

## 3.5 Dissolved inorganic carbon ( $C_T$ )

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### (2) Introduction

Concentrations of  $CO_2$  in the atmosphere are now increasing at a rate of  $1.5 \text{ ppmv y}^{-1}$  due to human activities such as burning of fossil fuels, deforestation, cement production, etc. It is an urgent task to estimate as accurately as possible the absorption capacity of the oceans against the increased atmospheric  $CO_2$ , and to clarify the mechanism of the  $CO_2$  absorption, because the magnitude of the predicted global warming depends on the levels of  $CO_2$  in the atmosphere, and because the ocean currently absorbs 1/3 of the 6 Gt of carbon emitted into the atmosphere each year by human activities.

In this cruise (BEAGLE), we were aimed at quantifying how much anthropogenic  $CO_2$  absorbed in the Southern Ocean, where intermediate and deep waters are formed, are transported and redistributed in the southern hemisphere subtropical oceans. For the purpose, we measured  $CO_2$ -system properties such as dissolved inorganic carbon ( $C_T$ ), total alkalinity ( $A_T$ ), pH and underway  $pCO_2$ .

In this section, we describe data on  $C_T$  obtained in the BEAGLE in detail.

### (3) Apparatus

Measurements of  $C_T$  were made with two total  $CO_2$  measuring systems (systems A and B; Nippon ANS,

Inc.), which are slightly different from each other. The systems comprise of a seawater dispensing system, a  $CO_2$  extraction system and a coulometer (Model 5012, UIC Inc.).

The seawater dispensing system has an auto-sampler (6 ports), which takes seawater in a 300 ml borosilicate glass bottle and dispenses the seawater to a pipette of nominal 20 ml volume by a PC control. The pipette is kept at  $20 \text{ }^\circ\text{C}$  by a water jacket, in which water from a water bath set at  $20 \text{ }^\circ\text{C}$  is circulated.

$CO_2$  dissolved in a seawater sample is extracted in a stripping chamber of the  $CO_2$  extraction system by adding phosphoric acid (10 % v/v). The stripping chamber is approx. 25 cm long and has a fine frit at the bottom. To degas  $CO_2$  as quickly as possible, a heating wire kept at  $40 \text{ }^\circ\text{C}$  was rolled from the bottom to a 1/3 height of the stripping chamber. The acid is added to the stripping chamber from the bottom of the chamber by pressurizing an acid bottle for a given time to push out the right amount of acid. The pressurizing is made with nitrogen gas (99.9999 %). After the acid is transferred to the stripping chamber, a seawater sample kept in a pipette is introduced to the stripping chamber by the same method as in adding an acid. The seawater reacted with phosphoric acid is stripped of  $CO_2$  by bubbling the nitrogen gas through a fine frit at the bottom of the stripping chamber. The  $CO_2$  stripped in the stripping chamber is carried by the nitrogen gas (flow rates of  $130 \text{ ml min}^{-1}$  and  $140 \text{ ml min}^{-1}$  for the systems A and B, respectively) to the coulometer through a dehydrating module. For the system A, the module consists of two electric dehumidifiers (kept at  $1 - 2 \text{ }^\circ\text{C}$ ) and a chemical desiccant ( $Mg(ClO_4)_2$ ). For the system B, it consists of three electric dehumidifiers with a chemical desiccant.

### (4) Shipboard measurement

#### *Sampling*

All seawater samples were collected from depth with 12 liter Niskin bottles basically at every other stations. The seawater samples for  $C_T$  were taken with a plastic drawing tube (PFA tubing connected to silicone rubber tubing) into a 300 ml borosilicate glass bottle. The glass bottle was filled with seawater smoothly from the bottom following a rinse with a seawater of 2 full, bottle volumes. The glass bottle was closed by a stopper, which was fitted to the bottle mouth gravimetrically without additional force.

At a chemical laboratory on the ship, a headspace of approx. 1 % of the bottle volume was made by removing seawater using a plastic pipette. A saturated mercuric chloride of 100  $\mu\text{l}$  was added to poison seawater samples. The glass bottles were sealed with a greased (Apiezon M, M&I Materials Ltd) ground glass stopper and the clips were secured. The seawater samples were kept at 4 °C in a refrigerator until analysis. A few hours just before analysis, the seawater samples were kept at 20 °C in a water bath.

### *Analysis*

At the start of each leg, we calibrated the measuring systems by blank and 5 kinds of  $\text{Na}_2\text{CO}_3$  solutions (nominally 500, 1000, 1500, 2000, 2500  $\mu\text{mol/L}$ ). As it was empirically known that coulometers do not show a stable signal (low repeatability) with fresh (low absorption of carbon) coulometer solutions. Therefore we measured 2 %  $\text{CO}_2$  gas repeatedly until the measurements became stable. Then we started the calibration.

The measurement sequence such as system blank (phosphoric acid blank), 2 %  $\text{CO}_2$  gas in a nitrogen base, seawater samples (6) was programmed to repeat. The measurement of 2 %  $\text{CO}_2$  gas was made to monitor response of coulometer solutions (from UIC, Inc.). For every renewal of coulometer solutions, certified reference materials (CRM, batch 60) provided by Prof. A. G. Dickson of Scripps Institution of Oceanography were analyzed. In addition, reference materials (RM) provided by JAMSTEC (2 kinds) and KANSO were measured at the initial, intermediate and end times of a coulometer solution's lifetime.

The preliminary values were reported in a data sheet on the ship. Repeatability and vertical profiles of  $C_T$  based on raw data for each station helped us check performances of the measuring systems.

In each leg, we finished all the analyses for  $C_T$  on board the ship. As we used two systems, we had not encountered such a situation as we had to abandon the measurement. However, we experienced some malfunctions of the measuring systems during the cruise, which are described in the followings:

In the leg 1, due to malfunction of the coulometer of the system B, we replaced it to a back-up coulometer;

There occurred lowering of repeatability, mostly due to dirt. This situation was recovered by cleaning the measuring systems;

The "undershooting" of coulometer detection was often found. This happened in measuring seawater samples subsequent to the measurement of phosphoric acid blank. To avoid the "undershooting" occurred in seawater sample measurement, we measured a dummy seawater sample subsequent to the blank measurement.

### **(5) Quality control**

#### *Leg 1*

Calibration factors of the systems A and B were listed in Table 3.5.1. With these factors, we calculated  $C_T$  of CRM (batch 60), and plotted the values as a function of sequential day (Fig. 3.5.1). From Fig. 3.5.1, it is found that there were no trends of CRM measurements for the system A during the leg 1. The average and standard deviation were 1991.0 and 1.5  $\mu\text{mol kg}^{-1}$  ( $n = 40$ ), respectively. Since the certified value of the batch 60 is 1991.24  $\mu\text{mol kg}^{-1}$ , very close to the average, it implies that the measurement had been conducted in a good condition.

For the system B, however, we had to replace the coulometer with a back-up one, because repeatability for the system B had been worse (3.0  $\mu\text{mol kg}^{-1}$  for CRM measurements) than usually expected value ( $\sim 1.5 \mu\text{mol kg}^{-1}$ ). Before and after the replacement, the calibration factor changed largely from 0.31322 to 0.31644 (Table 3.5.1). This change of a calibration factor caused CRM measurements to be  $2011.7 \pm 1.5 \mu\text{mol kg}^{-1}$ , which were 1991.9  $\mu\text{mol kg}^{-1}$  before the replacement.

Based on the results of CRM measurements stated above, we re-calculated the calibration factors so that measurements of seawater samples become traceable to the certified value of batch 60. For example, the initial factor of 0.31322 for the system A became 0.31333 by such a calculation as  $0.31322/(1990.24/1991.0)$ .

Temporal variations of RM measurements are shown in Fig. 3.5.2. From Fig. 3.5.2, it is evident that RM measurements included a linear trend, implying that measurements of seawater samples also have the trend. The trend was also found in temporal changes of 2 %  $\text{CO}_2$  gas measurements. The trend seems to be due to "cell age" change (Johnson et al., 1998) of a coulometer solution.

Considering the trends, we adjusted measurements of seawater samples so as to be traceable to the certified

value of batch 60, although the adjustments were usually slight.

Finally we surveyed vertical profiles of  $C_T$ . In particular, we examined whether systematic differences between measurements of the systems A and B existed or not. Then taking other information of analyses into account, we determined a flag of each value of  $C_T$ .

The average and standard deviation of absolute values of differences of  $C_T$  analyzed consecutively were 1.5 and  $1.3 \mu\text{mol kg}^{-1}$  ( $n = 203$ ), respectively.

#### *Leg 2*

Calibration factors of the systems A and B for the leg 2 are listed in Table 3.5.1, and temporal variations of CRM  $C_T$  are shown in Fig. 3.5.3.

From Fig. 3.5.3, it is found that the CRM  $C_T$  for the system A changes discontinuously at the 268th sequential day. In the former period, no trends are found, while in the latter period, a significant trend exists. We do not know the causes of this discontinuity and the subsequent trend. For the system B, no such a variation of CRM  $C_T$  is found (Fig. 3.5.3).

The average and standard deviation of CRM  $C_T$  in the former period (before the 268 sequential day) for the system A were calculated to be 1990.9 and  $1.2 \mu\text{mol kg}^{-1}$  ( $n = 16$ ), respectively. Those in the latter period were 1990.7 and  $1.4 \mu\text{mol kg}^{-1}$  ( $n = 20$ ), respectively. For the system B, the average and standard deviation were 1994.1 and  $1.9 \mu\text{mol kg}^{-1}$  ( $n = 34$ ), respectively.

Based on the information of CRM  $C_T$  stated above, we re-calculated the calibration factors as made for the leg 1, considering the trend.

Based on RM measurements, we adjusted the trend of  $C_T$  of seawater samples as conducted for the data on leg 1. Then, we checked the vertical profiles of  $C_T$ , and determined a flag of each  $C_T$  value.

The average and standard deviation of absolute values of differences of  $C_T$  analyzed consecutively were 1.5 and  $1.4 \mu\text{mol kg}^{-1}$  ( $n = 188$ ), respectively.

#### *Leg 4*

Calibration factors of the systems A and B for the leg 4 are listed in Table 3.5.1, and temporal variations of CRM  $C_T$  are shown in Fig. 3.5.4.

From Fig. 3.5.4, it is found that there existed no trends for the system A, but a slight decreasing trend for the system B, which was not significant statistically.

The average and standard deviation of CRM  $C_T$  for the system A were 1988.2 and  $1.1 \mu\text{mol kg}^{-1}$  ( $n = 35$ ), respectively, while those for the system B were 1998.6 and  $0.9 \mu\text{mol kg}^{-1}$  ( $n = 28$ ), respectively.

Based on the information of CRM  $C_T$  stated above, we re-calculated the calibration factors as made for the leg 1.

Based on RM measurements, we adjusted the trend of  $C_T$  of seawater samples as conducted for the data on leg 1. Then, we checked the vertical profiles of  $C_T$ , and determined a flag of each  $C_T$  value.

The average and standard deviation of absolute values of differences of  $C_T$  analyzed consecutively were 1.0 and  $0.8 \mu\text{mol kg}^{-1}$  ( $n = 166$ ), respectively.

#### *Leg 5*

Calibration factors of the systems A and B for the leg 5 are listed in Table 3.5.1, and temporal variations of CRM  $C_T$  are shown in Fig. 3.5.5. From this figure, it is found that for both the systems, the CRM  $C_T$ s show statistically significant increasing trends, but in a discontinuous manner. Therefore we divided the time series into the two periods. Then we calculated the averages and standard deviations of each period separately.

The average and standard deviation of CRM  $C_T$  for the former period (before the 367th sequential day) of the system A were 1989.7 and  $1.3 \mu\text{mol kg}^{-1}$  ( $n = 25$ ), respectively, while those for the latter period were 1990.1 and  $1.0 \mu\text{mol kg}^{-1}$  ( $n = 17$ ), respectively. For the system B, the average and standard deviation for the former period (before 377th sequential day) were 1988.6 and  $0.9 \mu\text{mol kg}^{-1}$  ( $n = 29$ ), respectively, while those for the latter period were 1990.1 and  $0.5 \mu\text{mol kg}^{-1}$  ( $n = 6$ ), respectively.

Based on RM measurements, we adjusted the trend of  $C_T$  of seawater samples as conducted for the data on

leg 1. Then, we checked the vertical profiles of  $C_T$ , and determined a flag of each  $C_T$  value.

The average and standard deviation of absolute values of differences of  $C_T$  analyzed consecutively were 0.9 and  $0.7 \mu\text{mol kg}^{-1}$  ( $n = 229$ ), respectively.

### Reference

Johnson, K.M., A.G. Dickson, G. Eiseid, C. Goyet, P. Guenther, R.M. Key, F. J. Millero, D. Purkerson, C.L.

Sabine, R.G. Schottle, D.W.R. Wallace, R.J. Wilke and C.D. Winn (1998): Coulometric total carbon dioxide analysis for marine studies: assessment of the quality of total inorganic carbon measurements made during the US Indian Ocean  $\text{CO}_2$  survey 1994-1996, Mar. Chem., 63, 21-37.

Table 3.5.1. Calibration factors determined from  $\text{Na}_2\text{CO}_3$  solutions.

Leg no.	Calibration factors		Remarks
	A	B	
1	0.31322	0.31322	Replacement of coulometer was conducted for the system B.
		0.31644	
2	0.31281	0.31589	
4	0.31399	0.30895	
5	0.31398	0.31140	

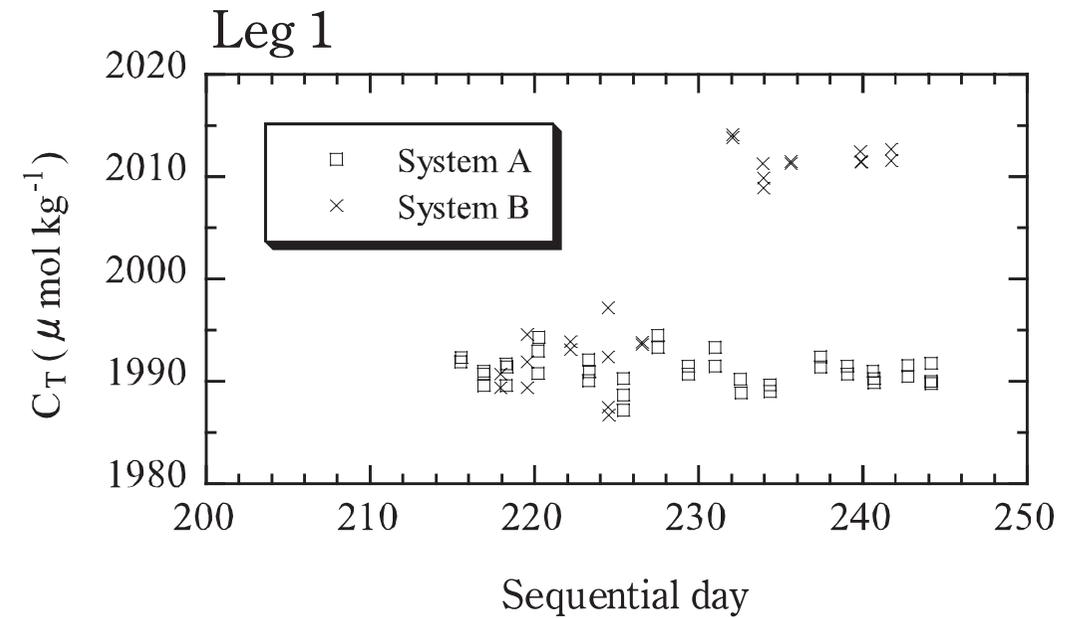


Figure 3.5.1. Temporal variations of CRM  $C_T$  measured by the systems A and B in the leg 1.

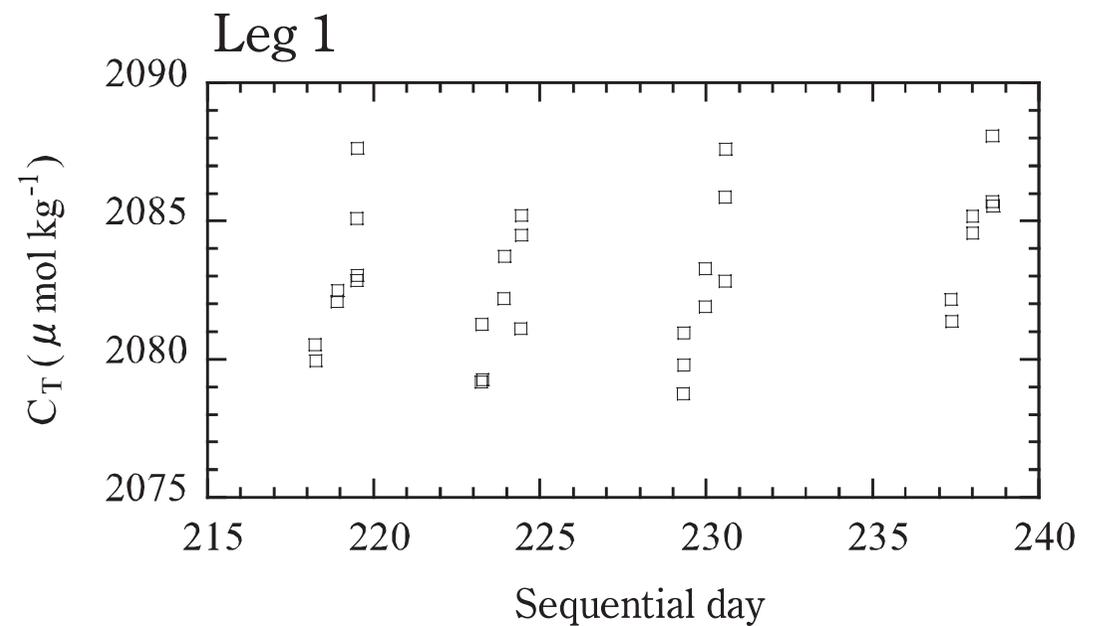


Figure 3.5.2. An example of temporal variations of RM  $C_T$ .

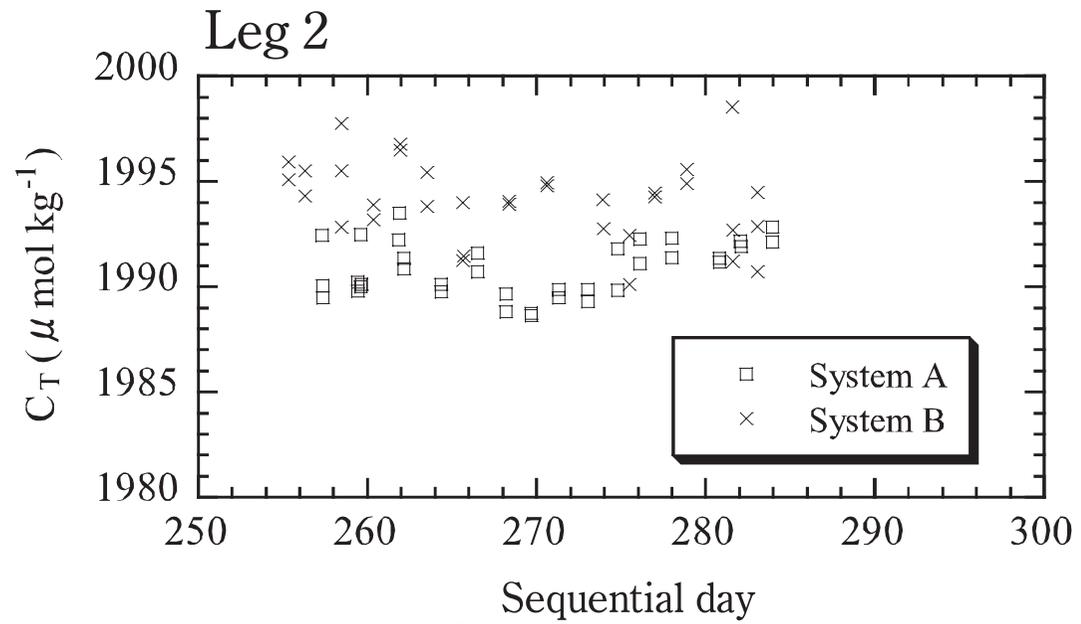


Figure 3.5.3. Temporal variations of CRM  $C_T$  measured by the systems A and B in the leg 2.

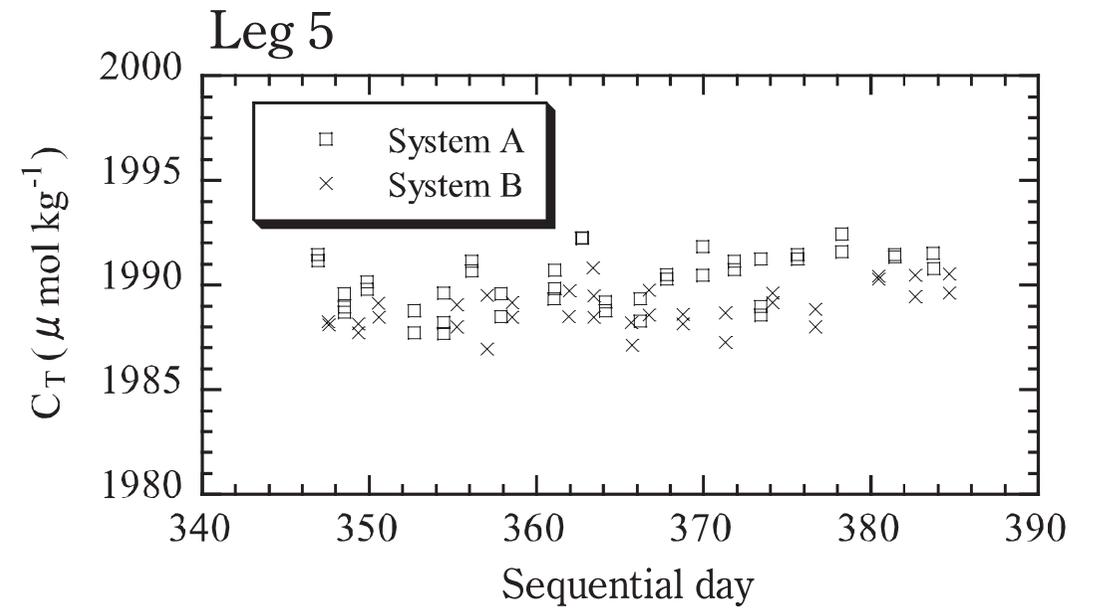


Figure 3.5.5. Temporal variations of CRM  $C_T$  measured by the systems A and B in the leg 5.

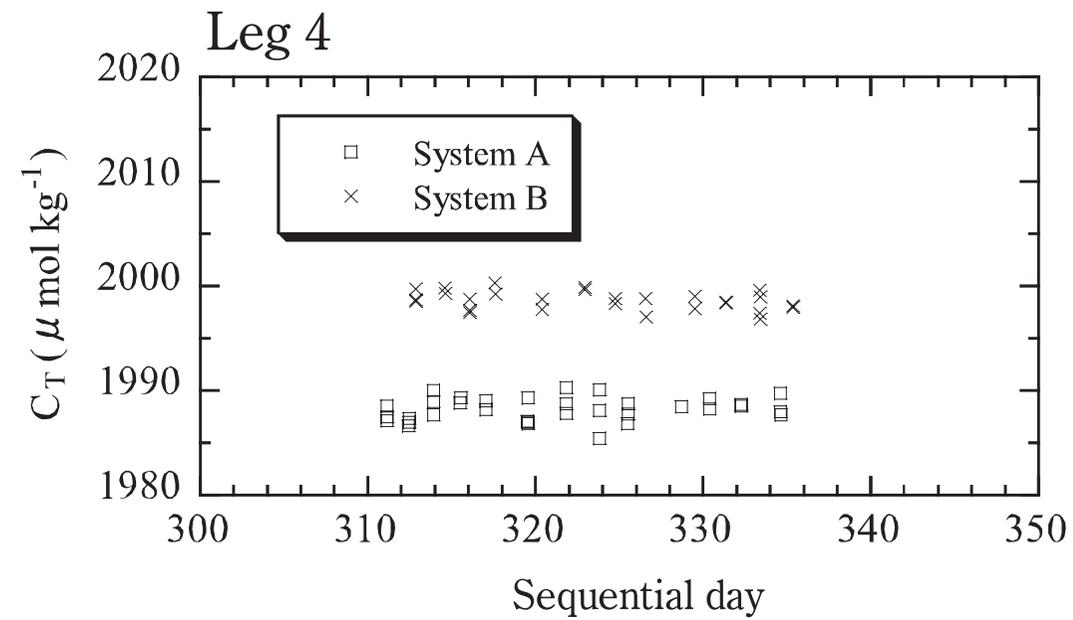


Figure 3.5.4. Temporal variations of CRM  $C_T$  measured by the systems A and B in the leg 4.

## 3.6 Total alkalinity ( $A_T$ )

3 February 2005

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### (2) Introduction

Concentrations of  $\text{CO}_2$  in the atmosphere are now increasing at a rate of  $1.5 \text{ ppmv y}^{-1}$  due to human activities such as burning of fossil fuels, deforestation, cement production, etc. It is an urgent task to estimate as accurately as possible the absorption capacity of the oceans against the increased atmospheric  $\text{CO}_2$ , and to clarify the mechanism of the  $\text{CO}_2$  absorption, because the magnitude of the predicted global warming depends on the levels of  $\text{CO}_2$  in the atmosphere, and because the ocean currently absorbs 1/3 of the 6 Gt of carbon emitted into the atmosphere each year by human activities.

In the BEAGLE, we were aimed at quantifying how much anthropogenic  $\text{CO}_2$  absorbed in the Southern Ocean, where intermediate and deep waters are formed, are transported and redistributed in the southern hemisphere subtropical oceans. For the purpose, we measured  $\text{CO}_2$ -system properties such as dissolved inorganic carbon ( $C_T$ ), total alkalinity ( $A_T$ ), pH and underway  $\text{pCO}_2$ .

In this section, we describe data on  $A_T$  obtained in the BEAGLE in detail.

### (3) Apparatus

The measuring system for  $A_T$  (customized by Nippon ANS, Inc.) comprises of a water dispensing unit with an auto-sampler (6 ports), an auto-burette (Metrohm) and a pH meter (Thermo Orion). They are automatically controlled by a PC. We prepared two systems for the BEAGLE, but a single system was enough

for the measurement except for the leg 1, because the system could perform a high speed titration (5-6 min.).

Combined electrodes (Model 8103BN ROSS™) were used through the cruise.

A seawater of approx. 40 ml is transferred from a sample bottle (borosilicate glass bottle; 130 ml) into a water-jacketed (25 °C) pipette by pressurized  $\text{N}_2$  gas, and is introduced into a water-jacketed (25 °C) titration cell. Next, a given volume of a titrant is injected into the titration cell so that pH of a seawater sample becomes 4.5 – 4.0. The seawater sample mixed with the titrant is stirred for three minutes by a stirring chip. Then an aliquot of titrant ( $\sim 0.1$  ml) is added consecutively until pH or e.m.f. reaches a given value. The concentration of the acid titrant is nominally 0.05 M HCl in 0.65 M NaCl.

Calculation of  $A_T$  is made based on a modified Gran approach.

### (4) Shipboard measurement

#### *Sampling*

All seawater samples were collected from depth using 12 liter Niskin bottles basically at every other stations. The seawater samples for  $A_T$  were taken with a plastic drawing tube (PFA tubing connected to silicone rubber tubing) into borosilicate glass bottles of 130 ml. The glass bottle was filled with seawater smoothly from the bottom after rinsing it with a seawater of half a or a full bottle volume. A few hours before analysis, the seawater samples were kept at 25 °C in a water bath.

#### *Analysis*

For the  $A_T$  measurement, we selected electrodes, which showed signals close to theoretical Nernstian behavior.

At the start of each leg, we conducted calibration of the acid titrant, which was prepared on land. The calibration was made by measuring  $A_T$  of 5 solutions of  $\text{Na}_2\text{CO}_3$  in 0.7 M NaCl solutions (nominally 0, 100, 1000, 2000 and 2500  $\mu\text{mol kg}^{-1}$ ). The measured values of  $A_T$  (calculated by assuming 0.05 M acid titrant) should be a linear function of the  $A_T$  computed from concentrations of the  $\text{Na}_2\text{CO}_3$  solutions. The linear function was fitted by

the method of least squares. Theoretically, the slope of the linear function should be unity. If the measured slope is not equal to one, the acid normality should be adjusted by dividing initial normality by the slope, and the whole set of calculations is repeated until the slope = 1.

Before starting analyses of seawater samples, we measured  $A_T$  of dummy seawater samples to confirm a condition of the measuring systems. If repeat measurements of  $A_T$  were constant within  $\sim 3 \mu\text{mol kg}^{-1}$ , we initiated measurement of seawater samples. We analyzed reference materials (RM), which were produced for  $C_T$  by JAMSTEC and KANSO, but were efficient also for the monitor of  $A_T$  measurement. In addition, certified reference materials (CRM, batch 60, certified value =  $2199.55 \mu\text{mol kg}^{-1}$ ) were also analyzed periodically to monitor systematic differences of measured  $A_T$ .

The preliminary values were reported in a data sheet on the ship. Repeatability calculated from replicate samples and vertical profiles of  $A_T$  based on raw data for each station helped us check performances of the measuring systems.

In each leg, we finished all the analyses for  $A_T$  on board the ship. We did not encounter so serious a problem as we had to give up the analyses. However, we experienced some malfunction of the system during the cruise, which are listed in the followings:

Small bubbles were often found in a pipette, probably due to stagnation of a seawater flow in the joint at an inlet of a pipette. In this case, we re-sealed the joint properly;

After analyses of a large number of samples, we often experienced a drift of an electrode, which appeared as differences of pH or e.m.f. in spite of an injection of a constant volume of an acid titrant into a seawater sample of almost a same  $A_T$ . In this case, we changed ranges of pH or e.m.f. used for the determination of  $A_T$ .

## (5) Quality control

### *Leg 1*

We used two systems (systems A and B) in this leg, but about 2/3 of the all the samples were analyzed by the system A.

Temporal variations of CRM  $A_T$  are displayed in Fig. 3.6.1. From this figure, it is found that for both the systems, such characteristic patterns as trend, discontinuity, etc. do not exist in the variations. Therefore, we re-calculated  $A_T$  of seawater samples using the concentration of HCl, which was re-calculated from the average of measured CRM  $A_T$  and the certified value of CRM  $A_T$ .

We surveyed vertical profiles of  $A_T$ . In particular, we examined whether systematic differences between measurements of the systems A and B existed or not. Then taking other information of analyses into account, we determined a flag of each value of  $A_T$ .

The average and standard deviation of absolute values of differences of  $A_T$  analyzed consecutively were 2.2 and  $1.8 \mu\text{mol kg}^{-1}$  ( $n = 188$ ), respectively.

We compared  $A_T$  measured in the BEAGLE with  $A_T$  calculated from  $C_T$  and  $p\text{CO}_2$  measured in the WOCE P6 (Fig. 3.6.5). We judged that differences of  $A_T$  between the two observation periods are due to analytical errors, because the differences are also found in the deep layer.

### *Leg 2*

We analyzed all seawater samples by the system B.

Temporal variations of CRM  $A_T$  are displayed in Fig. 3.6.2. From this figure, it is found that there exists a decreasing trend of  $A_T$ . In addition, we also found some gaps of measured  $A_T$ , when we examined the vertical profiles of  $A_T$ . Considering these results, we decided to calculate averages of CRM  $A_T$  separating the data into three periods. Since in the first period (before the 270th sequential day, Fig. 3.6.2), the  $A_T$  includes a decreasing trend, we determined the values of CRM  $A_T$  at each sequential day of measurements of seawater samples considering the trend. Then we determined concentration of HCl from the corrected values of CRM  $A_T$  and the certified value of CRM  $A_T$ .

We surveyed vertical profiles of  $A_T$ . Then taking other information of analyses into account, we determined a flag of each value of  $A_T$ .

The average and standard deviation of absolute values of differences of  $A_T$  analyzed consecutively were 2.5

and  $2.0 \mu\text{mol kg}^{-1}$  ( $n = 168$ ), respectively.

We compared  $A_T$  measured in the BEAGLE with  $A_T$  calculated from  $C_T$  and  $p\text{CO}_2$  measured in the WOCE P6 (Fig. 3.6.5). We judged that differences of  $A_T$  ( $5 - 10 \mu\text{mol kg}^{-1}$ ) between the two observation periods are due to analytical errors, because the differences are also found in the deep layer.

#### *Leg 4*

We analyzed all seawater samples by the system B.

Temporal variations of CRM  $A_T$  are displayed in Fig. 3.6.3. From this figure, it is found that there exists a discontinuous change of  $A_T$ . That is, before the 320 sequential day, the  $A_T$  shows a decreasing trend, but after the day, the  $A_T$  displays a stationary variation. From this characteristics of temporal variation, we re-calculated concentrations of HCl, separating the data for CRM  $A_T$  into two periods, as conducted in the quality control for the leg 2.

We surveyed vertical profiles of  $A_T$ . Then taking other information of analyses into account, we determined a flag of each value of  $A_T$ .

The average and standard deviation of absolute values of differences of  $A_T$  analyzed consecutively were  $2.2$  and  $1.7 \mu\text{mol kg}^{-1}$  ( $n = 162$ ), respectively.

We compared  $A_T$  measured in the BEAGLE with  $A_T$  measured in the WOCE A10 (Fig. 3.6.6). We judged that differences of  $A_T$  ( $5 - 10 \mu\text{mol kg}^{-1}$ ) between the two observation periods are due to analytical errors, except for the upper layer. The differences in the upper layer might be related to seasonal differences.

#### *Leg 5*

We analyzed all seawater samples by the system B.

Temporal variations of CRM  $A_T$  are displayed in Fig. 3.6.4. The  $A_T$  shows a decreasing trend. Therefore, we reflected the trend in re-determining concentration of HCl, as conducted in the quality control for the leg 2.

We surveyed vertical profiles of  $A_T$ . Then taking other information of analyses into account, we determined

a flag of each value of  $A_T$ .

The average and standard deviation of absolute values of differences of  $A_T$  analyzed consecutively were  $2.0$  and  $1.8 \mu\text{mol kg}^{-1}$  ( $n = 220$ ), respectively.

We compared  $A_T$  measured in the BEAGLE with  $A_T$  measured in the WOCE I3 and I4 (Fig. 3.6.7). It is evident that  $A_T$ s obtained in the BEAGLE are systematically lower by  $5 - 10 \mu\text{mol kg}^{-1}$  than those in the WOCE. At present, we do not know the reason why such a difference occurs.

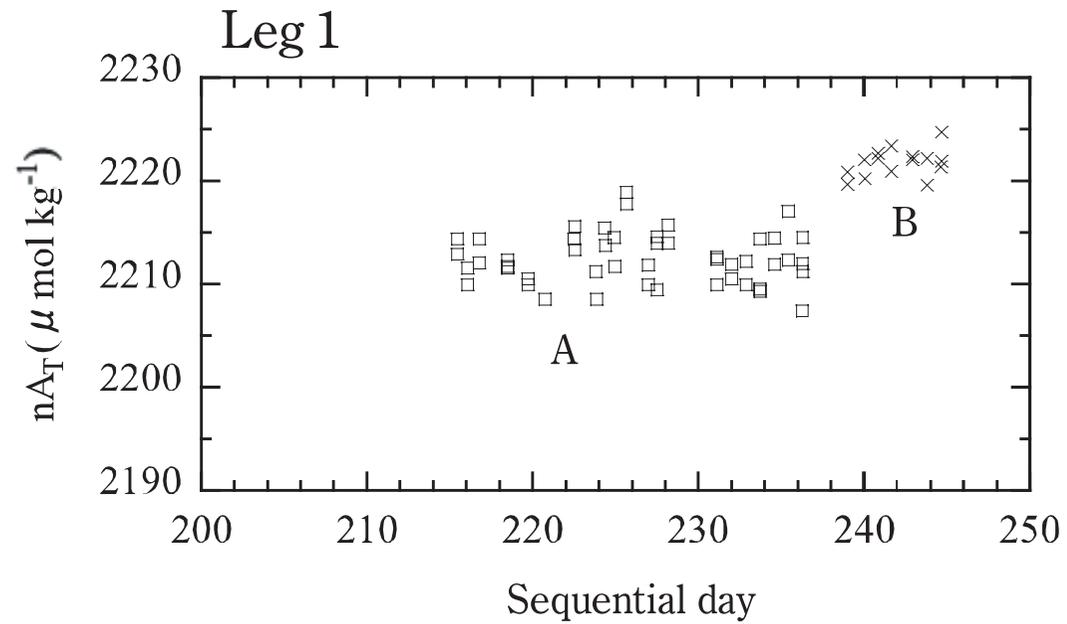


Figure 3.6.1. Temporal variations of CRM  $A_T$  measured in the leg 1. The sequential day is counted from 1 January, 2003. The "A" and "B" indicate results of the systems A and B, respectively.

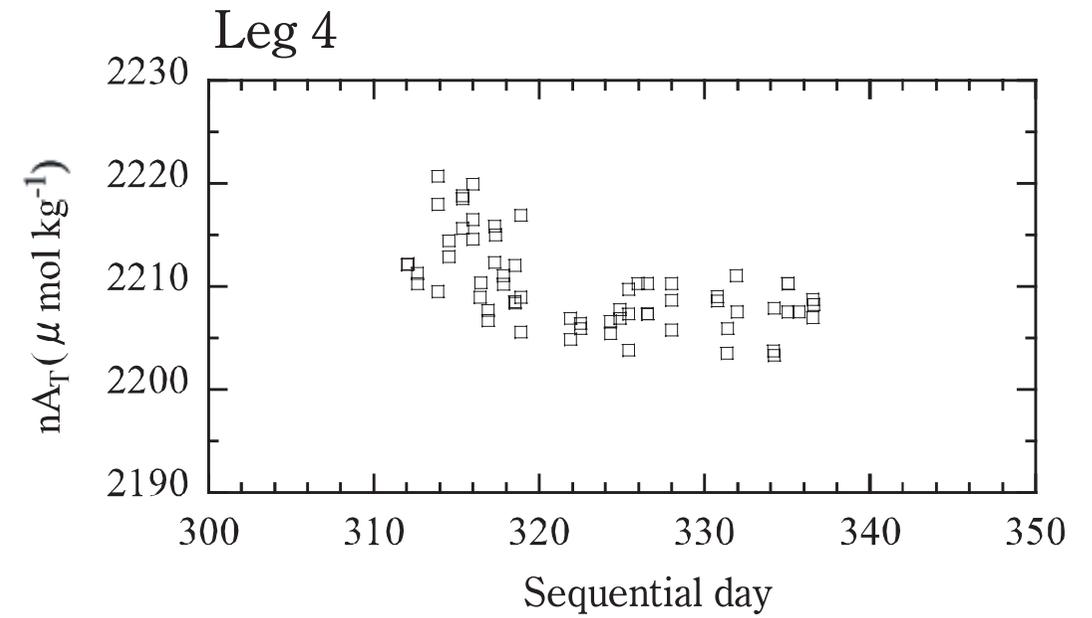


Figure 3.6.3. Temporal variations of CRM  $A_T$  measured in the leg 4.

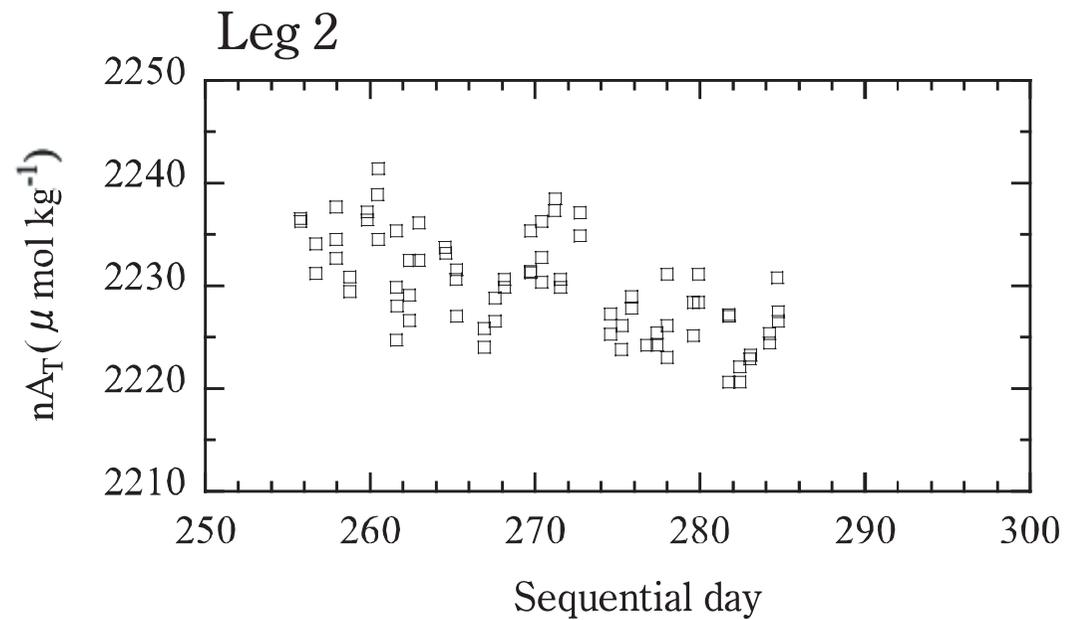


Figure 3.6.2. Temporal variations of CRM  $A_T$  measured in the leg 2.

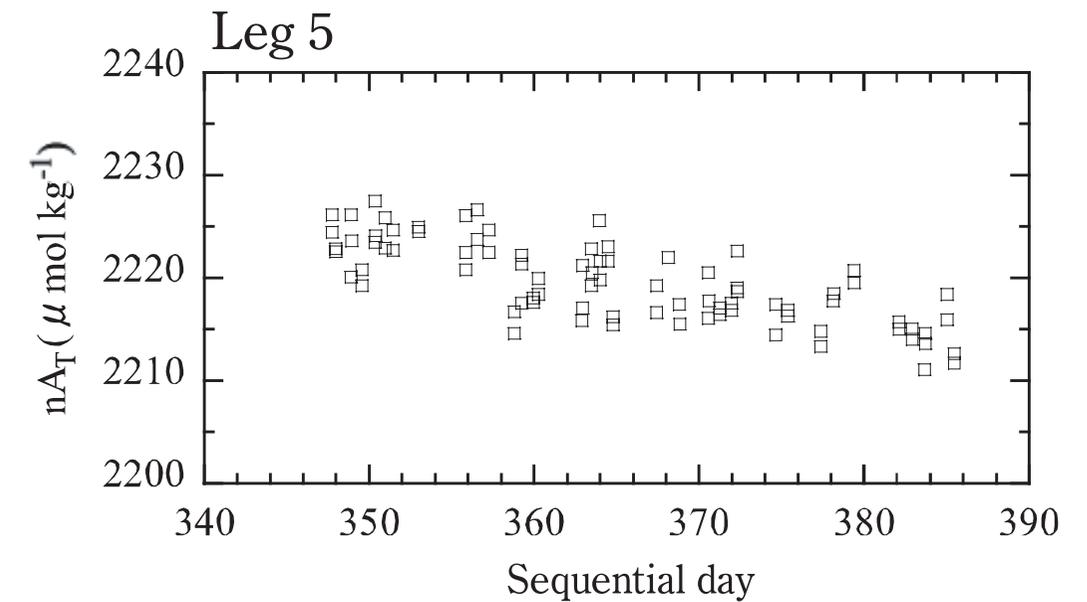


Figure 3.6.4. Temporal variations of CRM  $A_T$  measured in the leg 5.

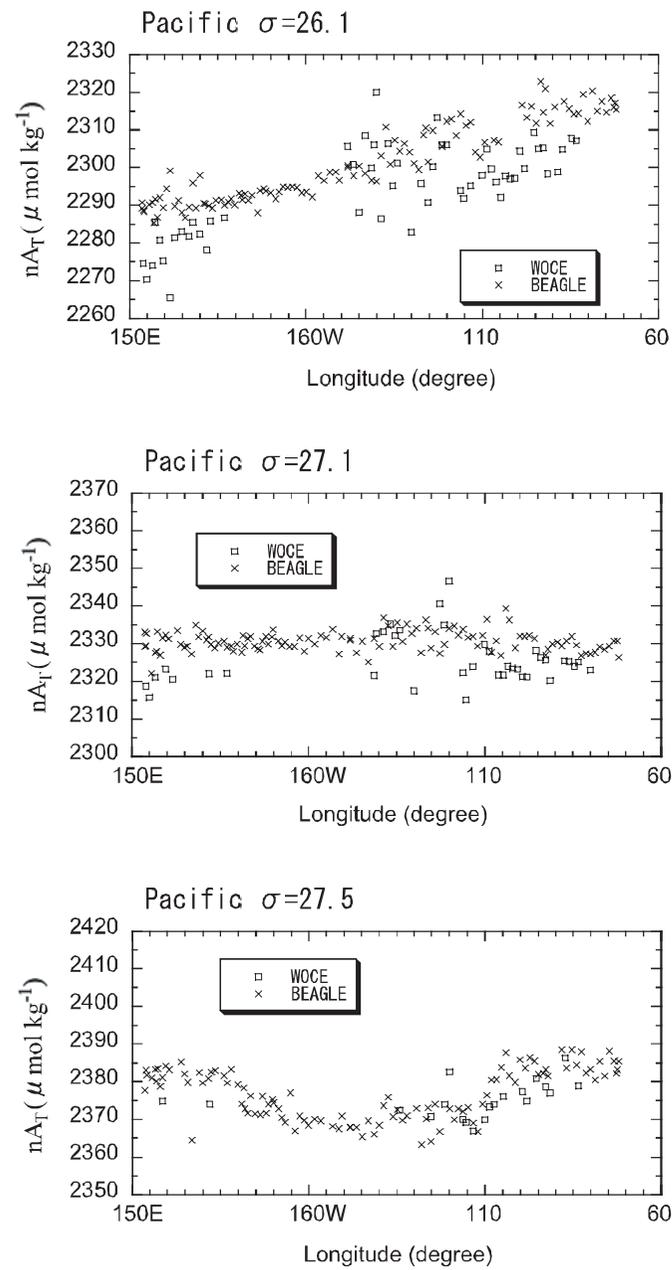


Figure 3.6.5. Comparisons of  $A_T$  measured in the BEAGLE with  $A_T$  calculated from  $C_T$  and  $p\text{CO}_2$  measured along the WOCE P6 on isopycnal surfaces of 26.1  $\sigma_0$  (top panel), 27.1  $\sigma_0$  (middle panel) and 27.5  $\sigma_0$  (bottom panel).

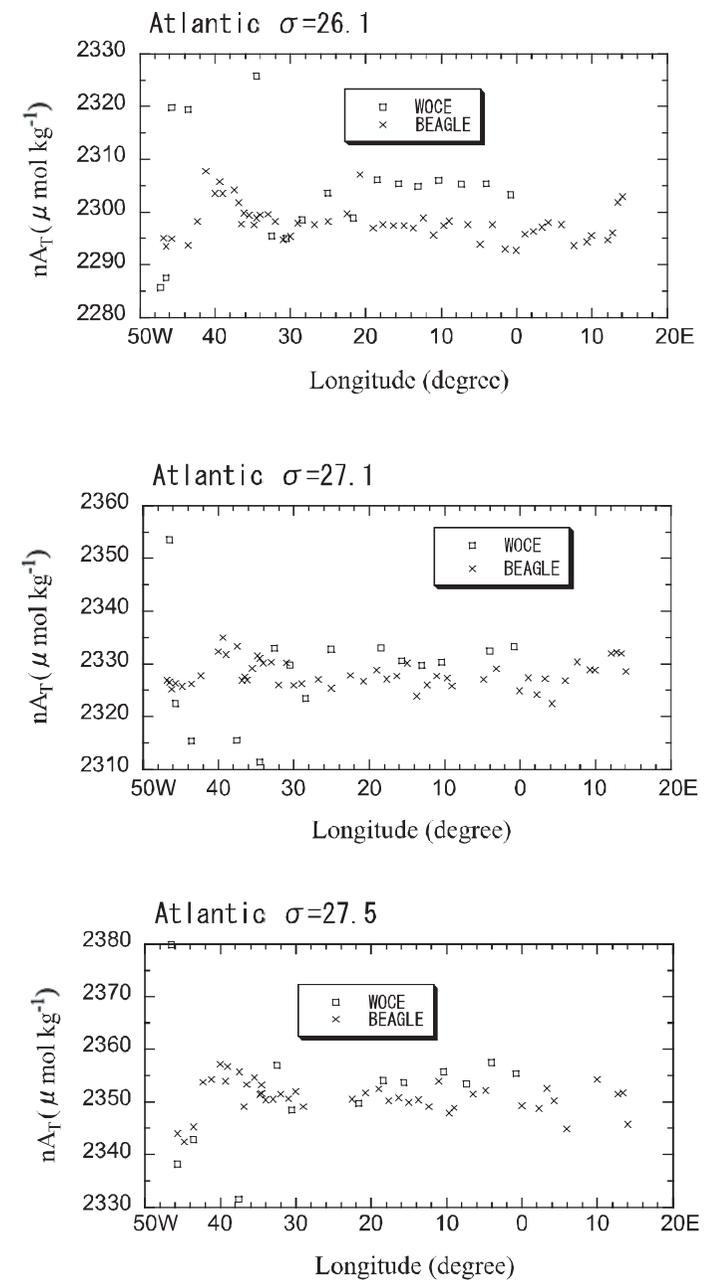


Figure 3.6.6. Comparisons of  $A_T$  measured in the BEAGLE with  $A_T$  calculated from  $C_T$  and  $p\text{CO}_2$  measured along the WOCE A10 on isopycnal surfaces of 26.1  $\sigma_0$  (top panel), 27.1  $\sigma_0$  (middle panel) and 27.5  $\sigma_0$  (bottom panel).

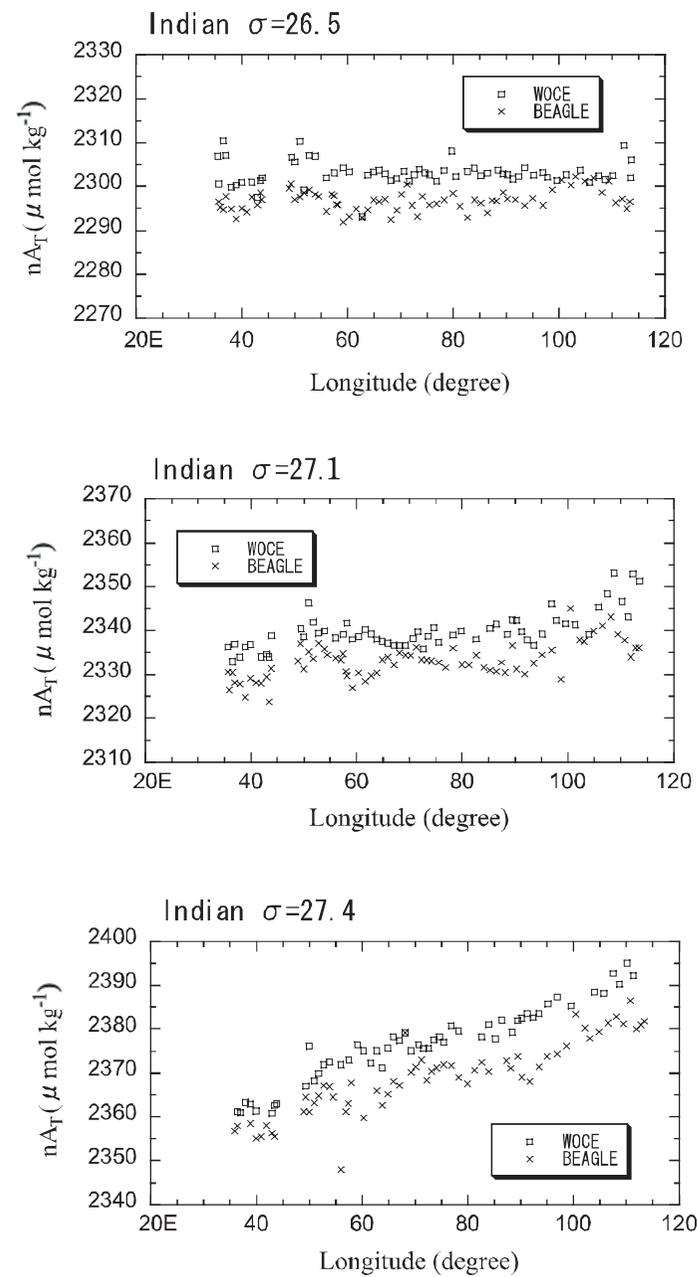


Figure 3.6.7. Comparisons of  $A_T$  measured in the BEAGLE with  $A_T$  calculated from  $C_T$  and  $p\text{CO}_2$  measured along the WOCE I3/14 on isopycnal surfaces of  $26.1 \sigma_\theta$  (top panel),  $27.1 \sigma_\theta$  (middle panel) and  $27.5 \sigma_\theta$  (bottom panel).

## 3.7 pH

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### (2) Introduction

Concentrations of CO<sub>2</sub> in the atmosphere are now increasing at a rate of 1.5 ppmv y<sup>-1</sup> due to human activities such as burning of fossil fuels, deforestation, cement production, etc. It is an urgent task to estimate as accurately as possible the absorption capacity of the oceans against the increased atmospheric CO<sub>2</sub>, and to clarify the mechanism of the CO<sub>2</sub> absorption, because the magnitude of the predicted global warming depends on the levels of CO<sub>2</sub> in the atmosphere, and because the ocean currently absorbs 1/3 of the 6 Gt of carbon emitted into the atmosphere each year by human activities.

In the BEAGLE, we were aimed at quantifying how much anthropogenic CO<sub>2</sub> absorbed in the Southern Ocean, where intermediate and deep waters are formed, are transported and redistributed in the southern hemisphere subtropical oceans. For the purpose, we measured CO<sub>2</sub>-system properties such as dissolved inorganic carbon (C<sub>T</sub>), total alkalinity (A<sub>T</sub>), pH and underway pCO<sub>2</sub>.

In this section, we describe data on pH obtained in the BEAGLE in detail.

### (3) Apparatus

Measurement of pH was made by a pH measuring system (Nippon ANS, Inc.), which adopts a method of the spectrophotometric determination. The measuring system comprises of a water dispensing unit with an auto-sampler and a spectrophotometer (Carry 50 Scan, Varian).

Seawater is transferred from borosilicate glass bottle (300 ml) to a sample cell in the spectrophotometer. The length and volume of the cell are 8 cm and 13 ml, respectively, and the sample cell is kept at 25.00 ± 0.05 °C in a thermostatic compartment. First, absorbance of seawater is measured at three wavelengths (730, 578 and 434 nm). Then an indicator solution is injected and circulated for about 4 minutes to mix the indicator solution and seawater sufficiently by a peristaltic pump. After the pump is stopped, the absorbance of seawater + indicator solution is measured at the three wavelengths. The pH is calculated based on the following equation (Clayton and Byrne, 1993):

$$pH = pK_2 + \log \left( \frac{A_1 / A_2 - 0.00691}{2.2220 - 0.1331(A_1 / A_2)} \right), \quad (1)$$

where A<sub>1</sub> and A<sub>2</sub> indicate absorbance at 578 and 434 nm, respectively, and pK<sub>2</sub> is calculated as a function of water temperature and salinity.

### (4) Shipboard measurement

#### Sampling

All seawater samples were collected from depth with 12 liter Niskin bottles basically at every other stations. The seawater samples for pH were taken with a plastic drawing tube (PFA tubing connected to silicone rubber tubing) into a 300 ml borosilicate glass bottle, which is the same as used for C<sub>T</sub> sampling. The glass bottle was filled with seawater smoothly from the bottom following a rinse with a sea water of 2 full, bottle volumes. The glass bottle was closed by a stopper, which was fitted to the bottle mouth gravimetrically without additional force.

We analyzed seawater samples as soon as possible within half a day.

#### Analysis

For an indicator solution, m-cresol purple (2 mM) was used. NaCl was added to the indicator solution so that

the solution had a density close to seawater. The indicator solution was produced on board the ship, and retained in a 1000 ml DURAN® laboratory bottle. To minimize absorption of CO<sub>2</sub> in an indicator solution, a holder of soda lime was attached. We renewed an indicator solution periodically when the headspace of the bottle became large, and monitored pH or absorbance ratio of the indicator solution by another spectrophotometer (Carry 50 Scan, Varian) using a cell with a short path length of 0.5 mm. In most indicator solutions, the absorbance ratios were initially in the range 1.4 – 1.6, and decreased to 1.1.

It is difficult to mix seawater with an indicator solution sufficiently under no headspace condition. However, by circulating the mixed solution with a peristaltic pump and by increasing density of indicator solutions, a well-mixed condition came to be attained rather shortly, leading to a rapid stabilization of absorbance (Fig. 3.7.1). We renewed a TYGON® tube of a peristaltic pump periodically, when the tube deteriorated in an impaired condition.

Absorbance of seawater only and seawater + indicator solutions was measured 12 and 30 times, respectively, and the last five values of absorbance were used for the calculation of pH (Equation 1).

The preliminary values of pH were reported in a data sheet on the ship. Repeatability calculated from replicate samples and vertical profiles of pH based on raw data for each station helped us check performance of the measuring system.

In each leg, we finished all the analyses for pH on board the ship. We did not encounter so serious a problem as we had to give up the analyses. However, we sometimes experienced malfunction of the system during the cruise:

The difference between absorbance of seawater only and absorbance of seawater + indicator solution was infrequently greater than ± 0.001. This implies dirt of the cell. In this case, we cleaned or replaced the cell.

#### (5) Quality control

It is recommended that correction for pH change resulting from addition of indicator solutions is made (DOE, 1994). To check the perturbation of pH due to the addition, we measured absorbance ratios by changing

the volume of indicator solutions added to a same seawater sample. We corrected absorbance ratios based on an empirical method (DOE, 1994).

We surveyed vertical profiles of pH. In particular, we examined whether systematic differences between before and after the renewal of indicator solutions existed or not. Then taking other information of analyses into account, we determined a flag of each value of pH.

The average and standard deviation of absolute values of differences of pH analyzed consecutively are listed in Table 3.7.1.

#### References

Clayton, T.D. and R.H. Byrne (1993): Spectrophotometric seawater pH measurements: total hydrogen ion concentration scale calibration of m-cresol purple and at-sea results. *Deep-Sea Research* 40, 2115-2129.  
 DOE (1994): Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water, version 2, A. G. Dickson & C. Goyet, eds. (unpublished manuscript).

Table 3.7.1. Averages and standard deviations (s.t.d.) of absolute values differences of pH analyzed consecutively, separately for legs 1, 2, 4 and 5.

Leg no.	N	Average	s.t.d
1	140	0.0014	0.0017
2	176	0.0017	0.0014
4	155	0.0010	0.0009
5	208	0.0008	0.0007

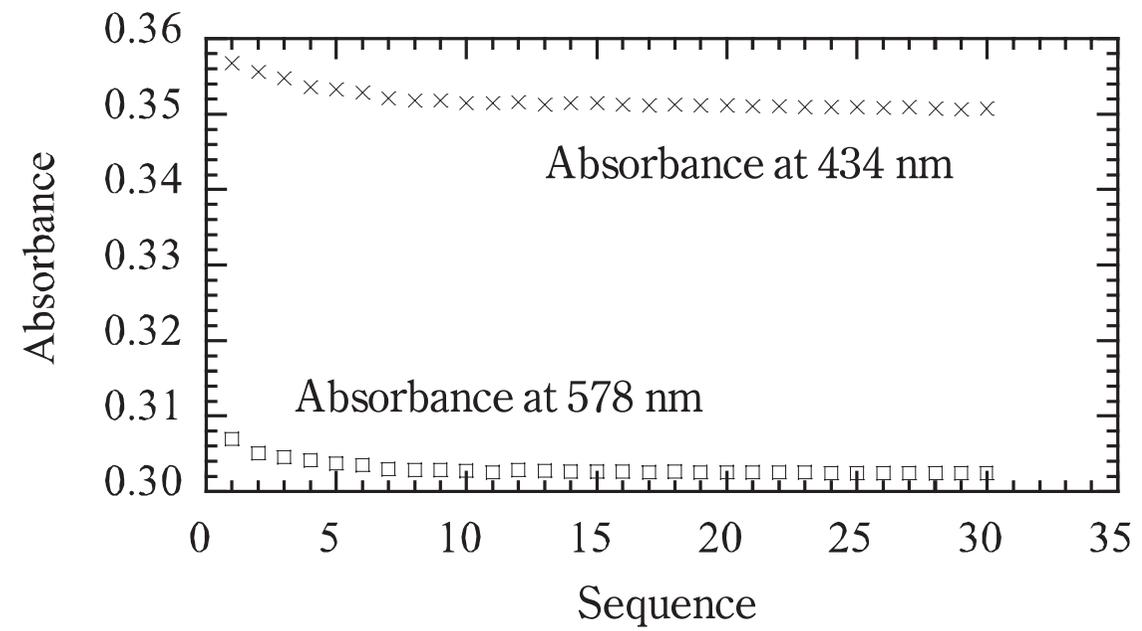


Figure 3.7.1. An example of temporal changes of absorbances. A unit of sequence corresponds to about 5 seconds.