

## Distribution of the partial pressure of CO<sub>2</sub> in surface water ( $p\text{CO}_2^{\text{w}}$ ) between Japan and the Hawaiian Islands: $p\text{CO}_2^{\text{w}}$ –SST relationship in the winter and summer

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### ABSTRACT

On the basis of measurements of the partial pressure of carbon dioxide in surface seawater ( $p\text{CO}_2^{\text{w}}$ ) between Japan and the Hawaiian Islands in winter and summer, we examined the relationship between  $p\text{CO}_2^{\text{w}}$  and the sea surface temperature (SST) in the North Pacific Subtropical Gyre (NPSG). In winter,  $p\text{CO}_2^{\text{w}}$  correlated well with the SST ( $0.14\text{--}0.24\% \text{ } ^\circ\text{C}^{-1}$ ), suggesting a monotonous change in the carbonate system. However, in summer, five different  $p\text{CO}_2^{\text{w}}$ –SST relationships were found in the NPSG (including the Kuroshio Extension) due to changes in the relative contribution of ocean dynamics (upwelling, vertical mixing and advection), biological activity in the absence (very low level) of macro-nutrients and thermodynamics. The increase in  $p\text{CO}_2^{\text{w}}$  corresponding to a unit increase in the SST from January to July was low ( $<2.5\% \text{ } ^\circ\text{C}^{-1}$ ) west (leeward side) of the Hawaiian Islands ( $19\text{--}22^\circ\text{N}$ ,  $158\text{--}168^\circ\text{W}$ ) and in the Kuroshio Extension ( $33\text{--}35^\circ\text{N}$ ,  $140\text{--}165^\circ\text{E}$ ), and high ( $\sim 3\% \text{ } ^\circ\text{C}^{-1}$ ) south of the Kuroshio Extension ( $25\text{--}30^\circ\text{N}$ ,  $180\text{--}165^\circ\text{W}$ ) and the Hawaiian Islands ( $15\text{--}19^\circ\text{N}$ ,  $157\text{--}162^\circ\text{W}$ ). This suggested that the drawdown of dissolved inorganic carbon was affected by the enhanced biological activity due to upwelling events associated with eddies and/or the transport of dissolved nutrients from gyre edges to the interior.

### 1. Introduction

The oligotrophic subtropical gyre of the Pacific Ocean acts as a sink for atmospheric CO<sub>2</sub> (see for example, Takahashi et al., 1997). In 1982 Weiss et al. reported the predominant role of thermodynamics in

determining seasonal variation in the fugacity (partial pressure) of CO<sub>2</sub> in the South and North Pacific Subtropical Gyres. Since then, it has been reported that seasonal variations in the partial pressure of CO<sub>2</sub> ( $p\text{CO}_2^{\text{w}}$ ) in the subtropics are mainly controlled by variations in sea surface temperature (Poisson et al., 1993; Inoue et al., 1995; Stephens et al., 1995; Metzl et al., 1998). At the time-series station in the North Atlantic Subtropical Gyre (Bermuda Atlantic Time-series Study site;  $31^\circ 50'\text{N}$ ,  $64^\circ 10'\text{W}$ ), Bates et al. (1996) reported the importance of biological activity relative to the spring–summer drawdown of total dissolved inorganic carbon (TCO<sub>2</sub>) in surface seawater that occurred in the absence of macro-nutrients. In the

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North Pacific Subtropical Gyre (NPSG), decreases of surface TCO<sub>2</sub> from winter to summer were also reported (Winn et al., 1994, 1998; Ishii et al., 2001). By taking into account vertical mixing and biological processes, Metzl et al. (1998) obtained better results on seasonal and interannual variations in the fugacity of CO<sub>2</sub> of the subtropical Indian Ocean.

Bates et al. (1996) indicated that the factors controlling the carbonate system in the subtropics are seasonally variable. However, to what extent these factors varied spatially and seasonally is poorly understood in the wide area of the subtropics. In this work, we examine the  $p\text{CO}_2^w$ -SST relationship between Japan

and the Hawaiian Islands (Fig. 1), mostly in the area of the NPSG in winter and summer, which will allow us to evaluate factors controlling changes in the surface carbonate system.

## 2. Observational data

From December 1990 to January 2001 measurements of the partial pressure of carbon dioxide in surface seawater ( $p\text{CO}_2^w$ ) and those of overlying air ( $p\text{CO}_2^a$ ) were made between Japan and the Hawaiian Islands in the boreal winter and summer (Fig. 1). The ships used were the R/V Natsushima and R/V

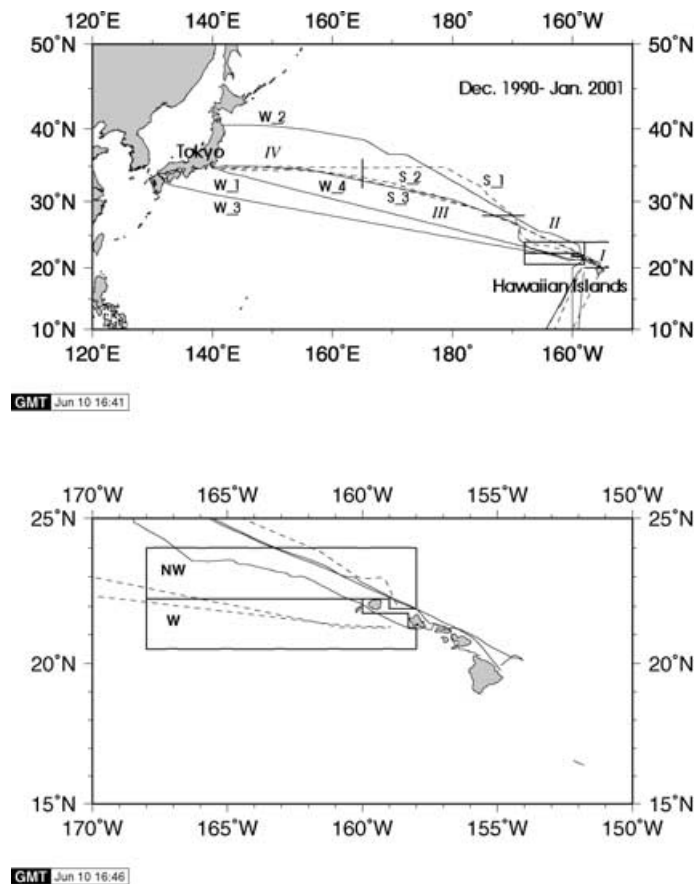


Fig. 1. Cruise tracks between Japan and the Hawaiian Islands. In the upper panel, W\_1 refers to the cruise track in December 1990–January 1991, W\_2 to that in January 1999, W\_3 to that in December 1999 and W\_4 to that in January 2001. S\_1 refers to the cruise track in July 1992, S\_2 to that in July 1993 and S\_3 to that in July 1996. In July four different temperature dependences of  $p\text{CO}_2^w$  occurred in Areas I–IV. Area I is northwest–east (windward side) of the Hawaiian Islands (see text). The lower panel is the area where the  $p\text{CO}_2^w$ -SST relationships are examined: (NW) is the area northwest of the Hawaiian Islands, and (W) is that west (leeward side) of the Hawaiian Islands.

Mirai, both of which belong to the Japan Marine Science Technology Center, and the M/S Hokuto-maru and M/S Taisei-maru, both of which belong to the National Institute for Sea Training, Independent Administrative Institution (formerly the Institute for Sea Training, Ministry of Transport). We also used oceanic CO<sub>2</sub> in surface seawater and auxiliary data taken in the northwest and west of the Hawaiian Islands during summer cruises of the North Pacific Carbon Cycle Study (NOPACCS) in 1995 and 1996 (Watai et al., 1999, <http://www.kanso.co.jp>).

Underway measurements of  $p\text{CO}_2^w$  and  $p\text{CO}_2^a$  were carried out with systems consisting of a non-dispersive infrared gas analyzer (NDIR gas analyzer, BINOS 4.1), a shower-head-type equilibrator, diaphragm pumps, electric dehumidifiers, Nafion tubing (Perma Pure Inc.), a chemical desiccant column [Mg(ClO<sub>4</sub>)<sub>2</sub>] and a data acquisition unit connected to a PC and associated instrumentation (Körtzinger et al., 2000). Four standard gases (typically 300, 340, 380 and 420 ppm CO<sub>2</sub> in natural air) traceable to the WMO mole fraction scale were used aboard the ship (Inoue et al., 1995; 1999). The water inlet was about 4 m below the surface for the M/S Hokuto-maru M/S Taisei-maru and R/V Natsushima and 5 m for the R/V Mirai. The increase in temperature from the sea surface to the equilibrator was typically 0.6 °C for the M/S Hokuto-maru and M/S Taisei-maru and 0.1 °C for the R/V Natsushima and R/V Mirai. To calculate  $p\text{CO}_2^w$  from the observed mixing ratio of CO<sub>2</sub> in the air equilibrated with seawater in the equilibrator, we used the equation given by Gordon and Jones (1973) for the cruises of the R/V Natsushima, M/S Hokuto-maru and M/S Taisei-maru and by Copin-Montégut (1988; 1989) for the cruises of the R/V Mirai. Because of a small temperature rise from the water inlet to the equilibrator (especially for the R/V Mirai), the difference in  $p\text{CO}_2^w$  derived from the two equations did not affect the results of the present study (see, for example, DOE, 1994).

The  $p\text{CO}_2$  data used in this work will be made available from WMO WDCGG (Tokyo, Japan) and CDIAC (Oak Ridge, USA) in the near future.

### 3. Results and discussion

#### 3.1. $p\text{CO}_2^w$ –SST relationship in winter

The data discussed in this paper represent a geographically extensive set of ocean  $p\text{CO}_2^w$  observa-

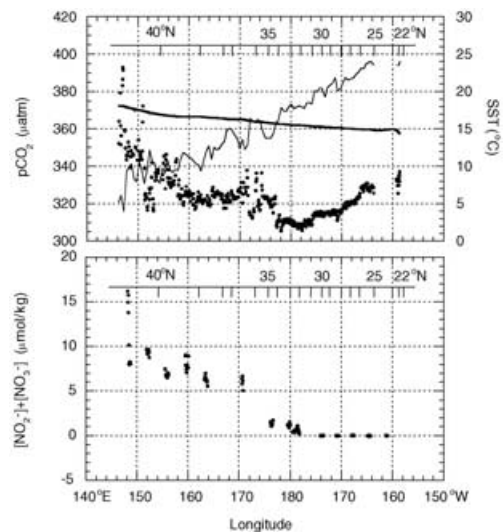


Fig. 2. Longitudinal distributions of  $p\text{CO}_2^w$ ,  $p\text{CO}_2^a$ , SST and nitrite and nitrate ( $\text{NO}_2^- + \text{NO}_3^-$ ) between Japan and the Hawaiian Islands (along W<sub>2</sub> in Fig. 1) in January 1999. In the upper panel,  $p\text{CO}_2^w$  is indicated by a solid circle,  $p\text{CO}_2^a$  by a heavy solid line and the SST by a lighter thinner line.

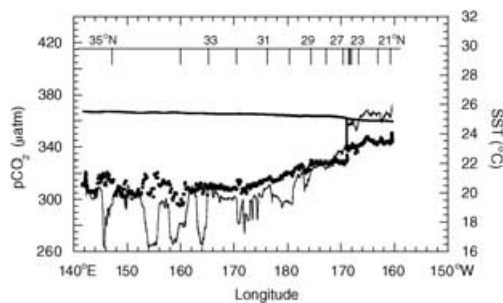


Fig. 3. Same as in the upper panel of Fig. 2, but in December 2000–January 2001 (along W<sub>4</sub> in Fig. 1).

tions for the NPSG (see, for example, Takahashi et al., 1997). Figures 2 and 3 show  $p\text{CO}_2^w$  distributions between Japan and the Hawaiian Islands in January 1999 (W<sub>2</sub> in Fig. 1) and December 2000–January 2001 (W<sub>4</sub> in Fig. 1). The ocean acted as a net sink for atmospheric CO<sub>2</sub> in a wide area of the North Pacific. Around 35°N, the Kuroshio left the coast of Japan and turned due east. The eastward continuation of the Kuroshio Extension is characterized by distorted meanders of its pass and numerous eddies of various sizes and durations (Kawai, 1972). South of the Kuroshio Extension,  $p\text{CO}_2^w$  increased gradually toward the south. In

the Kuroshio–Oyashio interfrontal zone between the Kuroshio Extension and the Oyashio (Subarctic) front (Yoshinari et al., 2001)  $p\text{CO}_2^w$  was fairly constant, and north of  $\sim 39^\circ\text{N}$  the  $p\text{CO}_2^w$  increased steeply toward the north.

Thermodynamics, ocean dynamics (upwelling, vertical mixing and advection) and biological activity are major factors controlling changes in  $p\text{CO}_2^w$ , which could correlate with the SST either directly or indirectly (Lee et al., 1998); the thermodynamic effect leads to a positive temperature dependence of  $p\text{CO}_2^w$ , while upwelling/vertical mixing with high CO<sub>2</sub> subsurface waters and biological activity lead to a negative one (Takahashi et al., 2002). The latter was due to the larger effect of the decrease in TCO<sub>2</sub> along with the SST increase (biological CO<sub>2</sub> uptake), as compared with that of the thermodynamics. Figure 4 illustrates the relationship between  $p\text{CO}_2^w$  and the SST in January 1999 and December 2000–January 2001. Along W<sub>2</sub>,  $p\text{CO}_2^w$  increased gradually and monotonously with SST higher than 19 °C (1.5% °C<sup>-1</sup>).  $p\text{CO}_2^w$  showed a broad minimum at an SST of 16–19 °C, caused by an opposite temperature effect between thermodynamics and vertical mixing with CO<sub>2</sub> and macro-nutrient rich subsurface water. The minimum  $p\text{CO}_2^w$  occurred in the formation area of Subtropical Mode Water (vertically homogeneous water found between the seasonal thermocline at the surface and the deeper main thermocline) south of

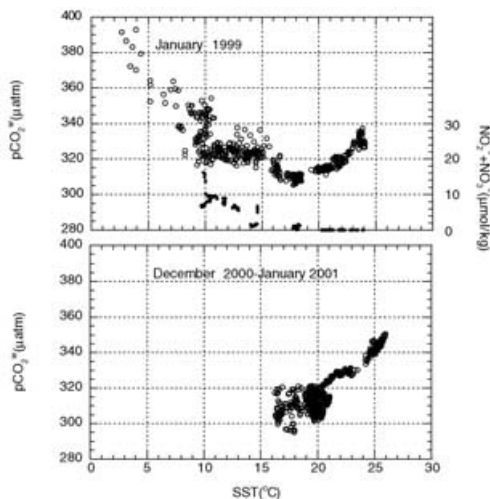


Fig. 4. Temperature dependence of  $p\text{CO}_2^w$  between Japan and the Hawaiian Islands in January 1999 (upper panel) and in December 2000–January 2001 (lower panel).

the Kuroshio Extension (Bingham, 1992; Suga and Hanawa, 1990).  $p\text{CO}_2^w$  and the nitrite and nitrate ( $\text{NO}_2^- + \text{NO}_3^-$ ) concentrations remained fairly constant against the SST change (11–16 °C) in the Kuroshio–Oyashio interfrontal zone, and north of  $39^\circ\text{N}$  they increased steeply with the decrease in SST. The relatively low or negative temperature dependence of  $p\text{CO}_2^w$  suggests that vertical mixing and biological activity played an important role in determining  $p\text{CO}_2^w$  north of the Kuroshio Extension, as reported earlier (Sasaki et al., 1998; Watai et al., 1999).

Around the Kuroshio Extension ( $35^\circ\text{N}$ ,  $140^\circ\text{E}$ – $33^\circ\text{N}$ ,  $165^\circ\text{E}$ ),  $p\text{CO}_2^w$  along W<sub>4</sub> did not correlate well with the SST ( $r < 0.2$ ), probably due to the difference in the carbonate system between Kuroshio (warm SST and constant salinity-normalized total alkalinity  $\sim 2320 \mu\text{mol kg}^{-1}$  at salinity  $S = 35$ ) and the Oyashio (cold SST and salinity-normalized total alkalinity higher than  $2350 \mu\text{mol kg}^{-1}$  at  $S = 35$ ; Midorikawa, personal communication); in the area with an SST higher than 19 °C,  $p\text{CO}_2^w$  also increased gradually with the SST (1.8% °C<sup>-1</sup>), as found in January 1999.

We also examined the  $p\text{CO}_2^w$ –SST relationships between Japan and the Hawaiian Islands in December 1990–January 1991 and December 1999 (Fig. 5). In the NPSG they showed a pattern similar to those of January 1999 and December 2000–January 2001, except for differences in the  $p\text{CO}_2^w$  level between two data sets. The  $p\text{CO}_2^w$  increased clearly from December 1990–January 1991 to December 1999 (Fig. 5). However, discussing the long-term trend in  $p\text{CO}_2^w$  on the basis of two data sets taken at different geographical positions (Fig. 1) is beyond the scope of this paper. In this work, we use the  $p\text{CO}_2^w$  long-term trend of

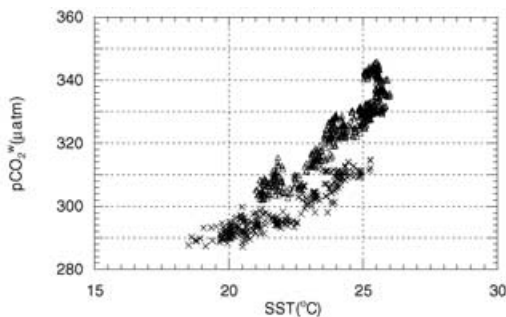


Fig. 5. Temperature dependence of  $p\text{CO}_2^w$  between Japan and the Hawaiian Islands in December 1990–January 1991 (cross) and December 1999 (open triangle).

$1.6 \mu\text{atm yr}^{-1}$  (Inoue et al., 1995; Nemoto, personal communication) to discuss the apparent temperature dependence of  $p\text{CO}_2^w$  between winter and summer.

### 3.2. $p\text{CO}_2^w$ –SST relationship in summer

Figure 6 shows the  $p\text{CO}_2^w$  distribution along the cruise track S\_2 (Fig. 1) in July 1993. In the areas east of  $166^\circ\text{W}$  and between  $140^\circ\text{E}$  and  $174^\circ\text{E}$ , the ocean generally acted as a sink for atmospheric  $\text{CO}_2$  and the remaining areas as the source. The temperature dependence of  $p\text{CO}_2^w$  differed significantly from that of winter and can be divided into four areas (Fig. 7). Northwest–east of the Hawaiian Islands ( $20^\circ\text{N}$ ,  $155^\circ\text{W}$

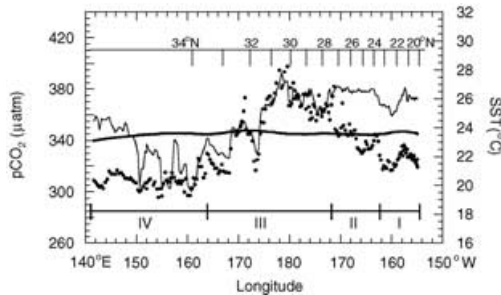


Fig. 6. Longitudinal distributions of  $p\text{CO}_2^w$ ,  $p\text{CO}_2^a$  and SST between Japan and the Hawaiian Islands (along S\_2 in Fig. 1) in July 1993.  $p\text{CO}_2^w$  is indicated by a solid circle,  $p\text{CO}_2^a$  by a heavy solid line, and the SST by a lighter thinner line.

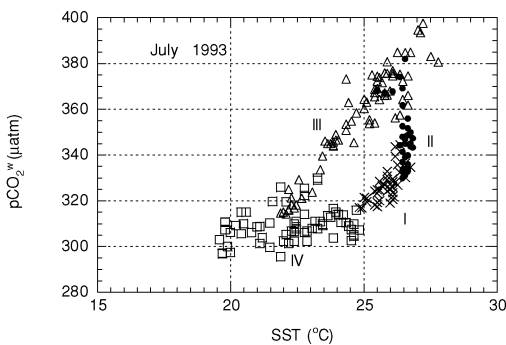


Fig. 7. Temperature dependence of  $p\text{CO}_2^w$  between Japan and the Hawaiian Islands in July 1993. A cross shows the data in Area I ( $20^\circ\text{N}$ ,  $155^\circ\text{W}$  –  $24^\circ\text{N}$ ,  $162^\circ\text{W}$ ), a solid circle those in Area II ( $24^\circ\text{N}$ ,  $162^\circ\text{W}$  –  $28^\circ\text{N}$ ,  $173^\circ\text{W}$ ), an open triangle those in Area III ( $28^\circ\text{N}$ ,  $173^\circ\text{W}$  –  $33.5^\circ\text{N}$ ,  $165^\circ\text{E}$ ) and the open square those in Area IV ( $33.5^\circ\text{N}$ ,  $165^\circ\text{E}$  –  $35^\circ\text{N}$ ,  $140^\circ\text{E}$ ).

–  $24^\circ\text{N}$ ,  $162^\circ\text{W}$ , Area I) and south of the Kuroshio Extension ( $28^\circ\text{N}$ ,  $173^\circ\text{W}$  –  $33.5^\circ\text{N}$ ,  $165^\circ\text{E}$ , Area III), we observed a larger temperature dependence of  $p\text{CO}_2^w$  ( $>3.5\% \text{ } ^\circ\text{C}^{-1}$ ) than that in winter ( $1.4$ – $2.4\% \text{ } ^\circ\text{C}^{-1}$ ). At a given SST between  $25$  and  $27^\circ\text{C}$ ,  $p\text{CO}_2^w$  northwest of the Hawaiian Islands was about  $39$ – $48 \mu\text{atm}$  lower than that south of the Kuroshio Extension. Around the Kuroshio Extension ( $33.5^\circ\text{N}$ ,  $165^\circ\text{E}$  –  $35^\circ\text{N}$ ,  $141^\circ\text{E}$ , Area IV),  $p\text{CO}_2^w$  increased slightly with the SST ( $<1\% \text{ } ^\circ\text{C}^{-1}$ ). In the area  $24^\circ\text{N}$ ,  $162^\circ\text{W}$  –  $28^\circ\text{N}$ ,  $173^\circ\text{W}$  (Area II),  $p\text{CO}_2^w$  varied largely with the SST at  $\sim 26.5^\circ\text{C}$  ( $r < 0.1$ ). In the subtropics there have been few studies of the low correlation between  $p\text{CO}_2^w$  and the SST (Landrum et al., 1996). In the area of the central North Pacific there occurred a strong northward wind during the summer season (see, for example, Plate 2 in Stephens et al., 1995). The surface current based on climatological data tends to be northward during the summer season (<http://www.jodc.go.jp>). Therefore, the  $p\text{CO}_2^w$ –SST relationship in Area II could be caused by the effect of the advection of surface water driven by a southerly wind with a low  $p\text{CO}_2^w$  at an SST of  $\sim 26.5^\circ\text{C}$ .

The temperature dependence of  $p\text{CO}_2^w$  between Japan and the Hawaiian Islands in July 1992 and July 1996 (Fig. 8) also showed the same pattern as that observed in July 1993 (Fig. 7). In July 1992 the cruise track showed a large deviation from those of July 1993 and July 1996 (Fig. 1).  $p\text{CO}_2^w$  east of Area IV (S\_1 in Fig. 1) increased with the SST ( $4\% \text{ } ^\circ\text{C}^{-1}$ ), which provided the same  $p\text{CO}_2^w$ –SST relationships north of  $28^\circ\text{N}$ . South of  $28^\circ\text{N}$  two different  $p\text{CO}_2^w$ –SST relationships occurred in nearly the same geographical positions as found in July 1993 and July 1996. In July 1996 data showing a large positive  $p\text{CO}_2^w$ –SST relationship in Area IV increased in number ( $\sim 60\%$ ) as compared with those in July 1992 and July 1993 (Figs. 7 and 8). This large positive  $p\text{CO}_2^w$ –SST relationship, the same as that in Area III, appeared every several tens of kilometres, which suggested a meso-scale phenomenon in the meandering Kuroshio Extension.

### 3.3. $p\text{CO}_2^w$ –SST relationship close to the Hawaiian Islands

A combination of prevailing north-easterly trade winds and island topography leads to the generation of vigorous eddies on the leeward side of the Hawaiian Islands and an eastward ocean current known as the subtropical countercurrent (Xie et al., 2001,

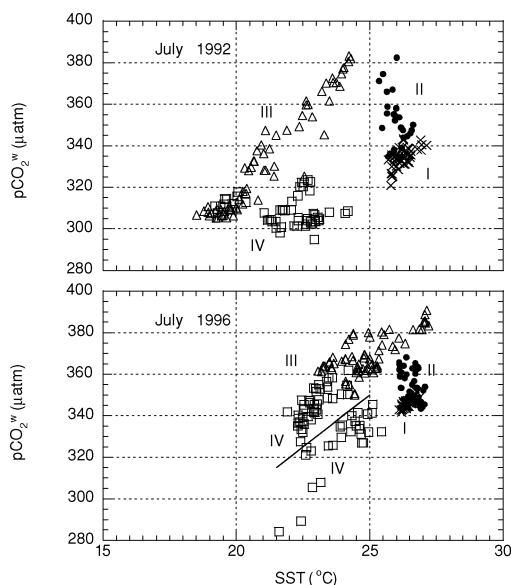


Fig. 8. Temperature dependence of  $p\text{CO}_2^w$  between Japan and the Hawaiian Islands in July 1992 (S.1 in Fig. 1) and July 1996 (S.3 in Fig. 1). In these figures, Areas I–III were determined by latitudes (20, 24, 28, 33.5°N) and Area IV by longitudes (140, 165°E) used in July 1993. In July 1996 the temperature dependence in Area IV was separated arbitrarily by  $p\text{CO}_2^w = 10 \times (\text{SST} - 20) + 300$  (thin solid line). Data in the leeward side of the Hawaiian Islands are omitted from the figure.

<http://www.jamstec.go.jp/frsgh/eng/Xie/010615/index.html>). Seki et al. (2001) have reported that the eddy pump and biological activity responses were likely to be the greatest during the summer, on the basis of archived satellite imagery. We examined the  $p\text{CO}_2^w$ –SST relationship close to the Hawaiian

Islands by diving into two areas measured during the summer (July and September): northwest of the Hawaiian Islands (windward side) and west of the Hawaiian Islands (leeward side, lower panel of Fig. 1). Northwest of the Hawaiian Islands,  $p\text{CO}_2^w$  correlated well with the SST (Table 1). However, on the leeward side, the temperature dependence of  $p\text{CO}_2^w$  was not clear, and the apparent increase in  $p\text{CO}_2^w$  against the change in the SST was smaller than that to the northwest (windward side) of the Hawaiian Islands (Table 1). This supports the idea of effect of biological activity on the surface carbonate system due to upwelling on the leeward side of the Hawaiian Islands. During winter, however, the  $p\text{CO}_2^w$ –SST relationship did not support any enhanced upwelling to the west of the Hawaiian Islands. Fresh water containing rich nutrients from the Hawaiian Islands may affect the  $\text{TCO}_2$  drawdown, but we could not detect a lower temperature dependence of  $p\text{CO}_2^w$  west of the Hawaiian Islands during winter. Therefore, fresh water input from the Hawaiian Islands was considered to be a minor factor controlling the  $p\text{CO}_2^w$  change.

#### 3.4. $p\text{CO}_2^w$ –SST relationship between January and July

On the basis of  $p\text{CO}_2^w$  and SST data measured within 4° of longitude, we examined an apparent increase in  $p\text{CO}_2^w$  against a unit increase of the SST from January to July (Fig. 9). Among combinations of January and July data, data between January 2001 and July 1992 and July 1993 and July 1996 were used because they covered a wide area between Japan and the Hawaiian Islands and might give an insight into the interannual variability of the carbonate system. The average apparent increase in  $p\text{CO}_2^w$  against a unit increase in the SST was usually lower than that of the

Table 1. The average apparent increase in  $p\text{CO}_2^w$  against a unit increase in the SST northwest (NW) and west (W) of the Hawaiian Islands (Fig. 1) in July and September<sup>a</sup>

Area	Month	$p\text{CO}_2^w$ <sup>b</sup> (μatm)	SST <sup>b</sup> (°C)	Salinity	Chl. a (μg L <sup>-1</sup> )	$p\text{CO}_2^w/\text{SST}^b$ [μatm °C <sup>-1</sup> (%°C <sup>-1</sup> )]	<i>r</i>	<i>n</i>
NW	July	347.0 ± 7.9	26.1 ± 0.5			13.7(4.0 ± 0.2)	0.91	57
W	July	344.8 ± 1.8	26.0 ± 0.1			3.2(0.9 ± 1.2)	0.27	10
NW	September	359.1 ± 4.5	26.4 ± 0.3	34.96 ± 0.14	0.10 ± 0.01	13.4(3.7 ± 0.4)	0.91	20
W	September	366.1 ± 2.3	27.8 ± 0.3	34.78 ± 0.09	0.11 ± 0.11	3.4(0.9 ± 0.2)	0.50	47

<sup>a</sup>The values in parentheses indicate the percentage of increase in  $p\text{CO}_2^w$  against the unit change in the SST. *r* indicates the correlation coefficient between  $p\text{CO}_2^w$  and the SST and *n* the number of data.

<sup>b</sup>Average ± 1 S.D.

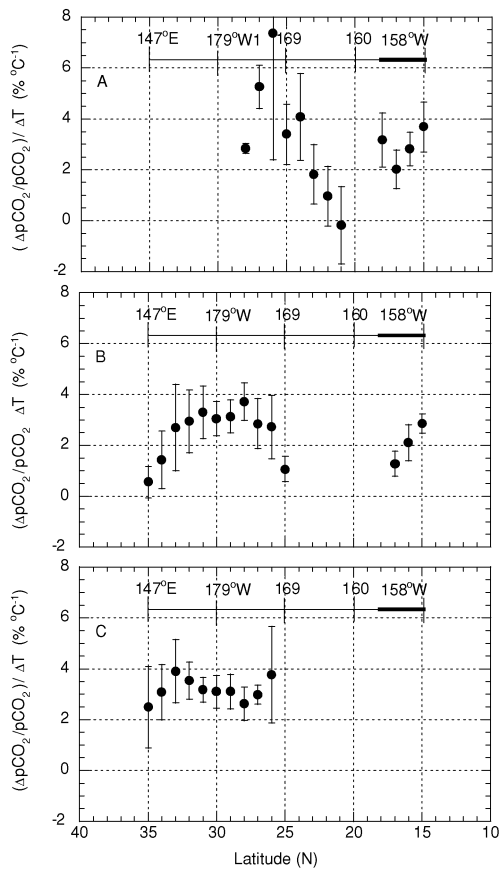


Fig. 9. Changes in  $p\text{CO}_2^w$  against a unit increase of the SST between Japan and the Hawaiian Islands calculated from data within  $4^\circ$  in longitude (Fig. 1). The top panel (A) shows the increase in  $p\text{CO}_2^w$  against a unit increase of the SST between July 1992 and December 2000–January 2001, the middle panel (B) that between July 1993 and December 2000–January 2001 and the bottom panel (C) that between July 1996 and December 2000–January 2001. In order to draw (A), (B) and (C), the long-term increase of  $p\text{CO}_2^w$  was assumed to be  $1.6 \mu\text{atm yr}^{-1}$  on the basis of observational data in the western North Pacific (Inoue et al., 1995; Nemoto, personal communication). The error bar represents the standard deviation of the average derived from the variability of  $p\text{CO}_2^w$  and the SST.

thermodynamic temperature effect ( $4.2\% \text{ } ^\circ\text{C}^{-1}$ ), especially in the Kuroshio Extension and on the leeward side of the Hawaiian Islands (Fig. 9). Besides a common pattern of spatial distribution sustained by large-scale, permanent processes (Poisson et al., 1993), a fairly large year-to-year difference in the apparent tem-

perature dependence of  $p\text{CO}_2^w$ , caused by the July data, occurred in the NPSG. Therefore, providing a  $p\text{CO}_2^w$ –SST relationship from data taken at the same time (month) in different years in order to estimate air–sea  $\text{CO}_2$  flux (Tans et al., 1990; Poisson et al., 1993; Inoue et al., 1995; Metzl et al., 1995; Takahashi et al., 2002) would yield an averaged (climatological)  $p\text{CO}_2^w$  at a given SST.

In the NPSG, from winter to summer, the  $\text{TCO}_2$  drawdown occurred due to biological activity (Winn et al., 1994, 1998; Ishii et al., 2001), leading to the lower temperature dependence of  $p\text{CO}_2^w$  than that of thermodynamic temperature effect. According to the climatological data in the summer season, the nitrate ( $\text{NO}_3^-$ ) in surface seawater was depleted (below the detection limit) south of  $35^\circ\text{N}$  ([http://www.nodc.noaa.gov/OC5/WOA98F/woaf\\_cd/search.html](http://www.nodc.noaa.gov/OC5/WOA98F/woaf_cd/search.html)). It has been reported that a significant fraction of the nitrogen required for photosynthesis in the NPSG is supplied via nitrogen fixation (Karl et al., 1997). This raised a question about the source of phosphorus necessary to support the observed biological nutrient export (Emerson et al., 2001). A relatively low  $p\text{CO}_2^w$  increase against the unit increase in the SST in the meandering Kuroshio Extension and leeward side of the Hawaiian Islands (Fig. 9) suggests that upwelling events associated with eddies (McGillicuddy et al., 1998) and/or the transport of dissolved nutrients from gyre edges to the interior (Williams and Follows, 1998) could be processes supporting biological activity in these areas. Within the Kuroshio Extension, cross-gyre mixing between the subpolar and subtropical waters occur (Joyce et al., 2001). This suggests that the latter process is at work. However, Ishii et al. (2001) reported that the role of the meridional component of the horizontal advection is insignificant in determining changes in  $\text{TCO}_2$  drawdown in the western North Pacific subtropical gyre.

Based on the assumptions of constant total alkalinity (Millero et al., 1998) and the climatological salinity field in July ([http://www.nodc.noaa.gov/OC5/data\\_woa.html](http://www.nodc.noaa.gov/OC5/data_woa.html)), the  $\text{TCO}_2$  drawdown was calculated using a thermodynamic model for the carbonate system in seawater (DOE, 1994). Data between January 2001 and July 1993 showed that the drawdown of the salinity-normalized  $\text{TCO}_2$  (at  $S = 35$ ) was within  $4\text{--}29 \mu\text{mol kg}^{-1}$  between  $15$  and  $35^\circ\text{N}$ . However, it varied widely depending on the combinations:  $-10$  to  $14 \mu\text{mol kg}^{-1}$  between  $15$  and  $28^\circ\text{N}$  for January 2001–July 1992 (a minus value indicates an increase of the normalized  $\text{TCO}_2$  corresponding to an extremely high

temperature dependence of the  $p\text{CO}_2^w$  at 26°N in the upper panel of Fig. 9) and 2–14  $\mu\text{mol kg}^{-1}$  between 25 and 35°N for January 2001–July 1996. The assumptions given above might significantly affect the results, but differences in TCO<sub>2</sub> drawdown among these three combinations were probably caused by the interannual variations in the carbonate system in the NPSG. The present results suggest that repeated measurements of the carbonate system in the wide area of the subtropics are necessary not only to interpolate/extrapolate  $p\text{CO}_2^w$  via the SST filed for the estimation of air–sea CO<sub>2</sub> flux but also to clarify the processes controlling the oceanic carbonate system.

#### 4. Summary

Over the period from December 1990 to January 2001, measurements of the partial pressure of carbon dioxide in surface seawater ( $p\text{CO}_2^w$ ) and overlying air ( $p\text{CO}_2^a$ ) have been made between Japan and the Hawaiian Islands, mainly in the North Pacific Subtropical Gyre (NPSG), in winter (four cruises) and summer (three cruises). In this work we examine spatial and temporal variations in the temperature dependence of  $p\text{CO}_2^w$  because factors controlling a  $p\text{CO}_2^w$  change could correlate with the SST either directly or indirectly (Lee et al., 1998).

In winter, south of the Kuroshio Extension,  $p\text{CO}_2^w$  correlated well with the SST, but the temperature dependence of  $p\text{CO}_2^w$  was significantly lower (1.4–2.4% °C<sup>-1</sup>) than that of the thermodynamic temperature effect. Around the Kuroshio Extension (33°N, 165°E – 35°N, 140°E),  $p\text{CO}_2^w$  did not correlate well with the SST ( $r < 0.2$ ), probably due to differences in the carbonate system between Kuroshio and Oyashio. In summer, the  $p\text{CO}_2^w$ –SST relationship differed significantly from that in winter. For example, in July 1993, northwest–east of the Hawaiian Islands (20°N, 155°W – 24°N, 162°W) and south of the Kuroshio Extension (28°N, 173°W – 33.5°N, 165°E), the temperature dependence of  $p\text{CO}_2^w$  was fairly large (>3.5% °C<sup>-1</sup>), which was attributable to the major role of

thermodynamics. However, in the former area,  $p\text{CO}_2^w$  was 39–48  $\mu\text{atm}$  lower than that of the latter over the range of SST between 25 and 27 °C. Around the Kuroshio Extension (33.5°N, 165°E – 35°N, 140°E), the apparent temperature dependence of  $p\text{CO}_2^w$  was small (<1% °C<sup>-1</sup>). In the remaining area (24°N, 162°W – 28°N, 173°W)  $p\text{CO}_2^w$  did not correlate with the SST ( $r < 0.1$ ), which was probably caused by the admixture of surface waters with different  $p\text{CO}_2^w$  values at the same SST mentioned above.

By compiling  $p\text{CO}_2^w$  data taken in July and September, we examined the  $p\text{CO}_2^w$ –SST relationship northwest (22–23.5°N, 158–168°W) and west (leeward side, 19–22°N, 158–168°W) of the Hawaiian Islands. West of the Hawaiian Islands, the  $p\text{CO}_2^w$ –SST relationship was affected by the leeward upwelling driven by the trade winds and island topography in summer.

The apparent temperature dependence of  $p\text{CO}_2^w$  between January and July suggests that, west of the Hawaiian Islands and in the Kuroshio Extension, a fairly large drawdown of the total dissolved inorganic carbon could occur, with a lesser one around 25–30°N and south of the Hawaiian Islands. The present results show a year-to-year variability of the seasonal  $p\text{CO}_2^w$ –SST relationship in the NPSG. Therefore, using the  $p\text{CO}_2^w$ –SST relationship obtained from data taken at the same time (month) in different years will simply provide an averaged (climatological) air–sea CO<sub>2</sub> flux at a given SST field. We need more investigations about factors controlling temporal and spatial variations in carbonate system in the subtropics.

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