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## Carbon dioxide along WOCE line A14: Water masses characterization and anthropogenic entry

A. F. Ríos,<sup>1</sup> X. A. Álvarez-Salgado,<sup>1</sup> F. F. Pérez,<sup>1</sup> L. S. Bingler,<sup>2</sup> J. Arístegui,<sup>3</sup> and L. Mémerly<sup>4</sup>

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[1] The meridional WOCE line A14, just east of the South Atlantic Mid-Atlantic Ridge, was surveyed during the austral summer of 1995 from 4°N to 45°S. Full-depth profiles of pH, total alkalinity (TA), and total inorganic carbon ( $C_T$ ) were measured, allowing a test of the internal consistency of the  $CO_2$  system parameters. The correlation between  $C_T$  measured and calculated from pH and TA was very good ( $r^2 = 0.998$ ), with an insignificant average difference of  $0.1 \pm 3.0 \mu\text{mol kg}^{-1}$  ( $n = 964$  data).  $CO_2$  certified reference materials (CRMs) and a collection of selected samples subsequently analyzed at the Scripps Institution of Oceanography were used to assess the accuracy of our measurements at sea with satisfactory results. The three measured  $CO_2$  system variables were then used to identify the characteristic array of zonal flows throughout the South Atlantic intersected by A14. Equatorial, subequatorial, subtropical, and subantarctic domains were identified at the depth range of the surface water, South Atlantic Central Water (SACW), Antarctic Intermediate Water (AAIW), Upper Circumpolar Water (UCPW), North Atlantic Deep Water (NADW) and Antarctic Bottom Water (AABW). The nonconservative  $CO_2$  system parameters (pH, TA,  $C_T$ ) have been useful in identifying the transition from aged subequatorial to ventilated subtropical surface, central and intermediate waters. They have been identified as good tracers of the zonal circulation of NADW, with marked flows at the equator, 13°S, and 22°S (the “Namib Col Current”) and the sharp transition from UNADW to UCPW at 23°S. The anthropogenic  $CO_2$  inventory ( $C_{ANT}$ ) was estimated and compared with CFC-derived apparent ages for different water masses along A14. The anthropogenic entry reached maximum in the relatively young and ventilated subantarctic and subtropical domains where AAIW was the most efficient  $CO_2$  trap. The calculated annual rate of  $C_{ANT}$  entry by AAIW was  $0.82 \mu\text{mol kg}^{-1} \text{y}^{-1}$ , in agreement with the annual rate estimated from the equilibrium between the atmospheric  $pCO_2$  increase and the upper mixed layer. **INDEX TERMS:** 4806 Oceanography: Biological and Chemical: Carbon cycling; 4283 Oceanography: General: Water masses; 4223 Oceanography: General: Descriptive and regional oceanography; 4536 Oceanography: Physical: Hydrography; **KEYWORDS:**  $CO_2$ , anthropogenic carbon, water masses, South Atlantic

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### 1. Introduction

[2] During the last decade, many oceanographers focused their efforts on global ocean circulation in relation to climate. They began the cooperative “World Ocean Circulation Experiment” (WOCE) to obtain high-quality hydro-

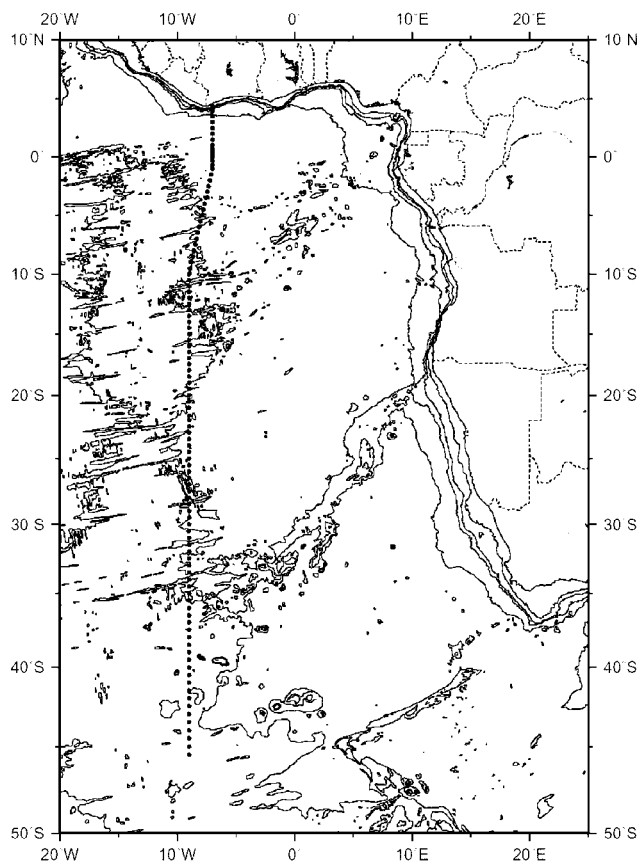
graphic data complemented with tracer measurements. Since ~30% of the anthropogenic emissions of the greenhouse gas  $CO_2$  seem to have been trapped by the oceans [Watson *et al.*, 1995], knowledge of the  $CO_2$  system parameters, partial pressure ( $pCO_2$ ), pH, total alkalinity (TA), and total inorganic carbon ( $C_T$ ), is essential for understanding the regulating action of the ocean on climate. Using the appropriate dissociation constants for carbonic acids [Millero, 1995], only two of the four parameters are needed to determine the  $CO_2$  system. Simultaneous measurements of at least one of the remaining two parameters allow a test of the internal consistency. However, field studies including measurements of more than two parameters are scarce [Millero *et al.*, 1993; Clayton *et al.*, 1995; Lee *et al.*, 1997; McElligott *et al.*, 1998; Johnson *et al.*, 1999].

<sup>1</sup>Consejo Superior de Investigaciones Científicas, Instituto de Investigaciones Marinas, Vigo, Spain.

<sup>2</sup>Pacific Northwest National Laboratory, Battelle Marine Sciences Laboratory, Sequim, Washington, USA.

<sup>3</sup>Universidad de las Palmas de Gran Canaria, Las Palmas de Gran Canaria, Spain.

<sup>4</sup>Laboratoire d’Océanographie Dynamique et Climatologie, Institut Pierre Simon Laplace, Paris, France.



**Figure 1.** Chart of the eastern South Atlantic Ocean with the position of the 107 full-depth stations surveyed along WOCE line A14. Isobaths 200 m and multiples of 1000 m are reported.

[3] Potentiometric pH and TA and coulometric  $C_T$  were measured at sea along WOCE line A14, in the Eastern Equatorial and South Atlantic (Figure 1). CO<sub>2</sub> “certified reference materials” (CRM) were used to test the accuracy of our measurements. In addition, duplicate analyses were performed to examine the precision of these methods. High internal consistency, accuracy, and precision of CO<sub>2</sub> parameters during the cruise allow us to characterize (1) the equatorial, subequatorial, subtropical, and subantarctic regimes imposed by the climatologically driven circulation in the upper ocean [Peterson and Stramma, 1991] and (2) the complex advection and mixing of intermediate, deep, and bottom waters of Antarctic origin with deep waters from the north Atlantic that exhibit opposing flow at different depths [Reid, 1989; Peterson and Whitworth, 1989].

[4] The initial concentrations of the CO<sub>2</sub> parameters in source regions of different water masses are modified by the oxidation of organic materials and the dissolution of carbonate skeletons [Broecker and Peng, 1982; Takahashi et al., 1985; Anderson and Sarmiento, 1994]. In addition, the initial pCO<sub>2</sub>, pH, and  $C_T$  of any water mass depend on the CO<sub>2</sub> levels in the overlying atmosphere, which have increased from preindustrial reference value of 278 ppm to 359 ppm in 1995 [Keeling et al., 1995]. The total amount of anthropogenic CO<sub>2</sub> dissolved in the ocean can be

estimated assuming that (1) dissolved oxygen and CO<sub>2</sub> are close to equilibrium with the atmosphere during water mass formation and (2) alkalinity is not significantly affected by the CO<sub>2</sub> increase [e.g., Chen and Millero, 1979; Poisson and Chen, 1987; Gruber et al., 1996]. On this basis we have examined the potential of the eastern South Atlantic as a sink for the anthropogenic CO<sub>2</sub> emitted throughout the industrial era. Finally, surface pCO<sub>2</sub> is compared with atmospheric concentration to establish the CO<sub>2</sub> sources and sinks at the time of the cruise in relation to the different zones observed in the upper ocean.

## 2. Methods

[5] The meridional line A14 was occupied during the first leg of cruise CITHER-3 (R/V L’Atalante, 13 January to 16 February 1995) from 4°N to 45°S along ~9°W (Figure 1). Data from a Neil-Brown Mark IIB CTD probe were acquired from the surface to 15 m above the bottom at 107 sampling stations. Water samples for chemical analyses were collected in 8 liter Niskin bottles at 30 depths throughout the water column. A comprehensive description of the cruise, sampling procedures, analytical techniques, and raw data are given by *Groupe CITHER-3* [1996, 1998]. Data are also available from the WOCE Hydrographic Program Office (<http://whpo.ucsd.edu/data/onetime/atlantic/a14>).

### 2.1. Sample Analyses

[6] Salinity was determined from conductivity measurements with a PORTASAL salinometer using the PSS78 equation [UNESCO, 1981] and dissolved oxygen was analyzed by the Winkler method following the recommendations of Joyce and Corry [1994]. Oxygen saturation for computing “apparent oxygen utilization” (AOU) was calculated using the equation of Benson and Krause [UNESCO, 1986]. Nutrients (nitrate + nitrite, phosphate, and silicate) were analyzed by segmented flow analysis following Hansen and Grasshoff [1983], with some modifications [Mouriño and Fraga, 1985; Alvarez-Salgado et al., 1992]. Salinity, dissolved oxygen (in  $\mu\text{mol kg}^{-1}$ ), and nutrients (in  $\mu\text{mol kg}^{-1}$ ) were determined in all samples collected. Chlorophyll *a* (Chl *a*) concentration in surface samples (in  $\text{mg m}^{-3}$ ) was estimated fluorometrically with a 10,000 R Turner fluorometer after 90% acetone extraction [Yentsch and Menzel, 1963]. Chlorofluoromethane CFC11 was measured using an extraction-trapping method in combination with gas chromatography using electron capture detection, as described by Bullister and Weiss [1988].

[7] The pH was measured with a Metrohm E-654 pH meter equipped with a Metrohm 6.0233.100 combination glass electrode and a Pt-100 probe for temperature control. The system was standardized with a National Bureau of Standards (NBS) phosphate buffer (pH = 7.413 at 25°C). The Nernstian response of the electrode was tested as described by Pérez and Fraga [1987a]. Total alkalinity (TA) was determined by automatic potentiometric titration with HCl ([HCl] = 0.1310) to a final pH of 4.44 [Pérez and Fraga, 1987b], using a “Titrino” Metrohm automatic potentiometric titrator with a Metrohm 6.0233.100 combined glass electrode and a Pt-100 probe. The [HCl] was potentiometrically titrated versus borax ( $\text{B}_4\text{O}_7\text{Na} \cdot 10\text{H}_2\text{O}$ )

**Table 1.** The pH<sub>15</sub>, TA, Measured C<sub>T</sub> (C<sub>T</sub>)<sub>M</sub>, Calculated C<sub>T</sub> (C<sub>T</sub>)<sub>C</sub> and Calculated pCO<sub>2</sub> on CRMs (Batch 24)<sup>a</sup>

Date	CRMs Analyzed	pH <sub>15</sub>	TA, μmol kg <sup>-1</sup>	(C <sub>T</sub> ) <sub>M</sub> , μmol kg <sup>-1</sup>	(C <sub>T</sub> ) <sub>C</sub> , μmol kg <sup>-1</sup>	pCO <sub>2</sub> , μatm
17-01-95	5	8.211 (±0.003)	2219 (±1.0)	1988.9 (±1.8)	1987.0 (±1.2)	345 (±3)
17-01-95	4	8.210 (±0.007)	2218 (±0.5)	1985.9 (±1.9)	1986.6 (±3.3)	346 (±6)
19-01-95	5	8.211 (±0.006)	2217 (±0.6)	1986.3 (±0.8)	1984.7 (±2.0)	345 (±5)
20-01-95	4	8.208 (±0.002)	2218 (±0.6)	1986.5 (±1.1)	1987.7 (±0.8)	348 (±2)
21-01-95	4	8.204 (±0.007)	2215 (±2.2)	1986.2 (±0.7)	1987.0 (±2.3)	351 (±5)
22-01-95	4	8.202 (±0.002)	2215 (±0.5)	1987.0 (±0.7)	1988.0 (±0.8)	354 (±2)
24-01-95	7	8.205 (±0.004)	2217 (±0.8)	1986.7 (±1.9)	1988.0 (±1.2)	351 (±4)
25-01-95	4	8.207 (±0.004)	2217 (±0.8)	1986.7 (±1.3)	1987.2 (±1.1)	349 (±4)
27-01-95	5	8.206 (±0.002)	2217 (±1.4)	1985.0 (±1.9)	1987.3 (±1.6)	350 (±2)
28-01-95	4	8.206 (±0.001)	2219 (±1.2)	1986.3 (±2.9)	1989.1 (±1.2)	350 (±1)
31-01-95	5	8.195 (±0.007)	2219 (±0.5)	1986.0 (±2.1)	1994.9 (±2.1)	361 (±4)
31-01-95	1	8.203	2214	1986.2	1986.7	352
2-02-95	4	8.200 (±0.002)	2217 (±0.5)	1984.9 (±3.4)	1990.4 (±2.1)	355 (±5)
4-02-95	5	8.204 (±0.003)	2218 (±1.4)	1984.9 (±1.3)	1989.3 (±1.5)	351 (±3)
6-02-95	4	8.210 (±0.004)	2219 (±1.6)	1985.5 (±0.7)	1987.3 (±2.6)	346 (±4)
9-02-95	8	8.211 (±0.004)	2217 (±1.1)	1986.3 (±1.6)	1985.5 (±1.9)	345 (±3)
10-02-95	3	8.208 (±0.004)	2216 (±0.5)	1986.6 (±3.8)	1986.0 (±2.4)	348 (±4)
Average		8.206 (±0.004)	2217.2 (±1.4)	1986.2 (±0.9)	1987.8 (±2.2)	350 (±4)
CRM	Batch 24	8.205 <sup>b</sup>	2216.0 (±1.0)	1987.55 (±1.3)		350.7 <sup>c</sup>

<sup>a</sup>Standard deviation of the CRMs analyzed per day (2nd column), in brackets. The pCO<sub>2</sub> was calculated using pH<sub>15</sub> and TA.

<sup>b</sup>The pH(NBS) calculated from C<sub>T</sub> and TA of CRM at 15°C. Independent measurements of pH(SWS) at 25°C were performed on CRMs and converted to the NBS scale at 15°C (pH<sub>15</sub> = 8.203) using the activity coefficient of *Mehrbach et al.* [1973].

<sup>c</sup>The pCO<sub>2</sub> was calculated from certified C<sub>T</sub> and TA at 15°C.

to a final pH of  $5.3 \pm 0.05$  [Pérez and Fraga, 1987b]. The pHs were measured at lab temperature and referred to 15°C (pH<sub>15</sub>) using the parameterisation of Pérez and Fraga [1987a], and TA results are expressed in μmol kg<sup>-1</sup>. Full water column profiles of pH<sub>15</sub> were produced at each of 107 stations occupied, whereas TA was determined at 39 stations. Additionally, TA of the surface sample was measured at each station.

[8] C<sub>T</sub> samples were collected following the procedure described by *U.S. Department of Energy* [1994] and preserved immediately with a saturated mercuric chloride solution to prevent biological production or consumption of CO<sub>2</sub>. Samples were analyzed within 14 h after collection; in the meantime they were kept cool and in the dark. The C<sub>T</sub> concentration was measured using a “Single Operator Multiparameter Metabolic Analyzer” (SOMMA) [Johnson *et al.*, 1987, 1993] coupled with coulometric detection. The seawater sample was drawn into a calibrated pipette and dispensed into a stripping chamber, where it was acidified with 8.5% phosphoric acid. The resultant CO<sub>2</sub> was carried into a coulometric cell with high purity N<sub>2</sub> gas (99.95%) where it was absorbed by and reacted with ethanolamine in dimethylsulfoxide. Seawater samples were collected at 42 stations to provide full C<sub>T</sub> profiles. Samples from the upper 1000 m were analyzed at 11 additional stations, to provide C<sub>T</sub> data in the main thermocline. C<sub>T</sub> and TA have been normalized to salinity 35.0 to produce the corresponding NC<sub>T</sub> and NTA parameters.

## 2.2. Precision, Accuracy, and Internal Consistency of Measured CO<sub>2</sub> Parameters

[9] At least one pair of Niskin bottles were closed at the same depth at each sampling station (field duplicate), providing a check of shipboard methodology precision. The average absolute difference between duplicate analyses was 0.003 for pH<sub>15</sub> and 1.1 μmol kg<sup>-1</sup> for TA, based on 174 and 61 field duplicates, respectively. In addition, each

of 30 bottles of the rosette sampler were closed at ~3000 m depth at station 45. The standard deviation of the 30 analyses of pH<sub>15</sub> and TA were 0.002 and 0.7 μmol kg<sup>-1</sup>, respectively. Analyses of C<sub>T</sub> field duplicates were performed ten times, with an average absolute difference of just 0.3 μmol kg<sup>-1</sup>. The average absolute difference of 80 laboratory duplicate C<sub>T</sub> analyses was 0.8 μmol kg<sup>-1</sup>. These laboratory analyses were performed by R. F. Keeling at Scripps Institution of Oceanography (SIO) immediately following the cruise.

[10] The accuracy of the measured CO<sub>2</sub> parameters was tested by means of “Certified Reference Materials” (CRMs) supplied by A. G. Dickson (University of California). CRMs (batch 24) were analyzed routinely every twenty samples for a total of 114 C<sub>T</sub> measurements. The average difference from the certified C<sub>T</sub> value (1987.55 μmol kg<sup>-1</sup>) was <0.94 μmol kg<sup>-1</sup>. The pH<sub>15</sub> and TA were also measured routinely using CRMs (Table 1). The average of 76 CRM analyses for TA ( $2217.2 \pm 1.4$  μmol kg<sup>-1</sup>) was in very good agreement with the certified concentration ( $2216.0 \pm 1.0$  μmol kg<sup>-1</sup>). In addition, ten selected C<sub>T</sub> samples were collected at seven stations along the cruise to be analyzed by P. Guenther (SIO) by the manometric method (Table 2). The results reinforce the accuracy of shipboard C<sub>T</sub> measurements, with  $0.9 \pm 2.4$  μmol kg<sup>-1</sup> as the average difference between samples analyzed at SIO and those analyzed on the ship.

[11] C<sub>T</sub> was calculated from pH<sub>15</sub> and TA using the thermodynamic equations of the carbonate system [Dickson, 1981] with the dissociation constants of *Mehrbach et al.* [1973], the pK<sub>B</sub> of *Lyman* [1956] recalculated by *Edmond and Gieskes* [1970], and K<sub>w</sub> of *Dickson and Riley* [1979]. Analytical errors of ±0.003 in pH and ±1.1 μmol kg<sup>-1</sup> in TA produce errors of ±1.2 and ±1.1 μmol kg<sup>-1</sup> in C<sub>T</sub>, estimated from the thermodynamic equations and the average values of pH<sub>15</sub>, TA, salinity, and temperature during the cruise. Consequently, the total error from the calculation of C<sub>T</sub> is

**Table 2.** Comparison of C<sub>T</sub> Measurements Performed by the Coulometric Method on Board and the Manometric Method at the Scripps Institution of Oceanography (SIO) at Ten Selected Samples<sup>a</sup>

Station	Bottle	(C <sub>T</sub> ) <sub>M</sub>	(C <sub>T</sub> ) <sub>C</sub>	(C <sub>T</sub> ) <sub>SIO</sub>	(C <sub>T</sub> ) <sub>SIO</sub> -(C <sub>T</sub> ) <sub>M</sub>	(C <sub>T</sub> ) <sub>SIO</sub> -(C <sub>T</sub> ) <sub>C</sub>
10	32	1906.7	1903.7	1910.0	3.4	6.4
22	32	2015.6	2015.6	2017.9	2.3	2.3
22	14	2188.9	2188.4	2189.8	0.8	1.3
49	22	2078.9	2077.1	2078.8	-0.1	1.7
49	4	2199.0	2202.1	2199.5	0.5	-2.6
55	32	2078.0	2075.5	2073.7	-4.2	-1.8
55	10	2199.2	2200.0	2197.3	-1.9	-2.8
76	31	2052.6	2056.0	2056.6	4.0	0.5
88	31	2041.6	2041.9	2043.8	2.3	1.9
100	31	2058.9	2059.0	2060.7	1.9	1.7
Average difference					0.9	0.9
Standard deviation					2.4	2.6

<sup>a</sup>C<sub>T</sub> calculated from pH and TA measurements on board are included as well. (C<sub>T</sub>)<sub>M</sub> and C<sub>T</sub> are measured coulometrically, (C<sub>T</sub>)<sub>C</sub> and C<sub>T</sub> are calculated from pH<sub>15</sub>-TA, and (C<sub>T</sub>)<sub>SIO</sub> and C<sub>T</sub> are measured manometrically at SIO. Concentrations in μmol kg<sup>-1</sup>.

±2.3 μmol kg<sup>-1</sup>. The regression between measured and calculated C<sub>T</sub> was very high (Figure 2). The average difference between calculated and measured C<sub>T</sub> during the cruise was 0.1 μmol kg<sup>-1</sup>, with an average error of the (C<sub>T</sub>)<sub>M</sub> estimate of ±3 μmol kg<sup>-1</sup>. Finally, calculated C<sub>T</sub> for 76 CRMs (Table 1) agrees well with the certified concentration and the average difference of the 10 C<sub>T</sub> samples measured at SIO and calculated from pH<sub>15</sub> and TA (Table 2) was only 0.9 ± 2.6 μmol kg<sup>-1</sup>. The results of these comparisons prove the high internal consistency of our data. Consequently, good precision, accuracy, and internal consistency of ship-board CO<sub>2</sub> measurements along line A14 make our data reliable for carbon studies in the South Atlantic.

[12] Surface pCO<sub>2</sub> can be calculated from pH<sub>15</sub>-TA, pH<sub>15</sub>-C<sub>T</sub>, and TA-C<sub>T</sub> using the thermodynamic equations of the carbonate system and the acid constants described above, together with the solubility coefficient of CO<sub>2</sub> in seawater [Weiss, 1974]. Analytical errors of ±0.003 in pH<sub>15</sub>, ±1.1 μmol kg<sup>-1</sup> in TA, and ±0.8 μmol kg<sup>-1</sup> in C<sub>T</sub> produced errors of ±3.5, ±0.2 and ±2 μatm in pCO<sub>2</sub>, respectively. The resultant total errors for the pH<sub>15</sub>-TA, C<sub>T</sub>-TA, and pH<sub>15</sub>-C<sub>T</sub> pairs were ±3.7, ±5.5, and ±2.2 μatm, respectively. Correlation between these three sets of calculated pCO<sub>2</sub> values was very high ( $r^2 > 0.98$ ) and the average difference was within the error of the pCO<sub>2</sub> estimate. For this study then, we have used the average of three estimates of surface pCO<sub>2</sub>. Calculated pCO<sub>2</sub> of CRMs from pH<sub>15</sub>-TA (Table 1) had an average standard deviation of ±4.0 μatm, in agreement with the expected error of the pCO<sub>2</sub> estimate.

### 3. Results and Discussion

#### 3.1. Imprint of the Eastern South Atlantic Circulation on Carbon System Variables

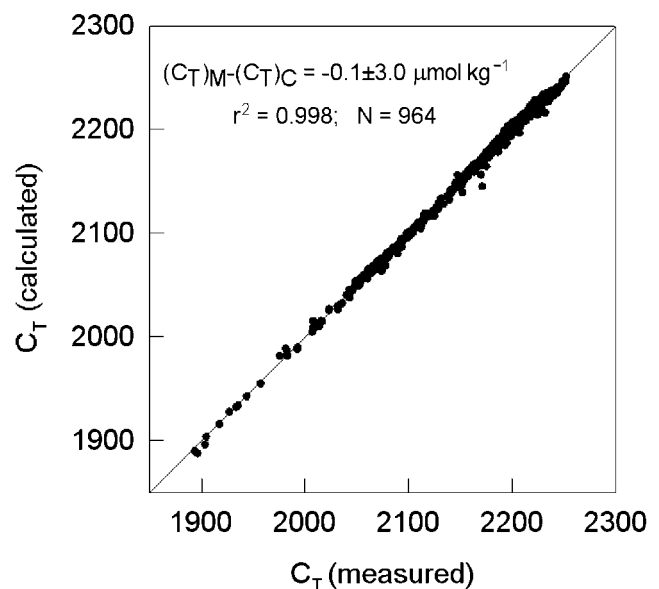
[13] A14 is the westernmost WOCE line in the eastern South Atlantic. It is situated just east of the Mid Atlantic Ridge (Figure 1) and affected by the well-defined zonal circulation of the South Atlantic Ocean [Peterson and Stramma, 1991]. The objective of this part is the identification of the main zonal regimes (equatorial, subequatorial, subtropical, and subantarctic) at the level of surface, central, intermediate, and deep waters along line A14, by means of measured and derived CO<sub>2</sub> system variables. The effect of

this zonation on the entry of anthropogenic carbon will be assessed in section 3.2.

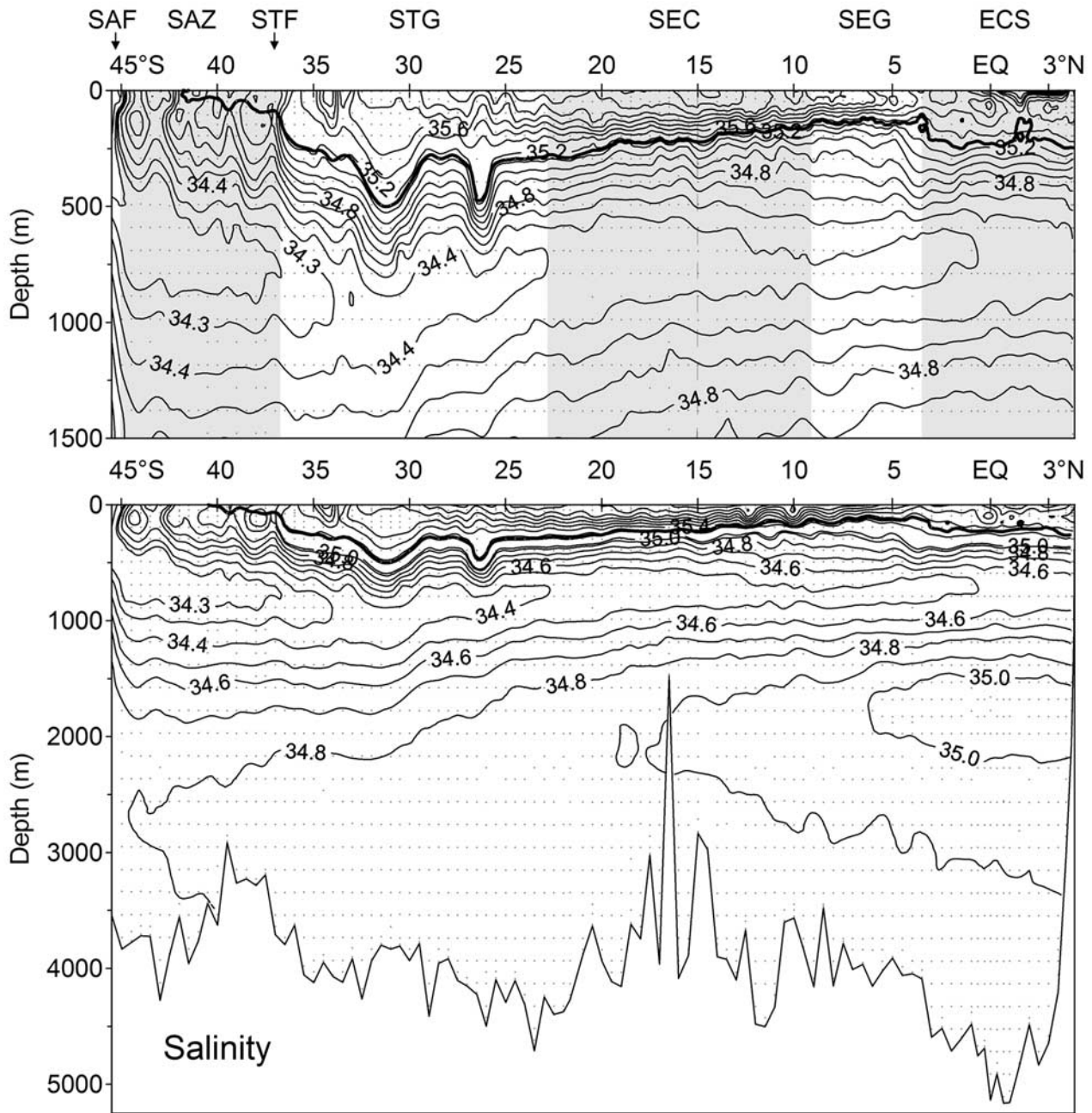
##### 3.1.1. Upper Ocean

[14] The climatologically driven upper ocean circulation originates a marked zonal array on thermocline waters, which produces a clear impact on the thermohaline and CO<sub>2</sub> system distributions (Figures 3, 4, 5, and 6). The 13°C isotherm, superimposed on the salinity distribution (Figure 3), was used to delimit the different zonal regimes observed along line A14 [Brea, 1998]. This isotherm is well within the South Atlantic Central Water (SACW) domain, which ranges from 10°C to 18°C [Gordon and Bosley, 1991].

[15] From north to south, line A14 began at 4°N (Figure 3). In the Equatorial Current System (ECS), between 4°N and 3°S, the 13°C isotherm was situated at ~250 m depth. Poleward rising to 100 m was observed near 3–4°S, which marks the eastward flowing South Equatorial Under-Current (SEUC) at the boundary between the ECS and the Sub-



**Figure 2.** Relationship between C<sub>T</sub> calculated and C<sub>T</sub> measured. The 1:1 line and the regression equation are reported.



**Figure 3.** Vertical distribution of salinity along line A14. The 13°C isotherm is depicted. ECS is Equatorial Current System, SEG is South Equatorial Gyre, SEC is South Equatorial Current, STG is Subtropical Gyre, STF is Subtropical Front, SAZ is Subantarctic zone, and SAF is Subantarctic Front. Vertical dashed line represents subtropical-subequatorial transition.

equatorial Gyre (SEG). The 13°C isotherm was present at 125–150 m in the SEG domain (4–9°S). Poleward deepening was observed from 9°S to 23°S, tracing the northwest flowing South Equatorial Current (SEC). The 13° isotherm reached 300 m depth at 23°S. In the Subtropical Gyre (STG), between 23°S and 36°S, the isotherm was found at ~325 m. Two V-shaped structures deepening about 200 m were evident at 26°S (stations 68–69) and 31.5°S (stations 77–79) that correspond with two eddies detached from the Agulhas current [Arhan *et al.*, 1999]. At 36–37°S

the 13°C isotherm rose abruptly from 250 to 100 m, denoting the Subtropical Front (STF). Further south, within the Subantarctic Zone, the isotherm rose to shallower depths (~40 m) and disappeared south of 41°S.

#### 3.1.1.1. Surface Waters

[16] Surface distributions of temperature, salinity, chlorophyll, and pCO<sub>2</sub> (Figure 7) are very sensitive to the observed zonal regimes. Therefore it is the objective of this section to study how the contemporary uptake of atmospheric CO<sub>2</sub> in the Eastern South Atlantic was affected by

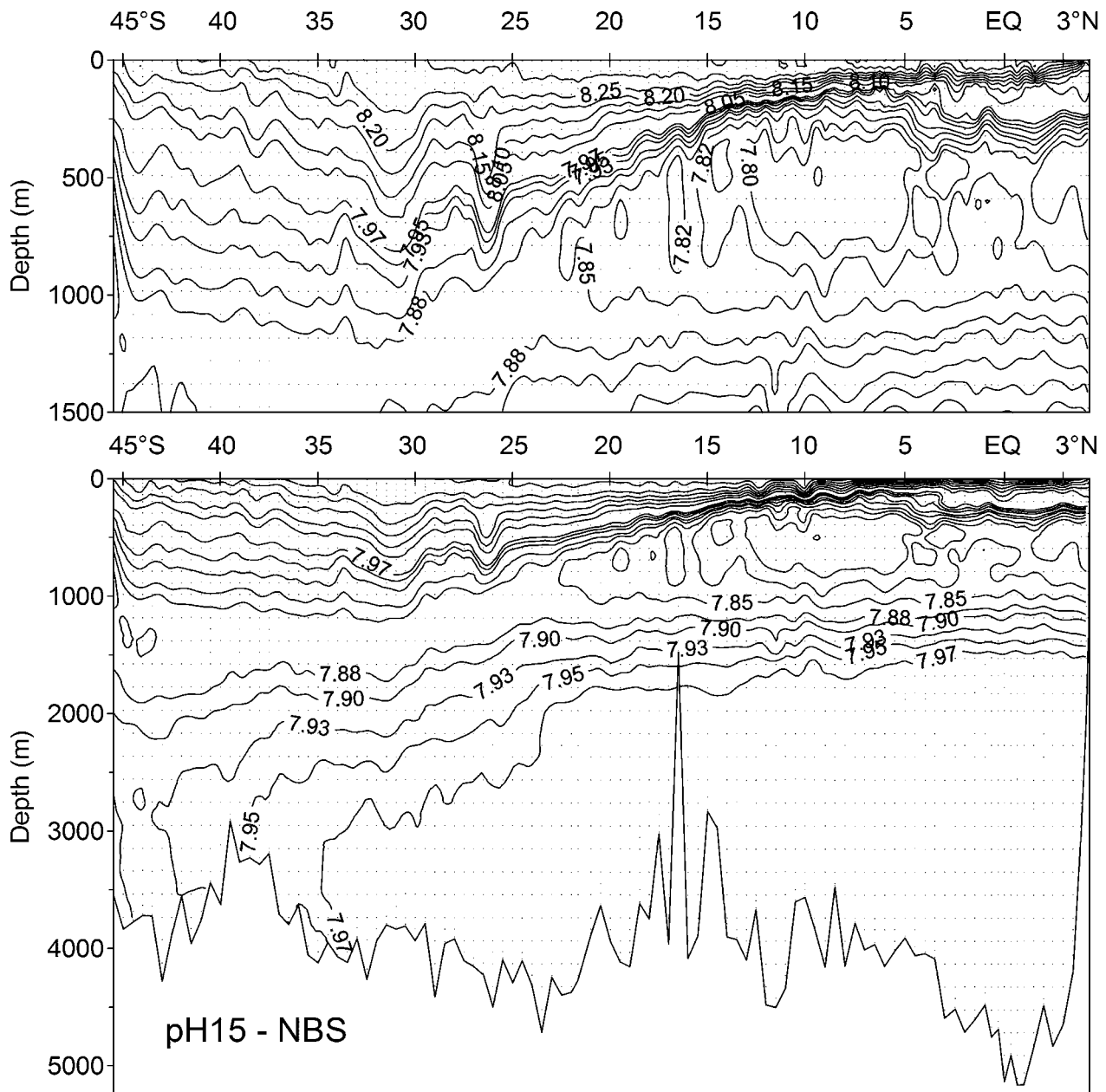
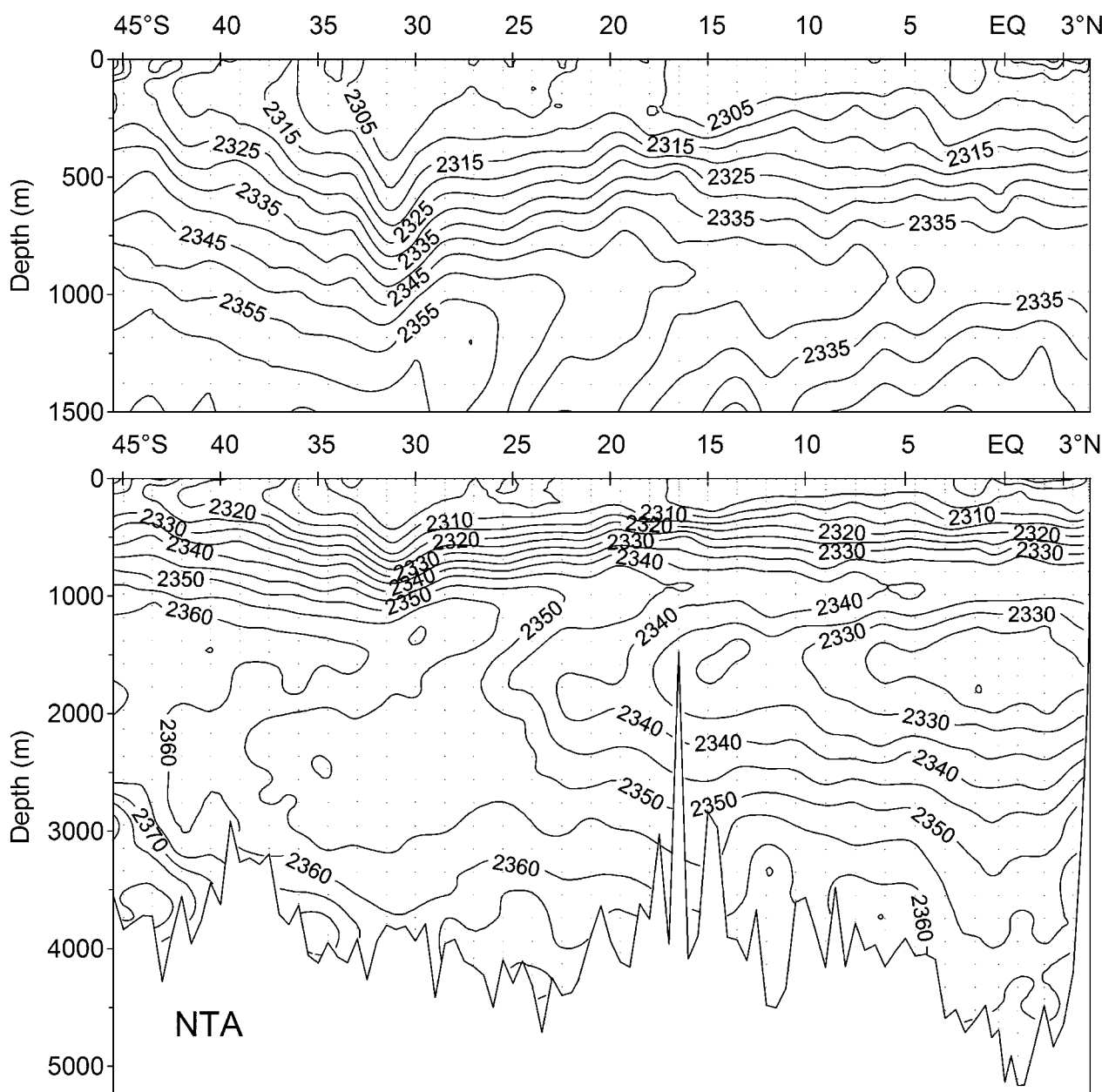


Figure 4. Vertical distribution of  $\text{pH}_{15}$  along the line A14.

such zonal arrangement. The average mole fraction in dry air of CO<sub>2</sub> ( $x_{\text{CO}_2}$ ) for 1995, 359 ppm according to Keeling *et al.* [1995], is represented by the dotted line in Figure 7b.

[17] Surface waters were  $\text{pCO}_2$  undersaturated north of the Equator, reaching a minimum of 313  $\mu\text{atm}$  at 4°16'N, where maximum surface chlorophyll *a* was recorded (3  $\text{mg m}^{-3}$ ). An area of constant surface  $\text{pCO}_2$  ( $\sim 330 \mu\text{atm}$ ) and very low chlorophyll concentrations ( $\sim 0.08 \text{ mg m}^{-3}$ ) appeared just south of the  $\text{pCO}_2$  minimum (Figure 7b) and extended up to 2°N. In this zone, nutrients were depleted at the surface and the nutricline was located at  $\sim 20 \text{ m}$  (not shown). Maximum surface temperature were recorded ( $>28^\circ\text{C}$ ) when salinity was  $<35$  (Figure 7a). The salinity minimum and temperature maximum in this region is known as the Low-Salinity Region (LSR) and is expected

to be  $\text{pCO}_2$  undersaturated [Bakker *et al.*, 1999]. The position of the LSR corresponds to the Intertropical Convergence Zone (ITCZ), where the wind systems of the two hemispheres converge producing high precipitation, lower salinity, and higher sea surface temperature. The position of this zone varies seasonally, being close to the equator in winter and moving northward in summer [Siedler *et al.*, 1992]. Similar results of low salinity accompanied by low  $\text{pCO}_2$  were found during several cruises executed in different seasons, suggesting that the LSR is a recurring or possibly a permanent feature [Oudot and Andrié, 1989; Lefèvre *et al.*, 1998; Bakker *et al.*, 1999]. Surface salinity and temperature at the LSR along A14 were 1 unit lower and 6°C higher than at 20 m depth, where  $\text{pCO}_2$  levels rose to 485  $\mu\text{atm}$ . Therefore the contribution of CO<sub>2</sub>-free rain-



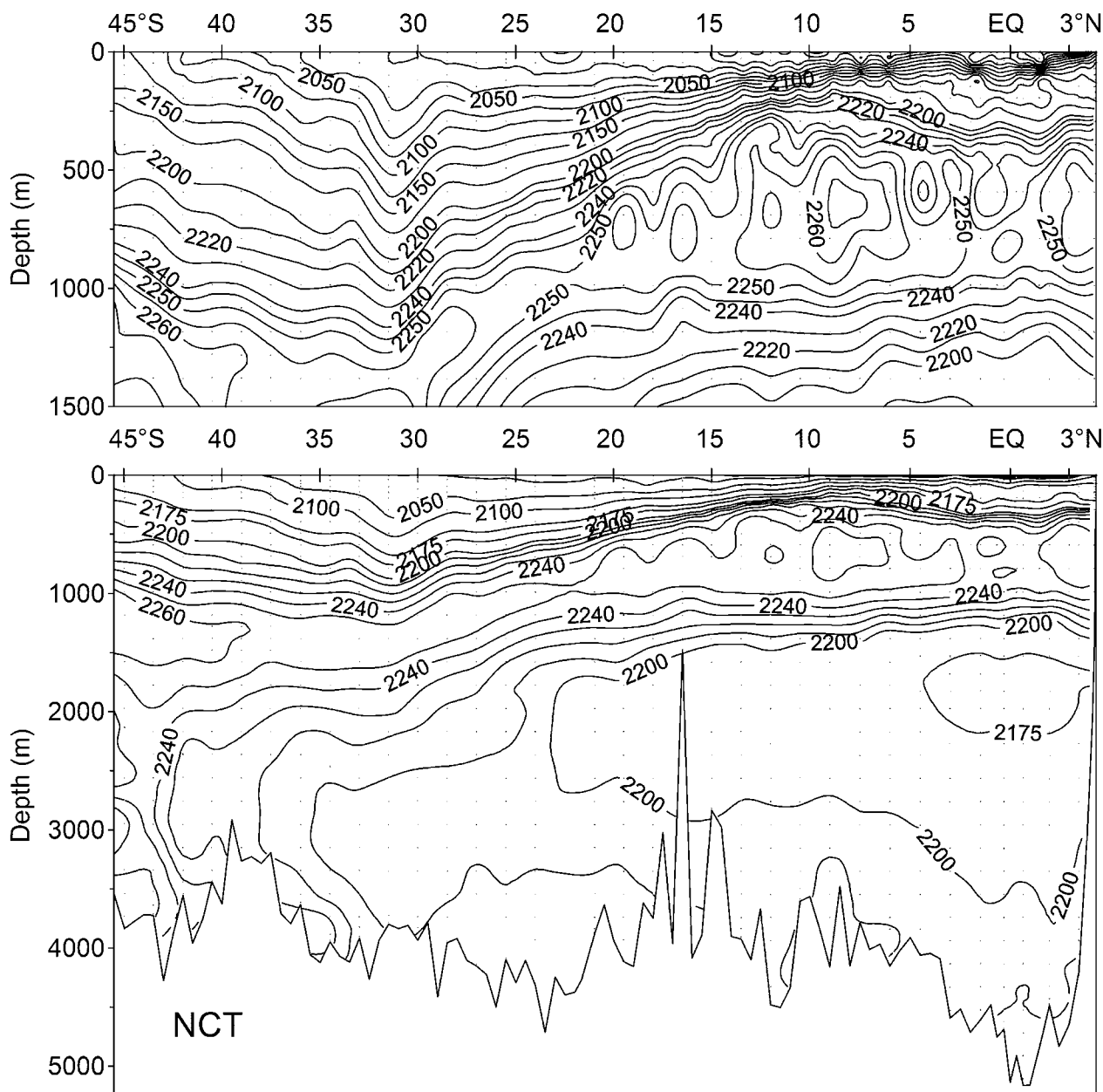
**Figure 5.** Vertical distribution of normalized total alkalinity (NTA) in  $\mu\text{mol kg}^{-1}$  along line A14. Dotted line represents meridional evolution of the UCPW NTA maximum.

water to the composition of surface waters in the LSR was about 3% compared with seawater at 20 m depth. This dilution produces a decrease of  $65.8 \mu\text{mol kg}^{-1}$  in TA and a corresponding  $\text{pCO}_2$  decrease of  $14 \mu\text{atm}$  (from 485 to 471  $\mu\text{atm}$ ). Since surface  $\text{pCO}_2$  in the LSR decreases to 330  $\mu\text{atm}$ , intense net primary production must be the cause of the observed low-surface  $\text{pCO}_2$ . This seems contradictory because chlorophyll concentrations in the LSR were quite low. However, it must be noted that (1) surface  $\text{pCO}_2$  does not depend only on surface chlorophyll but on its vertical distribution and (2) chlorophyll is not an index of primary production but an index of the biomass retained in the water column after grazing and sedimentation of primary producers. The fact that pH in surface waters was 0.24 units

higher than at the nutricline suggests intense net primary production in the LSR. This pH increase resulted in a  $\text{pCO}_2$  decrease of 294  $\mu\text{atm}$  (from 485 to 191  $\mu\text{atm}$ ). The difference between the observed (330  $\mu\text{atm}$ ) and the expected ( $485 - 14 - 294 = 177 \mu\text{atm}$ ) surface  $\text{pCO}_2$  levels after consideration of freshwater dilution and net primary production ( $330 - 177 = 153 \mu\text{atm}$ ) was due to the surface temperature increase of  $6^\circ\text{C}$ . Therefore the combination of thermohaline characteristics and biological activity can explain the low  $\text{pCO}_2$  values in the LSR at the time of A14 (January–February 1995).

[18] In the  $0-4^\circ\text{S}$  zone, salinity increased abruptly and temperature decreased slowly (Figure 7a), due to equatorial upwelling. Surface  $\text{pCO}_2$  also increased, reaching values near





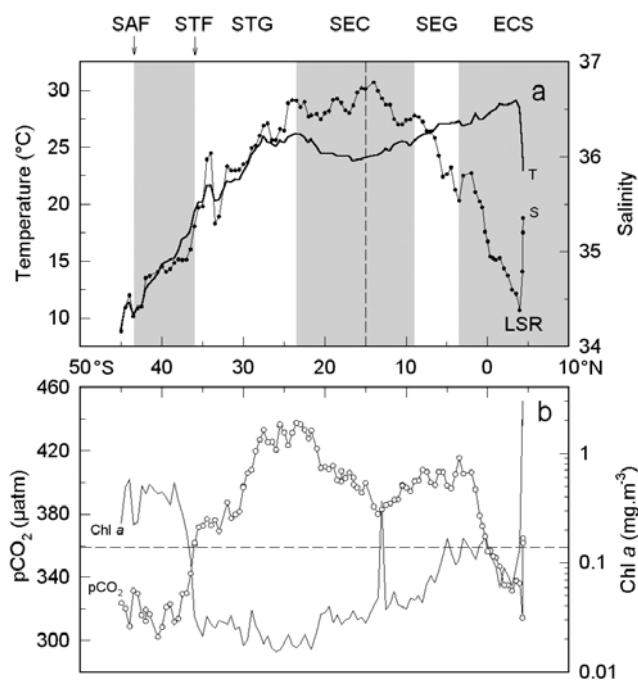
**Figure 6.** Vertical distribution of normalized total inorganic carbon ( $NC_T$ ) in  $\mu\text{mol kg}^{-1}$  along line A14. Dashed line represents equatorial/sub-equatorial SACW  $NC_T$  maximum. Dotted line represents meridional evolution of the UCPW  $NC_T$  maximum.

400  $\mu\text{atm}$ , whereas chlorophyll levels were  $\sim 0.15 \text{ mg m}^{-3}$  (Figure 7b). Despite low surface  $p\text{CO}_2$  levels in the LSR, the whole equatorial zone ( $4^\circ\text{N}$ – $4^\circ\text{S}$ ) was  $p\text{CO}_2$  oversaturated acting as a  $\text{CO}_2$  source to the atmosphere. The average  $\pm$  std oversaturation ( $\Delta p\text{CO}_2$ ) for the whole equatorial zone was  $9 \pm 29 \mu\text{atm}$  at the time of A14. *Andrié et al.* [1986] and *Smethie et al.* [1985] obtained similar values ( $8 \pm 19 \mu\text{atm}$  and  $11 \pm 17 \mu\text{atm}$ , respectively) at the same time of the year (January–February) farther east. The extremely high  $\Delta p\text{CO}_2$  ( $45 \pm 25 \mu\text{atm}$ ) recorded by *Oudot et al.* [1987] was attributed to a climate condition anomaly in 1984.

[19] Surface salinity increased while temperature decreased along the SEG zone ( $4$ – $9^\circ\text{S}$ ), where  $p\text{CO}_2$  values were constant ( $402 \pm 5 \mu\text{atm}$ ) and chlorophyll decreased

from 0.15 to  $0.03 \text{ mg m}^{-3}$ . The highest salinity values ( $36.5 \pm 0.1$ ) were observed in the SEC zone ( $9$ – $23^\circ\text{S}$ ) in combination with relatively low temperatures ( $24.6 \pm 0.6^\circ\text{C}$ ). The conspicuous V-shaped  $p\text{CO}_2$  distribution centered at  $\sim 13^\circ\text{S}$  traced the limit between the subtropical and sub-equatorial regimes. A local chlorophyll maximum ( $0.36 \text{ mg m}^{-3}$ ) was observed at that position, coinciding with local  $p\text{CO}_2$  minimum ( $383 \mu\text{atm}$ ). Temperature decrease and net primary production could be the causes of these relatively low  $p\text{CO}_2$  values. It should be noted that the depth of the nutricline at the center of the SEC was located at 137 m, while in the equatorial zone it was found at 20 m depth.

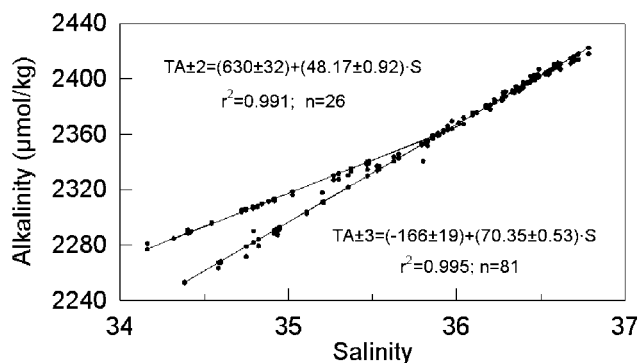
[20] Within the STG salinity, temperature, and  $p\text{CO}_2$  decreased by 1.3,  $1.3^\circ\text{C}$  and  $75 \mu\text{atm}$ , respectively, from



**Figure 7.** Distribution of (a) surface salinity and temperature ( $^{\circ}\text{C}$ ) and (b) surface  $\text{pCO}_2$  ( $\mu\text{atm}$ ) and chlorophyll *a* ( $\text{mg m}^{-3}$ ) along the line A14. ECS is Equatorial Current System, SEG is South Equatorial Gyre, SEC is South Equatorial Current, STG is Subtropical Gyre, STF is Subtropical Front, SAZ is Subantarctic zone, and SAF is Subantarctic Front. Vertical dashed line in Figure 7a represents subtropical/subequatorial transition. Horizontal dashed line represents the mole fraction in dry air ( $x\text{CO}_2$ ) for 1995 (359 ppm) according to Keeling *et al.* [1995].

23 $^{\circ}$ S to 36 $^{\circ}$ S. Chlorophyll concentrations were constant below the detection limit ( $\sim 0.03 \text{ mg m}^{-3}$ ). South of the STF (36–37 $^{\circ}$ S) a sharp decrease of surface  $\text{pCO}_2$  levels was observed, reaching values below saturation. The  $\text{pCO}_2$  undersaturation was caused by low temperatures associated with Subantarctic Surface Water and increased biological activity in the Subantarctic Zone, which produced high surface chlorophyll concentrations of  $\sim 0.4 \text{ mg m}^{-3}$ . Net primary production was favored in the Subantarctic Zone by a marked increase of surface nutrient concentrations; nitrate reached  $>15 \mu\text{mol kg}^{-1}$  in the southern end of A14 at the SAF (not shown). Although surface salinity in the Subantarctic and Equatorial zones was quite similar, TA clearly indicates the difference in origin of surface waters in these two regions. The TA-S plot shows two well-defined ( $r^2 > 0.99$ ) linear relationships north and south of 33 $^{\circ}$ S (Figure 8). For any salinity  $<36$ , TA was greater to the south (Subantarctic Surface Water influence) than to the north (Equatorial LSR influence).

[21] More than 80% of the total variability of surface  $\text{pCO}_2$  along A14 can be explained by a multiple linear regression with surface salinity and temperature ( $r^2 = 0.81$ ,  $n = 107$ ;  $p < 0.001$ ). The remaining 20% have to be due to the local effect of net primary production. In fact, a significant negative correlation was observed between surface  $\text{pCO}_2$  and chlorophyll ( $r^2 = 0.21$ ,  $n = 106$ ,  $p < 0.001$ ).

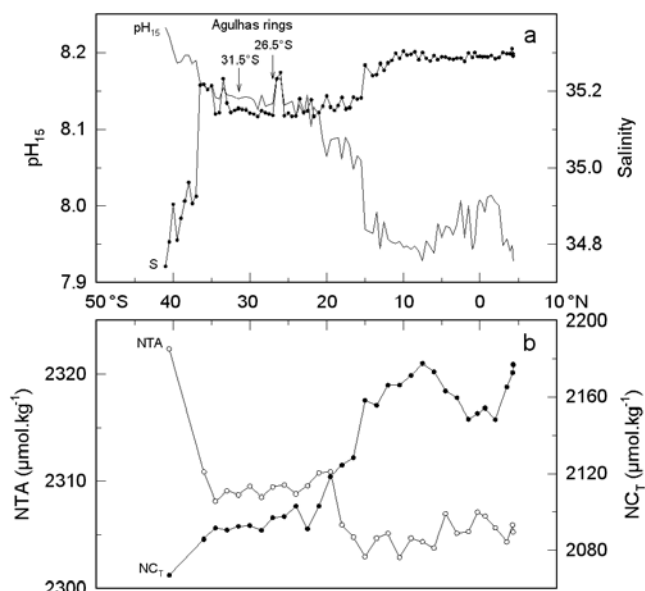


**Figure 8.** Relationship between total alkalinity ( $\mu\text{mol kg}^{-1}$ ) and salinity in surface waters along line A14. The corresponding linear regressions are reported.

However, the multiple regression of surface  $\text{pCO}_2$  with salinity, temperature, and chlorophyll did not significantly improve the regression with the thermohaline properties ( $r^2 = 0.82$ ,  $n = 106$ ,  $p < 0.001$ ) due to the inadequacy of chlorophyll measurements to represent net primary production.

### 3.1.1.2. Central Waters

[22] The evolution of salinity and  $\text{CO}_2$  system variables ( $\text{pH}_{15}$ ,  $\text{NC}_T$ , and NTA) along the 13 $^{\circ}\text{C}$  isotherm (Figure 9) clearly show the effect of different zonal regimes in the SACW domain. Salinity remained constant at  $35.29 \pm 0.01$  north of 15 $^{\circ}$ S where a sharp decrease of 0.13 was observed, denoting the abrupt transition from the subequatorial to the subtropical SACW branches. The observed salinity excess of subequatorial SACW on the eastern South Atlantic could be due to regional excess evaporation in the SEG [Gordon and Bosley, 1991] or transport of the Salinity Maximum Water formed in the tropical western South Atlantic by the



**Figure 9.** Meridional evolution of (a) salinity and  $\text{pH}_{15}$  and (b)  $\text{NC}_T$  and NTA in  $\mu\text{mol kg}^{-1}$  along the SACW 13 $^{\circ}\text{C}$  isotherm.

SECC [Mémery *et al.*, 2000]. Salinity along the 13°C isotherm was constant at ~35.16 from 15°S to the STF (36–37°S). South of the STF, salinity decreased abruptly coinciding with a sudden rise of the 13°C isotherm in the subantarctic zone.

[23] The pH<sub>15</sub> levels along the 13°C isotherm increased southwards. The most conspicuous features were a local maximum (excess of ~0.05 units) between 3°N and 3°S and successive steep increases of ~0.10 units at 15°S (subequatorial-subtropical transition) and ~0.05 units at 21–22°S (northern limb of the STG) and at 36–37°S (STF). Maximum pH<sub>15</sub> values (8.23) were recorded within the Subantarctic Zone, coinciding with an observed salinity minimum. The evolution of NC<sub>T</sub> was opposite that of pH<sub>15</sub> (Figure 9b), with an excess of ~60 μmol kg<sup>-1</sup> in the SEG compared to the STG as a result of a sudden NC<sub>T</sub> change between 15°S and 23°S. On the other hand, NTA concentrations showed a brief excess of ~4 μmol kg<sup>-1</sup> in the subtropical SACW domain. The observed ΔNC<sub>T</sub>/ΔNTA molar ratio of -15 between SACW at 13°C in the SEG and the STG indicates that >96% of the NC<sub>T</sub> excess in the SEG results from organic carbon oxidation rather than from CaCO<sub>3</sub> dissolution, as expected at these shallow levels (140 m). It should be noted that the NC<sub>T</sub> excess in the SEG is maximum at 400–700 m depth, where extreme pH<sub>15</sub> and NC<sub>T</sub> values of <7.80 and >2265 μmol kg<sup>-1</sup> were recorded (Figures 4 and 6). The low pH<sub>15</sub> and high NC<sub>T</sub> concentrations observed were due to the sedimentation associated with high net primary production rates in the surface water [Reid, 1989] and prolonged residence time (4.4 and 8.5 years) of thermocline waters in the SEG [Gordon and Bosley, 1991].

[24] The Agulhas ring centered at 26°S clearly affected salinity and pH<sub>15</sub> distributions along the 13°C isotherm (Figure 9a). The pH<sub>15</sub> values were 0.03 units higher than in the surrounding waters. Expected NC<sub>T</sub> and NTA minima were not observed (Figure 9b) because these variables were not measured at stations where the 26°S ring was located. On the contrary, although the 31.5°S ring was sampled, no indications of its presence appeared in any of the plotted distributions. According to Arhan *et al.* [1999], the 26°S ring remained at the higher latitudes of the Agulhas retro-reflection region during a winter, where it experienced a large heat loss (it is 3.5°C cooler than the second ring) and ventilation, causing an increase of oxygen (13 μmol kg<sup>-1</sup> higher than the ring centered at 31.5°S). This resulted in a net increase of pH<sub>15</sub> and therefore an expected decrease of NC<sub>T</sub>.

### 3.1.2. Intermediate and Deep Waters

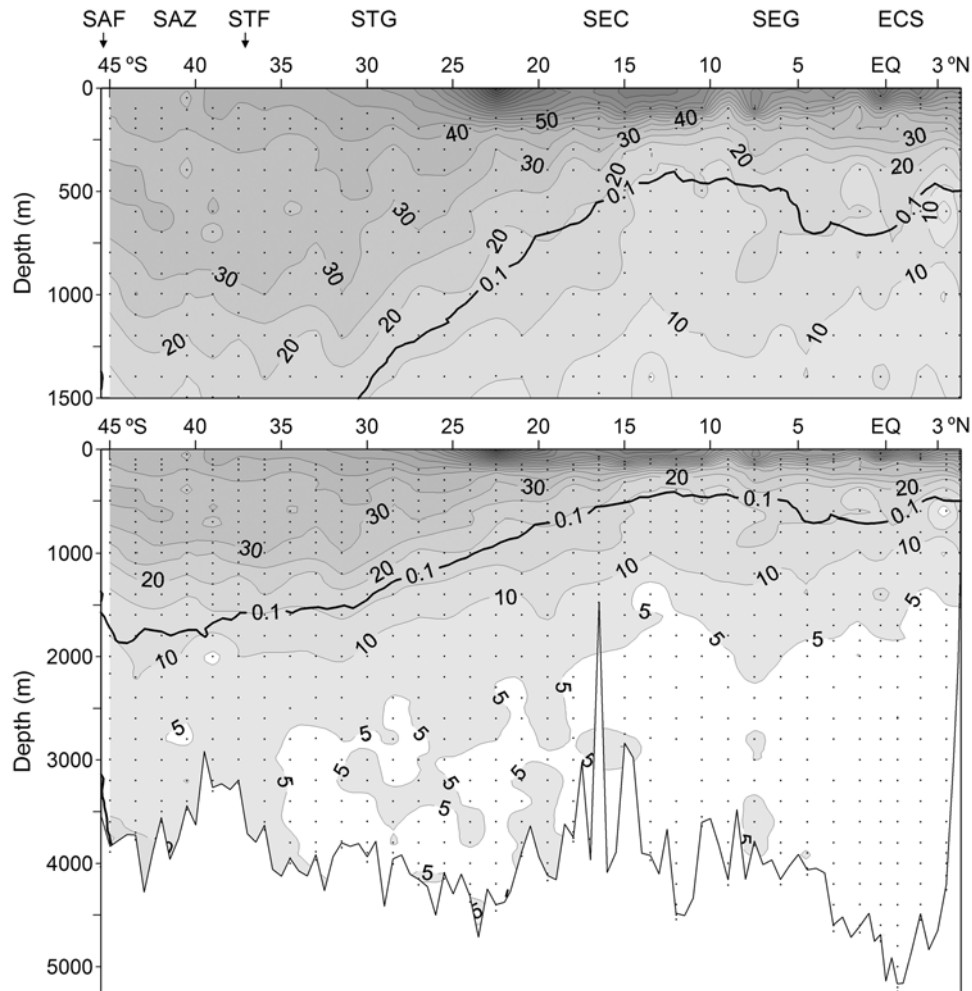
[25] Below the thermocline, carbon-rich waters of Antarctic origin mix with carbon-poor waters of North Atlantic origin. The northward spread of Antarctic Intermediate Water (AAIW) in the South Atlantic has been traditionally marked by a conspicuous salinity minimum clearly observed in Figure 3 [e.g., Wüst, 1935; Reid, 1989]. The meridional evolution of the AAIW salinity minimum denotes the sequence of zonal regimes observed in thermocline waters, as previously described in great detail by other authors [Warner and Weiss, 1992; Boebel *et al.*, 1997]. We note here a sudden pH<sub>15</sub>, NTA, and NC<sub>T</sub> changes at the level of the AAIW salinity minimum (not shown) denoting the transition from the ventilated subtropical to the aged

subequatorial AAIW domains that occurred at 23°S, i.e., 7° south of the transition in the overlying SACW domain.

[26] The northward spread of the aged Upper Circumpolar Water (UCPW) can be traced by the meridional evolution of the NTA and NC<sub>T</sub> maxima (Figures 4, 5, and 6) observed just below the AAIW salinity minimum at the southern end of A14. UCPW was present at ~1400 m from the SAF to the STF with NTA and NC<sub>T</sub> concentrations of 2364 and 2265 μmol kg<sup>-1</sup>, respectively. Equatorward rising of these extrema occurred throughout the STG up to ~1000 m at 23°S, where NTA and NC<sub>T</sub> concentrations were 2350 and 2250 μmol kg<sup>-1</sup>, respectively. North of 23°S the NTA and NC<sub>T</sub> extrema did not occur at the same depth. The NC<sub>T</sub> maximum coincided with the AAIW salinity minimum centered at 800 m. The NTA maximum (~2342 μmol kg<sup>-1</sup>) remained at 1000 m, coinciding with the silicate maximum (~34 μmol kg<sup>-1</sup>) and the CFCs minimum (~0.01 pmol kg<sup>-1</sup>) in the subequatorial and equatorial domains (not shown). The presence of appreciable volumes of UCPW north of the subtropical-subequatorial transition is still a matter of open discussion. McCartney [1993], Andrié *et al.* [1998], and Oudot *et al.* [1998] identified the property extrema at 1000 m depth as UCPW. Conversely, Tsuchiya *et al.* [1994] considered that they are really part of the AAIW domain, and Larqué *et al.* [1997] suggested that the UCPW progresses northward to about 24°S in the western basin and most of it returns southwards in the eastern basin. As a consequence of this controversy, Stramma and England [1999] give no circulation scheme in the most recent review of the South Atlantic circulation.

[27] The Deep Western Boundary Current (DWBC) transports North Atlantic Deep Water (NADW) from the Northern Hemisphere into the South Atlantic. Frequently, the NADW is separated into three layers: upper, middle, and lower NADW [e.g., Wüst, 1935; Friedrichs *et al.*, 1994; Stramma and England, 1999]. UNADW along A14 can be clearly distinguished by extreme values of all parameters (S > 35, pH<sub>15</sub> > 7.99, NTA < 2325 μmol kg<sup>-1</sup>, NC<sub>T</sub> < 2190 μmol kg<sup>-1</sup>) at 1500–2000 m depth in the Equatorial domain (Figures 3, 4, 5, and 6). Eastward deflection of the southward flowing DWBC along and just south of the equator has been observed in the NADW domain [Weiss *et al.*, 1985; Richardson and Schmitz, 1994; Rhein *et al.*, 1995; Andrié, 1996; Mercier and Arhan, 1997; Arhan *et al.*, 1998]. A uniform layer of S > 34.9, pH > 7.97, NTA < 2350 μmol kg<sup>-1</sup> and NC<sub>T</sub> < 2200 μmol kg<sup>-1</sup> was observed below the core of UNADW, which correspond to the deeper branches of NADW. A bend in the θ-S at ~2°C (not shown), coined as the Two-Degree Discontinuity (TDD) by Broecker *et al.* [1976], constitutes the lower limit of depth of the NADW. This limit is at ~4000 m on the northern end of A14, indicating that the deepest branches of NADW cross the Mid-Atlantic Ridge (MAR) through the Romanche Fracture Zone to enter the Eastern South Atlantic [Friedrichs *et al.*, 1994; Mercier and Morin, 1997].

[28] An isolate NTA minimum (<2330 μmol kg<sup>-1</sup>) at 1400–1700 m near 13°S (Figure 5) depicts the presence of a zonal jet transporting UNADW. According to Stramma and England [1999], NADW flows westward at ~15°S as a result of recirculation at the eastern flank of the MAR UNADW and UCPW encountered at 23°S, where they form a marked front that is easily observed in the distributions of



**Figure 10.** Vertical distribution of anthropogenic carbon ( $\mu\text{mol kg}^{-1}$ ) along line A14. Solid line represents CFC11 isopleth of  $0.1 \text{ pmol kg}^{-1}$ .

all the study properties (Figures 3, 4, 5, 6, and 10). As a consequence, NADW flows to the eastern basin through the Rio de Janeiro ( $22^{\circ}\text{S}$ ) and the Rio Grande ( $26^{\circ}\text{S}$ ) Fracture Zones of the MAR [Mercier *et al.*, 2000], and is deflected eastwards to meet a zonal jet that Warren and Speer [1991] called the “Namib Col Current” near  $22^{\circ}\text{S}$  in the Angola Basin. The existence of an eastward flow near  $25^{\circ}\text{S}$  centered at 2000 m, which transports NADW from the western South Atlantic, was first suggested by Reid [1989] and corroborated by Speer *et al.* [1995]. Local maxima of salinity and pH and minima of NTA and  $\text{NC}_T$  at  $\sim 22^{\circ}\text{S}$  in the UNADW domain ( $\sim 1800 \text{ m}$ ) traced the “Namib Col Current” along A14. To the south of  $23^{\circ}\text{S}$ , the deeper branches of NADW can be observed, centered at 2400 m, by the distributions of the measured variables (Figures 3, 4, 5, 6, and 10).

[29] Antarctic Bottom Water (AABW) along A14 consisted exclusively of Lower Circumpolar Water (LCPW) since the  $>46.04 \sigma_4$  characteristic density of Weddell Sea Deep Water (WDSW) was not observed. AABW can be distinguished in the southernmost side of the section by low  $\text{pH}_{15}$  (7.881–7.915) and high NTA (2370–2380  $\mu\text{mol kg}^{-1}$ ) and  $\text{NC}_T$  (2260–2270  $\mu\text{mol kg}^{-1}$ ) values in the bottom layer, spreading north to  $36^{\circ}\text{S}$ . At this point, the

Walvis ridge limits the northward extension of AABW. Minor volumes of this water mass were observed in abyssal depths ( $>4000 \text{ m}$ ,  $<2^{\circ}\text{C}$ ) at the equator, which enter from the western basins through the Romanche Fracture zone and can be traced by high NTA (2355–2360  $\mu\text{mol kg}^{-1}$ ) and  $\text{NC}_T$  (2210–2215  $\mu\text{mol kg}^{-1}$ ) concentrations.

### 3.2. Anthropogenic CO<sub>2</sub>

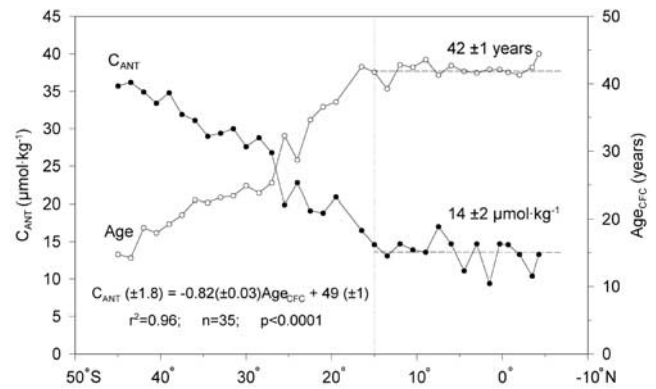
[30] The method used for calculating anthropogenic carbon ( $C_{\text{ANT}}$ ) is based on a modification of the back-calculation technique proposed by Brewer [1978] and Chen and Millero [1979], further modified by Gruber *et al.* [1996] and improved by Pérez *et al.* [2002]. In this technique, correction of the effect of organic carbon oxidation and  $\text{CaCO}_3$  dissolution processes on the distribution of  $C_T$  allows the determination of the initial  $\text{CO}_2$  ( $C_T^0$ ) of different water masses in source regions. In addition, assuming that dissolved oxygen and  $\text{CO}_2$  are close to equilibrium (or with the same disequilibrium) with the atmosphere during waters mass formation,  $C_T^0$  has progressively increased since the preindustrial era. Conversely,  $\text{TA}^0$  is not significantly affected by the entry of anthropogenic  $\text{CO}_2$  because in surface waters that are  $\text{CaCO}_3$  supersaturated,  $\text{CaCO}_3$  dissolution due to progressive acidification is negligible [Chen

and Millero, 1979; Poisson and Chen, 1987; Gruber et al., 1996]. The total amount of anthropogenic CO<sub>2</sub> trapped in any parcel of water ( $C_{ANT}$ ) according to Ríos et al. [2001] and Pérez et al. [2002] is calculated from  $C_T$ , TA and dissolved oxygen measured at the sea:

$$C_{ANT} = C_T - AOU/R_C - 1/2 \cdot (TA - TA^0 + AOU/R_N) - C_{T278}^0, \quad (4)$$

where  $AOU/R_C$  is the  $C_T$  increase by organic matter oxidation. Apparent Oxygen Utilization (AOU) is calculated with the oxygen saturation equation of Benson and Krause [UNESCO, 1986].  $R_C$  is a stoichiometric coefficient ( $=-\Delta O_2/\Delta C$ ). Additionally,  $1/2 \cdot (\Delta TA + AOU/R_N)$  is the  $C_T$  change due to CaCO<sub>3</sub> dissolution in deep ocean waters [Broecker and Peng, 1982], where  $\Delta TA$  is the total alkalinity change from the initial value during water mass formation ( $TA^0$ ), and  $R_N$  is a second stoichiometric coefficient ( $=-\Delta O_2/\Delta N$ ). For open ocean waters below 400 m  $R_C = 1.45$  and  $R_N = 10.6$  [Anderson and Sarmiento, 1994].  $TA^0$  stands for preformed alkalinity and was calculated using the A14 database, with an error of the estimation of  $4.4 \mu\text{mol kg}^{-1}$ , from salinity and “PO” for the layer between 50 and 200 m, as the best approximation to the winter mixed layer, using the empirical equation obtained:  $TA^0 = 336.86 + 56.23 \cdot S + 0.0200 \cdot \text{PO}$  ( $r^2 = 0.97$ ,  $n = 116$ ,  $p < 0.001$ ) where “PO” =  $O_2 + R_P \cdot \text{PO}_4$ .  $R_P$  is a stoichiometric coefficient ( $=-\Delta O_2/\Delta P$ ) with a constant value of  $170 \text{ mol O}_2/\text{mol P}$  [Anderson and Sarmiento, 1994].  $C_{T278}^0$  is the initial  $C_T$  of any water mass in the preindustrial era, which can be calculated from time-independent  $TA^0$  and the atmospheric  $p\text{CO}_2$  level at that time and water vapor pressure [Pérez et al., 2002], where  $p\text{CO}_2 = x\text{CO}_2 \cdot (\text{Patm} - \text{vapor pressure})$  according to U.S. Department of Energy [1994]. The mole fraction of CO<sub>2</sub> in the preindustrial atmosphere ( $x\text{CO}_2$ ) was 278.2 ppm [Neftel et al., 1994; Sarmiento et al., 1995]. The method to estimate  $C_{ANT}$  is subject to a number of uncertainties. Using an error propagation analysis for  $C_{ANT}$  as given by Gruber et al. [1996] and Sabine et al. [1999], the maximum error associated with the  $C_{ANT}$  calculation was  $\pm 5.6 \mu\text{mol kg}^{-1}$ .

[31] The distribution of  $C_{ANT}$  along A14 is shown in Figure 10. The  $0.1 \text{ pmol kg}^{-1}$  CFC11 isoline, corresponding roughly to an apparent age of 37–39 years, is traced along the  $C_{ANT}$  isoline of  $15 \mu\text{mol kg}^{-1}$ . In general,  $C_{ANT}$  was a maximum in the upper 200 m, with the highest values ( $45\text{--}75 \mu\text{mol kg}^{-1}$ ) to the north of  $23^\circ\text{S}$  (Figure 10). Minimum penetration of  $C_{ANT}$  was observed in the equatorial zone, where the  $C_{ANT}$  isoline of  $15 \mu\text{mol kg}^{-1}$  was situated at  $\sim 400 \text{ m}$  due to the upwelling of old waters. The reduced  $C_{ANT}$  penetration extended to  $15^\circ\text{S}$ , at the sub-equatorial-subtropical transition. Further south, within the STG, large-scale downwelling produced a relative sink of the  $C_{ANT}$  rich upper waters that contribute to the penetration of new water volumes which were ventilated to the south of the STF. Concentrations  $>10 \mu\text{mol kg}^{-1}$  were found above a depth of  $\sim 2000 \text{ m}$  in the STG, whereas south of the STF the isoline of  $10 \mu\text{mol kg}^{-1}$  extended to  $\sim 2200 \text{ m}$ . The invasion of  $C_{ANT}$  is remarkable south of  $23^\circ\text{S}$ , especially south of the STF where the isoline of  $5 \mu\text{mol kg}^{-1}$  reaches the bottom,



**Figure 11.** Meridional evolution of anthropogenic carbon ( $C_{ANT}$ ) and “apparent age” calculated through CFC11 ( $\text{Age}_{\text{CFC}}$ ) in the AAIW salinity minimum along A14. The linear regression between  $C_{ANT}$  and  $\text{Age}_{\text{CFC}}$  is reported.

corresponding with the penetration of AABW. It is interesting to note that the penetration of  $C_{ANT}$  at the NADW domain in the Eastern South Atlantic had already begun at the core of eastward flowing UNADW centered at  $\sim 1400 \text{ m}$  at the equator.

[32] The distribution of  $C_{ANT}$  along A14 (Figure 10), was similar to that described by Chen [1982] (GEOSECS 1973), Gruber [1998] (SAVE 1989) east of A14, and Wanninkhof et al. [1999] (NOAA/OACES 1991) west of A14, although with some remarkable differences. In general, the  $C_{ANT}$  penetration was deeper during A14 than found by these authors, mainly due to the time elapsed among different database used in the  $C_{ANT}$  estimates. In addition, the  $C_{ANT}$  estimates can vary depending on the method used [Wanninkhof et al., 1999].

[33] AAIW in the Subantarctic Zone (south of  $36\text{--}37^\circ\text{S}$ ) appears as a thick layer of salinity  $<34.2$  (Figure 3), which transports the high  $C_{ANT}$  concentrations ( $>30 \mu\text{mol kg}^{-1}$ ) acquired south of the SAF to the interior of the South Atlantic. Figure 11 shows the meridional evolution of  $C_{ANT}$  along the AAIW salinity minimum during A14. Maximum  $C_{ANT}$  values of  $36 \mu\text{mol kg}^{-1}$  were observed at the southern end of the section ( $45^\circ 30'\text{S}$ ) and decreased northward  $15^\circ\text{S}$ . North of  $15^\circ\text{S}$ ,  $C_{ANT}$  became constant at  $14 \pm 2 \mu\text{mol kg}^{-1}$ . CFC11 exhibited the same trend as  $C_{ANT}$  along the AAIW salinity minimum, as suggested by the corresponding linear regression ( $r^2 = 0.88$ ,  $n = 35$ ,  $p < 0.0001$ ):

$$C_{ANT}(\pm 2.9) = 15.2(\pm 0.6) + 7.5(\pm 0.5) \text{CFC11}. \quad (5)$$

[34] Warner and Weiss [1992] found similar CFC11 and CFC12 evolutions at the AAIW 27.2 isopycnal surface along the prime meridian during the Ajax expeditions (1983–1984). In their study the concentrations of both CFCs became constant at  $20^\circ\text{S}$  instead of at  $15^\circ\text{S}$ , which we observed 10 years later.

[35] CFC concentrations supply information on time scales of oceanic processes such as advection and mixing. Equilibration with the overlying atmosphere at the time of water mass formation is usually invoked during the estimation of water mass ages by means of CFC concentrations [Warner and Weiss, 1992]. The “apparent age” ( $\text{Age}_{\text{CFC}}$ ) of

AAIW at the salinity minimum can be calculated converting the measured CFC11 concentrations into CFC-11 partial pressures (pCFC11) [Doney and Bullister, 1992]:

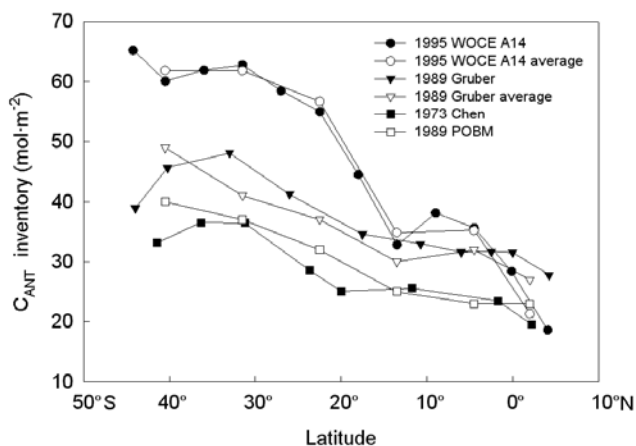
$$p\text{CFC} - 11 = [\text{CFC11}] \cdot F^{-1}, \quad (6)$$

where  $F$  is the solubility of CFC11, a function of potential temperature and salinity given by Warner and Weiss [1985].  $\text{Age}_{\text{CFC}}$  is then obtained matching the calculated pCFC11 with the atmospheric pCFC11 record. Reconstructed CFC11 annual mean dry air mole fractions in the Southern Hemisphere were used [Walker et al., 2000]. The course of  $\text{Age}_{\text{CFC}}$  at the AAIW salinity minimum along A14 referred to 1995 (Figure 11) is a mirror image of  $C_{\text{ANT}}$ . AAIW at 45°30'S was ~15 years old and became older as it evolved northwards. North of 15°S,  $\text{Age}_{\text{CFC}}$  was constant at 42 ± 1 year. There was a very good correlation between  $C_{\text{ANT}}$  and  $\text{Age}_{\text{CFC}}$  ( $r^2 = 0.96$ ,  $n = 35$ ,  $p < 0.001$ ).

[36] According to this regression, the annual rate of  $C_{\text{ANT}}$  entry in the ocean via AAIW is  $0.82 \mu\text{mol kg}^{-1} \text{y}^{-1}$ . This rate is in very good agreement with the annual rate of  $0.80 \mu\text{mol kg}^{-1} \text{y}^{-1}$  estimated from the equilibrium between the upper mixed layer and the average atmospheric  $x\text{CO}_2$  increase, according to Keeling et al. [1995]. In order to check the age of the AAIW salinity minimum at 45°S ( $C_{\text{ANT}} = 36 \mu\text{mol kg}^{-1}$  and  $\text{Age}_{\text{CFC}} = 15$  years) a back calculation was performed. Calculated  $C_{\text{T}}^0$  in the preindustrial time ( $x\text{CO}_2 = 278$  ppm) and in 1980 ( $x\text{CO}_2 = 336$  ppm) [Keeling et al., 1995], 15 years before A14, were  $2069 \mu\text{mol kg}^{-1}$  and  $2100 \mu\text{mol kg}^{-1}$ , respectively. Therefore the net anthropogenic carbon uptake was  $31 \mu\text{mol kg}^{-1}$  indicating that  $\text{Age}_{\text{CFC}}$  is comparable with the proper age of the water mass in this case. North of 15°S the CFC11 signal was below the detection limit. Consequently, we can only suggest that the AAIW was >42 years old in this zone.

[37] Similar  $C_{\text{ANT}}$  and  $\text{Age}_{\text{CFC}}$  calculations were performed for the overlying SACW 13°C isotherm along A14 (not shown). The average  $C_{\text{ANT}}$  entry along this isotherm was  $33 \pm 3 \mu\text{mol kg}^{-1}$ . The transition at 15°S separates the 22 ± 1 years old ( $\text{Age}_{\text{CFC}}$ ) subequatorial SACW to the north from the 10 ± 1 years old subtropical SACW to the south, with  $C_{\text{ANT}}$  entries of  $32 \pm 4$  and  $34 \pm 2 \mu\text{mol kg}^{-1}$ , respectively. The apparent age difference between the subtropical and subequatorial SACW branches (12 ± 2 years) exceeds the residence time of SACW in the SEG estimated by Gordon and Bosley [1991]. This indicates the time that subtropical SACW spends to arrive at the SEG through the SEC and then the ECS.

[38] Regarding the old and poorly ventilated UCPW just below the AAIW domain, the meridional evolution of  $C_{\text{ANT}}$  and  $\text{Age}_{\text{CFC}}$  have been examined along the core of maximum NTA (Figure 5). Constant  $C_{\text{ANT}}$  of  $17 \pm 2$  and  $13 \pm 1.6 \mu\text{mol kg}^{-1}$  were obtained south and north of 15°S, respectively. The corresponding  $\text{Age}_{\text{CFC}}$  were  $38 \pm 5$  and  $>45 \pm 2$  years. The youngest UCPW ( $33 \pm 1.4$  years) appeared south of the STF. The slight  $C_{\text{ANT}}$  penetration into the domain of the UNADW although coincident with the uncertainty ( $5.9 \pm 2.0 \mu\text{mol kg}^{-1}$ ), showed a systematic signal. This signal was also visible on the transect NOAA/OACES [Wanninkhof et al., 1999]. The penetration below 2500 m, south of 23°S, with AABW influence, showed an average  $C_{\text{ANT}}$  of  $5.7 \pm 2.0 \mu\text{mol kg}^{-1}$ , while



**Figure 12.** Meridional evolution of  $C_{\text{ANT}}$  inventories of WOCE A14 (black dots), averaged WOCE A14 (open dots), Gruber (black triangles down), averaged Gruber (open triangles down), Chen (black squares), and POBM (open squares).

north of 23°S in the domain of the aged middle and deep NADW, the  $C_{\text{ANT}}$  signal ( $2.6 \pm 2.4 \mu\text{mol kg}^{-1}$ ) is not significant. Since the standard deviation of  $C_{\text{ANT}}$  for this old water is  $2.4 \mu\text{mol kg}^{-1}$ , the uncertainty of  $5.6 \mu\text{mol kg}^{-1}$  obtained by calculation of error propagation is coherent.

[39] In order to estimate the inventory of anthropogenic carbon along A14, calculated  $C_{\text{ANT}}$  values were depth integrated from the surface (except the shallowest waters with  $\text{AOU} < 0$ ) to entire water column, erasing negative values. The average  $C_{\text{ANT}}$  inventory for the entire line A14 was  $540 \text{ gC m}^{-2}$ . Figure 12 provides the  $C_{\text{ANT}}$  specific inventory for the different zones intersected by A14. South of 15°S, the specific inventory is twice that north of 15°S so that nearly 70% of the  $C_{\text{ANT}}$  penetration occurred in the subantarctic and subtropical domains. A comparison of the  $C_{\text{ANT}}$  inventory by zonal bands between A14, Chen [1982], Gruber [1998] estimate for 1989, and Sarmiento et al. [1995] calculations with the Princeton Ocean Biogeochemistry Model (POBM) has been made (Figure 12). The  $C_{\text{ANT}}$  specific inventory for A14 (black dots) was binned (open dots) in the same latitude bands as Gruber [1998], represented by open triangles down, to facilitate the comparison. Inventory from Gruber [1998] was estimated from the zonal section of  $C_{\text{ANT}}$  of his Figure 10 and represented by black triangles down (Figure 12). The average inventory for 1989 obtained using a segment with the same range of latitude as the A14 line, was  $440 \text{ gC m}^{-2}$  that is in agreement with the average specific inventory ( $36 \text{ mol m}^{-2}$ ) taken from Table 4 of Gruber [1998]. In the same way we have estimated the inventory from Chen [1982], using the  $C_{\text{ANT}}$  vertical distribution of his Figure 4, obtaining an average inventory of  $342 \text{ gC m}^{-2}$  for 1973.

[40] The zonal distribution of our  $C_{\text{ANT}}$  specific inventory is higher than Gruber's [1998] and Chen's [1982] inventories, showing differences of 20 and 29  $\text{mol m}^{-2}$ , respectively, south of 15°S. The differences are lower north of 15°S (5 and 12  $\text{mol m}^{-2}$ , respectively). In the equatorial zone our  $C_{\text{ANT}}$  inventories are slightly lower (5  $\text{mol m}^{-2}$ ) than Gruber's and slightly higher (2  $\text{mol m}^{-2}$ ) than Chen's

estimations. In the equatorial zone the ocean could be acting as a source due to the upwelling in this zone, favoring that water loaded with C<sub>ANT</sub> reaches the surface water. Also, this decrease in the C<sub>ANT</sub> inventories in the equatorial zone could be affected by the differences in station locations with regard to the coast.

[41] The average C<sub>ANT</sub> specific inventory (45 mol m<sup>-2</sup>) for A14 is higher than the estimate by Gruber and Chen in 9 and 16 mol m<sup>-2</sup>, respectively. Our inventory is also higher in 15 mol m<sup>-2</sup> than the POBM model for the South Atlantic Ocean for 1989. The zonal distribution of the POBM corresponds very well with the Chen [1982] estimate for 1973. Taking into account these inventory differences from our data, increase rates of 0.73 mol m<sup>-2</sup> y<sup>-1</sup> with regard to Chen [1982] and 1.5 mol m<sup>-2</sup> y<sup>-1</sup> to Gruber [1998] were obtained. The inventory difference between Gruber [1998] and Chen [1982] of 7 mol m<sup>-2</sup>, results in an increase rate of 0.44 mol m<sup>-2</sup> y<sup>-1</sup>.

[42] Considering the annual rate of C<sub>ANT</sub> entry in the ocean via AAIW is 0.82 μmol m<sup>-2</sup> y<sup>-1</sup> and the maximum depth penetration of this water reaches about 800 m, the atmospheric input of C<sub>ANT</sub> is 0.67 mol m<sup>-2</sup> y<sup>-1</sup> that agrees with the increase rate estimated between A14 and Chen [1982] inventories for the period 1973–1995. Conversely, the increase rates calculated from Gruber [1998] inventory with regard to Chen [1982] and W14, for the periods 1973–1989 and 1989–1995, respectively, does not show this agreement. Although it can be expected that the penetration would increase in recent years, it seems to be very high for the period 1989–1995 and rather low between 1973 and 1989.

#### 4. Conclusions

[43] Accurate estimation of the CO<sub>2</sub> anthropogenic entry in the oceans requires an accurate, precise and consistent database. The accuracy was tested by means of CRMs and the precision by duplicate analyses. The consistency was assessed by in situ measurements of three CO<sub>2</sub> system parameters. Knowledge of the dependence of CO<sub>2</sub> system parameter distributions on water masses ventilation, circulation, and mixing patterns is needed to better understand how the anthropogenic CO<sub>2</sub> penetration is produced. On the basis of these considerations we can summarize the following conclusions regarding the meridional evolution of measured and derived CO<sub>2</sub> system parameters along line A14:

[44] 1. Simultaneous measurements of three CO<sub>2</sub> system variables, the systematic use of CO<sub>2</sub> certified reference materials, and the collection of samples for comparison with manometric C<sub>T</sub> measurements at SIO provided a means to test the accuracy and consistency of our shipboard measurements. CO<sub>2</sub> data produced during A14 were quite reliable to use for estimation of the potential of the Eastern South Atlantic as an anthropogenic CO<sub>2</sub> trap.

[45] 2. The power of CO<sub>2</sub> system parameters as tracers of the ventilation, circulation, and mixing patterns of water masses in the Eastern South Atlantic has been explored. The subtropical and subequatorial branches of SACW have been characterized by the pH<sub>15</sub>, NTA, and NC<sub>T</sub> meridional evolution along the 13°C isotherm. The CPW can be traced by the conspicuous NTA maximum. Maximum pH<sub>15</sub> and

minimum NTA and NC<sub>T</sub> values allows characterization of NADW, marking important zonal flows in the UNADW domains at the equator, 13°S and 22°S. CO<sub>2</sub> system variables also characterized AABW on the northern (Romanche Fracture Zone) and southern (south of the Walvis Ridge) sides of line A14.

[46] 3. About 70% of the anthropogenic CO<sub>2</sub> accumulated by the Eastern South Atlantic along A14 during the industrial era occurred in the subantarctic and subtropical domains, where penetration depths were maximum. Extreme values of C<sub>ANT</sub> are observed in the AAIW domain, being maximum in the relatively young AAIW of the subantarctic zone and minimum in the very old AAIW of the subequatorial gyre. The annual rate of C<sub>ANT</sub> incorporation by AAIW is 0.82 μmol kg<sup>-1</sup> y<sup>-1</sup>, in agreement with the annual rate (0.8 μmol kg<sup>-1</sup> y<sup>-1</sup>) estimated from the equilibrium between the upper mixed layer and the atmospheric pCO<sub>2</sub> increase in the section.

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X. A. Álvarez-Salgado, F. F. Pérez, and A. F. Ríos, CSIC, Instituto de Investigaciones Marinas, Eduardo Cabello 6, 36208-Vigo, Spain. (xsalgado@iim.csic.es; fiz@iim.csic.es; aida@iim.csic.es)

J. Aristegui, Universidad de las Palmas de Gran Canaria, Edificio de Ciencias Básicas, Campus Universitario Tafira, 35017 Las Palmas de Gran Canaria, Spain. (jaristegui@dbil.ulpgc.es)

L. S. Bingle, Pacific Northwest National Laboratory, Battelle Marine Sciences Laboratory, 1529 W. Sequim Bay Road, Sequim, WA 98382, USA. (l.bingle@pnl.gov)

L. Mémerly, Laboratoire d'Océanographie Dynamique et Climatologie, Institut Pierre Simon Laplace, CNRS-IRD-UPMC, Case 100, 4 Place Jussieu, 75252, Paris Cedex 05, France. (Laurent.Memery@ipsl.jussieu.fr)