



## Large accumulation of anthropogenic CO<sub>2</sub> in the East (Japan) Sea and its significant impact on carbonate chemistry

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Received 19 December 2005; revised 10 July 2006; accepted 26 July 2006; published 22 November 2006.

[1] This paper reports on a basin-wide inventory of anthropogenic CO<sub>2</sub> in the East (Japan) Sea determined from high-quality alkalinity, chlorofluorocarbon, and nutrient data collected during a summertime survey in 1999 and total dissolved inorganic carbon data calculated from pH and alkalinity measurements. The data set comprises measurements from 203 hydrographic stations and covers most of the East Sea with the exception of the northwestern boundary region. Anthropogenic CO<sub>2</sub> concentrations are estimated by separating this value from total dissolved inorganic carbon using a tracer-based (chlorofluorocarbon) separation technique. Wintertime surface CFC-12 data collected in regions of deep water formation off Vladivostok, Russia, improve the accuracy of estimates of anthropogenic CO<sub>2</sub> concentrations by providing improved air-sea CO<sub>2</sub> disequilibrium values for intermediate and deep waters. Our calculation yields a total anthropogenic CO<sub>2</sub> inventory in the East Sea of  $0.40 \pm 0.06$  petagrams of carbon as of 1999. Anthropogenic CO<sub>2</sub> has already reached the bottom of the East Sea, largely owing to the effective transport of anthropogenic CO<sub>2</sub> from the surface to the ocean interior via deep water formation in the waters off Vladivostok. The highest specific column inventory (vertically integrated inventory per square meter) of anthropogenic CO<sub>2</sub> of  $80 \text{ mol C m}^{-2}$  is found in the Japan Basin ( $40^{\circ}\text{N}$ – $44^{\circ}\text{N}$ ). Comparison of this inventory with those for other major basins of the same latitude band reveal that the East Sea values are much higher than the inventory for the Pacific Ocean ( $20$ – $30 \text{ mol C m}^{-2}$ ) and are similar to the inventory for the North Atlantic ( $66$ – $72 \text{ mol C m}^{-2}$ ). The substantial accumulation of anthropogenic CO<sub>2</sub> in the East Sea during the industrial era has caused the aragonite and calcite saturation horizons to move upward by  $80$ – $220 \text{ m}$  and  $500$ – $700 \text{ m}$ , respectively. These upward movements are approximately 5 times greater than those found in the North Pacific. Both the large accumulation of anthropogenic CO<sub>2</sub> and its significant impact on carbonate chemistry in the East Sea suggest that this sea is an important site for monitoring the future impact of the oceanic invasion of anthropogenic CO<sub>2</sub>.

**Citation:** Park, G.-H., K. Lee, P. Tishchenko, D.-H. Min, M. J. Warner, L. D. Talley, D.-J. Kang, and K.-R. Kim (2006), Large accumulation of anthropogenic CO<sub>2</sub> in the East (Japan) Sea and its significant impact on carbonate chemistry, *Global Biogeochem. Cycles*, 20, GB4013, doi:10.1029/2005GB002676.

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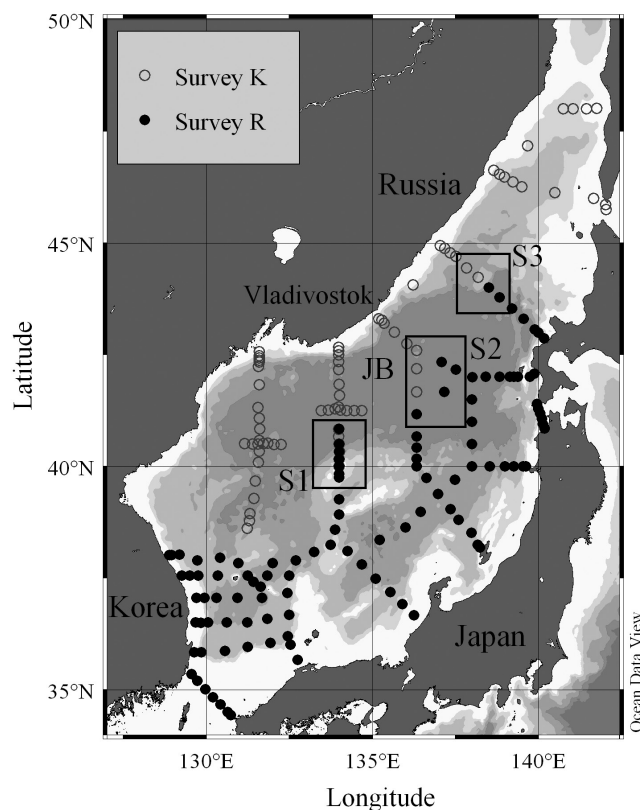
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### 1. Introduction

[2] Coastal and marginal seas potentially play an important role in absorbing atmospheric CO<sub>2</sub> because high inputs and an efficient use of nutrients from adjoining land result in a decrease in the surface water CO<sub>2</sub> concentration, which in turn drives CO<sub>2</sub> transfer from the atmosphere to the surface ocean. These seas also play a key role in the global carbon cycle by connecting terrestrial and oceanic carbon reservoirs [Tsunogai *et al.*, 1999; Thomas *et al.*, 2004]. Little attention has been devoted to the role of coastal and marginal seas as a sink of atmospheric CO<sub>2</sub> because these seas account for only 7% of the total area of the world ocean. As a result, only limited information is available regarding the amount of anthropogenic CO<sub>2</sub> stored in coastal and marginal seas and



**Figure 1.** Shaded topography map of the East Sea showing measurements sites. Data were collected by the Circulation Research of East Asian Marginal Seas project and U.S. Office of Naval Research’s Japan/East Sea Program from 24 June to 11 August 1999. Open circles represent sampling locations of Survey K conducted on the Russia *R/V Khromov*, while solid circles are sampling locations of Survey R conducted on the U.S. *R/V Roger Revelle*. JB indicates the Japan Basin. The three rectangular areas (S1–3) are discussed in Figure 2.

the mechanisms that underlie the transfer of atmospheric CO<sub>2</sub> to coastal and marginal seas and subsequently on to the open ocean.

[3] The East Sea is a marginal sea surrounded by Korea, Japan, and Russia, and is connected to the North Pacific via three straits with depths of less than 150 m. In early studies of the East Sea, Japanese investigators put forward the idea that waters deeper than ~300 m in this sea have uniform physical and chemical characteristics. This uniform water body was originally referred to as the Proper Water [Uda, 1934]; however, more recent investigations have revealed that this uniform water body can be further divided into three water masses, referred to as Central Water, Deep Water, and Bottom Water [Kim *et al.*, 1996; Kim and Kim, 1996]. A key physical feature of the East Sea is deep water formation at the continental shelf and slope off Vladivostok, Russia [Senjyu and Sudo, 1993; Kawamura and Wu, 1998; Kim *et al.*, 2002; Talley *et al.*, 2003]. Another unique feature of the East Sea is weak vertical stability compared to that in the open ocean; for example,

vertical variations in temperature and salinity found in the East Sea below the seasonal thermocline are one to two orders of magnitude smaller than those typically found in the Pacific Ocean [Kim and Kim, 1996; Kim *et al.*, 2001, 2002]. Both the deep water formation and weak vertical stability found in the East Sea lead to the formation of an active deep-convection system that vigorously transfers surface water loaded with anthropogenic CO<sub>2</sub> to the interior of the basin. On the basis of the features described above, the East Sea is potentially a significant reservoir for anthropogenic CO<sub>2</sub>.

[4] To verify this possibility, we applied a tracer-based separation technique [Gruber *et al.*, 1996] to CO<sub>2</sub> survey data collected from the East Sea. In the present paper, we report the basin-scale distribution of anthropogenic CO<sub>2</sub> in the East Sea and the effect of oceanic uptake of anthropogenic CO<sub>2</sub> on the saturation state of seawater with respect to biogenic calcium carbonate (CaCO<sub>3</sub>) particles.

## 2. Data and Calculation Methods

### 2.1. Survey Data

[5] The data used in the present study provide a dense coverage of the East Sea and were collected from 24 June to 11 August 1999 as part of the Circulation Research of East Asian Marginal Seas project and the U.S. Office of Naval Research’s Japan/East Sea Program. This field survey was jointly conducted by a multinational team of investigators from United States, Russia, and Korea. In the southern part of the East Sea, the survey (hereafter referred to as “Survey R”) was conducted on the U.S. *R/V Roger Revelle*, whereas in the northern part of the sea (referred to hereafter as “Survey K”) was carried out by Russian scientists on the Russia *R/V Professor Khromov* (Figure 1). A total of 203 hydrographic stations were established [Talley *et al.*, 2004]. Salinity, temperature, and nutrient concentrations were measured in all discrete samples, whereas concentrations of chlorofluorocarbons (CFC-11, CFC-12, and CFC-113) were determined in seawater samples collected from 110 of the 112 Survey R stations and 36 of the 91 Survey K stations. The precision of the chlorofluorocarbon measurements was about 0.005 pmol kg<sup>-1</sup> [Min and Warner, 2005].

[6] Total alkalinity (A<sub>T</sub>) and potentiometric pH were measured in nearly all discrete samples. The A<sub>T</sub> analysis followed Bruevich’s method, which utilizes colorimetric titration by hydrochloric acid in an open system using a mixed indicator (methylene blue and methyl red) [Bruevich, 1944]. The titrant concentration was monitored daily by titrating certified reference materials with known values of A<sub>T</sub> and total dissolved inorganic carbon (C<sub>T</sub>) (prepared and certified by A. Dickson of Scripps Institution of Oceanography, San Diego, California). The pH measurements were performed at 25°C in a potential cell without a liquid junction [Tishchenko *et al.*, 2001] and reported on the total scale, which considers the interaction of hydrogen ions with bisulfate ions [Hansson, 1973; Dickson, 1984]. To calculate C<sub>T</sub> from A<sub>T</sub> and pH measurements using the thermodynamic models, all pH values on the total hydro-

gen scale (pH<sub>T</sub>) were converted to the seawater scale (pH<sub>SWS</sub>) to be consistent with published dissociation constants of carbonic acid. The two scales are linked by the following equation:

$$\text{pH}_{\text{SWS}} = \text{pH}_{\text{T}} - \log \left\{ \frac{\left(1 + [\text{SO}_4^{2-}]_{\text{T}} / K_{\text{HSO}_4}\right) + [\text{F}]_{\text{T}} / K_{\text{HF}}}{\left(1 + [\text{SO}_4^{2-}]_{\text{T}} / K_{\text{HSO}_4}\right)} \right\}, \quad (1)$$

where  $[\text{SO}_4^{2-}]_{\text{T}}$  and  $[\text{F}]_{\text{T}}$  are the total concentrations of sulfate and fluoride in seawater, respectively, and  $K_{\text{HSO}_4}$  and  $K_{\text{HF}}$  are the dissociation constants of sulfate and hydrogen fluoride in seawater, respectively [Dickson and Riley, 1979].

[7] The measurement precisions were approximately  $\pm 4 \mu\text{mol kg}^{-1}$  for  $A_{\text{T}}$  and  $\pm 0.004$  units for pH [Talley et al., 2004]. The values of  $C_{\text{T}}$  used in the calculation of anthropogenic CO<sub>2</sub> concentration were calculated from  $A_{\text{T}}$  and pH measurements using the carbonic acid dissociation constants of Mehrbach et al. [1973] as refitted by Dickson and Millero [1987]. This set of carbonic acid dissociation constants provides the best correlation with global carbon measurements [Lee et al., 2000; Millero et al., 2002]; however, Talley et al. [2004] raised the concern that pH values used in the calculation of  $C_{\text{T}}$  may be biased by as much as 0.035 in pH. This bias was found to be the maximum difference in a comparison of two different pH measurement techniques (potentiometry versus spectrophotometry) applied to the same set of samples collected during the cruise. According to a comparison study, such a contrast in the two different pH data sets largely reflects unnecessary measurement steps associated with the spectrophotometric pH method (see auxiliary material<sup>1</sup>). These extra measurement steps were not included in the potentiometric pH measurement protocol. When these unnecessary steps are eliminated from the spectrophotometric measurement procedure, spectrophotometric pH values are in better agreement with potentiometric pH values. Therefore potentiometric pH values are sufficiently accurate to enable the calculation of  $C_{\text{T}}$ . The accuracy of the pH values is addressed in detail in the auxiliary material.

## 2.2. Systematic Differences in the Values of Carbon Parameters Measured During the Two Cruises

[8] We compared hydrographic and carbon parameter data obtained during Surveys R and K to assess systematic discrepancies between the two surveys. Three regions (labeled S1, S2, and S3 in Figure 1) for which the two surveys either overlap or collected data at proximate locations were arbitrarily chosen for comparison of the two data sets. Each of the three parameters,  $A_{\text{T}}$ ,  $C_{\text{T}}$ , and pH, was plotted against potential density ( $\sigma_{\theta}$ ) for each of the three overlapping or proximal regions (Figure 2). Comparisons of the two sets of survey data from each overlapping or proximal region were undertaken by fitting the data for  $\sigma_{\theta} > 27.2$  from each survey with a second-order polynomial function and then examining the differences between the

two curve fits (Figure 2). This method has been used previously to define systematic errors in global CO<sub>2</sub> survey data [Lamb et al., 2002; Sabine et al., 2005]. Systematic differences in measured parameters between the two data sets for the three overlap regions are summarized in Table 1. Differences in salinity (S), potential temperature ( $\theta$ ), oxygen concentration (O<sub>2</sub>), and  $A_{\text{T}}$  are within measurement uncertainties and thus no corrections were applied to these data; however, the calculated  $C_{\text{T}}$  values for Survey K are  $4.3 \mu\text{mol kg}^{-1}$  higher than those for Survey R. This systematic discrepancy is likely to reflect the mean pH difference of 0.014 between the two surveys. To correct for this difference in  $C_{\text{T}}$ ,  $4.3 \mu\text{mol kg}^{-1}$  was subtracted from the  $C_{\text{T}}$  values calculated for Survey K.

## 2.3. Calculation of Anthropogenic CO<sub>2</sub>

[9] The concentration of anthropogenic CO<sub>2</sub> within a given parcel of water was determined using a modified version of the  $\Delta C^*$  approach developed by Gruber et al. [1996]. Modification includes the use of an optimum multiparameter (OMP) analysis to more accurately determine the net air-sea disequilibrium for a given sample [Sabine et al., 2002; Lee et al., 2003]. In this method, anthropogenic CO<sub>2</sub> ( $C_{\text{T}}^{\text{ANT}}$ ) is separated out from  $C_{\text{T}}$  ( $C_{\text{T}}^{\text{CAL}}$ ; calculated from measured pH and  $A_{\text{T}}$  values using a thermodynamic model) via the following equation:

$$C_{\text{T}}^{\text{ANT}} = C_{\text{T}}^{\text{CAL}} - C_{\text{T}}^{\text{EQ}} - \Delta C^{\text{BIO}} - \Delta C^{\text{DISEQ}}, \quad (2)$$

where  $C_{\text{T}}^{\text{EQ}}$  is the total dissolved inorganic carbon in equilibrium with the preindustrial atmospheric CO<sub>2</sub> of 280  $\mu\text{atm}$  for the sample's potential temperature, salinity, and preformed total alkalinity ( $A_{\text{T}}^{\circ}$ ), where  $A_{\text{T}}^{\circ}$  represents the total alkalinity of a water parcel when it was last at the ocean surface;  $\Delta C^{\text{BIO}}$  is the change in total dissolved inorganic carbon resulting from the oxidation of organic matter and dissolution of calcium carbonate, which can be estimated from changes in apparent oxygen utilization (saturation O<sub>2</sub> – measured O<sub>2</sub>) and the difference between  $A_{\text{T}}$  and  $A_{\text{T}}^{\circ}$ , respectively; and  $\Delta C^{\text{DISEQ}}$  is the total dissolved inorganic carbon arising from disequilibrium of the fugacity of CO<sub>2</sub> ( $f\text{CO}_2$ ) between the atmosphere and ocean.

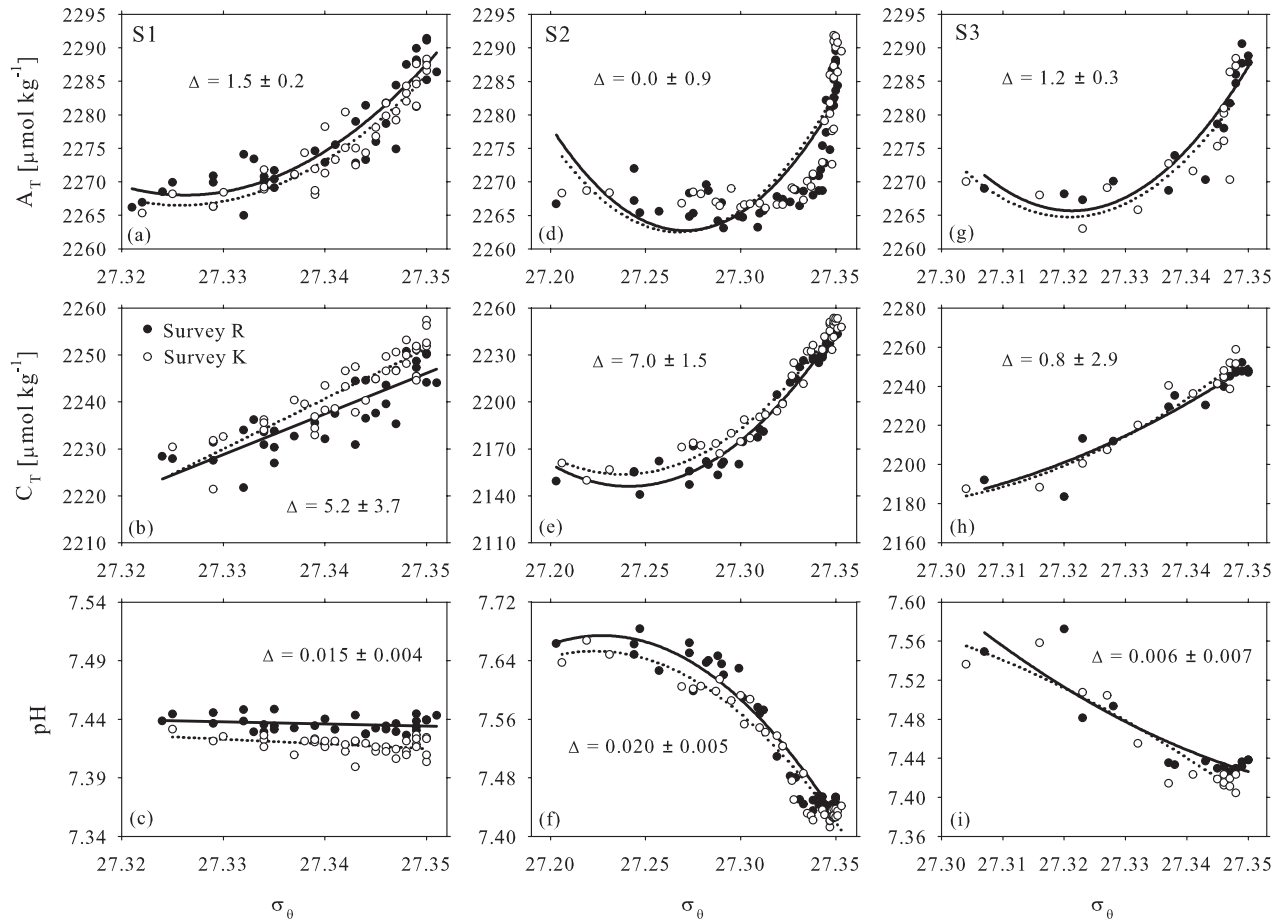
[10] The  $A_{\text{T}}^{\circ}$  values of subsurface samples were estimated from multilinear regression using salinity and NO ( $\text{NO} = \text{O}_2 - \text{R}_{\text{O}_2:\text{N}} \times \text{N}$ ) [Broecker, 1974]. We chose an  $\text{R}_{\text{O}_2:\text{N}}$  of  $-10.625$ , as given by Anderson and Sarmiento [1994]. An empirical equation for  $A_{\text{T}}^{\circ}$  was derived using surface water  $A_{\text{T}}$  data, including wintertime measurements ( $n = 1,177$ ) ( $< 100$  dbars),

$$A_{\text{T}}^{\circ} (\mu\text{mol kg}^{-1}) = 765.5 + 43.77 \times S + 0.03147 \times \text{NO}. \quad (3)$$

The standard deviation ( $1\sigma$ ) of the  $A_{\text{T}}^{\circ}$  value estimated using equation (3) is  $\pm 6.3 \mu\text{mol kg}^{-1}$ . We found that summer-winter differences in  $A_{\text{T}}$  are statistically insignificant.

[11] The value of  $C_{\text{T}}^{\text{EQ}}$  was calculated from the  $A_{\text{T}}^{\circ}$  estimated from equation (3) and  $f\text{CO}_2 = 280 \mu\text{atm}$  using the carbonic acid dissociation constants of Mehrbach et al. [1973], as refitted by Dickson and Millero [1987]. The

<sup>1</sup>Auxiliary materials are available in the HTML. doi:10.1029/2005GB002676.



**Figure 2.** Comparison plots of total alkalinity ( $A_T$ ), total dissolved inorganic carbon ( $C_T$ ), and pH for the regions (S1–S3 in Figure 1) where the two surveys either overlap or collected data at similar locations. Data collected for Survey R are fitted to a second-order polynomial function and plotted as solid symbols (solid lines), while those collected for Survey K are also fitted to a second-order polynomial function and shown as open symbols (dotted lines). Values ( $\Delta$ ) in shown in the figures denote the mean differences and standard deviations ( $1\sigma$ ) between the two curve fits.

calculated  $C_T^{\text{EQ}}$  values were then linearized by a least squares linear fit, yielding the equation

$$C_T^{\text{EQ}} = 2063 - 8.753(\theta - 5) + 95.64(S - 34) - 1.474(A_T^0 - 2270), \quad (4)$$

with a standard deviation ( $1\sigma$ ) between the linearized and calculated  $C_T^{\text{EQ}}$  of  $\pm 0.9 \mu\text{mol kg}^{-1}$ .

[12] The values of air-sea CO<sub>2</sub> disequilibrium ( $\Delta C^{\text{DISEQ}}$ ) were calculated according to the following equation:

$$\Delta C^{\text{DISEQ}} = C_T^{\text{CAL}} - \Delta C^{\text{BIO}} - C_T^{\text{EQ}}. \quad (5)$$

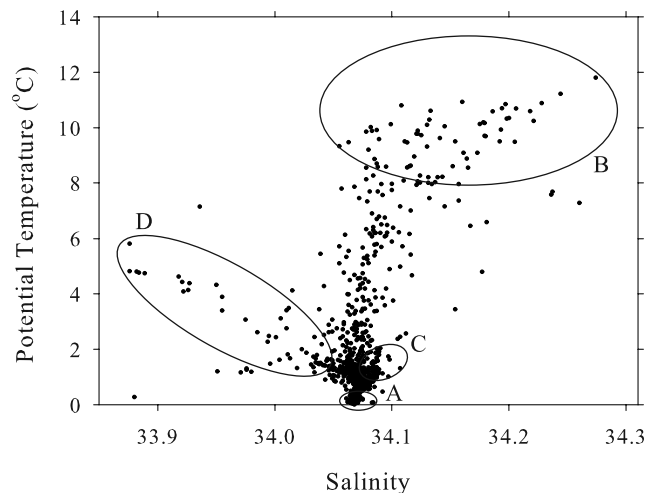
$C_T^{\text{EQ}}$  is the total dissolved inorganic carbon in equilibrium with the corresponding atmospheric fCO<sub>2</sub> at the time that the water parcel was at the ocean surface (sampling date –  $p\text{CFC-12}$  age). The apparent age of the subsurface water parcel using  $p\text{CFC-12}$  is defined as the time difference between the measurement year and the year when the water parcel was last in contact with the atmosphere. However, the

$p\text{CFC-12}$  water age is not necessarily identical to the true water age because of the nonlinear mixing of waters with different ages and possible undersaturation of CFC-12 at the surface when the surface water lost contact with the atmosphere during the winter [Min and Warner, 2005; Matsumoto and Gruber, 2005].

[13] Mixing between waters ventilated during the period 1960–1990 is expected to result in a relatively small age bias because  $p\text{CFC-12}$  in the atmosphere increased approx-

**Table 1.** Systematic Discrepancies (Survey R–Survey K) in Parameters Recorded in Regions For Which the Two Surveys Overlap

| Crossovers            | S       | $\theta$ | O <sub>2</sub> | pH    | $A_T$ | $C_T$ |
|-----------------------|---------|----------|----------------|-------|-------|-------|
| S1                    | 0.0003  | 0.0068   | −0.45          | 0.015 | 1.50  | −5.17 |
| S2                    | −0.0018 | −0.0263  | −1.92          | 0.020 | 0.01  | −6.98 |
| S3                    | −0.0004 | 0.0096   | −1.11          | 0.006 | 1.18  | −0.82 |
| Average discrepancies | −0.0006 | −0.0033  | −1.16          | 0.014 | 0.90  | −4.32 |
| S.D.                  | 0.0010  | 0.0199   | 0.74           | 0.007 | 0.78  | 3.17  |



**Figure 3.** Temperature-salinity diagram for all East Sea data points for which anthropogenic CO<sub>2</sub> can be estimated. Data within the four ovals were used to define the chemical properties of the four source waters (see Table 2 for a summary of results).

imately linearly during this period [Matsumoto and Gruber, 2005]. Therefore, in the present study we restricted the use of *p*CFC-12 based ages to waters younger than 40 years old. However, in the northern Japan Basin, in which the formation of deep water occurs, the surface CFC-12 concentrations observed during the winter are approximately 80% saturated with respect to atmospheric CFC-12 in 2000 [Min and Warner, 2005]. This 20% undersaturation of CFC-12 at the surface yielded resulting *p*CFC-12 water ages that are 2 to 5 years younger than those that would have resulted if the surface water had been in solubility equilibrium with respect to the overlying atmospheric *p*CFC-12. These *p*CFC-12 age biases result in a 1 to 2 μmol kg<sup>-1</sup> underestimation of anthropogenic CO<sub>2</sub> concentrations. In the present study, we applied these corrections only to waters colder than 1°C because CFC-12 concentrations were only measured for surface waters colder than 1°C during the winter. This cold surface water occupies most of the interior East Sea that is deeper than 600 m and approximately 30% of all waters shallower than 600 m.

[14] The net air-sea disequilibrium value for any given seawater sample is expressed as the sum of the disequilibrium values of different water mass end-members,

$$\Delta C^{\text{DISEQ}} = \sum_{i=1}^n x_i \Delta C^{\text{DISEQ}-i}, \quad (6)$$

where  $x_i$  ( $\sum x_i = 1$ ) is the relative contribution of the specific source water  $i$  to the sample and  $\Delta C^{\text{DISEQ}-i}$  is the unique

disequilibrium value for source water  $i$ . The OMP analysis was used to determine the net air-sea disequilibrium for a sample by more accurately estimating the relative contributions of the various source-water types contained in the sample. Source-water types are represented by unique values of measured conservative (temperature and salinity) and nonconservative (oxygen, silicate, phosphate, and nitrate concentrations) parameters. Four source-water types (A, B, C, and D) were identified from the  $\theta$ - $S$  diagram (Figure 3). Source water A includes nearly all waters deeper than 600 m. Waters deeper than 600 m consist of three different water masses: Central Water, Deep Water, and Bottom Water. We treated these as a single water mass (source water A) because their unique disequilibrium values are indistinguishable within  $\pm 3.0$  μmol kg<sup>-1</sup>. The mean values of the hydrographic properties and net air-sea disequilibrium for the four source-water types are summarized in Table 2.

## 2.4. Calculation of CaCO<sub>3</sub> Saturation State

[15] The degree of saturation of seawater with respect to aragonite and calcite is defined as the ion product of the concentrations of calcium ( $[\text{Ca}^{2+}]$ ) and carbonate ions ( $[\text{CO}_3^{2-}]$ ) at the in situ temperature, salinity, and pressure, divided by the stoichiometric solubility product ( $K^*sp$ ).

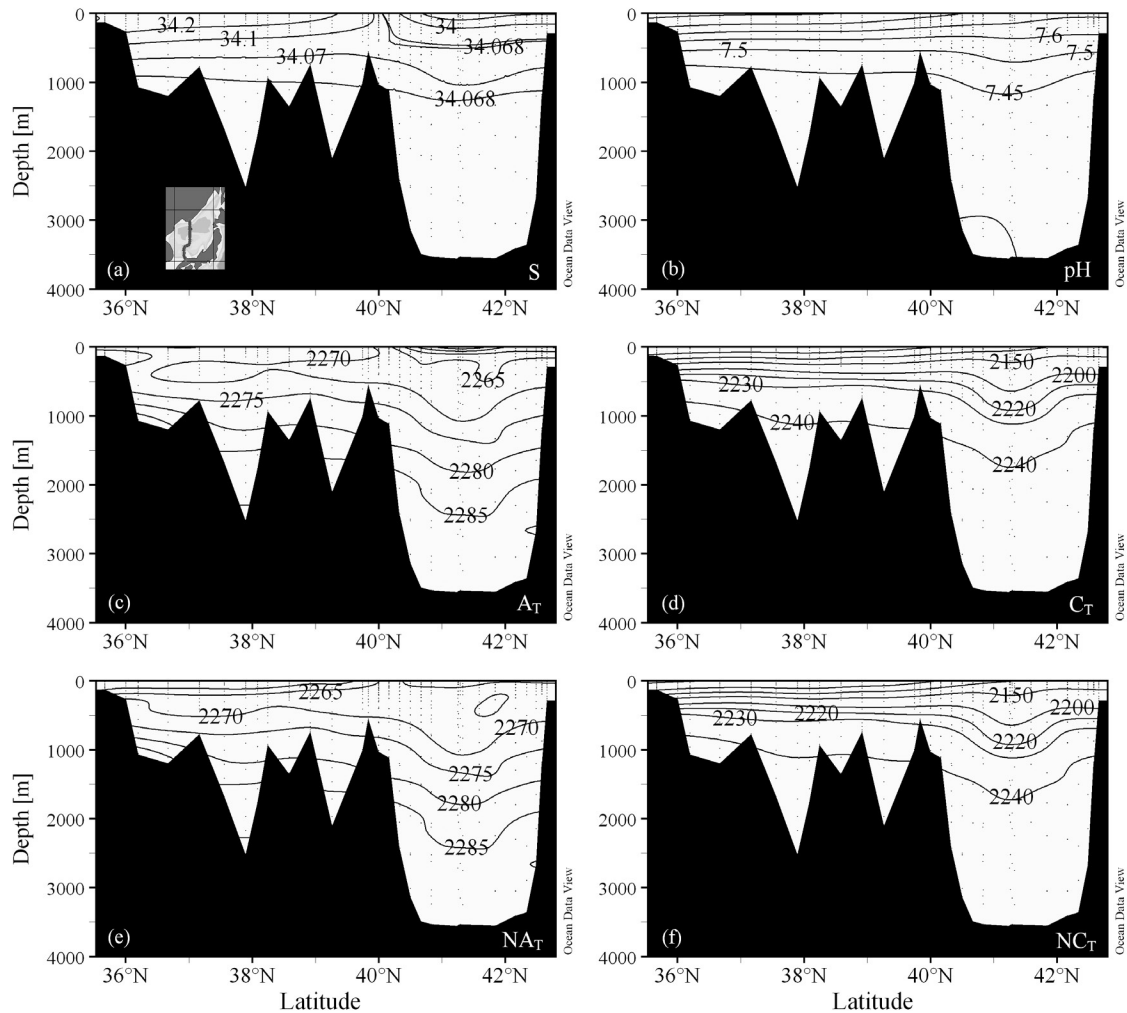
$$\Omega_{\text{arg}} = [\text{Ca}^{2+}] [\text{CO}_3^{2-}] / K^*sp\text{-arg} \quad (7)$$

$$\Omega_{\text{cal}} = [\text{Ca}^{2+}] [\text{CO}_3^{2-}] / K^*sp\text{-cal}, \quad (8)$$

where  $[\text{Ca}^{2+}]$  is estimated from salinity using the  $[\text{Ca}^{2+}]$ /salinity ratio of 0.00029377 [Riley and Tongudai, 1967], and  $[\text{CO}_3^{2-}]$  is calculated from  $A_T$  and  $C_T$  using the pressure-corrected thermodynamic constants that are consistent with the calibrated global field data [Lee et al., 2000; Millero et al., 2002]. These constants include the carbonic acid dissociation constants of Mehrbach et al. [1973] as refitted by Dickson and Millero [1987] and other ancillary constants as suggested by Millero [1995]. The effect of pressure on these dissociation constants has been estimated from partial molal volume and compressibility data [Millero, 1995]. The values of  $K^*sp$  were taken from Mucci [1983] at a given temperature and salinity at 1 atmosphere; the effect of pressure on  $K^*sp$  was also estimated from partial molal volume and compressibility data [Millero, 1995]. The preindustrial saturation horizons with respect to aragonite and calcite were calculated using measured  $A_T$  and

**Table 2.** Properties of the Four Source Waters Identified in the East Sea

| Identification | Latitude | $\theta$ | SD ( $\theta$ ) | S     | SD (S) | O <sub>2</sub> | SD (O <sub>2</sub> ) | PO <sub>4</sub> | SD (PO <sub>4</sub> ) | NO <sub>3</sub> | SD (NO <sub>3</sub> ) | Si    | SD (Si) | $\Delta C^{\text{DISEQ}}$ | SD ( $\Delta C^{\text{DISEQ}}$ ) |
|----------------|----------|----------|-----------------|-------|--------|----------------|----------------------|-----------------|-----------------------|-----------------|-----------------------|-------|---------|---------------------------|----------------------------------|
| A              | 40.30    | 0.18     | 0.12            | 34.07 | 0.01   | 214.72         | 6.90                 | 1.99            | 0.06                  | 25.12           | 0.62                  | 71.06 | 12.79   | 8.84                      | 3.02                             |
| B              | 38.67    | 9.20     | 0.98            | 34.13 | 0.04   | 260.22         | 5.97                 | 0.52            | 0.10                  | 6.90            | 1.30                  | 8.72  | 2.10    | -24.67                    | 5.17                             |
| C              | 42.88    | 1.14     | 0.25            | 34.09 | 0.00   | 281.49         | 17.36                | 1.36            | 0.17                  | 17.35           | 2.20                  | 28.56 | 5.04    | 2.00                      | 2.20                             |
| D              | 40.80    | 1.71     | 1.00            | 34.03 | 0.05   | 282.39         | 24.65                | 1.18            | 0.32                  | 14.96           | 4.25                  | 23.04 | 6.97    | 0.42                      | 4.27                             |



**Figure 4.** Meridional sections of (a) salinity, (b) pH, (c) total alkalinity ( $A_T$ ), (d) total dissolved inorganic carbon ( $C_T$ ), (e) salinity ( $S = 34.07$ )-normalized total alkalinity ( $NA_T = A_T \times 34.07/S$ ), and (f) salinity ( $S = 34.07$ )-normalized total dissolved inorganic carbon ( $NC_T = C_T \times 34.07/S$ ) nominally along  $134^\circ\text{E}$  in the East Sea. Dots indicate locations of measured data. The inset in Figure 4a shows the path of the cruise track.

preindustrial  $C_T$ , which was estimated by subtracting  $C_T^{\text{ANT}}$  from  $C_T^{\text{CAL}}$ .

### 3. Results and Discussion

#### 3.1. Distribution of Carbon Parameters ( $A_T$ , $C_T$ , and pH)

[16] Salinity is the dominant factor that affects  $A_T$  in the surface mixed layer of the oceans [Millero *et al.*, 1998; Lee *et al.*, 2006]. The highest values of surface water  $A_T$  ( $\sim 2270 \mu\text{mol kg}^{-1}$ ) are found in the southern East Sea ( $36^\circ\text{N}$ – $40^\circ\text{N}$ ) where salinity maxima as high as  $S > 34.2$  are observed (Figure 4a). These salinity maxima extend to the subarctic polar front (near  $40^\circ\text{N}$ ), which is formed from the interaction of subpolar water that originates from the northern part of the East Sea and subtropical water that flows into the East Sea through the Korea Strait [e.g., Legeckis, 1978; Kim *et al.*, 2001;

Tishchenko *et al.*, 2003]. From the Korea Strait to the northwestern part of the East Sea, salinity and  $A_T$  decrease to  $S = 33.0$ – $34.0$  and  $A_T = 2250$ – $2260 \mu\text{mol kg}^{-1}$ , respectively (Figures 4a and 4c). The surface water  $C_T$  concentration is also greatly affected by factors that influence salinity, as is surface water  $A_T$  [Lee *et al.*, 2000]. Biological activities also generate variations in surface water  $A_T$  in the East Sea; however, the magnitude of such biologically induced changes in  $A_T$  is likely to be negligible [Kim *et al.*, 2006] because calcifying organisms, which are the dominant biological contributors to  $A_T$ , are rarely found in the East Sea [Kang and Choi, 2002]. Biological activities affect  $C_T$  to a significantly greater extent than they affect surface water  $A_T$ .

[17] The values of  $A_T$  and  $C_T$  (as well as  $NA_T = A_T \times 34.07/S$  and  $NC_T = C_T \times 34.07/S$ ,  $S = 34.07$  was chosen as the mean salinity of the East Sea) increase gradually with depth up to 2500 m and 2000 m, respectively (Figures 4c

and 4d). For waters deeper than these depths,  $A_T$  and  $C_T$  remain almost constant to the ocean floor. To a first order approximation, a  $15 \mu\text{mol kg}^{-1}$  increase in  $NA_T$  with depth is probably related to the dissolution of  $\text{CaCO}_3$  particles within the water column or from sediments, whereas a  $90 \mu\text{mol kg}^{-1}$  increase in  $NC_T$  with depth is related to both the dissolution of  $\text{CaCO}_3$  and the oxidation of organic matter (Figures 4e and 4f). Thus, given that a  $15 \mu\text{mol kg}^{-1}$  increase in  $A_T$  is equivalent to an increase in  $C_T$  of approximately  $7.5 \mu\text{mol kg}^{-1}$ , the relative contribution of organic matter and biogenic  $\text{CaCO}_3$  to observed  $C_T$  increase in the East Sea is approximately 11:1. This ratio of 11:1 is approximately consistent with the global rain ratio of organic matter and  $\text{CaCO}_3$  at the bottom of the seasonal mixed layer [Lee, 2001; Sarmiento et al., 2002].

[18] The pH at  $25^\circ\text{C}$  in the East Sea decreases from 7.92 at the surface to 7.45 at 1000 m and then remains approximately constant for deeper waters (Figure 4b). Oxidation of organic matter within the water column is the main control on the vertical distribution of pH in the East Sea. The constant pH observed throughout the water column below 1000 m suggests that negligible organic matter is present below this depth and that any decrease in pH related to the oxidation of organic matter buried in the seafloor sediment is also negligible.

### 3.2. Air-Sea Disequilibrium ( $\Delta C^{\text{DISEQ}}$ )

[19] The mean air-sea disequilibrium values for the four types of source water are summarized in Table 2. Source water A probably forms during winter cooling in regions of relatively high latitude ( $40^\circ\text{N}$ – $42^\circ\text{N}$  and  $132^\circ\text{E}$ – $133^\circ\text{E}$ ) near Peter the Great Bay off Vladivostok, Russia. Source water A has a positive  $\Delta C^{\text{DISEQ}}$  value, suggesting that it was slightly supersaturated with respect to atmospheric  $f\text{CO}_2$  when it formed at the surface during wintertime. Deep convective mixing with subsurface waters during wintertime cooling would bring deep  $\text{CO}_2$ -rich waters to the surface and cause the surface water  $f\text{CO}_2$  value to increase above the atmospheric  $f\text{CO}_2$  level. During wintertime observations of the air-sea difference of  $f\text{CO}_2$  ( $\Delta f\text{CO}_2 = f\text{CO}_{2\text{AIR}} - f\text{CO}_{2\text{SEA}}$ ) in the East Sea [Oh et al., 1999; Tishchenko et al., 2003], negative  $\Delta f\text{CO}_2$  values (which are consistent with positive  $\Delta C^{\text{DISEQ}}$  values) were observed off Vladivostok in the northern part of the East Sea, where source water A probably forms. This positive  $\Delta C^{\text{DISEQ}}$  value for source water A in the region of deep water formation stands in contrast to the negative  $\Delta C^{\text{DISEQ}}$  value of  $-16 \mu\text{mol kg}^{-1}$  previously reported for North Atlantic Deep Water [Gruber, 1998; Lee et al., 2003]. This negative value of  $\Delta C^{\text{DISEQ}}$  implies that the surface waters in the deep water formation region of the North Atlantic are undersaturated with respect to atmospheric  $f\text{CO}_2$ .

[20] Source water B, which has a  $\Delta C^{\text{DISEQ}}$  value of  $-25 \mu\text{mol kg}^{-1}$ , is found in the southern part of the East Sea. The negative  $\Delta C^{\text{DISEQ}}$  value is explained by the following mechanism. A branch of the Tsushima warm current flows into the East Sea through the Korea Strait and then continues northward along the east coast of Korea as a western boundary current. During its northward movement, the warm water continues to interact

with cooler air and consequently cools considerably. This temperature decrease causes the  $f\text{CO}_2$  of the surface water to drop below the atmospheric  $f\text{CO}_2$  level, which would likely result in a negative  $\Delta C^{\text{DISEQ}}$  value for source water B. Active photosynthesis also contributes to the recorded decrease in the surface water  $f\text{CO}_2$  in this area [Kim et al., 2001; Gamo et al., 2001; Min and Warner, 2005]. The other two source waters, C and D, have approximately neutral  $\Delta C^{\text{DISEQ}}$  values. These two source waters probably correspond to the High Salinity Intermediate Water and East Sea Intermediate Water typically found at approximately 200–300 m depth in the Japan Basin [Kim et al., 2004].

### 3.3. Distribution of Anthropogenic CO<sub>2</sub>

[21] Figures 5a and 5b show the meridional and zonal distributions of anthropogenic  $\text{CO}_2$  in the East Sea. The highest concentrations of anthropogenic  $\text{CO}_2$  (typically  $50$ – $60 \mu\text{mol kg}^{-1}$ ) are found in the upper waters of the southern East Sea. In the southern East Sea, vertical mixing of surface waters and subsurface waters is limited by strongly developed stratification that leads to higher values of anthropogenic  $\text{CO}_2$  in the upper waters. In the northern East Sea, however, surface waters mix to a great extent with old waters that contain lower concentrations of anthropogenic  $\text{CO}_2$ , thus lowering the anthropogenic  $\text{CO}_2$  concentration of the upper waters.

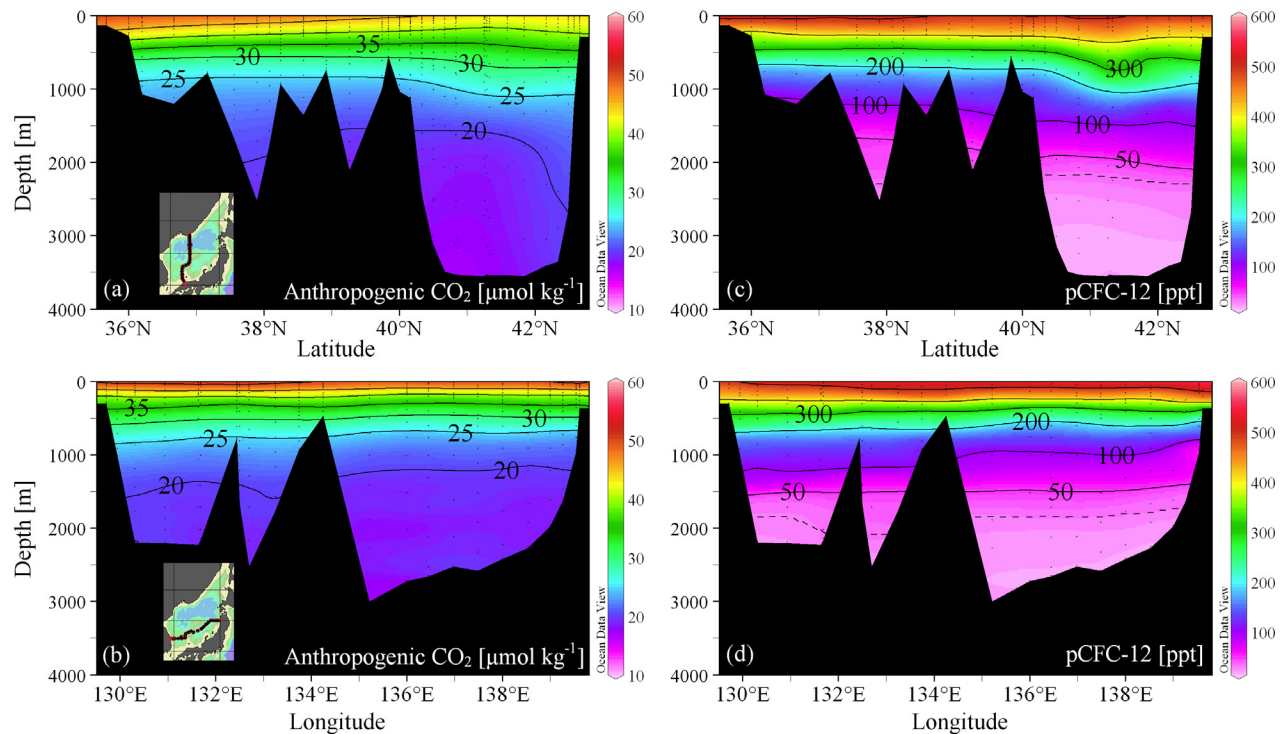
[22] Anthropogenic  $\text{CO}_2$  generally penetrates to the bottom of the entire basin of the East Sea, and its concentration in deep waters near the bottom reaches approximately  $10$ – $15 \mu\text{mol kg}^{-1}$ .  $p\text{CFC-12}$  tracer ages of deep waters that contain  $10$ – $15 \mu\text{mol kg}^{-1}$  of anthropogenic  $\text{CO}_2$  are approximately 40 years old (dotted lines in Figures 5c and 5d). There is a similarity in the meridional and zonal distributions of anthropogenic  $\text{CO}_2$  concentration and  $p\text{CFC-12}$  (Figures 5a–5d), because both anthropogenic gases penetrate to deep water levels via deep water formation. Deep water formation effectively transports surface waters loaded with anthropogenic gases to the interior of the basin during the winter cooling period. This transport mechanism is similar to that operating in the North Atlantic, where anthropogenic  $\text{CO}_2$  reaches depths greater than 3000 m [Lee et al., 2003]. In contrast, anthropogenic  $\text{CO}_2$  at the same latitude in the North Pacific Ocean does not penetrate beyond 1500 m, largely due to a lack of deep water formation [Sabine et al., 2002].

### 3.4. Inventory of Anthropogenic CO<sub>2</sub>

[23] The inventory of anthropogenic  $\text{CO}_2$  ( $\text{TOTAL} - C^{\text{ANT}}$ ) for each  $2.5^\circ$  latitude  $\times$   $2.5^\circ$  longitude grid element was determined by integrating the area-weighted mean profile of  $C^{\text{ANT}}$  ( $f - C^{\text{ANT}}$ ) from the surface (SFC) to the mean bottom depth (MEAN),

$$\text{TOTAL} - C^{\text{ANT}} = \int_{\text{SFC}}^{\text{MEAN}} A f - C^{\text{ANT}} dz, \quad (9)$$

where  $A$  ( $\text{m}^2$ ) is the area of each  $2.5^\circ$  latitude  $\times$   $2.5^\circ$  longitude grid element. The estimated inventories for each



**Figure 5.** (a, c) Meridional and (b, d) zonal sections of anthropogenic CO<sub>2</sub> and *p*CFC-12 nominally along 134°E and 38°N in the East Sea, respectively. Deep waters near the bottom (~3500 m depth) of the Japan Basin contain approximately 10–15  $\mu\text{mol kg}^{-1}$  of anthropogenic CO<sub>2</sub>. Dotted lines represent water masses of approximately 40 years in age. Anthropogenic CO<sub>2</sub> concentrations are not scaled down because corrections for the key systematic errors (inaccuracies in the assumption of the constant air-sea disequilibrium and the *p*CFC-12 age bias) differ for different water masses.

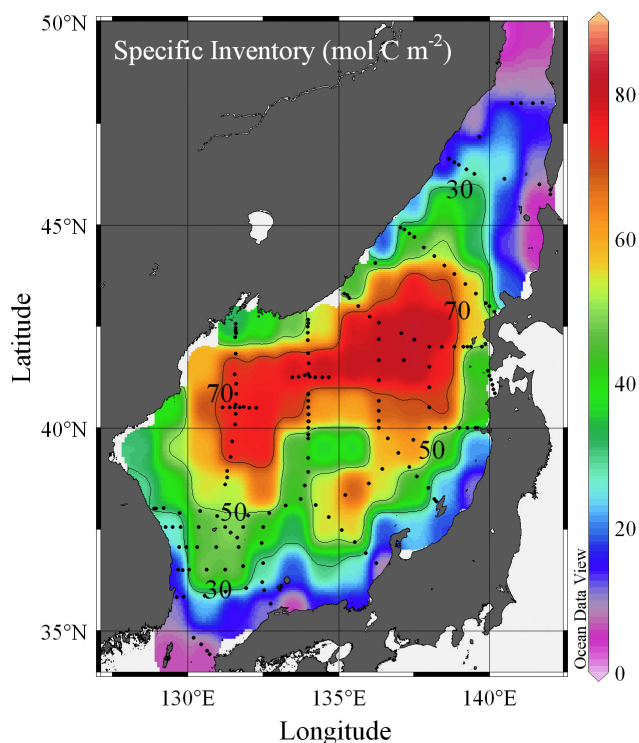
of the grid elements were then summed to produce the basin-wide inventory of anthropogenic CO<sub>2</sub>. The total amount of anthropogenic CO<sub>2</sub> that has accumulated in the East Sea between 1800 and 1999 is equal to 0.51 petagrams of carbon (Pg C, Pg = 10<sup>15</sup> g), which is just 0.01 Pg C more than the inventory obtained without correction for *p*CFC-12 age bias related to the 20% undersaturation of CFC-12 observed in the wintertime outcrop regions.

[24] The highest specific column inventory (TOTAL – C<sup>ANT</sup> divided by the area of each 2.5° latitude × 2.5° longitude grid element; moles of anthropogenic CO<sub>2</sub> per m<sup>2</sup>) is observed in the Japan Basin between 40°N and 44°N, and between 131°E and 139°E, with a mean value of 80 mol C m<sup>-2</sup> (Figure 6). This figure is much higher than the 20–30 mol C m<sup>-2</sup> observed in the adjacent North Pacific [Sabine et al., 2002]. The high specific column inventory in the East Sea compared to that at the same latitude band in the North Pacific can be attributed to the sinking of newly formed water into the interior that contains significant quantities of anthropogenic CO<sub>2</sub>. Such deep water formation was observed south of Vladivostok in the cold winter of 2001 [Kim et al., 2002; Talley et al., 2003]. Brine rejection into adjacent waters during the formation of sea ice resulted in dense surface waters that subsequently sank into the interior of the basin [Talley et al., 2003]. Within the Japan Basin, the specific column inventories in the central and western areas are lower than those in the

eastern area despite the fact that the deep water formation process is more active in the central and western parts of the Japan Basin. This pattern is directly attributable to the lower volumes of waters in the central and western basins compared to the eastern basin.

[25] We identified two key sources of systematic errors that could potentially have biased our estimation of anthropogenic CO<sub>2</sub> inventory. The first source of error arises from inaccuracies in the assumed value of the constant air-sea disequilibrium used in the  $\Delta C^*$  approach. This bias results in an overestimation of anthropogenic CO<sub>2</sub> in the younger waters that occupy much of the interior of the East Sea. We correct for this bias in the East Sea using the procedure proposed by Matsumoto and Gruber [2005], whereby the anthropogenic CO<sub>2</sub> inventory of 0.51 Pg C should be scaled down by approximately 14%. The second source of error is a *p*CFC-12 age bias related to the nonlinear mixing of waters of different ages. Although it is not possible to estimate the exact magnitude of this error, various modeling studies indicate that *p*CFC-12 based ages are 5–10 years younger than true ages, with the magnitude of the age bias being dependent on the degree of mixing in the interior [Matsumoto and Gruber, 2005; Hall et al., 2002, 2004; Waugh et al., 2004]. If this age bias is properly corrected, the revised inventory should be scaled down by approximately 8%. Considering these two corrections together, the inventory should be scaled down to as low as 0.40 Pg.





**Figure 6.** Map of anthropogenic CO<sub>2</sub> column inventory ( $\text{mol C m}^{-2}$ ) in the East Sea. The anthropogenic CO<sub>2</sub> inventory for waters in the northwestern East Sea near North Korea was estimated by extrapolating anthropogenic CO<sub>2</sub> concentrations from adjacent waters. Anthropogenic CO<sub>2</sub> column inventory are not scaled down because corrections for the key systematic errors (inaccuracies in the assumption of the constant air-sea disequilibrium and the  $p\text{CFC-12}$  age bias) differ for different water masses. Circles represent sampling locations of Surveys K and R.

[26] There are two additional sources of errors: uncertainty in the precision of various measurements required for the calculation of anthropogenic CO<sub>2</sub>, and uncertainties in the end-member disequilibrium values. The propagation of measurement errors indicates that any anthropogenic CO<sub>2</sub> estimate in the East Sea has an uncertainty of  $\pm 7.3 \mu\text{mol kg}^{-1}$ ; however, this random error should largely cancel out. Approximate upper (or lower) estimates of  $\Delta C^{\text{DISEQ}}$  for each data point were calculated by increasing (or decreasing) the mean  $\Delta C^{\text{DISEQ}}$  value by the standard deviation of the mean value for each source-water type. This analysis yielded an error of  $\pm 0.06 \text{ Pg C}$  in anthropogenic CO<sub>2</sub> inventory. Lee *et al.* [2003] applied this error estimation method to the Atlantic Ocean.

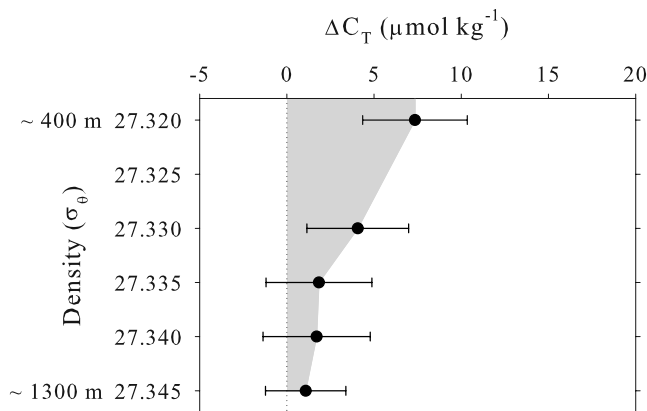
### 3.5. Uptake of Anthropogenic CO<sub>2</sub> Over the Period 1992 to 1999

[27] In conjunction with anthropogenic CO<sub>2</sub> results presented in this paper, results estimated from the  $A_T$  and  $C_T$  data sets collected during the Kuroshio Edge Exchange Processes-Marginal Sea Studies Expedition in the East Sea (July 28 to August 5, 1992) [Chen *et al.*, 1995] provide

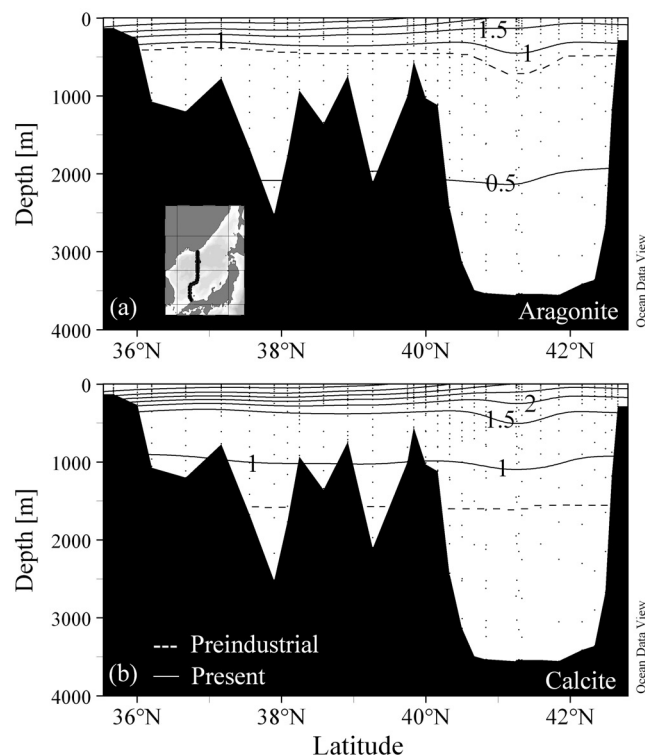
an opportunity to calculate the increase of anthropogenic CO<sub>2</sub> inventory over the 7-year period from 1992 to 1999. We used the isopycnal method to calculate the total anthropogenic CO<sub>2</sub> that accumulated in the East Sea over the 7-year period. This method was used previously to determine decadal rates of anthropogenic CO<sub>2</sub> uptake in the Indian and Pacific Oceans [Peng *et al.*, 1998, 2003]. The method directly compares  $C_T$  values measured at the same geographic location at two different times after correcting for CO<sub>2</sub> changes related to the oxidation of organic matter, dissolution of calcium carbonate, and variations in salinity. The net increase in corrected  $C_T$  at a selected isopycnal surface is assumed to represent the amount of anthropogenic CO<sub>2</sub> taken up during the time interval between the two different measurement dates.

[28] We only determined the anthropogenic CO<sub>2</sub> taken up by the East Sea and stored for the 7-year period for the Japan Basin owing to a lack of inorganic carbon data collected during the 1992 cruise. In comparing the 1992 and 1999 data, we found that the 1992 data contains systematic errors of  $21 \mu\text{mol kg}^{-1}$  in  $A_T$ ,  $13 \mu\text{mol kg}^{-1}$  in  $C_T$ , and  $6.5 \mu\text{mol kg}^{-1}$  in  $O_2$ . We then applied these discrepancies to the 1992 data. To avoid seasonal variations in  $C_T$  in the upper ocean, data collected for waters shallower than 300 m were not used in this calculation. We estimated the 7-year uptake rate of anthropogenic CO<sub>2</sub> for isopycnal surfaces, the potential densities of which range from  $\sigma_\theta = 27.320$  to  $27.345$ . This density range corresponds approximately to a depth range of 400–1300 m. The total inventory of anthropogenic CO<sub>2</sub> accumulated in the East Sea during this 7-year period was estimated by integrating the profile of anthropogenic CO<sub>2</sub> concentration from the surface to a depth of 1300 m (Figure 7); the resulting mean inventory is approximately  $4.6 \pm 2.7 \text{ mol m}^{-2}$ , which yields a mean annual uptake rate of  $0.66 \pm 0.38 \text{ mol m}^{-2} \text{ yr}^{-1}$ . The large degree of uncertainty associated with this estimate of annual uptake rate is primarily due to the lack of inorganic carbon data collected during the 1992 cruise.

[29] Our estimate of the accumulation rate of anthropogenic CO<sub>2</sub> in the Japan Basin is similar to that obtained for



**Figure 7.** Mean differences in  $C_T$  concentrations between the 1992 and 1999 data sets as a function of density surface. Error bars represent 1 standard deviation from the mean.



**Figure 8.** Meridional distributions of the degree of seawater saturation with respect to (a) aragonite and (b) calcite at the present day (solid lines), nominally along 134°E in the East Sea. The dotted lines denote the aragonite and calcite saturation horizons ( $\Omega = 1$ ) during the preindustrial era. The inset in Figure 8a shows the path of the cruise track.

the northeast Pacific using the same isopycnal method [Peng *et al.*, 2003], despite the much higher specific column inventory recorded in the East Sea compared to the North Pacific. This similarity probably reflects a weakening of deep water formation in the East Sea during the 1990s. Several previous studies suggest that deep water formation in the East Sea has weakened over the past several decades, resulting in outcrop waters being fed into the intermediate layer rather than the deep layer [Kim and Kim, 1996; Gamo *et al.*, 2001; Kim *et al.*, 2001, 1999, 2002; Talley *et al.*, 2003]. This weakening, which has been attributed to global warming [Kim and Kim, 1996; Gamo *et al.*, 2001], could lead to reduced efficiency in the transport of anthropogenic CO<sub>2</sub> to the interior of the East Sea. A similar decrease in the intensity of bottom water formation has also been observed for the North Atlantic Ocean [Wood *et al.*, 1999; Hansen *et al.*, 2001]. Such variations in the intensity of deep water formation and turnover time could potentially affect the sequestration of anthropogenic CO<sub>2</sub> by the oceans.

### 3.6. Comparisons With Other Marginal Seas

[30] Deep water formation occurs in various marginal seas, including the Arctic Ocean, East Sea, Labrador Sea, Mediterranean Sea, Okhotsk Sea, and Weddell Sea. Of these, the Sea of Okhotsk is a subpolar marginal sea located

northeast of the East Sea and contains the southernmost region of sea ice in the Northern Hemisphere. In the Okhotsk Sea, dense water produced as a result of brine rejection during the formation of sea ice is fed into the intermediate layer of the North Pacific [e.g., Talley, 1991; Yasuda, 1997; Shcherbina *et al.*, 2003]. This dense water carries some of the anthropogenic CO<sub>2</sub> taken up by the surface of the Okhotsk Sea. In contrast, there is only a limited exchange of waters between the East Sea and the North Pacific; hence, CO<sub>2</sub> taken up by the surface of the East Sea continuously accumulates at that site. These differences in deep water circulation patterns are the likely explanation for the fact that the annual accumulation rate of anthropogenic CO<sub>2</sub> in the Okhotsk Sea, which has been estimated to be  $0.78 \times 10^{-3}$  Pg C yr<sup>-1</sup> [Wakita *et al.*, 2003], is significantly lower than the rate of  $1.6 \times 10^{-3}$  Pg C yr<sup>-1</sup> recorded in the East Sea.

[31] In contrast, deep water formation in the abyssal Weddell Sea is believed to be less important with respect to the accumulation rate of anthropogenic CO<sub>2</sub> [Hoppema *et al.*, 2001; Poisson and Chen, 1987]. The concentration of anthropogenic CO<sub>2</sub> in the Weddell Sea falls sharply below  $5 \mu\text{mol kg}^{-1}$  at a depth of about 500 m [Hoppema *et al.*, 2001]. The shallower penetration and lower inventory of anthropogenic CO<sub>2</sub> in this sea is attributed to various factors. One of these factors is the limited exchange of CO<sub>2</sub> at the air-sea interface because of the fact that sea-ice covers the surface for much of the year, inhibiting air-sea CO<sub>2</sub> exchange and allowing only a short residence time for newly formed deep waters to absorb anthropogenic CO<sub>2</sub> from the atmosphere [Caldeira and Duffy, 2000; Hoppema *et al.*, 2001]. A second factor is the significant dilution of anthropogenic CO<sub>2</sub> by mixing with old Weddell Deep Water, which is poor in anthropogenic CO<sub>2</sub> [Poisson and Chen, 1987; Hoppema *et al.*, 2001].

[32] Until recently, the Arctic Ocean was believed to be an insignificant sink of anthropogenic CO<sub>2</sub> because much of the basin surface is covered with sea ice. However, a recent man-made tracer-based modeling study [Anderson *et al.*, 1998] indicated the active ventilation of intermediate water in the Arctic Ocean, through which a considerable amount of anthropogenic CO<sub>2</sub> is believed to be absorbed. On the basis of the results of this previous study, the mean inventory of anthropogenic CO<sub>2</sub> per unit area of the Arctic Ocean in the 1990s was estimated to be approximately  $360 \text{ g C m}^{-2}$  [Anderson *et al.*, 1998], which is similar to the value of  $400 \text{ g C m}^{-2}$  determined for the East Sea.

### 3.7. Upward Displacement of the Aragonite and Calcite Saturation Horizons

[33] Because some of the protons generated from the dissolution of anthropogenic CO<sub>2</sub> in seawater react with carbonate ions to form bicarbonate ions, the invasion of anthropogenic CO<sub>2</sub> into the ocean results in a decrease in the concentration of carbonate ion, which in turn acts to reduce the saturation states of seawater with respect to aragonite and calcite. The saturation horizons ( $\Omega = 1$ ) for aragonite and calcite in the East Sea for both present (solid lines) and preindustrial (dotted lines) levels are shown in Figure 8. The degree of saturation decreases

with depth because the solubility of aragonite and calcite generally increases with depth [Mucci, 1983]. The present-day saturation horizons of aragonite and calcite in the East Sea are located at depths of approximately 400 m and 1000 m, respectively. The depth of the aragonite saturation horizon in the East Sea is similar to that in the adjacent Pacific Ocean [Feely *et al.*, 2002]. In contrast, the saturation horizon for calcite is approximately 300–600 m deeper in the East Sea than that at the same latitude band in the North Pacific.

[34] Since the preindustrial era, the saturation horizons for aragonite and calcite in the East Sea have moved upward by approximately 80–220 m and 500–700 m, respectively, across the entire basin (Figure 8). These upward migrations of the saturation horizons are significantly greater than those observed for the same latitude band of the North Pacific (i.e., 40–50 m for aragonite and 100–150 m for calcite) [Feely *et al.*, 2002, 2004]. The greater upward shift of the saturation horizons in the East Sea compared to the North Pacific can be attributed to two main factors: the deeper penetration of anthropogenic CO<sub>2</sub> in the East Sea, and a significantly smaller vertical gradient in the degree of aragonite and calcite saturation in the East Sea. The interior of the East Sea at depths greater than 800 m has almost uniform aragonite and calcite saturation states throughout, with variation in the aragonite saturation state between 1000 m and 3500 m depth of slightly more than  $\Omega = 0.5$  and equivalent variation for calcite of  $\Omega = 0.5$ . As a result, a given amount of anthropogenic CO<sub>2</sub> will have a more profound effect on the aragonite and calcite saturation states in the East Sea than on those in the North Pacific. In the North Pacific, there is a significant vertical gradient in the degree of saturation of seawater with aragonite and calcite. Taken together, the above factors cause the aragonite and calcite saturation horizons in the East Sea to migrate upward to a significantly greater extent than those observed in other major basins of the global ocean.

#### 4. Conclusions

[35] In this study, we estimated the anthropogenic CO<sub>2</sub> inventory in the East Sea using a high-quality inorganic carbon data set collected during a comprehensive survey conducted in the summer of 1999. The distribution of anthropogenic CO<sub>2</sub> in the East Sea shows features that are consistent with the distributions found in other major basins within which deep water formation occurs (e.g., the North Atlantic); most notably, high column inventories of anthropogenic CO<sub>2</sub> were observed in the region of deep water formation near Peter the Great Bay off Vladivostok, Russia. The deep water formation process effectively carries anthropogenic CO<sub>2</sub> into the interior of the East Sea. In particular, the specific column inventory of anthropogenic CO<sub>2</sub> in the East Sea is two to three times greater than that in the North Pacific, in which only intermediate water formation occurs.

[36] The substantial accumulation of anthropogenic CO<sub>2</sub> in the East Sea has caused a significant change in the carbonate chemistry of the sea. In particular, the anthropogenic CO<sub>2</sub>-induced upward movement of the saturation

horizons for aragonite and calcite is significantly greater in the East Sea than in other major basins. This notable change in carbonate chemistry is likely driven by two unique characteristics of the East Sea: a fast turnover time (<100 years), which is directly related to active deep water formation; and a small dynamic range of temperature and salinity, which is one to two orders of magnitude smaller than the ranges found in the major oceans. This small degree of vertical variability suggests that the water column in the East Sea is relatively unstable. As a result, minor disturbances in the global or regional climate system will potentially change the intensity of deep water formation [Kim and Kim, 1996], which directly affects the uptake of anthropogenic CO<sub>2</sub> by the East Sea. Regular monitoring of carbon and hydrographic parameters in the East Sea will therefore provide information on variations that may occur in the global ocean at much longer time scales. In this way, the East Sea can serve as a site for monitoring decadal variability in oceanic CO<sub>2</sub> uptake.

[37] **Acknowledgments.** We are indebted to the hard work of the captains and crews of the *R/V Revelle* and *Khromov*, and scientific personnel from SIO/ODF, FEHRHI, and POI. The field work was financially supported by the U.S. Office of Naval Research (LDT), by U.S. National Science Foundation (MW), and by Russia Academy of Science (PT). The analysis of data and the preparation of the manuscript were supported by the National Research Laboratory (NRL) Program of the Korean Science and Engineering Foundation (KOSEF). Partial support was also provided by the Advanced Environmental Biotechnology Research Center (AEBRC) at POSTECH, the Korea Aerospace Research Institute, the Brain Korea 21 project, the KOSEF (R01-2002-000-00549-0, 2004), the Ministry of Education and Human Resources Development (MOEHRD) (KRF-2005-070-C00143), the Korea Polar Research Institute through a study on Arctic Environmental Characteristics (PE06030), the Ministry of Maritime Affairs and Fisheries (the Korea EAST-1 Program) (K.-R. Kim), and the Korea Meteorological Administration Research and Development Program under grant CATER 2006-4101 (K.-R. Kim).

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