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A. F. Ríos, X. A. Álvarez-Salgado, F. F. Pérez, L. S. Bingler, J. Arístegui, et al.. Carbon dioxide along WOCE line A14: Water masses characterization and anthropogenic entry. Journal of Geophysical Research. Oceans, 2003, 108, 10.1029/2000JC000366. hal-04110038

# HAL Id: hal-04110038 https://hal.science/hal-04110038

Submitted on 16 Jun 2023

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

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Received 12 April 2002; revised 31 May 2002; accepted 6 February 2003; published 22 April 2003.

[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  $0.1 \pm 3.0 \ \mu mol \ kg^{-1}$  (n = 964 data). CO<sub>2</sub> 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<sub>2</sub> 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 (CANT) 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 µmol  $kg^{-1} y^{-1}$ , 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: CO2, anthropogenic carbon, water masses, South Atlantic

Citation: Ríos, A. F., X. A. Álvarez-Salgado, F. F. Pérez, L. S. Bingler, J. Arístegui, and L. Mémery, Carbon dioxide along WOCE line A14: Water masses characterization and anthropogenic entry, *J. Geophys. Res.*, *108*(C4), 3123, doi:10.1029/2000JC000366, 2003.

#### 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-

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graphic data complemented with tracer measurements. Since  $\sim 30\%$  of the anthropogenic emissions of the greenhouse gas CO<sub>2</sub>, seem to have been trapped by the oceans [Watson et al., 1995], knowledge of the CO<sub>2</sub> 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<sub>2</sub> 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].

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**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). CO2 "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 carbonaceous skeletons [*Broecker and Peng*, 1982; *Takahashi et al.*, 1985; *Anderson and Sarmiento*, 1994]. In addition, the initial pCO<sub>2</sub>, pH, and C<sub>T</sub> 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  $CO_2$  are close to equilibrium with the atmosphere during water mass formation and (2) alkalinity is not significantly affected by the  $CO_2$  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  $CO_2$  emitted throughout the industrial era. Finally, surface  $pCO_2$  is compared with atmospheric concentration to establish the  $CO_2$  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  $\sim$ 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  $^{1}$ ), and al., 1992]. Salinity, dissolved oxygen (in µmol kg<sup>-</sup> nutrients (in  $\mu$ mol kg<sup>-1</sup>) were determined in all samples collected. Chlorophyll a (Chl a) concentration in surface samples (in mg m<sup>-3</sup>) 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 (B<sub>4</sub>O<sub>7</sub>Na · 10H<sub>2</sub>O)

Date	CRMs Analyzed	pH <sub>15</sub>	TA, $\mu mol \ kg^{-1}$	$(C_T)_M,$ µmol kg <sup>-1</sup>	$(C_T)_C$ , 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	$8.210 (\pm 0.007)$	2218 (±0.5)	$1985.9(\pm 1.9)$	$1986.6 (\pm 3.3)$	346 (±6)
19-01-95	5	8.211 (±0.006)	2217 (±0.6)	$1986.3 (\pm 0.8)$	$1984.7 (\pm 2.0)$	345 (±5)
20-01-95	4	$8.208 (\pm 0.002)$	2218 (±0.6)	$1986.5(\pm 1.1)$	$1987.7 (\pm 0.8)$	348 (±2)
21-01-95	4	8.204 (±0.007)	2215 (±2.2)	$1986.2 (\pm 0.7)$	$1987.0(\pm 2.3)$	351 (±5)
22-01-95	4	$8.202 (\pm 0.002)$	2215 (±0.5)	$1987.0 (\pm 0.7)$	$1988.0 (\pm 0.8)$	354 (±2)
24-01-95	7	$8.205 (\pm 0.004)$	2217 (±0.8)	$1986.7 (\pm 1.9)$	$1988.0 (\pm 1.2)$	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)	$2218(\pm 1.4)$	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>	$2216.0(\pm 1.0)$	$1987.55(\pm 1.3)$		350.7°

Table 1. The pH15, TA, Measured CT (CT)M, Calculated CT (CT)C and Calculated pCO2 on CRMs (Batch 24)<sup>a</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  $C_T$  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  $C_T$  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  $15^{\circ}$ 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  $C_T$ 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 CO2 was carried into a coulometric cell with high purity N2 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  $C_T$  data in the main thermocline.  $C_T$  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  $\mu$ mol 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  $\mu$ mol 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  $\mu$ mol kg<sup>-1</sup>. The average absolute difference of 80 laboratory duplicate C<sub>T</sub> analyses was 0.8  $\mu$ mol 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  $C_T$  value (1987.55  $\mu mol~kg^{-1})$  was <0.94  $\mu mol~kg^{-1}.$  The  $pH_{15}$  and TA were also measured routinely using CRMs (Table 1). The average of 76 CRM analyses for TA (2217.2  $\pm$  1.4  $\mu$ mol kg<sup>-1</sup>) was in very good agreement with the certified concentration  $(2216.0 \pm 1.0 \ \mu mol \ kg^{-1})$ . 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  $0.9 \pm 2.4 \ \mu mol \ kg^{-1}$  as the average difference between samples analyzed at SIO and those analyzed on the ship.

[11]  $C_T$  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

						-
Station	Bottle	$(C_T)_M$	$(C_T)_C$	$(C_T)_{SIO}$	$(C_T)_{SIO} - (C_T)_M$	$(C_T)_{SIO} - (C_T)_{O}$
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

**Table 2.** Comparison of  $C_T$  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>

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

 $\pm 2.3$  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  $\pm 3$  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 shipboard CO<sub>2</sub> measurements along line A14 make our data reliable for carbon studies in the South Atlantic.

[12] Surface  $pCO_2$  can be calculated from  $pH_{15}$ -TA,  $pH_{15}-C_T$  and  $TA-C_T$  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>,  $\pm 1.1 \text{ }\mu\text{mol kg}^{-1}$  in TA, and  $\pm 0.8 \text{ }\mu\text{mol kg}^{-1}$  in C<sub>T</sub> produced errors of  $\pm 3.5$ ,  $\pm 0.2$  and  $\pm 2$  µatm in pCO<sub>2</sub>. respectively. The resultant total errors for the  $pH_{15}$ -TA,  $C_T$ -TA, and  $pH_{15}$ - $C_T$  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  $CO_2$  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  $4^{\circ}N$  (Figure 3). In the Equatorial Current System (ECS), between  $4^{\circ}N$  and  $3^{\circ}S$ , the  $13^{\circ}C$  isotherm was situated at ~250 m depth. Poleward rising to 100 m was observed near  $3-4^{\circ}S$ , which marks the eastward flowing South Equatorial Under-Current (SEUC) at the boundary between the ECS and the Sub-



Figure 2. Relationship between  $C_T$  calculated and  $C_T$  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 ( $\sim$ 40 m) and disappeared south of 41°S.

### 3.1.1.1. Surface Waters

[16] Surface distributions of temperature, salinity, chlorophyll, and  $pCO_2$  (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  $CO_2$  in the Eastern South Atlantic was affected by



**Figure 4.** Vertical distribution of  $pH_{15}$  along the line A14.

such zonal arrangement. The average mole fraction in dry air of  $CO_2$  ( $xCO_2$ ) for 1995, 359 ppm according to *Keeling et al.* [1995], is represented by the dotted line in Figure 7b.

[17] Surface waters were pCO<sub>2</sub> undersaturated north of the Equator, reaching a minimum of 313 µatm at 4°16′N, where maximum surface chlorophyll *a* was recorded (3 mg m<sup>-3</sup>). An area of constant surface pCO<sub>2</sub> ( $\sim$ 330 µatm) and very low chlorophyll concentrations ( $\sim$ 0.08 mg m<sup>-3</sup>) appeared just south of the pCO<sub>2</sub> 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 m (not shown). Maximum surface temperature were recorded (>28°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  $pCO_2$  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  $pCO_2$  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  $pCO_2$  levels rose to 485 µatm. Therefore the contribution of  $CO_2$ -free rain-



**Figure 5.** Vertical distribution of normalized total alkalinity (NTA) in  $\mu$ mol kg<sup>-1</sup> 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  $\mu$ mol kg<sup>-1</sup> in TA and a corresponding pCO<sub>2</sub> decrease of 14  $\mu$ atm (from 485 to 471  $\mu$ atm). Since surface pCO<sub>2</sub> in the LSR decreases to 330  $\mu$ atm, intense net primary production must be the cause of the observed low-surface pCO<sub>2</sub>. This seems contradictory because chlorophyll concentrations in the LSR were quite low. However, it must be noted that (1) surface pCO<sub>2</sub> 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 pCO<sub>2</sub> decrease of 294 µatm (from 485 to 191 µatm). The difference between the observed (330 µatm) and the expected (485 - 14 - 294 = 177 µatm) surface pCO<sub>2</sub> levels after consideration of freshwater dilution and net primary production (330 - 177 = 153 µatm) was due to the surface temperature increase of 6°C. Therefore the combination of thermohaline characteristics and biological activity can explain the low pCO<sub>2</sub> values in the LSR at the time of A14 (January–February 1995).

[18] In the  $0-4^{\circ}$ S zone, salinity increased abruptly and temperature decreased slowly (Figure 7a), due to equatorial upwelling. Surface pCO<sub>2</sub> also increased, reaching values near

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**Figure 6.** Vertical distribution of normalized total inorganic carbon (NC<sub>T</sub>) in  $\mu$ mol kg<sup>-1</sup> along line A14. Dashed line represents equatorial/subequatorial SACW NC<sub>T</sub> maximum. Dotted line represents meridional evolution of the UCPW NC<sub>T</sub> maximum.

400 µatm, whereas chlorophyll levels were ~0.15 mg m<sup>-3</sup> (Figure 7b). Despite low surface pCO<sub>2</sub> levels in the LSR, the whole equatorial zone (4°N-4°S) was pCO<sub>2</sub> oversaturated acting as a CO<sub>2</sub> source to the atmosphere. The average ± std oversaturation ( $\Delta$ pCO<sub>2</sub>) for the whole equatorial zone was 9 ± 29 µatm at the time of A14. *Andrié et al.* [1986] and *Smethie et al.* [1985] obtained similar values (8 ± 19 µatm and 11 ± 17 µatm, respectively) at the same time of the year (January–February) farther east. The extremely high  $\Delta$ pCO<sub>2</sub> (45 ± 25 µatm) 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°S), where pCO<sub>2</sub> values were constant (402  $\pm$  5 µatm) and chlorophyll decreased

from 0.15 to 0.03 mg m<sup>-3</sup>. The highest salinity values (36.5  $\pm$  0.1) were observed in the SEC zone (9–23°S) in combination with relatively low temperatures (24.6  $\pm$  0.6 °C). The conspicuous V-shaped pCO<sub>2</sub> distribution centered at ~13°S traced the limit between the subtropical and subequatorial regimes. A local chlorophyll maximum (0.36 mg m<sup>-3</sup>) was observed at that position, coinciding with local pCO<sub>2</sub> minimum (383 µatm). Temperature decrease and net primary production could be the causes of these relatively low pCO<sub>2</sub> 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 pCO<sub>2</sub> decreased by 1.3,  $1.3^{\circ}$ C and 75 µatm, respectively, from



**Figure 7.** Distribution of (a) surface salinity and temperature (°C) and (b) surface  $pCO_2$  (µatm) and chlorophyll a (mg m<sup>-3</sup>) 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 (xCO<sub>2</sub>) for 1995 (359 ppm) according to *Keeling et al.* [1995].

23°S to 36°S. Chlorophyll concentrations were constant below the detection limit ( $\sim 0.03 \text{ mg m}^{-3}$ ). South of the STF (36-37°S) a sharp decrease of surface pCO<sub>2</sub> levels was observed, reaching values below saturation. The pCO<sub>2</sub> 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  $\sim 0.4$  mg m<sup>-3</sup>. Net primary production was favored in the Subantarctic Zone by a marked increase of surface nutrient concentrations; nitrate reached >15  $\mu$ mol kg<sup>-1</sup> 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 welldefined ( $r^2 > 0.99$ ) 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 pCO<sub>2</sub> 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 pCO<sub>2</sub> and chlorophyll ( $r^2 = 0.21$ , n = 106, p < 0.001).



**Figure 8.** Relationship between total alkalinity ( $\mu$ mol kg<sup>-1</sup>) and salinity in surface waters along line A14. The corresponding linear regressions are reported.

However, the multiple regression of surface  $pCO_2$  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 CO<sub>2</sub> system variables (pH<sub>15</sub>, NC<sub>T</sub>, and NTA) along the 13°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°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  $pH_{15}$  and (b) NC<sub>T</sub> and NTA in  $\mu$ mol kg<sup>-1</sup> along the SACW 13°C isotherm.

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

[23] The pH<sub>15</sub> levels along the  $13^{\circ}$ 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  $\sim 0.10$  units at 15°S (subequatorial-subtropical transition) and  $\sim 0.05$  units at  $21-22^{\circ}S$ (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  $\sim 60 \ \mu mol \ kg^{-1}$  in the SEG compared to the STG as a result of a sudden  $NC_T$ change between 15°S and 23°S. On the other hand, NTA concentrations showed a brief excess of  $\sim 4 \ \mu mol \ kg^{-1}$  in the subtropical SACW domain. The observed  $\Delta NC_T$  $\Delta$ NTA 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  $NC_T$  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  $>2265 \ \mu mol \ kg^{-1}$  were recorded (Figures 4 and 6). The low  $pH_{15}$  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  $pH_{15}$  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 retroflection 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 kghigher than the ring centered at 31.5°S). This resulted in a net increase of pH15 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  $\sim$ 1400 m from the SAF to the STF with NTA and NC<sub>T</sub> concentrations of 2364 and 2265  $\mu$ mol kg<sup>-1</sup>, respectively. Equatorward rising of these extrema occurred throughout the STG up to  $\sim 1000$ m at 23°S, where NTA and NC<sub>T</sub> concentrations were 2350 and 2250  $\mu$ mol kg<sup>-1</sup>, respectively. North of 23°S the NTA and  $NC_T$  extrema did not occur at the same depth. The  $NC_T$ maximum coincided with the AAIW salinity minimum centered at 800 m. The NTA maximum (~2342 µmol  $kg^{-1})$  remained at 1000 m, coinciding with the silicate maximum (~34  $\mu mol~kg^{-1})$  and the CFCs minimum  $(\sim 0.01 \text{ pmol kg}^{-1})$  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  $(S > 35, pH_{15} > 7.99, NTA < 2325 \ \mu mol \ kg^{-1}, NC_T < 2190$  $\mu$ mol 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  $\mu mol~kg^{-1}$  and  $NC_T$  < 2200  $\mu mol~kg^{-1}$  was observed below the core of UNADW, which correspond to the deeper branches of NADW. A bend in the  $\theta$ -S at  $\sim 2^{\circ}$ 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  $\sim$ 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  $\mu$ mol 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 ( $\mu$ mol kg<sup>-1</sup>) along line A14. Solid line represents CFC11 isoline of 0.1 pmol kg<sup>-1</sup>.

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°S) and the Río Grande (26°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°S in the Angola Basin. The existence of an eastward flow near 25°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 NC<sub>T</sub> at  $\sim 22^{\circ}$ S in the UNADW domain ( $\sim$ 1800 m) traced the "Namib Col Current" along A14. To the south of 23°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 pH<sub>15</sub> (7.881–7.915) and high NTA (2370–2380 µmol kg<sup>-1</sup>) and NC<sub>T</sub> (2260–2270µmol kg<sup>-1</sup>) values in the bottom layer, spreading north to 36°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 m, <2°C) at the equator, which enter from the western basins through the Romanche Fracture zone and can be traced by high NTA (2355–2360  $\mu$ mol kg<sup>-1</sup>) and NC<sub>T</sub> (2210–2215  $\mu$ mol kg<sup>-1</sup>) concentrations.

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

[30] The method used for calculating anthropogenic carbon (CANT) 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 CaCO<sub>3</sub> dissolution processes on the distribution of  $C_T$  allows the determination of the initial  $CO_2$  ( $C_T^0$ ) of different water masses in source regions. In addition, assuming that dissolved oxygen and CO<sub>2</sub> 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, TA<sup>0</sup> is not significantly affected by the entry of anthropogenic CO<sub>2</sub> because in surface waters that are CaCO<sub>3</sub> supersaturated, CaCO<sub>3</sub> dissolution due to progressive acidification is negligible [Chen

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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 *Rios et al.* [2001] and *Pérez et al.* [2002] is calculated from C<sub>T</sub>, TA and dissolved oxygen measured at the sea:

$$C_{ANT} = C_T - AOU/R_C - 1/2 \cdot (TA - TA^0 + AOU/R_N) - C_{T278}^0$$
(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<sub>C</sub> is a stoichiometric coefficient  $(=-\Delta O_2/\Delta C)$ . Additionally,  $1/2 \cdot (\Delta TA + AOU/R_N)$  is the C<sub>T</sub> 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<sup>0</sup>), and R<sub>N</sub> 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<sup>0</sup> stands for preformed alkalinity and was calculated using the A14 database, with an error of the estimation of 4.4 µmol kg<sup>-1</sup>, 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:  $TA^0 = 336.86 + 56.23 \cdot S + 0.0200 \cdot PO'$  ( $r^2 =$ 0.97, n = 116, p < 0.001) where "PO" =  $O_2 + R_P \cdot PO_4$ .  $R_P$  is a stoichiometric coefficient (=  $-\Delta O_2/\Delta P$ ) with a constant value of 170 molO<sub>2</sub>/molP [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<sup>0</sup> and the atmospheric pCO<sub>2</sub> level at that time and water vapor pressure [*Pérez et al.*, 2002], where  $pCO_2 = xCO_2^{0}$ ·(Patmvapor pressure) according to U.S. Department of Energy [1994]. The mole fraction of  $CO_2$  in the preindustrial atmosphere ( $xCO_2^0$ ) 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  $\pm 5.6 \ \mu mol \cdot kg^{-1}$ .

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



**Figure 11.** Meridional evolution of anthropogenic carbon  $(C_{ANT})$  and "apparent age" calculated through CFC11  $(Age_{CFC})$  in the AAIW salinity minimum along A14. The linear regression between  $C_{ANT}$  and  $Age_{CFC}$  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 ~1400 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  $36-37^{\circ}$ S) appears as a thick layer of salinity <34.2 (Figure 3), which transports the high C<sub>ANT</sub> concentrations (>30 µmol kg<sup>-1</sup>) acquired south of the SAF to the interior of the South Atlantic. Figure 11 shows the meridional evolution of C<sub>ANT</sub> along the AAIW salinity minimum during A14. Maximum C<sub>ANT</sub> values of 36 µmol kg<sup>-1</sup> were observed at the southern end of the section (45°30'S) and decreased northward 15°S. North of 15°S, C<sub>ANT</sub> became constant at  $14 \pm 2$  µmol kg<sup>-1</sup>. CFC11 exhibited the same trend as C<sub>ANT</sub> along the AAIW salinity minimum, as suggested by the corresponding linear regression ( $r^2 = 0.88$ , n = 35, p < 0.0001):

$$C_{ANT}(\pm 2.9) = 15.2(\pm 0.6) + 7.5(\pm 0.5)$$
 CFC11. (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°S instead of at 15°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" (Age<sub>CFC</sub>) of

$$pCFC - 11 = [CFC11] \cdot F^{-1}, \tag{6}$$

where F is the solubility of CFC11, a function of potential temperature and salinity given by Warner and Weiss [1985]. Age<sub>CFC</sub> 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 Age<sub>CFC</sub> at the AAIW salinity minimum along A14 referred to 1995 (Figure 11) is a mirror image of CANT. AAIW at 45°30'S was  $\sim$ 15 years old and became older as it evolved northwards. North of 15°S, Age<sub>CFC</sub> was constant at  $42 \pm 1$  year. There was a very good correlation between  $C_{ANT}$  and  $Age_{CFC}$  ( $r^2 = 0.96$ , n = 35, p < 0.001).

[36] According to this regression, the annual rate of  $C_{ANT}$ entry in the ocean via AAIW is 0.82  $\mu$ mol kg<sup>-1</sup> y<sup>-1</sup>. This rate is in very good agreement with the annual rate of 0.80  $\mu$ mol kg<sup>-1</sup> y<sup>-1</sup> estimated from the equilibrium between the upper mixed layer and the average atmospheric xCO<sub>2</sub> increase, according to Keeling et al. [1995]. In order to check the age of the AAIW salinity minimum at  $45^{\circ}$ S (C<sub>ANT</sub> = 36  $\mu$ mol kg<sup>-1</sup> and Age<sub>CFC</sub> = 15 years) a back calculation was performed. Calculated C<sub>T</sub><sup>0</sup> in the preindustrial time ( $xCO_2 = 278$  ppm) and in 1980 ( $xCO_2 = 336$  ppm) [Keeling et al., 1995], 15 years before A14, were 2069 µmol  $kg^{-1}$  and 2100 µmol  $kg^{-1}$ , respectively. Therefore the net anthropogenic carbon uptake was 31  $\mu$ mol kg<sup>-1</sup> indicating that  $Age_{CFC}$  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 CANT and Age<sub>CFC</sub> calculations were performed for the overlying SACW 13°C isotherm along A14 (not shown). The average CANT entry along this isotherm was  $33 \pm 3 \ \mu mol \ kg^{-1}$ . The transition at  $15^{\circ}S$ separates the 22  $\pm$  1 years old (Age<sub>CFC</sub>) subequatorial SACW to the north from the  $10 \pm 1$  years old subtropical SACW to the south, with  $C_{ANT}$  entries of  $32 \pm 4$  and  $34 \pm 2$  $\mu$ mol kg<sup>-1</sup>, respectively. The apparent age difference between the subtropical and subequatorial SACW branches  $(12 \pm 2 \text{ years})$  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 CANT and Age<sub>CFC</sub> have been examined along the core of maximum NTA (Figure 5). Constant  $C_{ANT}$  of 17  $\pm$  2 and  $13 \pm 1.6 \ \mu mol \ kg^{-1}$  were obtained south and north of 15°S, respectively. The corresponding  $Age_{CFC}$  were  $38 \pm 5$ and >45  $\pm$  2 years. The youngest UCPW (33  $\pm$  1.4 years) appeared south of the STF. The slight CANT penetration into the domain of the UNADW although coincident with the uncertainty (5.9  $\pm$  2.0  $\mu$ mol kg<sup>-1</sup>), 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  $C_{ANT}$  of 5.7  $\pm$  2.0  $\mu$ mol kg<sup>-1</sup>, while

north of 23°S in the domain of the aged middle and deep NADW, the  $C_{ANT}$  signal (2.6 ± 2.4 µmol kg<sup>-1</sup>) is not significant. Since the standard deviation of CANT for this old water is 2.4  $\mu$ mol kg<sup>-1</sup>, the uncertainty of 5.6  $\mu$ mol kg<sup>-1</sup>

obtained by calculation of error propagation is coherent. [39] In order to estimate the inventory of anthropogenic carbon along A14, calculated  $C_{ANT}$  values were depth integrated from the surface (except the shallowest waters with AOU < 0) to entire water column, erasing negative values. The average  $C_{ANT}$  inventory for the entire line A14 was 540 gC m<sup>-2</sup>. Figure 12 provides the C<sub>ANT</sub> 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 CANT penetration occurred in the subantarctic and subtropical domains. A comparison of the C<sub>ANT</sub> 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 CANT 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  $C_{ANT}$  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 gC m<sup>-2</sup> that is in agreement with the average specific inventory (36 mol  $m^{-2}$ ) taken from Table 4 of Gruber [1998]. In the same way we have estimated the inventory from Chen [1982], using the CANT 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<sub>ANT</sub> specific inventory is higher than Gruber's [1998] and Chen's [1982] inventories, showing differences of 20 and 29 mol m<sup>-2</sup>, respectively, south of 15°S. The differences are lower north of 15°S (5 and 12 mol m<sup>-2</sup>, respectively). In the equatorial zone our C<sub>ANT</sub> inventories are slightly lower (5 mol m<sup>-2</sup>) than Gruber's and slightly higher (2 mol  $m^{-2}$ ) than Chen's

20 10 50° S 30 20 10°N 40 10 0 Latitude Figure 12. Meridional evolution of C<sub>ANT</sub> 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).



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  $C_{ANT}$  reaches the surface water. Also, this decrease in the  $C_{ANT}$  inventories in the equatorial zone could be affected by the differences in station locations with regard to the coast.

[41] The average  $C_{ANT}$  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  $C_{ANT}$  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  $C_{ANT}$  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  $CO_2$  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  $CO_2$  system parameters. Knowledge of the dependence of  $CO_2$  system parameter distributions on water masses ventilation, circulation, and mixing patterns is needed to better understand how the anthropogenic  $CO_2$  penetration is produced. On the basis of these considerations we can summarize the following conclusions regarding the meridional evolution of measured and derived  $CO_2$  system parameters along line A14:

[44] 1. Simultaneous measurements of three  $CO_2$  system variables, the systematic use of  $CO_2$  certified reference materials, and the collection of samples for comparison with manometric  $C_T$  measurements at SIO provided a means to test the accuracy and consistency of our shipboard measurements.  $CO_2$  data produced during A14 were quite reliable to use for estimation of the potential of the Eastern South Atlantic as an anthropogenic  $CO_2$  trap.

[45] 2. The power of  $CO_2$  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  $NC_T$  values allows characterization of NADW, marking important zonal flows in the UNADW domains at the equator, 13°S and 22°S.  $CO_2$  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  $C_{ANT}$  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  $C_{ANT}$  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.

[47] Acknowledgments. We would like to thank the master, officers, and crew of R/V L'Atalante and all the participants on the cruise CITHER-3. We are very grateful to T. Rellán for pH and alkalinity measurements and preparation of figures, A. Billant and J.P. Gouillou in charge of the CTD, M.J. Messias for CFC measurements, M.J. Pazó for nutrients and chlor-ophyll determinations, and Melchor González-Dávila for providing pH<sub>SWS</sub> measured on CRM batch 24. Special thanks to M. Arhan (coordinator of the WOCE-France program CITHER) and H. Mercier (chief scientist of cruise CITHER 3). This work was supported by the Spanish CICYT (grant ANT94-1168-E) and IFREMER (University contract 94 1430 087).

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