Carbonate chemistry and the anthropogenic CO_2 in the South China Sea

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Abstract—— In order to understand the water mass exchange between the South China Sea and the West Philippine Sea, and to study the dissolved carbonate system in the seas surrounding Taiwan Island, we participated in five WOCE cruises (Cruises 257, 262, 266, 287 and 316) aboard R/V *Ocean Researcher* 1. The areas studied were the South China Sea, the West Philippine Sea and the Bashi Channel. Temperature, salinity, pH, alkalinity and total CO_2 were measured.

Our data indicate that because of the interference of the submarine topography and the Kuroshio axis, there exists a "front" south of the Lanyu Islet. East of it, the water mass belongs to the West Philippine Sea, on the west in the mixed water of the South China Sea and the West Philippine Sea.

The South China Sea deep water should have the characteristics similar to the water at about 2 200 m in the West Philippine Sea. The calculated results from the residence time, the inorganic carbon dissolution rate and the organic carbon decomposition rate show that the differences between these two water masses should be between 0.008~0.023 in pH, 5.2~15.0 $\mu mol/kg$ in apparent oxygen utilization, 3.6~10.2 $\mu mol/kg$ in alkalinity and 6.4~18.4 $\mu mol/kg$ in total CO_2, respectively. The measured results show that there are no distinguishable differences between these two water masses, implying a short deep water residence time of approximately 40 a.

The anthropogenic CO_2 penetrates to roughly 500 m, slightly shallower than found in the West Philippine Sea. The entire South China Sea contains $(0.38\pm0.1) \times 10^{15}$ g excess CO_2.

INTRODUCTION

The South China Sea (SCS) is one of the major marginal seas in the world and has attracted early attention of the oceanographic community. The US R/V *Vincennes* ventured into it as early as 1842. The world famed British HRS *Challenger* studied the SCS in 1872 (State Oceanic Administration, 1988a), followed by many American, Chinese, Japanese and Russian studies. Wyrtki (1961) summarized the early results.

Most of the studies, however, were related to the biological or physical oceanography. Chemical oceanography received less attention (Han *et al.*, 1980; State Oceanic Administration, 1988a, b). Even less is known about the carbonate chemistry of sea water. We hereby report the prelimi-

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nary results from some of our recent investigations.

STUDY AREA

We participated in 5 cruises of R/V *Ocean Researcher* 1. The 257th cruise (OR 257) was part of the WOCE PR-20 (World Ocean Circulation Experiment Pacific Repeated Line 20). It occurred between 11 and 18 October, 1990.

OR 262 was a WOCE test cruise between 17 and 22 November, 1990. OR 266 was part of the WOCE PR-21, which occurred between 16 and 30 December, 1990. OR 287 occupied PR-20 and PR-21 between 23 June and 11 July, 1991. OR 316 occupied PR-20 between 7 and 16 May, 1992. The station locations mentioned in this report are given in Fig. 1. Details of the cruises are given in Chen *et al*. (1993), Chen *et al*. (1993) and Chen *et al*. (1993).
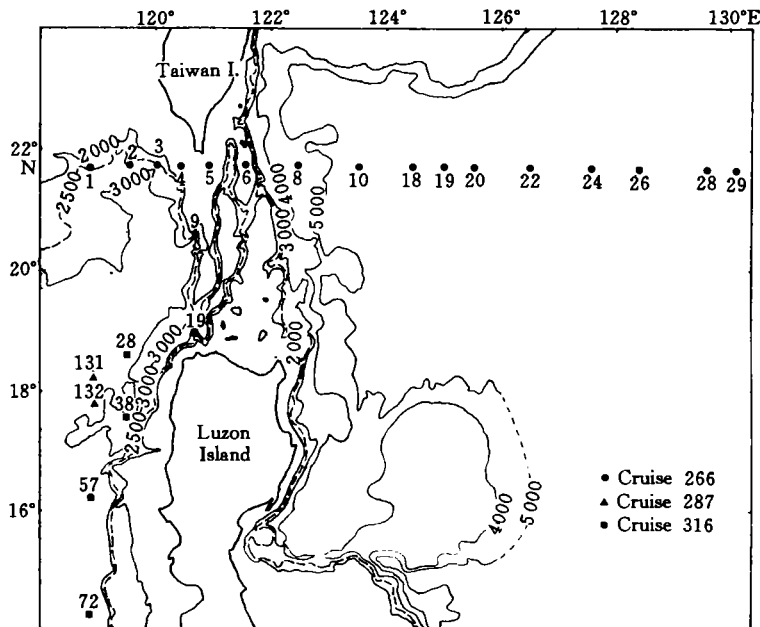

Fig. 1.   Station locations.

EXPERIMENTAL METHOD

pH was measured at $25 \pm 0.05\,°C$ by a radiometer PHM-85 pH meter using a GK 24001C combination electrode. The US National Institute of Standards and Technology 4.006, 6.863 or 7.400 buffers were used for calibrating the electrode. The precision was better than ± 0.003 pH unit (Chen, 1984).

The potentiometric alkalinity (TA) and total $CO_2 (T_{CO_2})$ were measured by a PC-controlled automatic titration system composed of a radiometer PHM-84 pH meter, a GK 2401C combination electrode, an ABU 80 autoburet, a titration cell and a temperature controlled water bath set at $25 \pm 0.05\,°C$. The end points were determined by the Gran function with a precision of 3 $\mu mol/$

kg for TA and 6 μmol/kg for T_{CO_2}, respectively (Bradshaw *et al.*, 1981; Chen *et al.*, 1993; Chen *et al.*, 1993; Chen *et al.*, 1993). The coulometric method was also used to measure T_{CO_2} on OR 316 with a precision of 2 μmol/kg (Chen *et al.*, 1993).

THE INORGANIC CARBON/ORGANIC CARBON RATIO

Decomposition of $CaCO_3$ (inorganic carbon, IC) and organic carbon (OC) both contribute to the increase of T_{CO_2} in the subsurface waters. We use the following equation to calculate the IC/OC ratio (Chen, 1990).

$$IC/OC = [0.160\ 38 \times (\triangle NT_{CO_2} + 40) + \triangle NTA]/[2 \times (\triangle NT_{CO_2} + 40) - \triangle NTA],$$

where $NTA = TA \times 35/S$, $NT_{CO_2} = T_{CO_2} \times 35/S$, $\triangle NTA = NTA$ (measured) $- NTA°$, $\triangle NT_{CO_2} = NT_{CO_2}$ (measured) $- NT_{CO_2}^\cdot$. The node denotes preformed values. For deep and bottom waters:

$$NTA°(\mu mol/kg) = 2\ 384 - 4.2 \times \theta(\pm 9),$$

$$NT_{CO_2}^\cdot(\mu mol/kg) = 2\ 219 - 11 \times \theta(\pm 16).$$

For salinity minimum waters:

$$NTA°(\mu mol/kg) = 2\ 384 - 3.36 \times \theta(\pm 11),$$

$$NT_{CO_2}^\cdot(\mu mol/kg) = 2\ 242 - 12.08 \times \theta(\pm 18).$$

RECOGNIZING THE ANTHROPOGENIC CO_2 SIGNAL IN THE OCEAN

The CO_2 increase in the ocean can be estimated from observations by reconstructing the increase from measurements of the oceanic carbon system. The approach was suggested by Brewer (1978), Chen and Millero (1978, 1979) and used by many others (Chen and Drake, 1986; Chen, 1993a, b, c). To determine the fossil fuel CO_2 signal, it is necessary to subtract the contributions to T_{CO_2} and TA due to biological activity, i. e., from respiration and calcium carbonate dissolution. The respiration contribution can be estimated from the apparent oxygen utilization, since the change in T_{CO_2} and O_2 are linked by a fixed ratio (Redfield ratio) (Redfield *et al.*, 1963; Chen *et al.*, 1982). The original (preformed) NTA ($NTA°$) of the sea water can be calculated from potential temperature since in a given ocean basin the two properties are very well correlated. The NTA is also slightly affected by respiration (addition of NO_3 and PO_4); but this contribution can also be obtained from the apparent oxygen utilization (AOU) (Chen, 1981; Chen *et al.* 1982). In summary, the changes in NT_{CO_2} and in NTA due to biological activity can be estimated as:

$$T_{CO_2}^\cdot(\text{old}) = T_{CO_2}(\text{measured}) + 0.5[TA°(\text{present}) - TA(\text{measured})] - 0.78AOU,$$

$$\triangle T_{CO_2}^\cdot(\mu mol/kg) = T_{CO_2}^\cdot(\text{old}) - T_{CO_2}^\cdot(\text{present})$$

$$= T_{CO_2}(\text{measured}) - 0.5\ TA\ (\text{measured}) - 0.78AOU$$

$$+ 0.5\ TA°(\text{present}) - T_{CO_2}^\cdot(\text{present}).$$

In this way, the preformed composition of the water parcel (i. e., its composition at the time when it was last in contact with the atmosphere) can be reconstructed, and therefore the preformed NT_{CO_2} determined.

The earlier studies using this (or a similar) approach were partly criticized because of uncer-

tainties in the data and in the coefficients involved in the above equations. However, the signal is quite large by now—surface water NT_{CO_2} is typically 40 μmol/kg higher than in pre-industrial time—and the measurement accuracy has considerably improved to ± 1 μmol/kg for T_{CO_2} (SCOR, 1991).

RESULTS AND DISCUSSION

A typical salinity cross-section for PR-20 is shown in **Fig. 2**. There is a shallow salinity maximum centered at approximately 200 m at 130° E, shoaling toward west to roughly 100 m at 120° E. A minimum salinity core (the North Pacific intermediate water, NPIW) extends to a lesser degree across the Bashi Channel into the SCS. Intensive upwelling and vertical mixing tend to reduce the extreme signals.
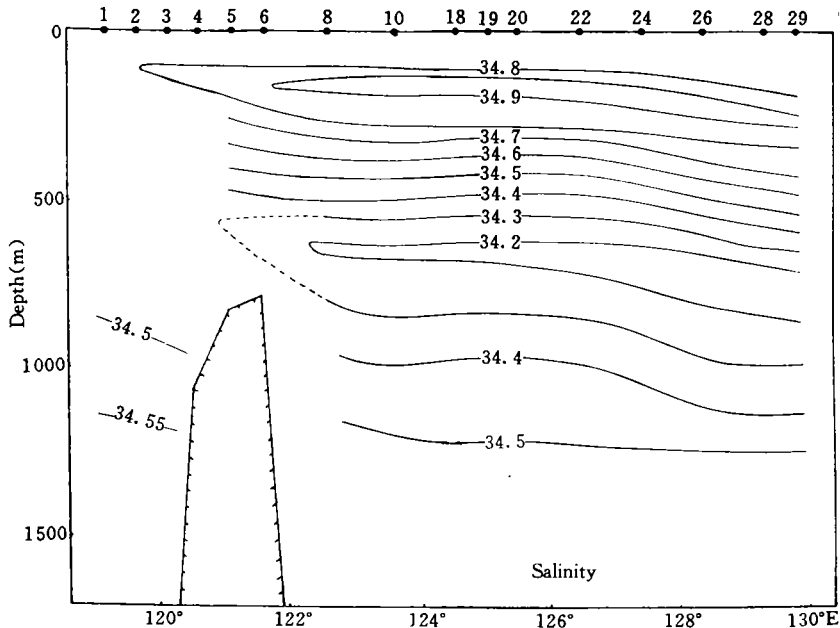

Fig. 2.   WOCE PR-20 salinity cross-section.

Figure 3 shows a typical pH cross-section for PR-20. The shallow pH contours tend to shoal towards west. The pH minimum east of the ridge is typical in the North Pacific Ocean (Chen *et al.*, 1986) but the signal disappears in the SCS. This is because the pH minimum core, slightly deeper than NPIW, has received much end products of the organic carbon decomposition, thus increasing the acidity. On the other hand, the Antarctic Bottom Water and its deep return water (the Pacific deep water, PDW) have higher preformed pH values and do not experience much organic carbon decomposition. As a result, a pH minimum is formed at mid-depth in the West Philippine Sea. There is no AABW in the SCS and the PDW influence is small. Intensive upwelling further diminishes any remnant pH minimum from the West Philippine Sea.

Figure 4 shows a typical NTA cross-section for the same east-west PR-20 line. Westward
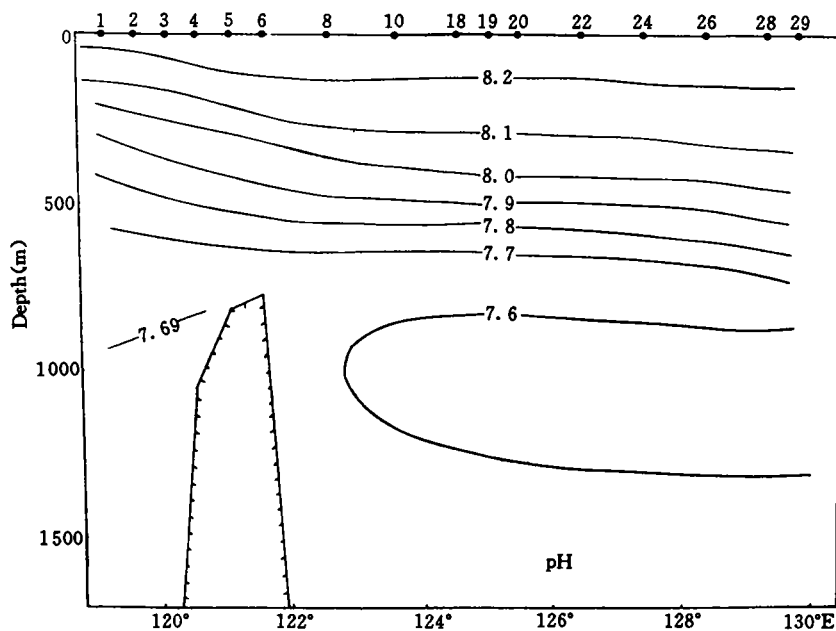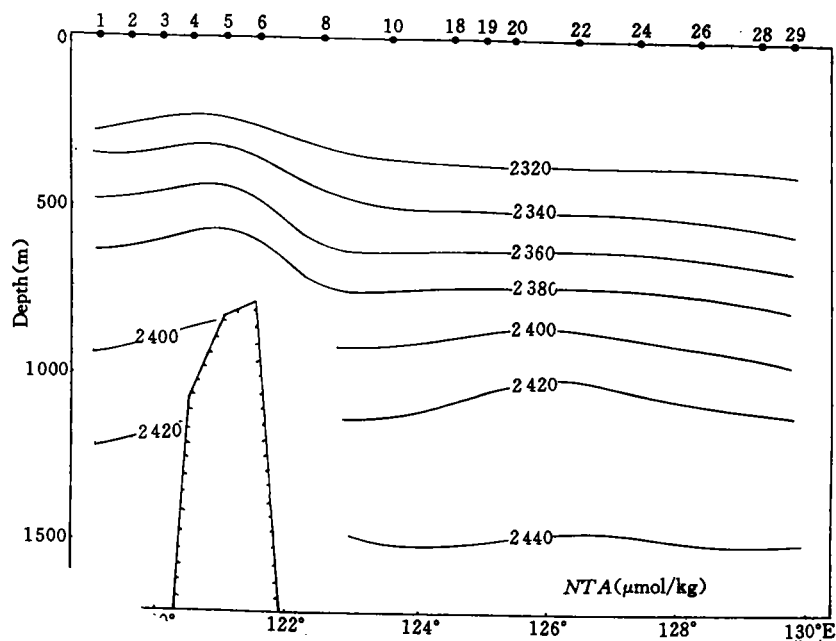
Fig. 3.   WOCE PR-20 pH cross-section.

Fig. 4.   WOCE PR-20 normalized alkalinity cross-section.

shoaling of the contour lines is evident. Above 800 m, the SCS water has higher NTA values than the Philippine Sea water at the same depth but the relation is reversed below 800 m. The rather deep NTA maximum in the North Pacific Ocean is not found here because the sampling is not deep enough.

Figure 5 shows the NT_{CO_2} cross-section for OR 316. The NT_{CO_2} distribution is similar to NTA. Westward shoaling of NT_{CO_2} contours makes the NT_{CO_2} above 600 m in the SCS higher than that in the West Philippine Sea. The reverse is true below 600 m. The typical NT_{CO_2} maximum in the Pacific Ocean is lacking in the SCS.
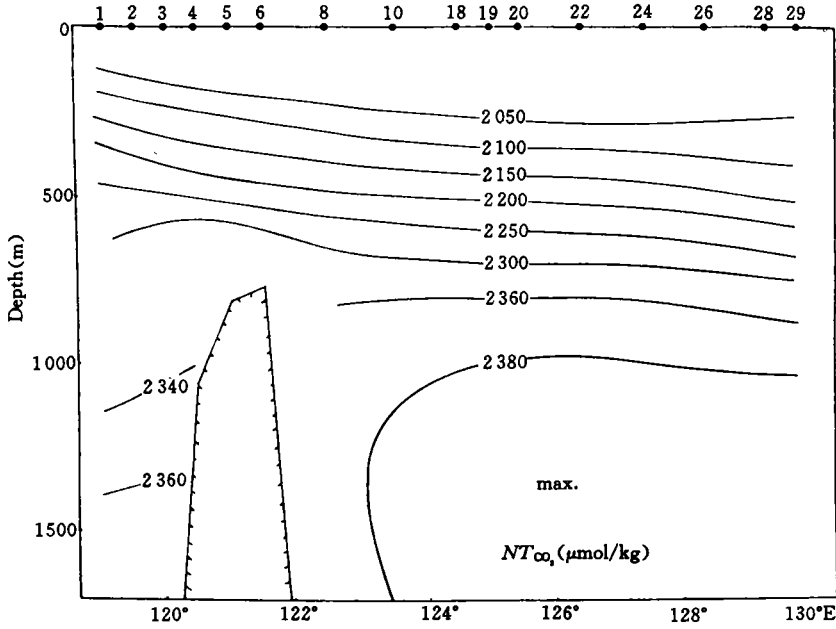
Fig. 5.   WOCE PR-20 normalized total CO₂ cross-section.
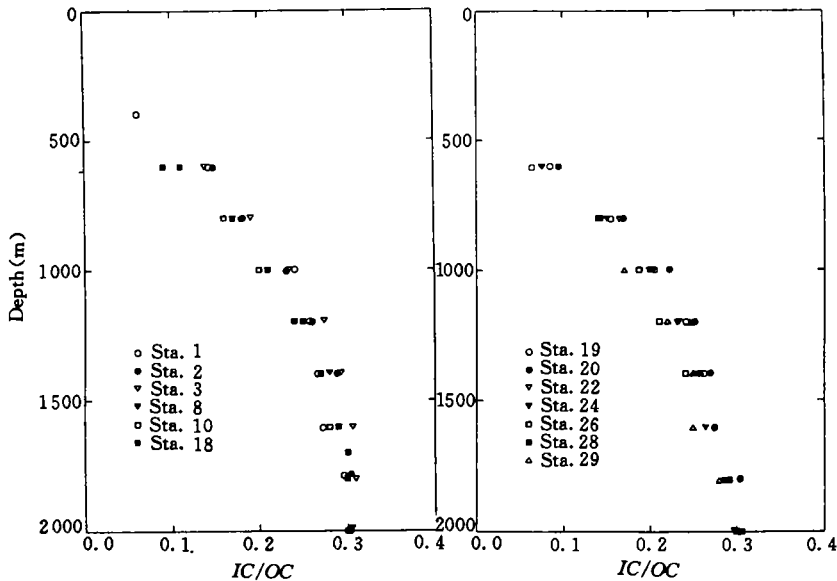
Fig. 6.   The inorganic carbon/organic carbon ratio for WOCE PR-20 stations.

The IC/OC ratios for OR 316 stations are between 0. 17 to 0. 22 at 1 000 m, 0. 27 to 0. 30

at 2 000 m (see Fig. 6) and remain relatively constant below 2 000 m, reaching 0. 31 to 0. 33 at 3 000 m and deeper.

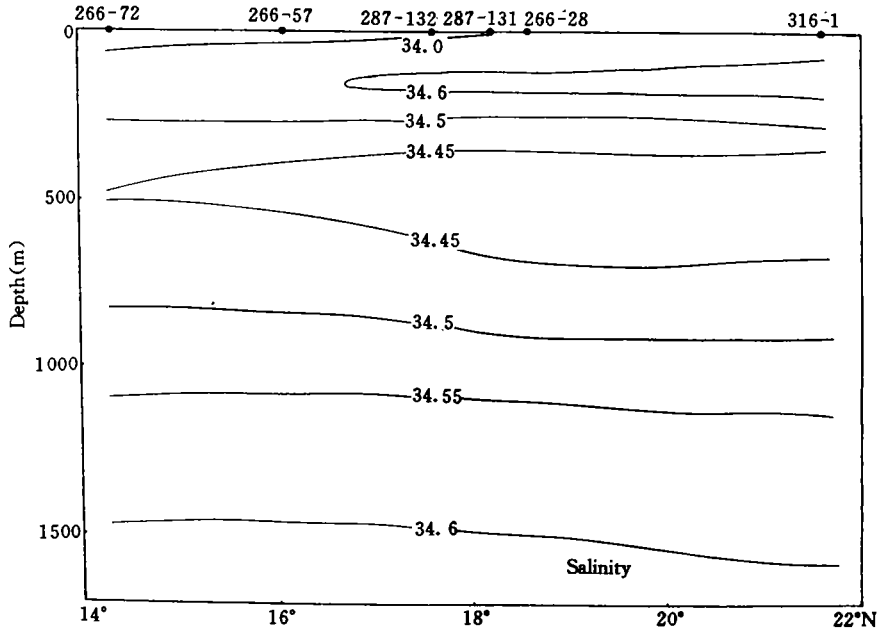The north-south salinity cross-section in the northeast SCS is shown in Fig. 7. The shallow

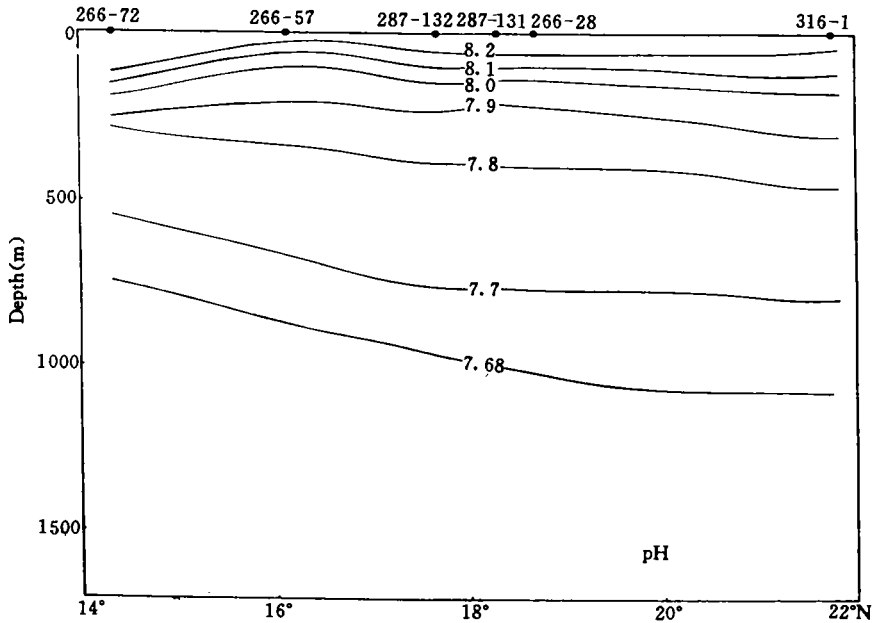Fig. 7.   North-south salinity cross-section in the northeast SCS.

Fig. 8.   North-south pH cross-section in the northeast SCS.

salinity maximum layer between $100 \sim 200$ m is thinner in the more southern stations, suggesting diminishing role of the West Philippine Sea water. The salinity minimum layer between $350 \sim 700$ m also becomes thinner in the south. It was noted above that the extremes in the distributions of physico-chemical properties become weaker in the SCS proper.

Figure 8 shows the north-south cross-section for pH, which is uncharacteristic with essentially no change below 1 000 m. Han *et al.* (1980) reported pH minimum at $800 \sim 990$ m in the SCS. Neither our data nor the data of the State Oceanic Administration (1988a, b) show the signal.

Figures 9 and 10 show the NTA and NT_{CO_2} cross-sections. Again they are uncharacteristic with values increasing monotonically with depth. The water becomes relatively homogeneous below 1 200 m. No maximum was detected.
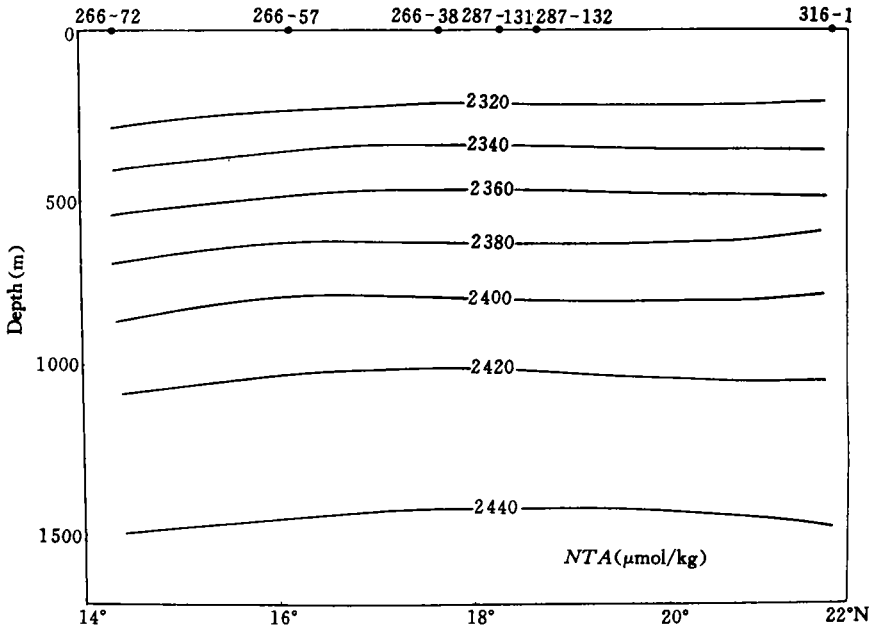

Fig. 9.   North-south normalized alkalinity cross-section in the northeast SCS.

Figure 11 shows the IC/OC ratios for stations in the northeast SCS. This figure is similar to Fig. 6 and the values are similar to those found in the North Pacific Ocean (Chen, 1990).

The residence time of the SCS water below 1 500 m has been estimated to be between $40 \sim 155$ a (Gong *et al.*, 1993). Han and Lin (1992) reported the residence time for waters below 1 000 m as 76 a. Based on the inorganic carbon dissolution rate of $0.053 \ \mu mol/(kg \cdot a)$, the organic carbon decomposition rate of $0.107 \mu mol/(kg \cdot a)$, and the oxygen consumption rate of $0.13 \ \mu mol/(kg \cdot a)$ (Chen *et al.*, 1986), the increase in pH, AOU, NTA and NT_{CO_2} of the West Philippine Sea water entering the SCS should be between $0.008 \sim 0.023$ pH unit, $5.2 \sim 15.0$, $3.6 \sim 10.2$ and $6.4 \sim 18.4 \ \mu mol/kg$, respectively.
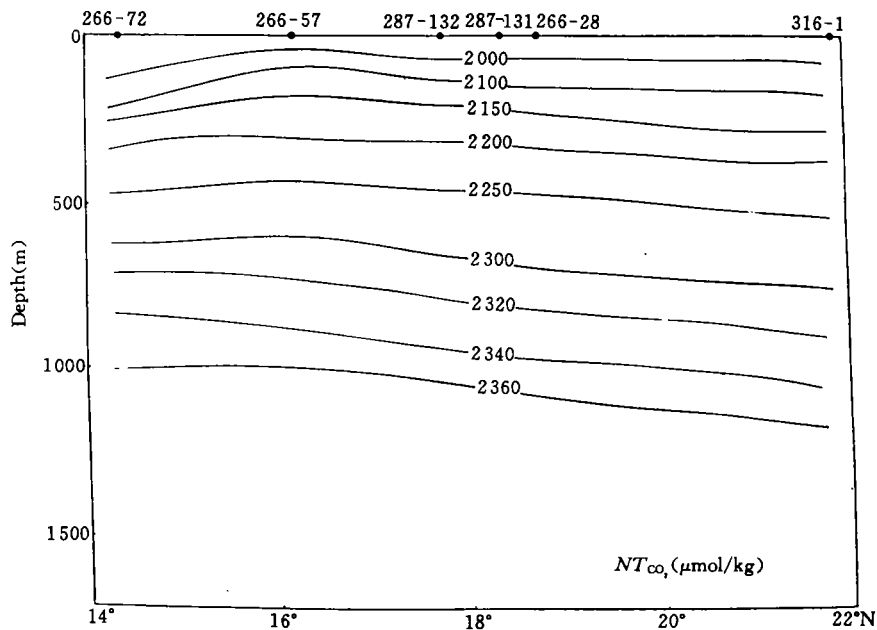
Fig. 10.   North-south normalized total CO_2 cross-section in the northeast SCS.
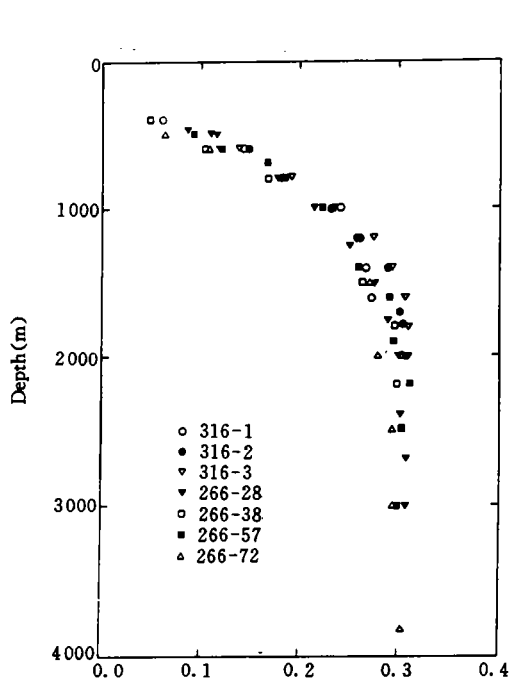

Fig. 11.   The inorganic carbon/organic carbon ratio for the stations in the northeast SCS.
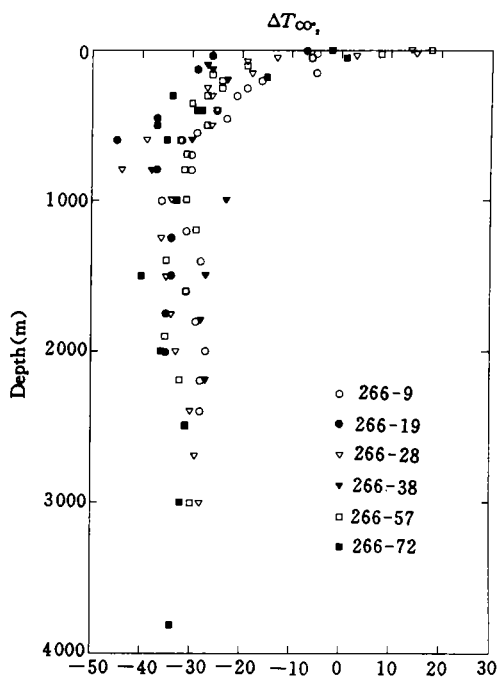

Fig. 12.   Vertical distribution of $\triangle T_{CO_2}$ in the SCS.

The actual data, however, indicate that the differences between the SCS water and the West Philippine Sea water are near the combined precision of our determinations, thus the residence

time of the SCS deep water is more likely closer to 40 a than 115 a.

The vertical distribution of the excess CO_2 in the northeast SCS is shown in Fig. 12. Excess CO_2 does not seem to penetrate more than 500 m deep, shallower than in the West Philippine Sea. Since it is almost certain that the shelf area is fully penetrated by excess CO_2 (Chen, 1993b), we can safely assume that on the average the excess CO_2 penetrates to 300 m in the SCS. This amounts to $(0.38\pm0.1)\times10^{15}$ g anthropogenic carbon in the SCS.

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