27.2\sigma_\theta$ (cross) surfaces at Station KNOT during the period from 1992 to 2001. We show the linear regression lines on $26.9\sigma_\theta$ (solid line), $27.0\sigma_\theta$ (dashed line), $27.1\sigma_\theta$ (dashed-dotted line), $27.2\sigma_\theta$ (dotted line) and $27.3\sigma_\theta$ (thin line). In addition, we also show the correlation coefficient (r) and the probability value (p) for the linear regression lines of θ and salinity on each isopycnal surface.

In the water mass shallower than $26.8\sigma_\theta$ (about 180 m), the recorded values of θ and salinity in 01/6 and 01/7 were the minimum in our dataset, while the values in 98/6-1, 98/6-2, 99/6-1, and 99/7 were the maximum values recorded (Figs. 2 and 3). The higher values of θ and salinity in 98/6-1, 98/6-2, 99/6-1 and 99/7 might be due to the migration of subtropical water from the south (Tsurushima *et al.*, 2002), because Station KNOT is located just north of the Subpolar Front (Kono, 1997; Isoda *et al.*, 2002).

The values of θ and salinity deeper than $26.9\sigma_\theta$ (about 230 m) were not greatly different from year to year during the last ten years (Figs. 2 and 3). We could not detect decadal changes of the θ and salinity from $26.9\sigma_\theta$ to $27.3\sigma_\theta$ (about 630 m). Their standard errors from $26.9\sigma_\theta$ to $27.3\sigma_\theta$ were $\pm 0.02 \sim \pm 0.05^\circ\text{C}$ and $\pm 0.002 \sim \pm 0.006$, respectively, during last ten years, which is comparable to values deeper than $27.4\sigma_\theta$ ($\pm 0.01 \sim \pm 0.02^\circ\text{C}$ (θ) and $\pm 0.001 \sim \pm 0.002$ (salinity)) (Fig. 4). We thus assumed that the structure of intermediate water from $26.9\sigma_\theta$ to $27.3\sigma_\theta$ did not change during the period from 1992 to 2001.

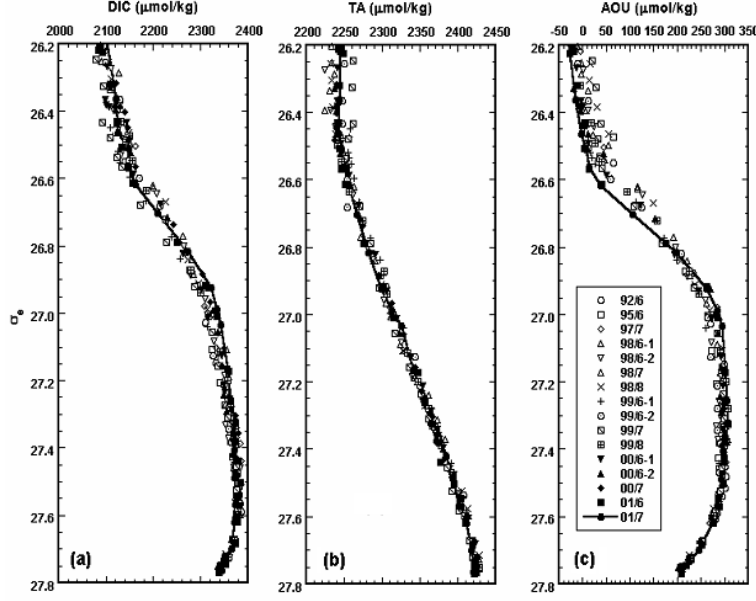


Fig. 5. Profiles of (a) DIC, (b) TA and (c) AOU against density (σ_θ) at Station KNOT from 1992 to 2001. We show the vertical profiles of DIC, AOU and TA in the most recent observation (01/7) as a solid line to clarify these temporal changes.

Table 4. Increase rate of DIC and other properties on the 26.9–27.3 σ_θ surfaces at Station KNOT. Error shows the standard error of the slope of linear regression.

Isopycnal surface	Depth (ave.) ^(a) (m)	$d\text{DIC}_{\text{obs}}/dt$ ($\mu\text{mol/kg/yr}$)	$d_{\text{anth}}\text{DIC}_{\text{air-sea}}/dt$ ($\mu\text{mol/kg/yr}$)	$d\text{DIC}_{\text{org}}/dt$ ^(b) ($\mu\text{mol/kg/yr}$)	$d\text{AOU}_{\text{obs}}/dt$ ($\mu\text{mol/kg/yr}$)	$d_{\text{non-anth}}\text{DIC}_{\text{air-sea}}/dt$ ^(c) ($\mu\text{mol/kg/yr}$)
26.9 σ_θ	230 ± 37	2.3 ± 1.0	0.6 ± 0.2	0.8 ± 0.8	1.1 ± 1.1	0.9 ± 1.3
27.0 σ_θ	293 ± 41	2.6 ± 0.9	0.5 ± 0.1	1.2 ± 0.8	1.8 ± 1.2	0.9 ± 1.2
27.1 σ_θ	379 ± 43	2.5 ± 0.9	0.6 ± 0.1	0.8 ± 0.7	1.2 ± 1.0	1.1 ± 1.1
27.2 σ_θ	487 ± 48	1.3 ± 0.6	0.7 ± 0.1	0.6 ± 0.5	0.8 ± 0.7	0.0 ± 0.8
27.3 σ_θ	626 ± 47	1.3 ± 0.6	0.6 ± 0.1	0.5 ± 0.6	0.7 ± 0.8	0.2 ± 0.9

^(a)Averages and standard deviations at the isopycnal surfaces.

^(b) $d\text{DIC}_{\text{org}}/dt = 0.69d(\text{AOU})/dt : 0.69 = C_{\text{org}}/O_2$ (Anderson and Sarmiento, 1994).

^(c) $d_{\text{non-anth}}\text{DIC}_{\text{air-sea}}/dt = d(\text{DIC}_{\text{obs}})/dt - d(\text{DIC}_{\text{org}})/dt - d_{\text{anth}}\text{DIC}_{\text{air-sea}}/dt$.

3.2 Decadal variations in the vertical profile in DIC, TA and AOU

The vertical profile of DIC was similar to that of AOU due to decomposition of organic matter (Figs. 5(a) and (b)). DIC and AOU were at their minima in the surface water due to photosynthesis and gas exchange of CO_2 and O_2 across the air-sea interface. Both properties increased with density, and decreased slightly below 27.6 σ_θ . On the other hand, TA increased with density and had a strong correlation with salinity ($\text{TA} = 106.9 \text{ salinity} - 1296$, $r = 0.98$) (Figs. 3(b) and 5(c)).

Comparing the vertical profiles of DIC, TA and AOU in the most recent observation (01/7) with the other data

obtained in the last ten years, we found that the temporal changes in DIC and AOU below 26.9 σ_θ decreased with increasing density (Fig. 5). AOU in 01/7 above 26.8 σ_θ was smaller than that in the other data, while the temporal change of DIC above 26.8 σ_θ had a large variation. These changes of AOU and DIC in the mixed layer (above 26.8 σ_θ) may be caused by the large variation of water mass structure. It is thus difficult to detect decadal changes above 26.8 σ_θ . In the next section we focus on the decadal changes in AOU, TA and DIC on 26.9~27.3 σ_θ for the period from 1992 to 2001, since NPIW is generally seen from 26.8 σ_θ to 27.4 σ_θ .

3.3 Rate of increase of DIC in the intermediate water (26.9~27.3 σ_θ)

We found that DIC between 26.9 σ_θ and 27.3 σ_θ increased at rates of 1.3~2.3 (ave. 2.0 ± 0.8) $\mu\text{mol/kg/yr}$, based on linear regression (Fig. 6 and Table 4). The values of DIC on each isopycnal surface were obtained by linear interpolation. The rates in the upper intermediate water (26.9~27.1 σ_θ) were higher than these in the lower water (27.2~27.3 σ_θ) (Table 4).

If oceanic physical and biological conditions are in a steady state, the rate of DIC increase on any isopycnal surface is the rate of anthropogenic CO_2 increase absorbed in seawater. In the steady state, the average rate of increase of anthropogenic CO_2 was estimated to be 2.0 ± 0.8 $\mu\text{mol/kg/yr}$ on 26.9~27.3 σ_θ at Station KNOT. However, Watanabe *et al.* (2000) reported that the rate of anthropogenic CO_2 increase was estimated to be 0.3~0.6 $\mu\text{mol/kg/yr}$ in the 1990s on 26.9~27.3 σ_θ in the western North Pacific subpolar region, on the assumption of oceanic conditions steady-state, based on the thermodynamic method using temperature, salinity, the TA and the rate of increase of atmospheric CO_2 . Our estimate is three times higher than theirs. It is thus difficult to explain the rate of increase of DIC on 26.9~27.3 σ_θ at Station KNOT only in terms of the rate of increase of anthropogenic CO_2 , based on the assumption of steady-state oceanic physical and biological conditions during the observation period.

3.4 Rate of increase of TA in the intermediate water (26.9~27.3 σ_θ)

The values of TA on 26.9~27.3 σ_θ were statistically insignificant during the period from 1992 to 2001 (Fig. 6(b)). The values of TA on each isopycnal surface were obtained by linear interpolation. The standard deviation of TA on 26.9~27.3 σ_θ was 2~4 $\mu\text{mol/kg}$, which is close to the analytical error of TA. This suggests that the rate of dissolution of particulate carbonate has not changed over these isopycnal surfaces during the period from 1992 to 2001 at Station KNOT. Bates (2001) and Winn *et al.* (1998) also reported that the temporal change of TA in the mixed layer is insignificant at the subtropical stations BATS (31°50' N, 64°10' W) and HOT (22°45' N, 158°00' W). This is consistent with the observational results that the saturation depths of calcite and aragonite are about 750 m and 500 m, respectively, in North Pacific (Millero, 1996) and the depth of 26.9~27.3 σ_θ surface at Station KNOT (about 200~600 m) is almost shallower than these saturation depths. Thus these isopycnal surfaces are not sensitive to the effect of dissolution of particulate carbonate.

3.5 Rate of increase of AOU in the intermediate water (26.9~27.3 σ_θ)

The rate of AOU increase on 26.9~27.3 σ_θ was the

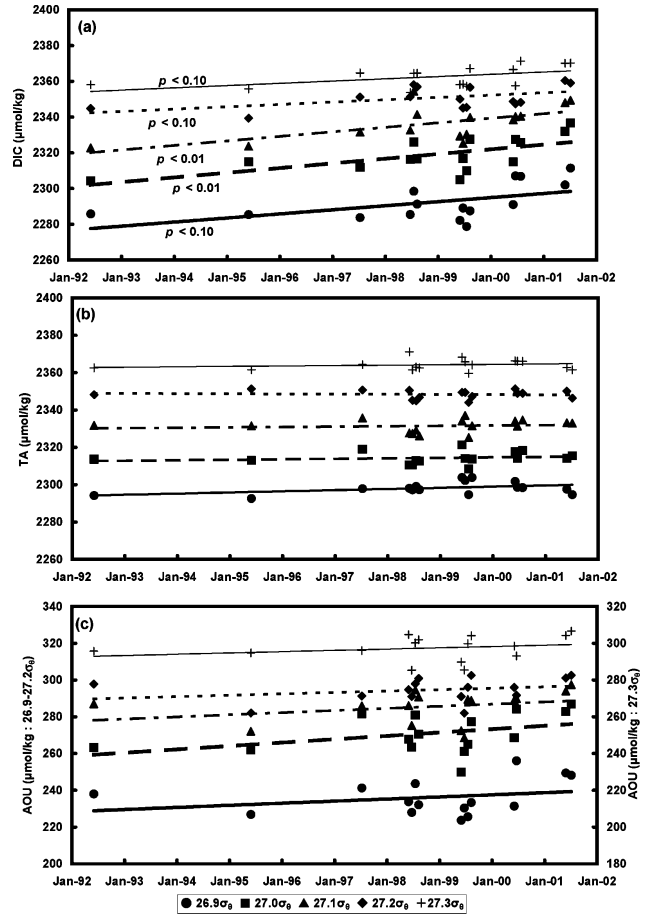


Fig. 6. Temporal changes in (a) DIC, (b) TA and (c) AOU on the isopycnal surface of 26.9 σ_θ (solid circles), 27.0 σ_θ (solid squares), 27.1 σ_θ (solid triangles), 27.2 σ_θ (solid diamonds) and 27.3 σ_θ (plus) surfaces at Station KNOT from 1992 to 2001. We show the linear regression lines on 26.9 σ_θ (solid line), 27.0 σ_θ (dashed line), 27.1 σ_θ (dashed-dotted line), 27.2 σ_θ (dotted line) and 27.3 σ_θ (thin line). In addition, we also show the probability value (p) for the linear regression lines of DIC on each isopycnal surface. The values of TA from 1992 to 1997 were computed using the strong correlation between TA and salinity on 26.9~27.3 σ_θ from 1998 to 2001 ($\text{TA}/\mu\text{mol/kg} = 140.4 \text{ salinity} - 2447$, $r = 0.99$).

range 0.7~1.8 (ave. 1.1 ± 1.0) $\mu\text{mol/kg/yr}$ and decreased with increasing density (Fig. 6(c) and Table 4). The trend of AOU increase on 27.0~27.1 σ_θ was significant at the 80% confidence level, while the other isopycnal surfaces (26.9 σ_θ , 27.2 σ_θ and 27.3 σ_θ) show no trend of AOU increase. Ono *et al.* (2001) reported that AOU has increased in the range from 0.6 to 1.3 $\mu\text{mol/kg/yr}$ between 26.7 σ_θ and 27.2 σ_θ from 1968 to 1998 in the western North Pacific subpolar region (near the area east of Japan). The rates of increase of AOU in our study agreed well with their results.

The increase of AOU could be caused by the change in the physical and biological conditions of the ocean. To clarify whether or not oceanic biological activity changed at Station KNOT in the period from 1992 to 2001, we examined the change in primary production due to biological activity and the export flux of carbon from the surface to the ocean interior. According to Honda *et al.* (2002), the equations of vertical change in particulate organic carbon (POC) flux based on observed data are as follows at Station KNOT,

$$\text{POC} = 1120.9Z^{-0.63} \text{ (Nov.–Dec. 1998)} \quad (1)$$

$$\text{POC} = 1691.5Z^{-0.63} \text{ (May–June 1999)} \quad (2)$$

where Z is water depth. Using the above equations, we can estimate the flux of decomposition of POC from 230 m ($26.9\sigma_\theta$) to 626 m ($27.3\sigma_\theta$) to be 6–9 gC/m²/yr in the intermediate water ($26.9\sim 27.3\sigma_\theta$). On the other hand, the rate of increase of AOU in this study was an average of 1.1 $\mu\text{mol/kg/yr}$ between this intermediate water at Station KNOT (Fig. 6(c) and Table 4). The temporal increase in the flux of decomposition of POC is calculated to be about 4 g C/m²/yr, using our rate of increase of AOU (1.1 $\mu\text{mol/kg/yr}$) and the stoichiometric ratios for carbon to oxygen ($C_{\text{org}}/-O_2 = 0.69$; Anderson and Sarmiento, 1994). The temporal increase of flux of decomposition (4 g C/m²/yr) is comparable to 44–67% of flux of decomposition (6–9 gC/m²/yr) from $26.9\sigma_\theta$ to $27.3\sigma_\theta$, which is not reasonable. The flux of POC observed at 1000 m at Station KNOT during the period from 1989/June to 1990/January (average 11 gC/m²/day) agreed with values found during the period from 2000/June to 2001/January (Noriki, personal communication). Ono *et al.* (2002) also reported that the net rate of biological phosphate consumption from February to August decreased linearly at 0.40 mmol P/m²/yr (0.51 g C/m²/yr) in the surface of the western North Pacific subpolar region during the last three decades. Thus the increase of primary production and the export flux due to biological activity may not have caused the rate of increase of AOU in the intermediate water at Station KNOT in the past decade.

In addition, Watanabe *et al.* (2001) suggested that the formation rate of the intermediate water in the North Pacific has reduced at least during past fifteen years. Watanabe *et al.* (2003) showed that both the linear trends and the oscillations of DO, phosphate and temperature in the North Pacific Intermediate Water in the last four decades showed a strong correlation with the North Pacific Index, an anomaly of sea surface level pressure in the wintertime in the North Pacific (Minobe, 1999). They suggested that atmospheric oscillations and/or artificial greenhouse warming effects simultaneously caused the reduction of the formation rate of the subsurface water in

the ocean. Thus, the rate of increase of AOU on $26.9\sim 27.3\sigma_\theta$ may be due to the increase of residence time of intermediate water.

3.6 Factors controlling the rate of increase of DIC in the intermediate water ($26.9\sim 27.3\sigma_\theta$)

In general, observed DIC (DIC_{obs}) along an isopycnal surface is the sum of the changes of DIC due to the gas exchange of CO₂ at the air-sea interface ($\text{DIC}_{\text{air-sea}}$), the decomposition of organic matter (DIC_{org}) and the dissolution of calcium carbonate ($\text{DIC}_{\text{CaCO}_3}$). To clarify the factors controlling the rate of increase of DIC, we can express Eqs. (3)–(5), as follows (e.g., Brewer, 1978; Chen and Millero, 1979),

$$\begin{aligned} d(\text{DIC}_{\text{obs}})/dt \\ = d(\text{DIC}_{\text{air-sea}})/dt + d(\text{DIC}_{\text{org}})/dt + d(\text{DIC}_{\text{CaCO}_3})/dt \end{aligned} \quad (3)$$

$$\begin{aligned} d(\text{DIC}_{\text{air-sea}})/dt \\ = d(\text{DIC}_{\text{obs}})/dt - (C_{\text{org}}/-O_2)d(\text{AOU}_{\text{obs}})/dt - 0.5d(\text{TA}_{\text{obs}})/dt \end{aligned} \quad (4)$$

$$= d(\text{anth-DIC}_{\text{air-sea}})/dt + d(\text{non-anth-DIC}_{\text{air-sea}})/dt \quad (5)$$

where $d(\text{DIC}_{\text{obs}})/dt$, $d(\text{AOU}_{\text{obs}})/dt$ and $d(\text{TA}_{\text{obs}})/dt$ are the rates of increase of DIC, AOU and TA observed on any isopycnal surfaces. $C_{\text{org}}/-O_2$ is the stoichiometric ratio of carbon to oxygen at the organic matter decomposition (Redfield *et al.*, 1963; Anderson and Sarmiento, 1994). The term $d(\text{anth-DIC}_{\text{air-sea}})/dt$ is the rate of increase of DIC due to the gas exchange of the anthropogenic CO₂ at the air-sea interface and is defined that the near-surface water in the region of the formation of this intermediate water has followed the atmospheric perturbation and therefore has taken up anthropogenic CO₂ in equilibrium with the atmospheric CO₂ increase. The term $d(\text{non-anth-DIC}_{\text{air-sea}})/dt$ is defined as the rate of increase of DIC due to the uptake of non-anthropogenic CO₂ through gas exchange at the air-sea interface in the region of the intermediate water formation, because $\text{non-anth-DIC}_{\text{air-sea}}$ fluxes estimated by Gloor *et al.* (2003) showed a large influx in the North Pacific, acting as a CO₂ sink. The term $d(\text{TA}_{\text{obs}})/dt$ can be eliminated, because TA has not changed over the isopycnal surfaces ($26.9\sim 27.3\sigma_\theta$) during the period from 1992 to 2001 at Station KNOT. Thus, in the intermediate water ($26.9\sim 27.3\sigma_\theta$) at Station KNOT from 1992 to 2001, the factors causing the rate of increase of DIC were the rate of increase of AOU, $\text{anth-DIC}_{\text{air-sea}}$ and $\text{non-anth-DIC}_{\text{air-sea}}$, and we can express these factors with Eqs. (3)–(5) and $(C_{\text{org}}/-O_2) = 0.69$ (Anderson and Sarmiento, 1994), as following,

$$\begin{aligned} d(\text{non-anth-DIC}_{\text{air-sea}})/dt \\ = d(\text{DIC}_{\text{obs}})/dt - 0.69d(\text{AOU}_{\text{obs}})/dt - d(\text{anth-DIC}_{\text{air-sea}})/dt. \end{aligned} \quad (6)$$

We calculated the rate of increase of ${}_{\text{anth}}\text{DIC}_{\text{air-sea}}$ using observed temperature, salinity and the average values of TA on each isopycnal surface ($26.9\sim 27.3\sigma_\theta$) and the rate of increase of atmospheric CO_2 between 1992 and 2001 (1.7 ppm/yr, Keeling and Whorf, 2002). In this calculation we have used the dissociation constants of carbonic acid originally given by Mehrbach *et al.* (1973) and refitted by Dickson and Millero (1987). This yields the increase rate of ${}_{\text{anth}}\text{DIC}_{\text{air-sea}}$ at $0.5\sim 0.7\ \mu\text{mol/kg/yr}$ (Table 4), which agrees with values estimated by Watanabe *et al.* (2000). On the basis of Eq. (6), the remainder of $d({}_{\text{non-anth}}\text{DIC}_{\text{air-sea}})/dt$ was estimated to be $0.9\sim 1.1\ \mu\text{mol/kg/yr}$ in the upper intermediate water ($26.9\sim 27.1\sigma_\theta$) (Table 4). Thus, the rate of increase of DIC on $26.9\sim 27.3\sigma_\theta$ (ave. $2.0 \pm 0.8\ \mu\text{mol/kg/yr}$) has been controlled by the increase of anthropogenic CO_2 (ave. $0.6 \pm 0.1\ \mu\text{mol/kg/yr}$), the decomposition of organic matter due to AOU increase (ave. $0.8 \pm 0.7\ \mu\text{mol/kg/yr}$) and the uptake of non-anthropogenic CO_2 through gas exchange at the region of intermediate water formation (ave. $0.6 \pm 1.1\ \mu\text{mol/kg/yr}$).

Since the increase of non-anthropogenic CO_2 must have resulted from the recent changes due to the artificial greenhouse warming effect and/or the natural climate change at the region of the upper intermediate water formation, we can suggest the following possibilities for the factors controlling the increase of non-anthropogenic CO_2 : the accumulation of non-anthropogenic CO_2 liberated back to atmosphere at this region due to 1) the decrease of difference between DIC in the winter mixed layer and DIC under equilibrium with the atmospheric CO_2 increase (Tsunogai, 2000) and 2) the reduction of diapycnal vertical water exchange between mixed layer and pycnocline waters.

The intermediate water ($26.9\sim 27.1\sigma_\theta$) at KNOT existed in the layer of maximum temperature. This water mass was transported from the area east of Japan to the Gulf of Alaska (Ueno and Yasuda, 2000), which indicates that the region of the upper intermediate water formation at KNOT is derived from the area east of Japan. Midorikawa *et al.* (2003) reported that the partial pressure of oceanic CO_2 in winter ($p\text{CO}_2^{\text{sea}}_{\text{win}}$) was higher than $400\ \mu\text{atm}$ from 1998 to 2001 in the area east of Japan, which was a source of atmospheric CO_2 . However, because of the increase of atmospheric CO_2 concentration, the temporal difference between $p\text{CO}_2^{\text{sea}}_{\text{win}}$ and atmospheric CO_2 must have decreased in the area east of Japan, which indicates that non-anthropogenic CO_2 liberated back to atmosphere has accumulated in the winter mixed layer. To examine this possibility, we calculated DIC in winter at the area east of Japan (DIC_{win}) and DIC in equilibrium with the atmospheric CO_2 increase (${}_{\text{anth}}\text{DIC}_{\text{air-sea}}$), and estimated the difference between DIC_{win} and ${}_{\text{anth}}\text{DIC}_{\text{air-sea}}$. In this test calculation, because

the values of θ , salinity and TA in the intermediate water at KNOT had not changed for the period from 1992 to 2001, and we cannot estimate the elapsed time from the area east of Japan to KNOT, we calculated DIC_{win} and ${}_{\text{anth}}\text{DIC}_{\text{air-sea}}$ for convenience by using $p\text{CO}_2^{\text{sea}}_{\text{win}}$ in the area east of Japan and the atmospheric CO_2 concentrations from 1998 to 2001 and observed temperature, salinity and the average values of TA on $26.9\sigma_\theta$ at KNOT. As a result, the difference between DIC_{win} ($2110\sim 2120\ \mu\text{mol/kg}$ normalized to a salinity of 33) and ${}_{\text{anth}}\text{DIC}_{\text{air-sea}}$ ($2100\sim 2110\ \mu\text{mol/kg}$ normalized to a salinity of 33) from 1998 to 2001 could have decreased by about $2.0\ \mu\text{mol/kg/yr}$, which almost agrees with $d({}_{\text{non-anth}}\text{DIC}_{\text{air-sea}})/dt$ ($0.9\sim 1.1\ \mu\text{mol/kg/yr}$) in the upper intermediate water ($26.9\sim 27.1\sigma_\theta$) at KNOT. Thus, possibility 1) has some possibility to explain the increase of non-anthropogenic CO_2 in the upper intermediate water ($26.9\sim 27.1\sigma_\theta$) at KNOT.

We now examine possibility 2). Ono *et al.* (2001) suggested that the linear increase of AOU, phosphate and salinity between $26.7\sigma_\theta$ and $27.2\sigma_\theta$ from 1968 to 1998 was caused by the reduction of diapycnal vertical water exchange between mixed layer and pycnocline waters in the western North Pacific subpolar region (near the area east of Japan), based on the linear decrease of salinity and density in the winter mixed layer. This suggestion agrees with the surface stratification in winter induced by the linear decrease of phosphate in the winter mixed layer of the same region from 1968 to 1998 (Ono *et al.*, 2002). The reduction of diapycnal vertical water exchange between mixed layer and pycnocline waters could affect the upper intermediate water at KNOT, because the region of the upper intermediate water formation at KNOT is similar to that obtained by Ono *et al.* (2001) and Ono *et al.* (2002). If the temporal change of $p\text{CO}_2^{\text{sea}}_{\text{win}}$ near the area east of Japan could be controlled basically by the depth of the winter mixed layer, the temporal trend of $p\text{CO}_2^{\text{sea}}_{\text{win}}$ would have decreased due to the linear decrease of the depth of winter mixed layer (Ono *et al.*, 2001). This would lead us to expect a decrease of DIC in the winter mixed layer and an increase of DIC in the upper intermediate water. We suggest that the increase of DIC in the upper intermediate water over time near the area east of Japan is responsible for the accumulation of non-anthropogenic CO_2 liberated back to the atmosphere. Thus, possibility 2) also has some possibility to explain the increase of non-anthropogenic CO_2 in the upper intermediate water ($26.9\sim 27.1\sigma_\theta$) at KNOT.

The greater DIC of the winter mixed layer would have decreased due to the shoaling of the depth of the layer (Ono *et al.*, 2001), the more the difference between $p\text{CO}_2^{\text{sea}}_{\text{win}}$ and atmospheric CO_2 would have decreased, according to the possibility 1), which would facilitate the accumulation of non-anthropogenic CO_2 in the upper in-

intermediate water. However, the temporal change of $p\text{CO}_2^{\text{sea}}_{\text{win}}$ was insignificant during the period from 1998 to 2001 (Midorikawa *et al.*, 2003). An additional time series dataset is required to understand the linkage of the accumulation of non-anthropogenic CO_2 between the area east of Japan and KNOT, and clarify which of the possibilities 1) or 2) affects the factors controlling the increase of non-anthropogenic CO_2 .

This paper first showed the decadal linear increase of DIC in the intermediate water ($26.7\text{--}27.2\sigma_\theta$) at KNOT in the western North Pacific subpolar region. Since Ono *et al.* (2000) reported that the linear increase of AOU and phosphate superimposed on bidecadal oscillation from $26.7\sigma_\theta$ to $27.2\sigma_\theta$ of the western North Pacific subpolar region (near the area east of Japan), the increase of DIC from $26.9\sigma_\theta$ to $27.3\sigma_\theta$ at Station KNOT also possibly has a bidecadal oscillation. Thus the rate of increase of DIC in the intermediate water at Station KNOT may be an overestimate according to the ten years' time series data during the period from 1992 to 2001. In future, more accurate and longer time series data will be required to confirm our results. Similarly, by using a decadal dataset of DIC in the subtropical mode water of the North Atlantic Ocean, Bates *et al.* (2002) suggested that the rate of increase of DIC in this region is caused by the increase of anthropogenic CO_2 and the increase in the accumulation of non-anthropogenic CO_2 due to the reduction of vertical water exchange. We suggest that this phenomenon might have happened in the ocean of the North Hemisphere and is likely to contribute substantially to the interannual variability in oceanic CO_2 uptake.

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Reference

Anderson, L. A. and J. L. Sarmiento (1994): Redfield ratios of remineralization determined by nutrient data analysis. *Global Biogeochem. Cycles*, **8**, 65–80.
 Bates, N. R. (2001): Interannual variability of oceanic CO_2 and biogeochemical properties in the Western North Atlantic

subtropical gyre. *Deep-Sea Res., Parts II*, **48**, 1507–1528.
 Bates, N. R., A. C. Pequignot, R. J. Johnson and N. Gruber (2002): A short-term sink for atmospheric CO_2 in subtropical mode water of the North Atlantic. *Nature*, **420**, 489–493.
 Brewer, P. G. (1978): Direct observation of the oceanic CO_2 increase. *Geophys. Res. Lett.*, **5**, 997–1000.
 Chen, C. T. A. and F. J. Millero (1979): Gradual increase of oceanic carbon dioxide. *Nature*, **227**, 205–206.
 Culbertson, C., R. M. Pytkowicz and J. E. Hawley (1970): Seawater alkalinity determination by the pH method. *J. Mar. Res.*, **28**, 15–21.
 Dickson, A. G. and F. J. Millero (1987): A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media. *Deep-Sea Res.*, **40**, 107–118.
 Dickson, A. G., G. C. Anderson and J. D. Afghan (2003): Reference materials for oceanic CO_2 analysis: 1. Preparation, distribution and use. *Mar. Chem.* (submitted).
 DOE (1994): *Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide in Sea Water; Ver. 2*, ed. by A. G. Dickson and C. Goyet.
 Favorite, F., A. J. Dodimead and K. Nasu (1976): Oceanography of the subarctic Pacific region, 1960–1971. *INPFC*, **33**, 1–187, Vancouver.
 Gloor, M., N. Gruber, J. Sarmiento, C. L. Sabine, R. A. Feely and C. Rodenbeck (2003): A first estimate of present and preindustrial air-sea CO_2 flux patterns based on oceanic interior carbon measurements and models. *Geophys. Res. Lett.*, **30**, 1010, doi:10.1029/2002GL015594.
 Honda, M. C., K. Imai, Y. Nojiri, F. Hoshi, T. Sugawara and M. Kusakabe (2002): The biological pump in the northwestern North Pacific based on fluxes and major components of particulate matter obtained by sediment-trap experiments (1997–2000). *Deep-Sea Res. II*, **49**, 5595–5625.
 Imai, K., Y. Nojiri, N. Tsurushima and T. Saino (2002): Time series of seasonal variation of primary productivity at station KNOT (44°N , 155°E) in the sub-arctic western North Pacific. *Deep-Sea Res. II*, **49**, 5395–5408.
 Isoda, Y., S. Shimizu, T. Izawa and T. Azumaya (2002): Interannual variations of North Pacific Intermediate Water across 155°E and 180°E sections in the subarctic North Pacific. *Umi to Sora*, **77**, 143–151.
 Johnson, K., A. E. King and J. M. Sieburth (1985): Coulometric TCO_2 analyses for marine studies: An introduction. *Mar. Chem.*, **16**, 61–81.
 Keeling, C. D. and T. P. Whorf (2002): Atmospheric CO_2 records from sites in the SIO air sampling network. In *Trends, A Compendium of Data on Global Change, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tenn., U.S.A.*
 Knap, A., A. Michaels, A. Close, H. Ducklow and A. Dickson (eds.) (1996): Protocols for the Joint Global Ocean Flux Study (JGOFS) core measurements. JGOFS Report No. 19, vi + 170 pp. Reprint of the IOC manuals and guides No. 29, UNESCO.
 Kono, T. (1997): Modification of the Oyashio Water in the Hokkaido and Tohoku areas. *Deep-Sea Res. I*, **44**, 669–688.
 McNeil, B. I., R. J. Matear, R. M. Key, J. L. Bullister and J. L. Sarmiento (2003): Anthropogenic CO_2 uptake by the ocean

- based on the global chlorofluorocarbon data set. *Science*, **299**, 235–239.
- Mehrbach, C., C. H. Culbertson, J. E. Hawley and R. M. Pytkowicz (1973): Measurement of the apparent dissociation constants of carbonic acid in the seawater at atmospheric pressure. *Limnol. Oceanogr.*, **18**, 897–907.
- Midorikawa, T., S. Sonoki, K. Saito, H. Takano, H. Kamiya, M. Ishii and H. I. Inoue (2003): Seasonal changes in oceanic $p\text{CO}_2$ in the Oyashio region from winter to spring. *J. Oceanogr.*, **59**, 871–882.
- Millero, F. J. (1996): *Chemical Oceanography*. CRC Press, Boca Raton, Florida, 272 pp.
- Minobe, S. (1999): Resonance in bidecadal and pentadecadal climate oscillations over the North Pacific: role in climate regime shifts. *Geophys. Res. Lett.*, **26**, 855–858.
- Ono, T., S. Watanabe, K. Okuda and M. Fukasawa (1998): Distribution of total carbonate and related properties in the North Pacific along 30°N. *J. Geophys. Res.*, **103**, 30873–30883.
- Ono, T., Y. W. Watanabe and S. Watanabe (2000): Recent increase of DIC in the western North Pacific. *Mar. Chem.*, **72**, 317–328.
- Ono, T., T. Midorikawa, Y. W. Watanabe, K. Tadokoro and T. Saito (2001): Temporal increases of phosphate and apparent oxygen utilization in the subsurface waters of western subarctic Pacific from 1968 to 1998. *Geophys. Res. Lett.*, **28**, 3285–3288.
- Ono, T., K. Tadokoro, T. Midorikawa, J. Nishioka and T. Saino (2002): Multi-decadal decrease of net community production in western subarctic North Pacific. *Geophys. Res. Lett.*, **29**, 10.1029/2001GL014332.
- Redfield, A. C., B. H. Ketchum and F. A. Richards (1963): The influence of organisms on the composition of seawater. p. 26–77. In *The Sea*, ed. by M. H. Hill, Wiley-Interscience, New York.
- Reid, J. L. (1965): Intermediate waters of the Pacific Ocean. *The John Hopkins Oceanographic Study*, **2**, Baltimore, p. 85.
- Slansky, C. M., R. A. Feely and R. H. Wanninkhof (1997): The stepwise linear regression method for calculating anthropogenic CO_2 invasion into the North Pacific Ocean. *Proceeding of International Marine Science Symposium on Biogeochemical Processes in the North Pacific*, 70–79, Japan.
- Takahashi, Y., E. Matsumoto and Y. Watanabe (1999): Improved method for calculating anthropogenic CO_2 in the upper layer of the North Pacific subtropical gyre along 175°E. *J. Oceanogr.*, **55**, 717–730.
- Talley, L. D. (1991): An Okhotsk Sea anomaly: implications for ventilation in the North Pacific. *Deep-Sea Res. A*, **38**, Suppl., S171–S190.
- Tsunogai, S. (2000): North Pacific water's larger potential sink capacity for absorbing anthropogenic CO_2 and the processes recovering it. p. 533–560. In *Dynamics and Characterization of Marine Organic Matter*, ed. by N. Handa, E. Tanoue and T. Hama, TERRAPUB, Tokyo.
- Tsunogai, S., T. Ono and S. Watanabe (1993): Increase in the total carbonate in the western North Pacific water and a hypothesis on the missing sink of anthropogenic carbon. *J. Oceanogr.*, **49**, 305–315.
- Tsurushima, N., Y. Nogiri, K. Imai and S. Watanabe (2002): Seasonal variations of carbon dioxide system and nutrients in the surface mixed layer at Station KNOT (44°N, 155°E) in the subarctic North Pacific. *Deep-Sea Res. II*, **49**, 5377–5394.
- Ueno, H. and I. Yasuda (2000): Distribution and formation of the mesothermal structure (temperature inversions) in the North Pacific subarctic region. *J. Geophys. Res.*, **105**, 16885–16898.
- Watanabe, Y. W., Y. Takahashi, T. Kitao and K. Harada (1996): Total amount of oceanic excess CO_2 taken from the North Pacific Subpolar Region. *J. Oceanogr.*, **52**, 301–312.
- Watanabe, Y. W., T. Ono and A. Shimamoto (2000): Increase in the uptake rate of oceanic anthropogenic carbon in the North Pacific determined by CFC ages. *Mar. Chem.*, **72**, 297–315.
- Watanabe, Y. W., T. Ono, A. Shimamoto, T. Sugimoto, M. Wakita and S. Watanabe (2001): Probability of a reduction in the formation rate of the subsurface water in the North Pacific during the 1980s and 1990s. *Geophys. Res. Lett.*, **28**, 3289–3292.
- Watanabe, Y. W., T. Ono, M. Wakita, N. Maeda and T. Gamo (2003): Synchronous bidecadal periodic changes of oxygen, phosphate and temperature between the Japan Sea deep water and the North Pacific intermediate water. *Geophys. Res. Lett.*, **30**, 10.1029/2003GL018338.
- Weiss, R. F. (1970): The solubility of nitrogen, oxygen and argon in water and seawater. *Deep-Sea Res.*, **17**, 721–735.
- Winn, C. D., Y. H. Lee, F. T. Mackenzie and D. M. Karl (1998): Rising surface ocean dissolved inorganic carbon at the Hawaii Ocean Time-series site. *Mar. Chem.*, **60**, 33–47.