

Carbonate Chemistry of the South China Sea

南海之碳化學

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Abstract

In order to study the dissolved carbonate system in the South China Sea (SCS) and to understand the water mass exchange between the SCS and the West Philippine Sea (WPS), pH, total alkalinity and total CO₂ were measured aboard R/V Ocean Researcher 1. Because of the sill separating these two seas with a maximum depth of 2200 m, the SCS Deep Water has the characteristics similar to the water at about 2200 m in the WPS. The minimum in pH and the maxima in normalized alkalinity and total CO₂ commonly found in the open oceans at mid-depth are also prominent in the WPS but are very weak in the SCS. Mass balance calculations indicate that the SCS is a weak CO₂ sink in the wet season but a weak CO₂ source in the dry season. The anthropogenic CO₂ penetrates to at least 1000 m deep in the SCS, slightly shallower than found in the WPS. The entire SCS contains $0.50 \pm 0.15 \times 10^{15}$ g excess CO₂.

1. Introduction

The South China Sea (SCS) is the largest marginal sea in the world, with an area of 3.5×10^6 km² and a maximum depth of 5559 m. Because of the wide shelves on the northwestern and southern ends, the average depth is only 1350 m. The SCS connects with the East China Sea (ECS) through the Taiwan Strait, which is about 150 km wide and averages only 50 m deep. The deep Bashi Channel with a sill depth of about 2200 m is the major connection with the Pacific Ocean. The 420 m deep Mindoro Strait connects the SCS with the Sulu Sea which is itself semi-enclosed with only shallower connections with other seas. The southern end of the SCS is the wide Sunda Shelf which is rather shallow and flat, being about 40 m deep at its periphery and only up to 100 m in its central part. Because of the topography, the SCS exchanges only surface waters with the outside through the Taiwan Strait and over the Sunda Shelf. Exchange of intermediate waters occurs mainly through the Bashi Channel although some upper intermediate water is exchanged with the Sulu Sea. Between 420 m and 2200 m, the

waters only exchange with the West Philippine Sea (WPS) through the Bashi Channel.

The SCS 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, followed by many American, Chinese, Japanese and Russian studies. Wyrki (1961) summarized the early results. Most of these studies, however, were related to the biological or physical oceanography. Chemical oceanography has received less attention until recently (State Oceanic Administration, 1988a, b; Chen, 1995; Chen and Huang, 1995; Chen and Wang, 1997; Chen et al., 2000). However, still not much is known about the carbonate chemistry of seawater because of the dearth of high quality data. We hereby report the preliminary results from some of our recent investigations.

2. Study Area

We participated in several 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 Oct., 1990. OR 262 was a WOCE test cruise between 17 and 22 Nov., 1990. PR20 was reoccupied by OR 287 between 23 and 30 June, 1991; OR 316 between 7 and 16 May, 1992; OR 418B between 11 and 17 May, 1995; OR 433 between 15 and 21 Oct., 1995; OR 462 between 4 and 13 Sept., 1996.

OR 266 was part of the WOCE PR-21, which occurred between 16 and 30 Dec., 1990. It was repeated by OR 287 between 1 and 11 July, 1991; OR 403 between 5 and 7 Oct., 1994; OR 434 between 26 and 29 Oct., 1995. OR 508 and OR 546 ventured into the interior of the SCS between 15 and 24 Nov., 1997 and between 7 and 20 April, 1999, respectively. The station locations mentioned in this report are given in Fig. 1. Details of the cruises are given in Chen et al. (1993a,b,c; 1995, 1996, 1997, 1998, 2000).

3. Experimental method

pH was measured at $25 \pm 0.05^\circ\text{C}$ by a Radiometer PHM-85 pH meter using a GK 2401C combination electrode. TRIS seawater buffer was used to calibrate the electrode. IAPSO Standard seawater was used as a running standard to calibrate the electrode shift. The precision was better than ± 0.003 pH unit.

The potentiometric alkalinity (TA) was 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 $25 \pm 0.05^\circ\text{C}$. The end points were determined by the Gran Function with a precision of $3\mu\text{mol/kg}$ for TA (Chen et al., 1993a, b, c). The coulometric method was used to measure TCO_2 with a precision of 0.05% (Chen et al., 1993c, 1995, 1996). The single operator multiparameter metabolic analyzer (SOMMA) system was used to extract CO_2 gas from acidified seawater, then the CO_2 gas was measured by the UIC, Coulometrics, Inc. model 5011 coulometric detector (Dickson and Goyet, 1991). Reference material prepared by A. Dickson was used for calibration.

4. The Inorganic Carbon/Organic Carbon Ratio

Decomposition of CaCO_3 (inorganic carbon, IC) and organic carbon (OC) both contribute to the increase of TCO_2 in the subsurface waters. We used the following

equations to calculate the IC/OC ratio (Chen, 1990).

$$\text{IC/OC} = [0.16038 \times (\Delta\text{NTCO}_2 + 40) + \Delta\text{NTA}] / [2 \times (\Delta\text{NTCO}_2 + 40) - \Delta\text{NTA}]$$

where $\text{NTA} = \text{TA} \times 35/\text{S}$

$$\text{NTCO}_2 = \text{TCO}_2 \times 35/\text{S}$$

$$\Delta\text{NTA} = \text{NTA} (\text{measured}) - \text{NTA}^\circ;$$

$$\Delta\text{NTCO}_2 = \text{NTCO}_2 (\text{measured}) - \text{NTCO}_2^\circ$$

The node denotes preformed values (Chen, 1984). For deep and bottom waters:

$$\text{NTA}^\circ (\mu\text{mol/kg}) = 2384 - 4.2 \times \theta (\pm 9)$$

$$\text{NTCO}_2^\circ (\mu\text{mol/kg}) = 2219 - 11 \times \theta (\pm 16)$$

For salinity minimum waters:

$$\text{NTA}^\circ (\mu\text{mol/kg}) = 2384 - 3.36 \times \theta (\pm 11)$$

$$\text{NTCO}_2^\circ (\mu\text{mol/kg}) = 2242 - 12.08 \times \theta (\pm 18)$$

Since the anthropogenic CO_2 increase in the oceans affects NTCO_2 , the contribution must be subtracted from NTCO_2 in order to get the portion that comes from the decomposition of CaCO_3 .

The anthropogenic CO_2 increase in the oceans can be estimated from observations by reconstructing the increase from measurements of the oceanic carbonate system. To determine the fossil fuel CO_2 signal, it is necessary to subtract the contributions to TCO_2 and TA due to biological activity, i.e., from respiration and calcium carbonate dissolution. The respiration contribution can be estimated from AOU since changes in TCO_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 seawater 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 AOU. In summary, the changes in NTCO_2 and in NTA due to biological activity can be estimated as:

$$\text{NTCO}_2^\circ (\text{old}) = \text{NTCO}_2 (\text{measured}) + 0.5 [\text{NTA}^\circ (\text{present}) - \text{NTA} (\text{measured})] - 0.78 \text{ AOU}$$

$$\Delta\text{NTCO}_2^\circ (\mu\text{mol/kg}) = \text{NTCO}_2^\circ (\text{old}) - \text{NTCO}_2^\circ (\text{present}) = \text{NTCO}_2 (\text{measured}) - 0.5 \text{ NTA} (\text{measured}) - 0.78 \text{ AOU} + 0.5 \text{ NTA}^\circ (\text{present}) - \text{NTCO}_2^\circ (\text{present})$$

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 NTCO_2 determined.

The earlier studies using this (or a similar) approach were criticized because of uncertainties 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 more than 45 $\mu\text{mol/kg}$ higher than in pre-industrial time -- and the measurement accuracy has considerably improved to $\pm 1 \mu\text{mol/kg}$ for TCO_2 .

The IC/OC ratios for the WPS based on the OR 316 stations are between 0.17 to 0.22 at 1000m, 0.27 to 0.30 at 2000 m (Fig.2a) and remain relatively constant below 2000 m, reaching 0.31 to 0.33 at 3000 m and deeper. Fig. 2b shows the IC/OC ratios for stations in the SCS. This figure is similar to Fig.2a and the values are similar to those found in the North Pacific Ocean (Chen, 1990).

The residence time of the SCS water below 1500 m has been estimated to be between 40-115 yr (Gong et al., 1992). Han and Lin (1992) reported the residence time for waters below 1000 m as 76 yr. Based on the inorganic carbon dissolution rate of 0.053 $\mu\text{mol/kg/yr}$, the organic carbon decomposition rate of 0.107 $\mu\text{mol/kg/yr}$, and the oxygen consumption rate of 0.13 $\mu\text{mol/kg/yr}$ for Pacific Deep Waters (Chen et al., 1986), the increase in pH, AOU, NTA and NT CO_2 of the West Philippine seawater after it enters the SCS should be between 0.008-0.023 pH unit, 5.2-15.0 $\mu\text{mol/kg}$, 3.6-10.2 $\mu\text{mol/kg}$ and 6.4-18.4 $\mu\text{mol/kg}$, respectively. The actual data, however, indicate that the differences between the SCS and the WPS waters are near the combined precision of our determinations, thus the residence time of the SCS deep water is more likely closer to 40 yr than 115 yr.

The vertical distribution of the $\Delta\text{NTCO}_2^\circ$ in the SCS is shown in Fig.3. Excess CO_2 seem to penetrate more than 1000 m deep. Since it is almost certain that the shelf area is fully penetrated by excess CO_2 (Chen 1993a, b), we can safely assume that on the average the excess CO_2 penetrates to 500 m in the SCS. This amounts to $0.50 \pm 0.15 \times 10^{15}$ g anthropogenic carbon in the SCS.

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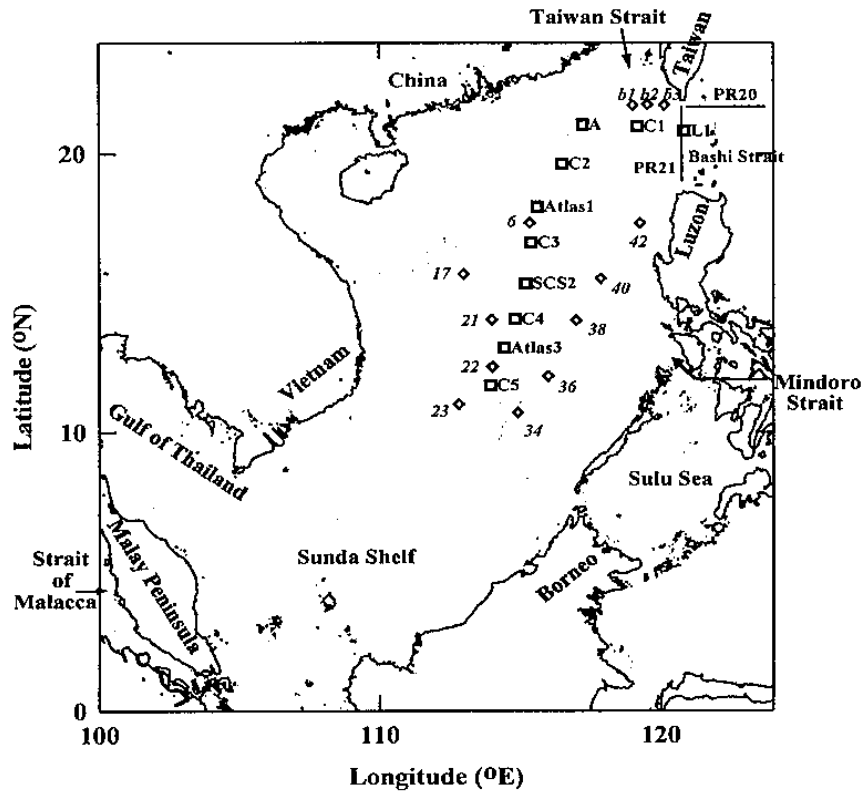


Fig. 1. Station locations and the WOCE PR 20 and PR 21 lines (Stations on these lines are not shown).

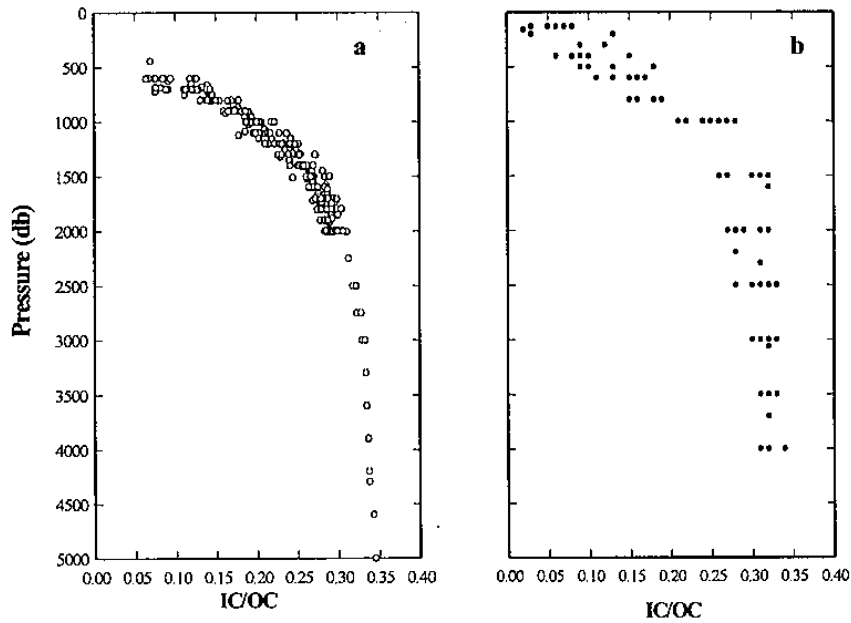


Fig. 2. The typical IC/OC profiles in (a) the West Philippine Sea and (b) the South China Sea.

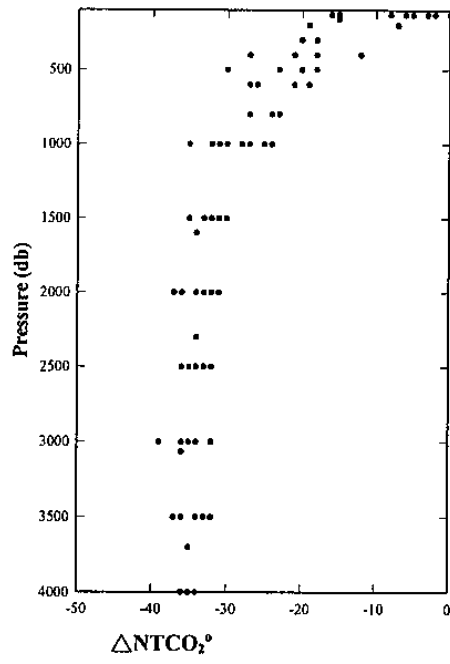


Fig. 3. Vertical distributions of $\Delta\text{NTCO}_2^\circ$ in the South China Sea.