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Variations and trends of CO<sub>2</sub> in the surface seawater in the Southern Ocean south of Australia  
between 1969 and 2002

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## ABSTRACT

Measurements of the partial pressure of CO<sub>2</sub> in surface seawater ( $p\text{CO}_2^{\text{sw}}$ ) were made in the Southern Ocean south of Australia during four cruises in January to February 1969, December 1983 to January 1984, December 1994 to January 1995, and January 2002. The spatial distribution of  $p\text{CO}_2^{\text{sw}}$  for the four cruises showed the same pattern north of the Subantarctic Front (SAF), while year-to-year changes were noted south of the SAF. We evaluated the long-term trend of the  $p\text{CO}_2^{\text{sw}}$  representative of the zone between oceanographic fronts by taking into account changes in the seasonal variation in  $p\text{CO}_2^{\text{sw}}$  and the long-term increase of the sea surface temperature (SST) of the Southern Hemisphere. The observed growth rate of  $p\text{CO}_2^{\text{sw}}$  was  $0.7\pm 0.1\mu\text{atm/yr}$  at its minimum, which was observed at the SST of 15°C north of the Subtropical Front (STF),  $1.0\pm 0.5\mu\text{atm/yr}$  in the Subantarctic Zone (SAZ) between STF and SAF,  $1.5\pm 0.4\mu\text{atm/yr}$  in the Polar Frontal Zone (PFZ) between SAF and the Polar Front (PF), and  $1.8\pm 0.2\mu\text{atm/yr}$  in the Polar Zone (PZ) between PF and 62°S, determined as the northern edge of the Seasonal Sea Ice Zone (SSIZ) on the basis of surface salinity and satellite images. These increases were caused by the uptake of anthropogenic CO<sub>2</sub> as well as variations in the thermodynamic temperature effect, ocean transport, and biological activity. In the SSIZ between 62 and 66.5°S, we could not clearly evaluate the long-term trend of  $p\text{CO}_2^{\text{sw}}$  due to the remarkable CO<sub>2</sub> drawdown by the biological activity in January 2002. The relatively low growth rates of  $p\text{CO}_2^{\text{sw}}$  close to the STF and in the SAZ are probably associated with the formation

of Subtropical Mode Water and Subantarctic Mode Water in their respective zones. Between the north of the STF and PZ, the growth rate of total dissolved inorganic carbon (DIC) was calculated to be about 0.5-0.8  $\mu\text{mol/kg/yr}$  via the buffer factor.

## 1. Introduction

The ocean plays an important role in determining the atmospheric CO<sub>2</sub> level, which has been currently increasing due to human activities (IPCC, 2001). Because of the large surface area and regional wind velocity, the Southern Ocean is considered to be an area showing a large CO<sub>2</sub> flux between the sea and the air (Sabine and Key, 1998). Furthermore, water formed in the Southern Ocean ventilates the intermediate and abyssal depths of much of the world's oceans (Rintoul and Bullister, 1999).

On the basis of measurements of the difference in the partial pressure (fugacity) of CO<sub>2</sub> between the sea and the overlying air ( $\Delta p\text{CO}_2$ ), CO<sub>2</sub> uptakes in the Southern Ocean south of 50°S were estimated to be in the range of 0.2 to 0.6Gt-C/yr (Tans et al., 1990; Takahashi et al., 1997; 1999), while atmospheric inverse models, which use spatial distributions of atmospheric CO<sub>2</sub> for inferring surface CO<sub>2</sub> fluxes, gave lower atmospheric CO<sub>2</sub> uptakes of about 0.1Gt-C/yr (Rayner et al., 1999). Takahashi et al. (2002) reported that the uptake of the Southern Ocean (south of 50°S) is larger than 20% of the total, although it occupies about 10% of the global ocean. However, most  $\Delta p\text{CO}_2$  measurements are made only in the Austral summer (see, for example, Metzl et al., 1999), which is insufficient to elucidate the annual CO<sub>2</sub> uptake in the Southern Ocean. A lower value of oceanic uptake close to that of the atmospheric inversion model and ocean inversion model (Gloor et al., 2003) has been estimated by adding the observed  $\Delta p\text{CO}_2$  data in the Austral winter (Metzl, after

Fig. 1 of Roy et al., 2003). This does not reconcile the numerical model result of a small Southern Hemisphere CO<sub>2</sub> uptake with the observations because numerical model studies that examined the distributions of CO<sub>2</sub> sources and sinks have large uncertainties in estimating the regional CO<sub>2</sub> sources and sinks (Sabine and Key, 1998). As was pointed out by Roy et al. (2003), at present, potential errors in these estimates have not been quantified enough to claim consistency among various recent results.

By taking into account the annual cycle of the fugacity of CO<sub>2</sub> in surface seawater, Metzler et al. (1999) suggested a CO<sub>2</sub> uptake of about 1Gt-C/yr in the circumpolar Subantarctic Zone (SAZ), which lies between the Subtropical Front (STF) and the Subantarctic Front (SAF). Takahashi et al. (2002) estimated a CO<sub>2</sub> uptake of 1.51Gt-C/yr between 14°S and 50°S, which was concentrated in the transition zone between the subtropical gyre and subpolar waters. Most atmospheric models gave a strong sink for atmospheric CO<sub>2</sub> at latitudes ~30-50°S (Ciais et al., 1995; Enting et al., 1995; Rayner et al., 1999; Roy et al., 2003). On the basis of total dissolved inorganic carbon (DIC) data below 200m measured in 1968 and 1996, McNeil et al. (2001) estimated an anthropogenic CO<sub>2</sub> uptake of 0.07-0.08Gt-C/yr in the circumpolar SAZ, which is the area where deep penetration of anthropogenic CO<sub>2</sub> occurs (<1900m). This corresponded to about 10% of the total annual CO<sub>2</sub> uptake in the circumpolar SAZ. They also reported that the anthropogenic CO<sub>2</sub> accumulated less across the Polar Frontal Zone (PFZ) toward the south and remained relatively constant from 53 to

58°S in the upper water column because of strong density gradients; furthermore, it accumulated significantly in the Antarctic Bottom Water, a dense water mass that sinks to abyssal depths along the Antarctic continental slope.

It is important to clarify the long-term trend of the carbonate system in surface seawater of the Southern Ocean, which has been thought to exhibit larger uptake rates, in order to understand the role in the global carbon budget. This will provide a constraint for the simulation of global carbon cycle models.

The thermodynamic effect, ocean transport (lateral flow, vertical mixing, and upwelling of water), biological activity, and CO<sub>2</sub> exchange between the sea and the overlying air are the processes (Poisson et al., 1993; Lee et al., 1998) affecting pCO<sub>2</sub><sup>sw</sup> via changes in the total dissolved inorganic carbon, total alkalinity, pH, temperature, and salinity. One approach for evaluating the long-term trend due to the uptake of anthropogenic CO<sub>2</sub> is to compare the pCO<sub>2</sub><sup>sw</sup> data taken at the same condition of the thermodynamics, ocean transport, and biological activity. In order to attain these conditions, Feely et al. (1999) examined the long-term trend of pCO<sub>2</sub><sup>sw</sup> for the core of upwelled water in the region of the temperature minimum near the equator, between 140 and 160°W, by using the pCO<sub>2</sub><sup>sw</sup>-SST relationship.

The IPCC (2001) reported an increase of global SST in the Northern Hemisphere of 0.18°C per decade and Southern Hemisphere of 0.10°C per decade from 1976 to 2000. The rate of

change in the observed  $p\text{CO}_2^{\text{sw}}$  over a few decades, therefore, can be caused by variations in all four processes mentioned above.

After correcting for SST changes and the annual uptake of atmospheric  $\text{CO}_2$ , Takahashi et al. (2003) reported the rates of change in  $p\text{CO}_2^{\text{sw}}$  in the central and western equatorial Pacific between the 1980s and 1990s. They determined that there were decreases in  $p\text{CO}_2^{\text{sw}}$  at a mean rate of  $-20\mu\text{atm}$  per decade before the phase shift of the Pacific Decadal Oscillation (PDO) and increases at about  $15\mu\text{atm}$  per decade after that, which can be caused by variations in ocean transport and biological activity.

In this paper, the distributions and variations in the partial pressure of  $\text{CO}_2$  of surface seawater ( $p\text{CO}_2^{\text{sw}}$ ) in the Southern Ocean will be reported by using Austral summer (December-February) data measured in 1968/69, 1983/84, 1994/95, and 2002; moreover, the long-term trend of  $p\text{CO}_2^{\text{sw}}$  and the uptake of anthropogenic  $\text{CO}_2$  in the mixed layer will be discussed.

## 2. Experiment

As shown in Fig. 1, this study covered the region extending from  $33^\circ\text{S}$  to  $66^\circ\text{S}$  south of Australia. Data of  $p\text{CO}_2^{\text{sw}}$  and those of overlying air ( $p\text{CO}_2^{\text{air}}$ ) were collected over the period from January to February 1969, December 1983 to January 1984, December 1994 to January 1995, and



January 2002 along with auxiliary hydrographic data (Oceanographic Data of KH68-4, 1970; Nakai et al., 1986; Kawaguchi, 1996; Terazaki et al., 2003). Analysis of DIC was made coulometrically using an automated CO<sub>2</sub> extraction unit and a coulometer for the cruises from December 1994 to January 1995 and January 2002 (Ishii et al., 1998; 2002). The ship used was the R/V Hakuho-maru, which belongs to the Ocean Research Institute, University of Tokyo.

Underway measurements of pCO<sub>2</sub><sup>sw</sup> and pCO<sub>2</sub><sup>air</sup> for these cruises were carried out with systems reported earlier (Miyake et al., 1974; Inoue and Sugimura, 1988; Inoue, 2000; Körtzinger et al., 2000). For the four cruises, the heart of the underway measurements of pCO<sub>2</sub><sup>sw</sup> and pCO<sub>2</sub><sup>air</sup> was the same. They consisted of a non-dispersive infra-red gas analyzer, a shower-head-type equilibrator, diaphragm pumps, and a unit for the removal of water vapor in sample air. Uncontaminated water from the inlet of sample seawater about 5m below the surface was introduced into the equilibrator at approximately 10L/min. CO<sub>2</sub> in the water is equilibrated with re-circulated air in a shower-head-type equilibrator. Taking factors affecting pCO<sub>2</sub><sup>sw</sup> measurements into account, we retrieved pCO<sub>2</sub><sup>sw</sup> data measured in 1968/69 and 1983/84 to compare the results with those obtained most recently (Inoue et al., 1999). Four standard gases (typically 290, 340, 370, 420 ppm CO<sub>2</sub> in natural air, Nippon Sanso Co. Ltd.) traceable to the WMO mole fraction scale were used aboard the ship (Inoue et al., 1995, 1999) during cruises in 1994/95 and 2002. The partial pressure of CO<sub>2</sub> in the equilibrator (pCO<sub>2</sub><sup>eq</sup>) was calculated from the CO<sub>2</sub> mole fraction in dry air equilibrated with seawater in the equilibrator

( $xCO_2^{eq}$ ),

$$pCO_2^{eq} = xCO_2^{eq} \times (P_{bar} - W), \quad (1)$$

where  $P_{bar}$  is the barometric pressure at the air-sea boundary and  $W$  is the water vapor pressure equilibrated with seawater. In order to calculate  $pCO_2^{sw}$  from  $pCO_2^{eq}$ , we used the equation given by Gordon and Jones (1973) for the three cruises in 1968/69, 1983/84, and 1994/95 and by Copin-Montégut (1988; 1989) for the cruise in 2002. The increase in temperature from the sea surface to the equilibrator was typically 0.7°C in 1968/69, 0.3°C in 1983/84, 0.5°C in 1994/95, and 0.4°C in 2002. The two equations expressing the temperature dependence of  $pCO_2^{sw}$  might lead to a difference of 1 $\mu$ atm, but this was within the estimated precision of measurements (better than 3.6 $\mu$ atm, Inoue et al., 1999). Our results and discussion remain unchanged because they do not depend critically on the two different equations.

The barometric pressure varied spatially and temporally. For example, in the SAZ, the  $P_{bar}$  ranged from 1007.1 to 1022.3 hPa with a median value of 1016.6 hPa in January 1969, 996.7 to 1026.3 hPa with 1000.1 hPa in December 1983/January 1984, 996.2 to 1029.2 hPa with 1017.3 hPa in December 1994/January 1995, and 1005.6 to 1011.5 hPa with 1009.2 hPa in January 2002. The observed barometric pressure is simply related to weather systems. In this work, we focused on variations in the carbonate system in the surface mixed layer. In order to avoid any effects of the weather system on the long-term variations in  $pCO_2^{air}$  and  $pCO_2^{sw}$ , we used an average  $P_{bar}$  in each

zone for four cruises (Sections 4.2 and 4.3).

The  $\text{pCO}_2^{\text{sw}}$  data in 1968/69, 1983/84, and 1994/95 were sent to the WMO WDCGG (Tokyo, Japan), and those in 2002 will be sent in the near future.

### 3. Oceanographic Setting

Three major fronts were observed south of 40°S (Rintoul et al., 1997; Rintoul and Bullister, 1999; Yaremchuk et al., 2001). The STF, marked as the boundary between warm, salty subtropical water and cool, fresh Subantarctic water, was located in the range of 44.5-46.5°S. The SAF, characterized by a steep horizontal temperature gradient, was found in the range of 49-51.5°S. This SAF marks the northern edge of the eastward flowing Antarctic Circumpolar Current. The Polar front (PF), which marks the steep temperature gradient of the surface seawater and the northern limit of minimum-temperature water with temperatures of less than 2°C near 200m depth, was found in 53-56.5°S. South of Australia, Rintoul and Bullister (1999) described two distinct deep-reaching fronts, one at 53°S and one between 57 and 59°S on the SR3 section of the World Ocean Circulation Experiment (WOCE). However, the southern branch was less clearly defined than the northern one. The PF used in this work corresponds to the northern branch of the PF.

Chaigneau and Morrow (2002) reported that the STF, SAF, and PF determined by continuous measurements of SST and sea surface salinity (SSS) between Tasmania and Antarctica

were located further north than their subsurface counterparts. In this work, we will use the criteria given by Chaigneau and Morrow (2002) as far as SST and SSS data were available, because we discuss the long-term trend of the carbonate system in surface seawater. Three major fronts observed for the four cruises are summarized in Table 1.

The zones between the fronts are commonly referred to as the SAZ between the STF and the SAF and the PFZ between the SAF and the PF. The Polar Zone (PZ) extends southward from the PF to the Antarctic Divergence, which may be called the Permanently Open Ocean Zone (POOZ, Tréguer and Jacques, 1992). The Antarctic Divergence marks the transition from prevailing westerlies to coastal Antarctic easterlies as well as the location of upwelling of circumpolar deep water (Popp et al., 1999). However, the colder, less saline surface water close to the ice edge often overwhelmed the Antarctic Divergence (Ishii et al., 2002). The Seasonal Sea-Ice Zone (SSIZ) is the zone affected by the ice-melt from receding sea ice (Popp et al., 1999). In this work, the northern boundary of SSIZ was assumed to be 62°S on the basis of the distribution of surface salinity and satellite images (Enomoto and Ohmura, 1990).

## 4. Results and Discussion

### 4.1. Distribution and seasonal variation in $p\text{CO}_2^{\text{sw}}$

Figure 2 illustrates the latitudinal distribution of  $p\text{CO}_2^{\text{sw}}$  in January/February 1969, January 1984, January 1995, and January 2002. North of the SAF,  $p\text{CO}_2^{\text{sw}}$  showed a coherent meridional pattern in the Austral summer. In the subtropics north of the STF,  $p\text{CO}_2^{\text{sw}}$  decreased toward the south as the sea surface temperature (SST) decreased. The minimum  $p\text{CO}_2^{\text{sw}}$  occurred at 44.5°S in 1969 and 1984, 45°S in 1995, and 45.5°S in 2002. These were latitudes at the SST of ~15°C (Fig. 3), which was equal to the lower limit of temperature of the Subtropical Mode Waters (15-19°C) in the southwestern Pacific Ocean (Roemmich and Cornuelle, 1992). Our results show that the minimum  $p\text{CO}_2^{\text{sw}}$  occurred slightly north of the STF or at the STF (Table 1). In this area,  $p\text{CO}_2^{\text{sw}}$  decreased due to the cooling of warm subtropical water and biological drawdown of  $\text{CO}_2$  in the nutrient-rich subpolar waters (Takahashi et al., 2002).

In the area of the SAZ,  $p\text{CO}_2^{\text{sw}}$  increased toward the south as the SST decreased (Fig. 4). The  $p\text{CO}_2^{\text{sw}}$  data measured during repeated occasions in Austral summer show that both temporal and spatial variations can be approximated well by a single  $p\text{CO}_2^{\text{sw}}$ -SST relationship for each cruise (Table 2). We will use the  $p\text{CO}_2^{\text{sw}}$ -SST relationship to elucidate the long-term increase of  $p\text{CO}_2^{\text{sw}}$  due to uptake of anthropogenic  $\text{CO}_2$  (Section 4.2).

The maximum  $p\text{CO}_2^{\text{sw}}$ , which was higher than  $p\text{CO}_2^{\text{air}}$ , occurred close to the SAF (Fig. 2), while Sabine and Key (1998) reported that the SAF was associated with a local minimum in  $f\text{CO}_2^{\text{sw}}$  along 126 and 88°W in December 1992 and January 1993. South of the maximum in  $p\text{CO}_2^{\text{sw}}$ ,

$p\text{CO}_2^{\text{sw}}$  showed a distribution that differed from year to year (Fig. 2). In the PFZ, for example, the  $p\text{CO}_2^{\text{sw}}$  in January 1984 tended to increase toward the south, and, in January 2002, it decreased. In the PZ, the  $p\text{CO}_2^{\text{sw}}$  in January 1969 generally decreased to a lower level with large variability on small spatial scales. A local maximum of SSS occurred at  $56^\circ\text{S}$ , where corresponded to the sub-surface PF (Chaigneau and Morrow, 2002). In this area the SSS increased along with the SST. Warm water with high SSS and different carbonate system was probably transported southward due to an eddy. Around the minimum SSS at  $59^\circ\text{S}$  the SST remained constant, and the  $p\text{CO}_2^{\text{sw}}$  decreased with the decrease in SSS. In January 2002, the  $p\text{CO}_2^{\text{sw}}$  in the PZ was remarkably constant and equal to  $p\text{CO}_2^{\text{air}}$ . In the SSIZ, the  $p\text{CO}_2^{\text{sw}}$  in January 2002 decreased significantly toward the south from 360 to  $150\mu\text{atm}$  along with decreases in macro-nutrients (Terazaki et al., 2003); this was associated with the  $\text{CO}_2$  uptake by the biological activity in summer (Poisson et al., 1994). Metzl et al. (1999) showed a pattern similar to that of January 2002, i.e., changes from 370 to  $230\mu\text{atm}$  along  $30^\circ\text{E}$  and from 370 to  $270\mu\text{atm}$  along  $145^\circ\text{E}$  in February-March 1993 (the  $f\text{CO}_2^{\text{sw}}$  values were taken from Fig. 2 of Metzl et al. (1999)). In January 2002, temperature and salinity data indicated that waters showing steep changes in  $p\text{CO}_2^{\text{sw}}$  and macro-nutrients were associated with an eddy and had been transported from an area close to Antarctica (Aoki, personal communication).

Inoue and Sugimura (1988) reported that the  $p\text{CO}_2^{\text{sw}}$  in the PFZ, PZ, and SSIZ remained almost constant for about one month, starting from the middle of December 1983. In these zones,

$p\text{CO}_2^{\text{sw}}$  also remained fairly constant from December 1994 to January 1995 and in January 2002.

The  $p\text{CO}_2^{\text{sw}}$  in the Austral summer varied independently from changes in the SST both spatially and temporally (Fig. 4), which was mainly caused by variations in the SST rise and carbon uptake by the biological activity (Ishii et al., 1998; 2002).

#### 4.2. Long-term trend of the $p\text{CO}_2^{\text{sw}}$ in the Southern Ocean

In the Southern Ocean, major fronts shifted interannually and longitudinally (Table 1). This would lead to a large error if we tried to evaluate the long-term trend of  $p\text{CO}_2^{\text{sw}}$  at the given geographical position close to the major front. If the same water mass remained at that location for a few decades, we could calculate the long-term trend of  $p\text{CO}_2^{\text{sw}}$  at fixed latitudes. However, selecting the latitude covered with the same water mass considerably decreases the amount of available data. For example, in the SAZ, only a small amount of data (around 48°S) was available in January 1969 and January 1984. Therefore, we determined the representative  $p\text{CO}_2^{\text{sw}}$  value in the water mass with uniform properties in each zone by using  $p\text{CO}_2^{\text{sw}}$  data as much as possible and evaluating the long-term trend in the Southern Ocean.

We summarize  $p\text{CO}_2^{\text{air}}$ ,  $p\text{CO}_2^{\text{sw}}$ , and thermodynamically temperature-normalized  $p\text{CO}_2^{\text{sw}}$  ( $N\text{-}p\text{CO}_2^{\text{sw}}$ ) in each zone measured in January (Table 3). The increases of the  $p\text{CO}_2^{\text{sw}}$  minimum at the SST of 15°C north of the STF were always smaller than those of  $p\text{CO}_2^{\text{air}}$ . South of SAZ, the

variations in  $p\text{CO}_2^{\text{sw}}$  differ largely from not only those of  $p\text{CO}_2^{\text{air}}$  but also those of adjacent zones (Table 3). The  $N\text{-}p\text{CO}_2^{\text{sw}}$  at an average SST for each zone tended to vary more than  $p\text{CO}_2^{\text{sw}}$ . The larger variability of the  $N\text{-}p\text{CO}_2^{\text{sw}}$  was due to the removal of the thermodynamic temperature effect, which compensates for the effect of the ocean transport and biological activity on  $p\text{CO}_2^{\text{sw}}$ . The  $p\text{CO}_2^{\text{sw}}$  and  $N\text{-}p\text{CO}_2^{\text{sw}}$  data show large interannual/decadal variations superimposed on the long-term increase. However, the present data were not enough to examine interannual/decadal variations in the carbonate system in the surface mixed layer of the Southern Ocean. In this work, therefore, we decided to figure out the average feature of the long-term  $p\text{CO}_2^{\text{sw}}$  increase. By assuming the linear long-term trend of  $p\text{CO}_2^{\text{sw}}$ , we calculated the growth rate of  $p\text{CO}_2^{\text{sw}}$  in each zone (Table 4).

Here, we adiabatically divide the variations in  $p\text{CO}_2^{\text{sw}}$  into those of the processes affecting  $p\text{CO}_2^{\text{sw}}$ : the uptake of anthropogenic  $\text{CO}_2$ , variations in thermodynamics, ocean transport, and biological activity. In Table 4, we list the rate of change in  $p\text{CO}_2^{\text{sw}}$  due to the long-term increase of SST ( $0.10^\circ\text{C}$  per decade, IPCC, 2001) on the basis of the thermodynamic temperature effect ( $4.23\% \text{ } ^\circ\text{C}^{-1}$ , Takahashi et al., 2003).

The growth rate of the observed  $p\text{CO}_2^{\text{sw}}$  tended to increase toward the south from the north of the STF, where the  $p\text{CO}_2^{\text{sw}}$  minimum occurs, to the PZ (Fig. 5). The  $p\text{CO}_2^{\text{sw}}$  minimum increased at a rate of  $0.7\mu\text{atm/yr}$ , which was a half of the  $p\text{CO}_2^{\text{air}}$  ( $1.4\mu\text{atm/yr}$ ) over the same period. In the SAZ, the growth rate of the observed  $p\text{CO}_2^{\text{sw}}$  was  $1.0\mu\text{atm/yr}$ , which could be affected by the annual



uptake of anthropogenic CO<sub>2</sub> as well as by the thermodynamics, ocean transport, and biological activity. We calculated the pCO<sub>2</sub><sup>sw</sup> value at the same SST on the basis of the pCO<sub>2</sub><sup>sw</sup>-SST relationship for each cruise (Table 2). Because, either directly or indirectly, the thermodynamics, ocean transport, and biological activity are correlated with the SST (Lee et al., 1998), the pCO<sub>2</sub><sup>sw</sup> at the same SST might allow us to evaluate the pCO<sub>2</sub><sup>sw</sup> increase at the same conditions of them: the pCO<sub>2</sub><sup>sw</sup> increase can be caused by the annual uptake of anthropogenic CO<sub>2</sub>. If pCO<sub>2</sub><sup>sw</sup> were calculated at exactly the same conditions, the growth rate of pCO<sub>2</sub><sup>sw</sup> due to the annual uptake of anthropogenic CO<sub>2</sub> should remain constant against a given SST. Within a standard deviation ( $\pm 1.0^{\circ}\text{C}$ ) of the mean SST for four cruises (11.4°C), the growth rate of pCO<sub>2</sub><sup>sw</sup> remained constant (1.2 $\mu\text{atm}/\text{yr}$ ). The growth rate of pCO<sub>2</sub><sup>sw</sup> due to the thermodynamic temperature effect is calculated to be 0.1 $\mu\text{atm}/\text{yr}$ . Therefore, the effect of the ocean transport and biological activity due to the SST increase is estimated to be  $-0.3 \pm 0.5 \mu\text{atm}/\text{yr}$ . The rate of change in N-pCO<sub>2</sub><sup>sw</sup> (0.9 $\mu\text{atm}/\text{yr}$ ) could be caused by the annual uptake of anthropogenic CO<sub>2</sub>, ocean transport, and biological activity, as mentioned by Takahashi et al. (2003). In the SAZ, the growth rate of pCO<sub>2</sub><sup>sw</sup> at the same SST was slightly lower than that of pCO<sub>2</sub><sup>air</sup>. The relatively lower value of the long-term trend is probably caused by the formation of Subantarctic Mode Water in this zone (McNeil et al., 2001). Because of increases in  $\Delta\text{pCO}_2$ , the area at SST of  $\sim 15^{\circ}\text{C}$  north of the STF and SAZ can be oceanic sinks for atmospheric CO<sub>2</sub>, where the uptake of anthropogenic CO<sub>2</sub> has been increasing (Le Quéré et al.,

2003).

In the PFZ, the growth rate of  $p\text{CO}_2^{\text{sw}}$  was nearly equal to that of  $p\text{CO}_2^{\text{air}}$ , and, in the PZ, the rate was slightly larger than that of  $p\text{CO}_2^{\text{air}}$  and reached the same level as that of the  $p\text{CO}_2^{\text{air}}$  in January 2002. In the SSIZ, the distribution of the  $p\text{CO}_2^{\text{sw}}$  in January 2002 differed remarkably from those obtained on the other three cruises due to the  $\text{CO}_2$  uptake by biological activity, which was supported by the steep changes in macro-nutrients. For example, the concentration of nitrate in surface seawater decreased from 25  $\mu\text{mol/kg}$  at 62°S to 14 $\mu\text{mol/kg}$  at 65°S. The limited data and distribution did not allow us to evaluate the long-term trend clearly. If we selected the  $p\text{CO}_2^{\text{sw}}$  data between 62 and 63.5°S, where the macro-nutrients in surface seawater were comparable (23 $\mu\text{mol/kg}$  at 63.5°S) to those of the three cruises in the SSIZ, we would obtain a growth rate of  $0.8\pm 0.8\mu\text{atm/yr}$ .

#### 4.3. Annual uptake of anthropogenic $\text{CO}_2$

Takahashi et al. (2003) implicitly assumed the increase of  $p\text{CO}_2^{\text{sw}}$  caused by the uptake of anthropogenic  $\text{CO}_2$  (1.5 $\mu\text{atm/yr}$ ) in the central and western equatorial Pacific and determined the  $p\text{CO}_2^{\text{sw}}$  variations before and after the PDO shift. Our objective in this work is to elucidate the increase of  $p\text{CO}_2^{\text{sw}}$  caused by the uptake of anthropogenic  $\text{CO}_2$ . In the Southern Hemisphere, the absolute value of the variation in SST is smaller than those of the central and western equatorial

Pacific, reported to be in the range between  $-0.03$  and  $0.1^{\circ}\text{C}/\text{yr}$  (Takahashi et al., 2003). After 1991, a slower rate of SST increase was reported in the area where this study was conducted (IPCC, 2001). This suggests relatively small long-term variations in  $\text{pCO}_2^{\text{sw}}$  due to variations in ocean transport and biological activity. Hereafter, we assume that the effect of ocean transport and biological activity on the long-term increase in  $\text{pCO}_2^{\text{sw}}$  offsets that of thermodynamics.

On the basis of DIC,  $\text{pCO}_2^{\text{sw}}$ , SST, and SSS data measured in January 2002, we evaluated the rate of the DIC increase (Table 5) via the buffer factor (DOE, 1994). The buffer factor in this work was calculated to be in the range from 9.9 close to the STF and 14.4 in the SSIZ. The growth rate of the DIC was  $0.5\text{-}0.8\mu\text{mol}/\text{kg}/\text{yr}$  between the area close to the STF and PZ. If we assume that the growth rate of DIC in surface seawater is equal to that of the mixed layer, we can evaluate the annual uptake of anthropogenic  $\text{CO}_2$  in the mixed layer. In this work, the mixed layer depth (MLD) was taken from McNeil et al. (2001). Extrapolating our estimate of the DIC increase to the circumpolar zones, the annual uptake of anthropogenic  $\text{CO}_2$  in the mixed layer can be estimated to be  $0.17\text{Gt-C}/\text{yr}$  in the SAZ and  $0.03\text{Gt-C}/\text{yr}$  in the PFZ and PZ (Table 6). McNeil et al. (2001) estimated that the circumpolar anthropogenic  $\text{CO}_2$  uptake for the area between  $45$  and  $50^{\circ}\text{S}$  (SAZ) is  $0.07\text{-}0.08\text{Gt-C}/\text{yr}$ . Because of the vertical transport of  $\text{CO}_2$  to the middle/deep water, our estimate is the lower limit of the  $\text{CO}_2$  uptake in the Southern Ocean south of the STF. The estimation given in this work is the first step toward the precise estimation of the anthropogenic  $\text{CO}_2$  uptake in the

mixed layer of the Southern Ocean. It is necessary to observe the carbonate system in the wide area of the Southern Ocean systematically and repeatedly in order to better understand the oceanic uptake of anthropogenic CO<sub>2</sub> as well as the natural variability of the carbon cycle on a time scale of months to a few decades.

## 5. Summary

On the basis of Austral summer data of pCO<sub>2</sub><sup>air</sup> and pCO<sub>2</sub><sup>sw</sup> measured in 1968/69, 1983/84, 1994/95, and 2002, we have reported the distributions and long-term variations in the pCO<sub>2</sub><sup>sw</sup> in the Southern Ocean by dividing it into five zones between major fronts. Prior to this work, Inoue and Sugimura (1988) reported that the pCO<sub>2</sub><sup>sw</sup> in high latitudes increased much more than in lower latitudes by comparing pCO<sub>2</sub><sup>sw</sup> data between 1968/69 and 1983/84, and Inoue et al. (1999) suggested large interannual/decadal variations in the pCO<sub>2</sub><sup>sw</sup> south of the STF.

By adding the pCO<sub>2</sub><sup>air</sup> and pCO<sub>2</sub><sup>sw</sup> data in January 2002 to these three data sets, we could discuss the spatial distribution of the long-term trend of pCO<sub>2</sub><sup>sw</sup>. The growth rate of the pCO<sub>2</sub><sup>sw</sup> minimum at the SST of 15 °C north of the STF was calculated to be a half (0.7±0.1 μatm/yr) of that of pCO<sub>2</sub><sup>air</sup> (1.4±0.1 μatm/yr). The observed growth rate of pCO<sub>2</sub><sup>sw</sup> tended to increase from the SAZ (1.0±0.5 μatm/yr) to the PZ (1.8±0.2 μatm/yr). From 1976 to 2000, which was nearly equal to the

period of our work, the SST in the Southern Hemisphere increased at a rate of 0.10°C per decade, though that in high latitudes could be low (IPCC, 2001). This suggests that the rate of  $p\text{CO}_2^{\text{sw}}$  increase is caused by the uptake of anthropogenic  $\text{CO}_2$  as well as variations in the thermodynamics, ocean transport, and biological activity.

The relatively low growth rates of the  $p\text{CO}_2^{\text{sw}}$  minimum north of the STF and that in the SAZ are probably associated with the formation of Subtropical Mode Water and Subantarctic Mode Water in their respective zones. The effect of the increasing atmospheric  $\text{CO}_2$  on the  $p\text{CO}_2^{\text{sw}}$  is relatively low due to waters with a deep mixed layer as compared with those of subtropics, where the  $p\text{CO}_2^{\text{sw}}$  has been increasing at a rate parallel with or larger than that of the  $p\text{CO}_2^{\text{air}}$  (Inoue et al., 1995; 1999; Bates, 2001; Dore et al., 2003). In the SSIZ, because of the large effect of biological activity in January 2002, we could not detect the long-term trend of  $p\text{CO}_2^{\text{sw}}$ . In high latitudes, continuous measurements of the concentrations of macro-nutrients, as well as of  $p\text{CO}_2^{\text{sw}}$ , must be conducted. Such measurements will allow us to estimate the contribution of biological activity on the carbonate system.

In the Southern Ocean, the long-term variations in  $p\text{CO}_2^{\text{sw}}$  are considered to be mostly caused by the uptake of anthropogenic  $\text{CO}_2$ . By using the buffer factor, we could estimate the growth rate of surface DIC in the range of 0.5-0.8  $\mu\text{mol}/\text{kg}/\text{yr}$  between the area close to the STF and PZ (Table 5). On the basis of the growth rate of the DIC, the annual uptake of anthropogenic  $\text{CO}_2$  in the

mixed layer, estimated as a first step, is 0.17Gt-C/yr in the SAZ and 0.03Gt-C/yr in the PFZ and PZ.

This leads to the lower limit of the annual uptake of anthropogenic CO<sub>2</sub> in the Southern Ocean because CO<sub>2</sub> transferred from the surface mixed layer to the deeper layer was not taken into account.

In order to evaluate the total annual uptake of CO<sub>2</sub> in the Southern Ocean more precisely, it is necessary to examine the temporal and spatial (vertical) distribution of the carbonate system in the wide area of the Southern Ocean repeatedly and systematically at least over a few decades.

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Table 1. Location of three major fronts south of Australia determined on the basis of hydrographic data (Oceanographic Data of KH68-4, 1970; Nakai et al., 1986; Kawaguchi, 1996; Terazaki et al., 2003).

Year	Observation period	STF	SAF	PF	SSIZ**
1969	Jan. 23-Feb. 4	44.5°S, 155°E	51.5°S, 155°E	54°S, 155°E	62°S, 155°E
1983/84	Dec. 11-Jan. 15	45.5°S, 150°E	49°S, 150°E	54.5°S, 150°E*	62°S, 150°E
1994/95	Dec. 15-Jan. 27	45.5°S, 147°E	50°S, 142°E	51°S, 140°E	62°S, 140°E
2002	Jan. 4-Jan. 20	46.5°S, 141°E	49.5°S, 140°E	52.5°S, 140°E	62°S, 140°E

\* In the PZ, the  $p\text{CO}_2^{\text{sw}}$  data with SSS higher than 34 should be removed.

\*\* Northern latitude of the SSIZ

Table 2. The  $p\text{CO}_2^{\text{sw}}$  -SST relationships in the SAZ.

Period	$p\text{CO}_2^{\text{sw}}$ *-SST relationship	$1\sigma/\mu\text{atm}$	$r$
January 1969	$p\text{CO}_2^{\text{sw}}=407.6-9.90x\text{SST}$ , $n=43$ , $p<0.001$	4.3	0.912
December 1983-January 1984	$p\text{CO}_2^{\text{sw}}=404.7-8.30x\text{SST}$ , $n=70$ , $p<0.001$	6.1	0.858
December 1994-January 1995	$p\text{CO}_2^{\text{sw}}=444.4-10.1x\text{SST}$ , $n=121$ , $p<0.001$	8.8	0.780
January 2002	$p\text{CO}_2^{\text{sw}}=456.5-10.9x\text{SST}$ , $n=82$ , $p<0.001$	5.3	0.895

\* In the SAZ, the average  $P_{\text{bar}}$  was 1012.5 hPa.

Table 3. The  $p\text{CO}_2^{\text{air}}$ ,  $p\text{CO}_2^{\text{sw}}$ ,  $\text{N-pCO}_2^{\text{sw}}$ , and SST in the area of the  $p\text{CO}_2^{\text{sw}}$  minimum north of the STF, SAZ, PFZ, PZ, and SSIZ in January observed for the period from 1969 to 2002. Differences in  $p\text{CO}_2^{\text{air}}$ ,  $p\text{CO}_2^{\text{sw}}$ , and  $\text{N-pCO}_2^{\text{sw}}$  between two cruises are given by  $\Delta^{\text{air}}$ ,  $\Delta^{\text{sw}}$ , and  $\text{N-}\Delta^{\text{sw}}$ , respectively. The  $\text{N-pCO}_2^{\text{sw}}$  was calculated at the average SST of 11.4°C for four cruises in the SAZ, the average SST of 8.7°C in the PFZ, the average SST of 3.8°C in the PZ, and the average SST of 0.9°C in the SSIZ.

$p\text{CO}_2^{\text{sw}}$ minimum at 15°C north of the STF <sup>1)</sup>							
Period	$p\text{CO}_2^{\text{air}}/\mu\text{atm}^{2)}$	$\Delta^{\text{air}}/\mu\text{atm}$	$p\text{CO}_2^{\text{sw}}/\mu\text{atm}^{2)}$	$\Delta^{\text{sw}}/\mu\text{atm}$	$\text{N-pCO}_2^{\text{sw}}/\mu\text{atm}$	$\text{N-}\Delta^{\text{sw}}/\mu\text{atm}$	SST/°C
1969 <sup>3)</sup>	317.2±0.1, n=10		280.4±2.7, n=10				14.5-15.5
1984	336.9±0.7, n=15	19.7±0.7	287.2±5.7, n=16	6.8±6.3			14.5-15.5
1995	351.9±0.3, n=11	15.0±0.8	295.8±3.3, n=10	8.6±6.6			14.5-15.5
2002	364.1±0.2, n=21	12.2±0.3	304.5±3.5, n=16	8.7±6.6			14.5-15.5
SAZ							
Period	$p\text{CO}_2^{\text{air}}/\mu\text{atm}^{2)}$	$\Delta^{\text{air}}/\mu\text{atm}$	$p\text{CO}_2^{\text{sw}}/\mu\text{atm}^{2)}$	$\Delta^{\text{sw}}/\mu\text{atm}$	$\text{N-pCO}_2^{\text{sw}}/\mu\text{atm}$	$\text{N-}\Delta^{\text{sw}}/\mu\text{atm}$	SST/°C
1969 <sup>3)</sup>	317.7±0.3, n=44		294.1±10.3, n=43		292.9		11.5±1.0, n=44
1984	337.8±0.5, n=21	20.1±0.6	315.5±11.0, n=21	21.4±15.1	316.8	23.9	11.0±1.5, n=21
1995	352.7±0.5, n=40	14.9±0.7	337.9±13.3, n=39	22.4±17.3	357.0	40.2	10.3±1.4, n=39
2002	363.8±0.4, n=36	11.1±0.6	318.9±11.7, n=82	-19.0±17.7	303.1	-53.9	12.6±1.0, n=82
$p\text{CO}_2^{\text{sw}}$ -SST							
1969 <sup>3)</sup>			294.7±4.3, n=44				11.5±1.0, n=44
1984			310.1±6.1, n=76	15.4±7.5			11.3±1.3, n=76
1995			329.3±8.8, n=121	19.2±10.7			10.1±1.1, n=121
2002			332.2±5.3, n=122	2.9±10.2			12.6±0.9, n=122
PFZ							
Period	$p\text{CO}_2^{\text{air}}/\mu\text{atm}^{2)}$	$\Delta^{\text{air}}/\mu\text{atm}$	$p\text{CO}_2^{\text{sw}}/\mu\text{atm}^{2)}$	$\Delta^{\text{sw}}/\mu\text{atm}$	$\text{N-pCO}_2^{\text{sw}}/\mu\text{atm}$	$\text{N-}\Delta^{\text{sw}}/\mu\text{atm}$	SST/°C
1969 <sup>3)</sup>	316.8±0.1, n=17		318.9±4.1, n=16		328.5		8.0±0.6, n=16
1984	336.5±0.5, n=33	19.7±0.5	326.9±9.3, n=19	8.0±10.2	326.9	-1.6	8.7±0.9, n=33
1995	351.1±0.3, n=16	14.6±0.6	348.1±4.6, n=15	21.2±10.4	343.7	16.8	9.0±0.5, n=15
2002	363.0±0.3, n=32	11.9±0.4	368.0±2.9, n=62	19.9±5.4	360.3	16.6	9.2±0.8, n=62

continued



PZ

Period	pCO <sub>2</sub> <sup>air</sup> /μatm <sup>2)</sup>	Δ <sup>air</sup> /μatm	pCO <sub>2</sub> <sup>sw</sup> /μatm <sup>2)</sup>	Δ <sup>sw</sup> /μatm	N-pCO <sub>2</sub> <sup>sw</sup> /μatm	N-Δ <sup>sw</sup> /μatm	SST/°C
1969 <sup>3)</sup>	314.4±0.3, n=47		298.5±14.7, n=44		284.9		4.9±1.7, n=47
1984	335.0±0.6, n=36	20.6±0.7	331.9±6.7, n=62	33.4±0.7	343.3	58.4	3.0±2.7, n=62
1995	348.8±0.7, n=151	13.8±0.9	340.6±6.9, n=152	8.7±9.6	334.9	-8.4	4.2±1.1, n=152
2002	361.1±0.4, n=126	12.3±0.8	361.6±3.2, n=255	21.0±7.6	370.9	36.0	3.2±2.0, n=255

SSIZ<sup>4)</sup>

Period	pCO <sub>2</sub> <sup>air</sup> /μatm <sup>2)</sup>	Δ <sup>air</sup>	pCO <sub>2</sub> <sup>sw</sup> /μatm <sup>2)</sup>	Δ <sup>sw</sup>	N-pCO <sub>2</sub> <sup>sw</sup> /μatm	N-Δ <sup>sw</sup> /μatm	SST
1969 <sup>3)</sup>	314.6±0.1, n=21		298.5 (282.7, 354.4), n=21		296.0		1.0±0.8, n=21
1984	334.7±0.6, n=29	20.1±0.6	340.0 (326.2, 345.9), n=36	41.5	347.3	51.3	0.4±0.6, n=36
1995	348.9±0.4, n=262	14.2±0.7	337.7 (333.1, 343.8), n=270	-2.3	334.9	-12.4	1.1±1.5, n=270
2002	360.6±0.3, n=232	11.7±0.5	282.2 (218.2, 318.5), n=480	-55.5	282.2	-52.7	0.9±0.4, n=722
2002	360.7±0.2, n=81	11.8±0.4	326.1 (316.6, 337.1), n=167	-11.6	322.0	-12.9	1.2±0.3, n=253

<sup>1)</sup> Average pCO<sub>2</sub><sup>sw</sup> for SSTs between 14.5 and 15.5°C. The selection of the temperature range does not considerably affect the results. If we select the SST range between 14 and 16°C, the average pCO<sub>2</sub><sup>sw</sup> is 281.4±4.1 μatm (n=17) for January 1969, 286.4±5.9 μatm (n=18) for January 1984, 298.5±3.9 μatm (n=12) for January 1995, and 304.9±5.2 μatm (n=41) for January 2002.

<sup>2)</sup> The average barometric pressure used was 1014.5hPa in the area close to the STF, 1006.9hPa in the PFZ, 997.3hPa in the PZ, and 996.1hPa in the SSIZ.

<sup>3)</sup> In 1969, we used the atmospheric CO<sub>2</sub> data at baseline stations (Inoue et al., 1999).

<sup>4)</sup> We examined the frequency distribution of the pCO<sub>2</sub><sup>sw</sup> in the SSIZ. In January 2002, the frequency distribution of the pCO<sub>2</sub><sup>sw</sup> showed a different pattern from that of the normal distribution. In the SSIZ, therefore, the median of the pCO<sub>2</sub><sup>sw</sup> is given along with the 25 and 75 percentiles.

Table 4. Rates of change in the  $p\text{CO}_2^{\text{air}}$  and  $p\text{CO}_2^{\text{sw}}$  ( $\mu\text{atm/yr}$ ) in the zone between major fronts of the Southern Ocean.

Rate of change <sup>1)</sup>	$\delta p\text{CO}_2^{\text{air}}/\delta t$	$\delta p\text{CO}_2^{\text{sw}}/\delta t^2$	$\delta p\text{CO}_2^{\text{sw}}(\text{A\_CO}_2)/\delta t$	$\delta p\text{CO}_2^{\text{sw}}(\text{Thermo})/\delta t$	$\delta p\text{CO}_2^{\text{sw}}(\text{O\_bio})/\delta t$
$p\text{CO}_2^{\text{sw}}$ minimum	1.4±0.1		0.7±0.1		
SAZ	1.4±0.1	1.0±0.5 (0.8±1.2)	1.2±0.1 <sup>3)</sup>	0.1±0.1	-0.3±0.5
PFZ	1.4±0.1	1.5±0.4 (0.9±0.4)		0.1±0.1	
PZ	1.4±0.1	1.8±0.2 (2.3±0.7)		0.1±0.1	
SSIZ <sup>4)</sup>	1.4±0.1	0.8±0.8 (0.7±0.9)		0.1±0.1	

<sup>1)</sup> The rates of change in the  $p\text{CO}_2^{\text{air}}$  and  $p\text{CO}_2^{\text{sw}}$  are expressed as  $\delta p\text{CO}_2^{\text{sw}}/\delta t$ . In the parentheses, A\_CO<sub>2</sub> means the annual uptake of anthropogenic CO<sub>2</sub>, Thermo, the thermodynamic temperature effect by the SST increase in the Southern Hemisphere (0.1±0.05°C per decade), and O\_bio, the ocean transport and biological activity.

<sup>2)</sup> The rate of change in N- $p\text{CO}_2^{\text{sw}}$  is given in the parentheses along with a standard deviation. The N- $p\text{CO}_2^{\text{sw}}$  was normalized to the average SST in each zone for four cruises (Table 3).

<sup>3)</sup> We used the  $p\text{CO}_2^{\text{sw}}$ -SST relationship to evaluate the  $p\text{CO}_2^{\text{sw}}$  at the same SST for four cruises (11.4°C).

<sup>4)</sup> In January 2002, the  $p\text{CO}_2^{\text{sw}}$  data between 62 and 63.5°S were used. If all  $p\text{CO}_2^{\text{sw}}$  data were used, the long-term trend of the  $p\text{CO}_2^{\text{sw}}$  would be calculated as  $-0.1\pm 1.4\mu\text{atm/yr}$ . If we omitted the  $p\text{CO}_2^{\text{sw}}$  data of January 2002, it would be  $1.6\pm 0.8\mu\text{atm/yr}$ .

Table 5. Growth rate of DIC in the surface seawater of the Southern Ocean, which was calculated on the basis of the growth rate of the  $p\text{CO}_2^{\text{sw}}$ , DIC, SST, and SSS data measured in January 1995 and 2002.

Zone	SST	SSS	$p\text{CO}_2^{\text{sw}}$ $\mu\text{atm}$	$\delta p\text{CO}_2^{\text{sw}}(\text{A\_CO}_2)/\delta t$ $\mu\text{atm/yr}$	N-DIC <sup>1)</sup> $\mu\text{mol/kg}$	Buffer Factor	$\delta\text{DIC}(\text{A\_CO}_2)/\delta t$ $\mu\text{mol/kg/yr}$
$p\text{CO}_2^{\text{sw}}$ minimum <sup>2)</sup>	°C						
	15.0	34.92	295.8	0.7±0.1	1975.1	9.9	0.47±0.14
SAZ	12.6	34.86	318.9	1.2±0.1	2013.4	10.7	0.71±0.09
PFZ	9.2	34.07	368.0	1.7±0.4	2094.9	12.3	0.69±0.27
PZ	3.2	33.82	361.6	2.0±0.2	2138.2	14.1	0.75±0.11
SSIZ	1.2	33.65	326.1	(1.0±0.8)	2149.6	14.4	(0.37±1.00)

<sup>1)</sup> Normalized to the SSS of 34.

<sup>2)</sup> Data in January 1995.

Table 6. Anthropogenic CO<sub>2</sub> uptake in the mixed layer of the Southern Ocean.

Zone	MLD <sup>1)</sup>	Area	$\delta\text{DIC}(\text{A\_CO}_2)/\delta t$	CO <sub>2</sub> uptake
	m	10 <sup>6</sup> km <sup>2</sup>	$\mu\text{mol/kg/yr}$	Gt-C/yr
pCO <sub>2</sub> <sup>sw</sup> minimum	150		0.47±0.14	
45-50°S	500	13.4	0.71±0.09	0.058±0.007
SAZ	500	39 <sup>2)</sup>	0.71±0.09	0.17±0.02
PFZ	500	3 <sup>3)</sup>	0.69±0.27	0.013±0.005
PZ	150	14 <sup>3)</sup>	0.75±0.11	0.019±0.003
SSIZ	(50)	16 <sup>3)</sup>	(0.37±1.00)	(0.004±0.011)

<sup>1)</sup> Mixed layer depth, McNeil et al. (2001).

<sup>2)</sup> Hoshiai (1982).

<sup>3)</sup> Tréguer and Jacques (1992).

## Figure Captions

Fig. 1. Cruise tracks of the R/V Hakuho-maru in the Southern Ocean. In the left panel, the dotted line shows the cruise track from December 1969 to February 1969, and the solid line, that from December 1994 to January 1995. In the right panel, the dotted line shows the cruise track from December 1983 to January 1984, and the solid line, that in January 2002. Temporal and spatial variations in  $p\text{CO}_2^{\text{sw}}$  were examined in the area surrounded by the thin solid line. The geographical position of the STF, SAF, and PF was drawn on the basis of Sokolov and Rintoul (2002).

Fig. 2. Latitudinal distributions of  $p\text{CO}_2^{\text{air}}$  and  $p\text{CO}_2^{\text{sw}}$ , SSS, and SST observed in January/February 1969, January 1984, January 1995, and January 2002. In the upper panel, red open circles show the  $p\text{CO}_2^{\text{sw}}$  in January/February 1969, green crosses, that in January 1984, brown open squares, that in January 1995, and blue open triangles, that in January 2002, and the solid lines show the  $p\text{CO}_2^{\text{air}}$ . In the middle and lower panels, the color of the line is the same as that in the upper panel. In January 2002, the  $p\text{CO}_2^{\text{sw}}$  decreased steeply to the level of  $150\mu\text{atm}$  south of  $65^\circ\text{S}$ .

Fig. 3. Temperature dependence of  $p\text{CO}_2^{\text{sw}}$  in the SST range between  $10$  and  $20^\circ\text{C}$  for the subtropics and SAZ. Open circles show the  $p\text{CO}_2^{\text{sw}}$  in January 1969, open triangles, that in January 1984, open

squares, that in January 1995, and cross symbols, that in January 2002. The average  $p\text{CO}_2^{\text{sw}}$  surrounded by the thin solid line was used to calculate the  $p\text{CO}_2^{\text{sw}}$  minimum value north of the STF.

Fig. 4. Temperature dependence of the  $p\text{CO}_2^{\text{sw}}$  in the area north of the STF to the SSIZ measured in January 1995 (upper panel) and January 2002 (lower panel). Open circles show the data measured in the SSIZ, crosses, those in the PZ, open triangles, those in the PFZ, open squares, those in the SAZ, and solid circles, those in the north of the STF.

Fig. 5. Variations in the  $p\text{CO}_2^{\text{air}}$  and  $p\text{CO}_2^{\text{sw}}$  in the area from the  $p\text{CO}_2^{\text{sw}}$  minimum at the SST of  $15^\circ\text{C}$  north of the STF to the SSIZ during the period from 1969 to 2002. Open circles show the  $p\text{CO}_2^{\text{air}}$ , solid circles, the  $p\text{CO}_2^{\text{sw}}$ , and open triangles, the  $\text{N-}p\text{CO}_2^{\text{sw}}$ . The dotted line shows the long-term trend of  $p\text{CO}_2^{\text{air}}$  expressed as the second-degree polynomial function, the solid line, the linear long-term trend of the  $p\text{CO}_2^{\text{sw}}$ , and the dashed line, changes in  $\text{N-}p\text{CO}_2^{\text{sw}}$  between two cruises. In the SAZ, the cross symbols mean the  $p\text{CO}_2^{\text{sw}}$  calculated by using the  $p\text{CO}_2^{\text{sw}}$ -SST relationship; in the SSIZ, the solid square means the  $p\text{CO}_2^{\text{sw}}$  between  $62$  and  $63.5^\circ\text{S}$ , and the open square, the  $\text{N-}p\text{CO}_2^{\text{sw}}$  between  $62$  and  $63.5^\circ\text{S}$ .

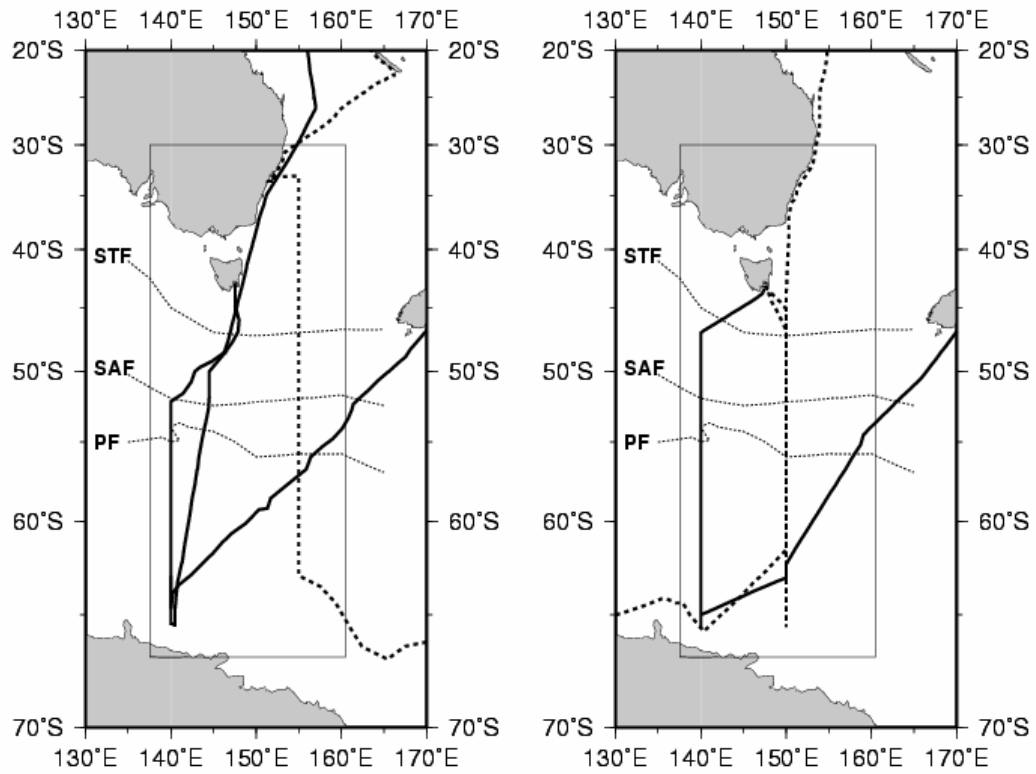


Fig. 1. Inoue and Ishii

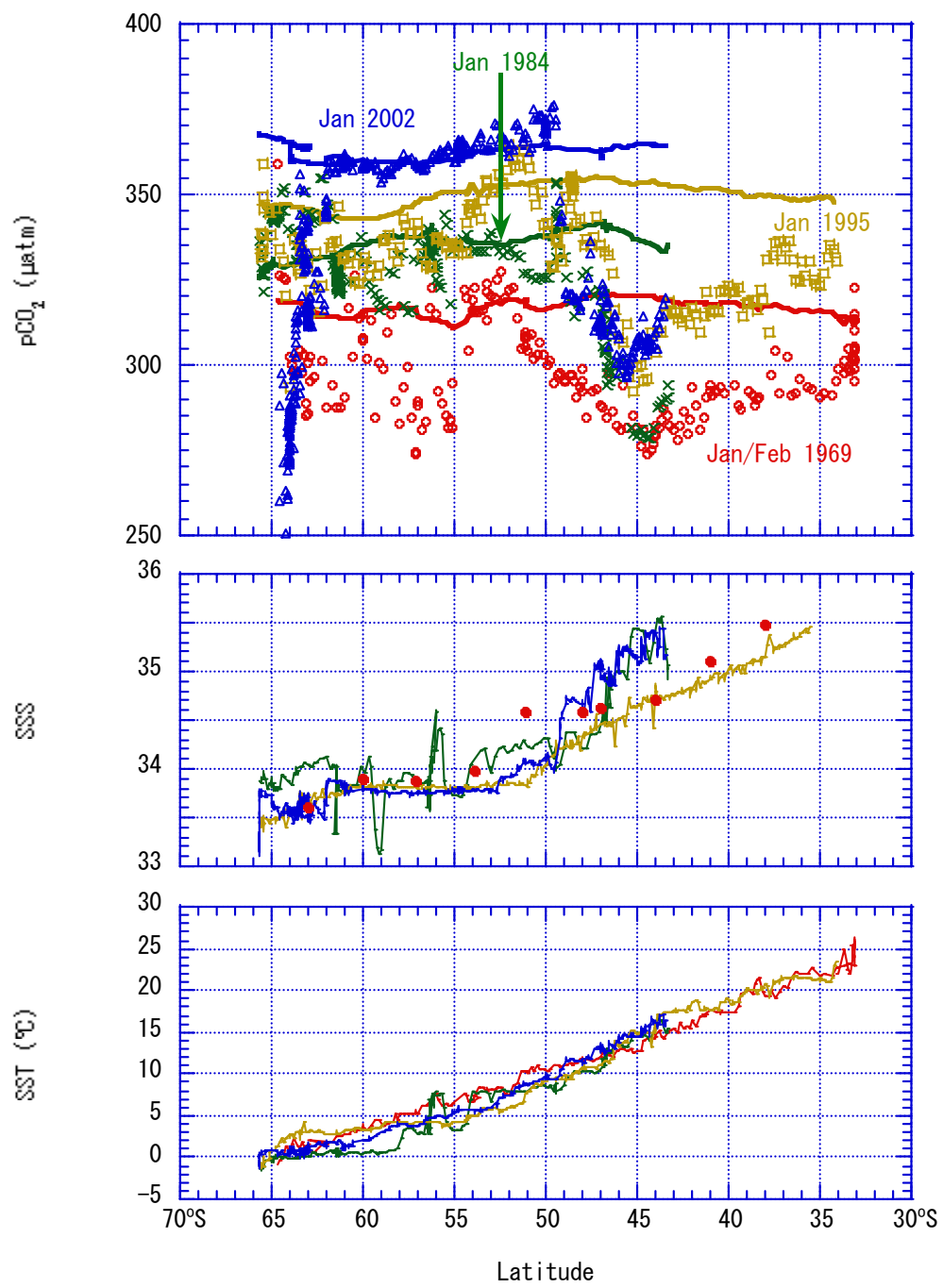


Fig. 2. Inoue and Ishii



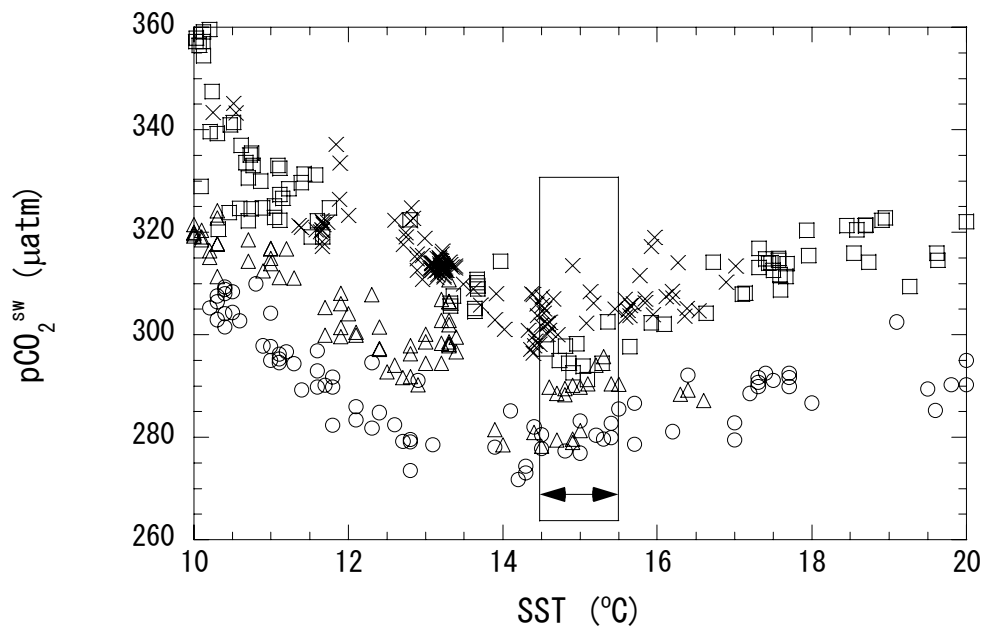


Fig. 3. Inoue and Ishii

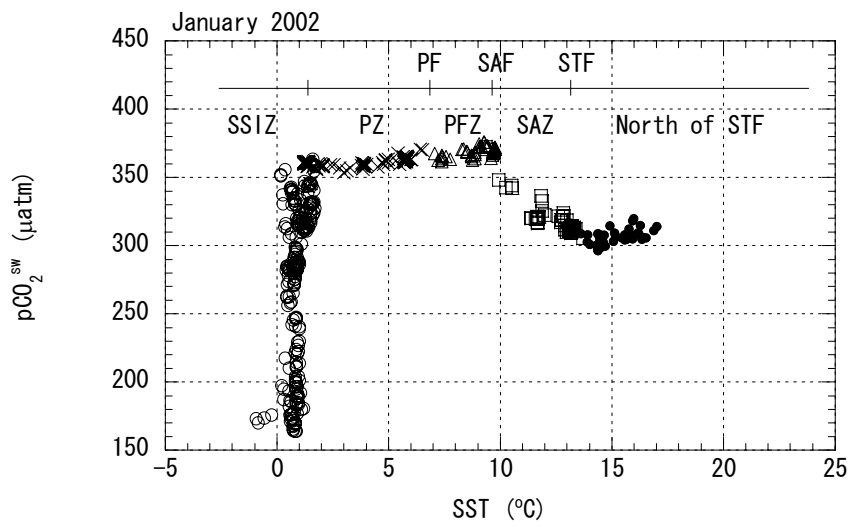
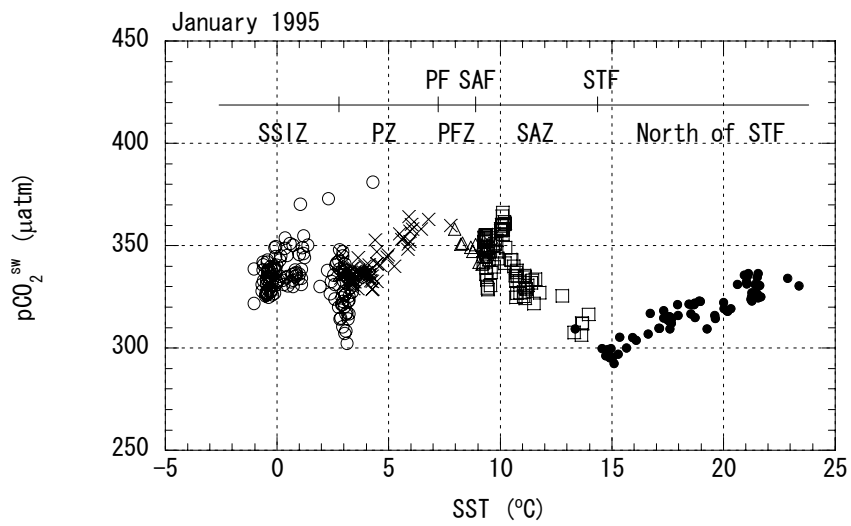


Fig. 4. Inoue and Ishii

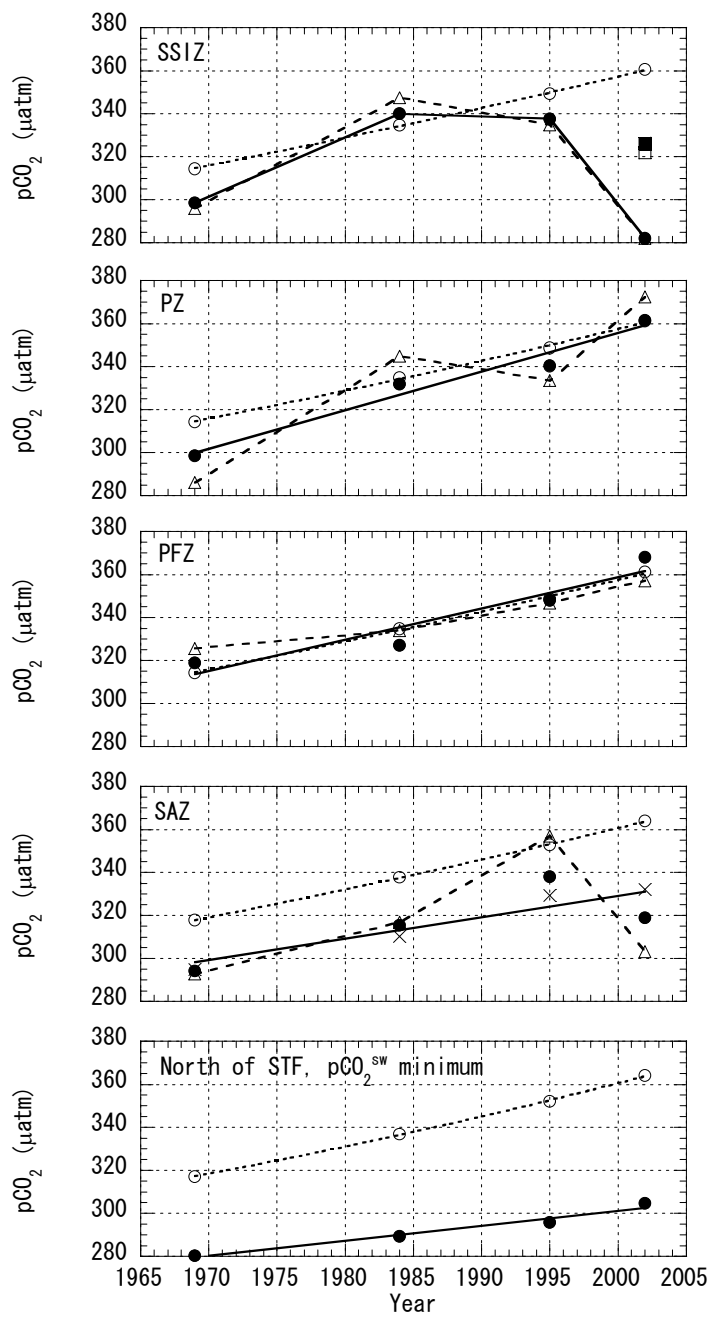


Fig. 5. Inoue and Ishii

