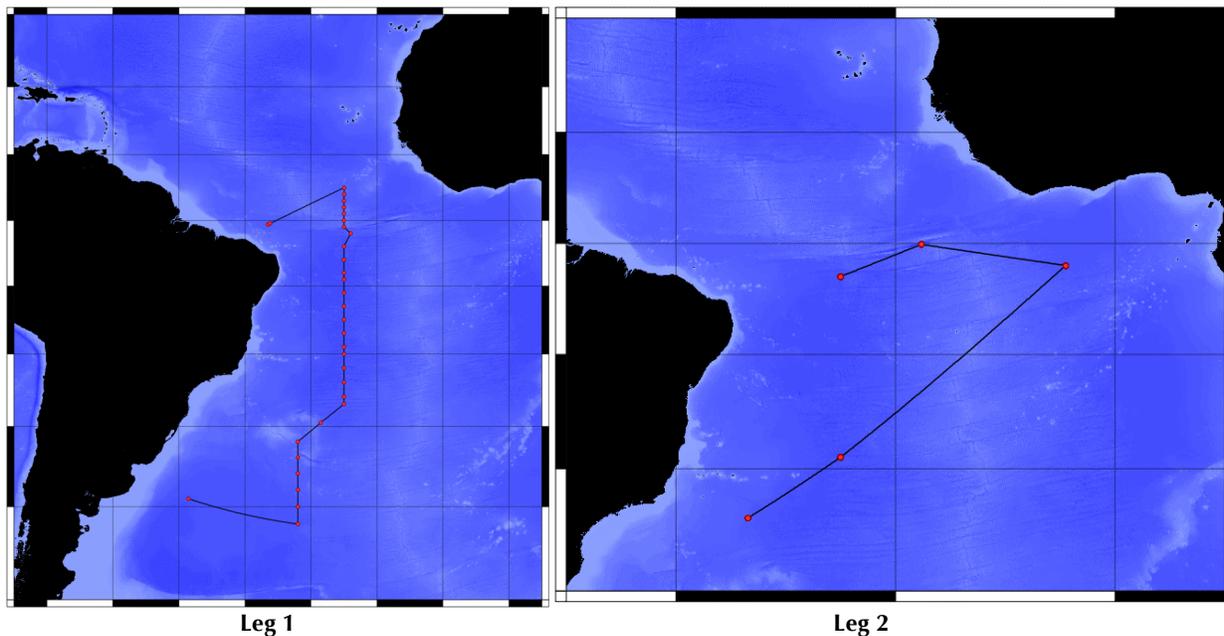


# CRUISE REPORT: AR21

(Updated APR 2012)



## Highlights

### Cruise Summary Information

WOCE Section Designation	AR21 Leg 1	AR21 Leg 2
Aliases	OACES91, SATL-91	
Expedition designation (ExpoCodes)	3175MB91	3175MB91_2
Chief Scientists	Donald K. Atwood/AOML	Dr. Alex Pszenny/AOML
Dates	1991 JUL 11 - 1991 AUG 05	1991 AUG 13 - 1991 SEP 2
Ship	<i>R/V Malcolm Baldrige</i>	
Ports of call	Fortaleza, Brazil to Montevideo, Uruguay	
Geographic Boundaries	48° 33' W 5° N 24° 58.2' W 42° S	0° 5.64' S 33° 27.3' W 4° 30' W 24° 7.68' S
Stations	33	5
Floats and drifters deployed	0	
Moorings deployed or recovered	0	

#### Recent Contact Information:

Donald K. Atwood  
 NESDIS Office of Research and Applications • World Weather Bldg. Room 601-18  
 5200 Auth Road • Camp Springs • MD • 20746-4304  
 Phone: 301-763-8102 Ext 206 • Fax 305-763-8580 • Email: Don.Atwood@noaa.gov

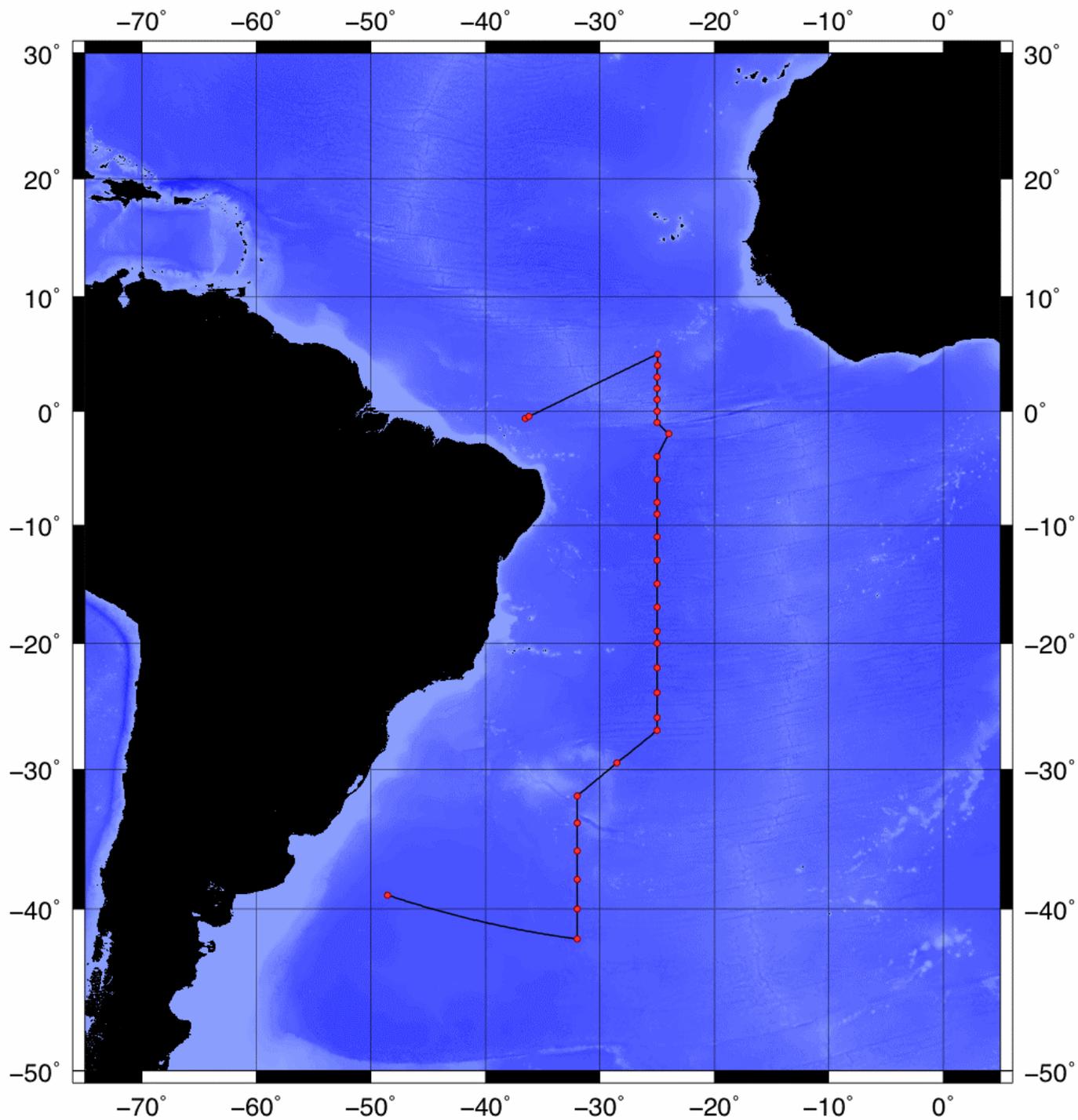
Dr. Alex Pszenny  
 Institute for the Study of Earth, Oceans, and Space  
 Morse Hall • University of New Hampshire • 8 College Road • Durham, NH 03824-3525  
 Tel: 603-862-1994 • Fax: 603-862-1915 • Email: alex.pszenny@unh.edu

## LINKS TO SELECT LOCATIONS

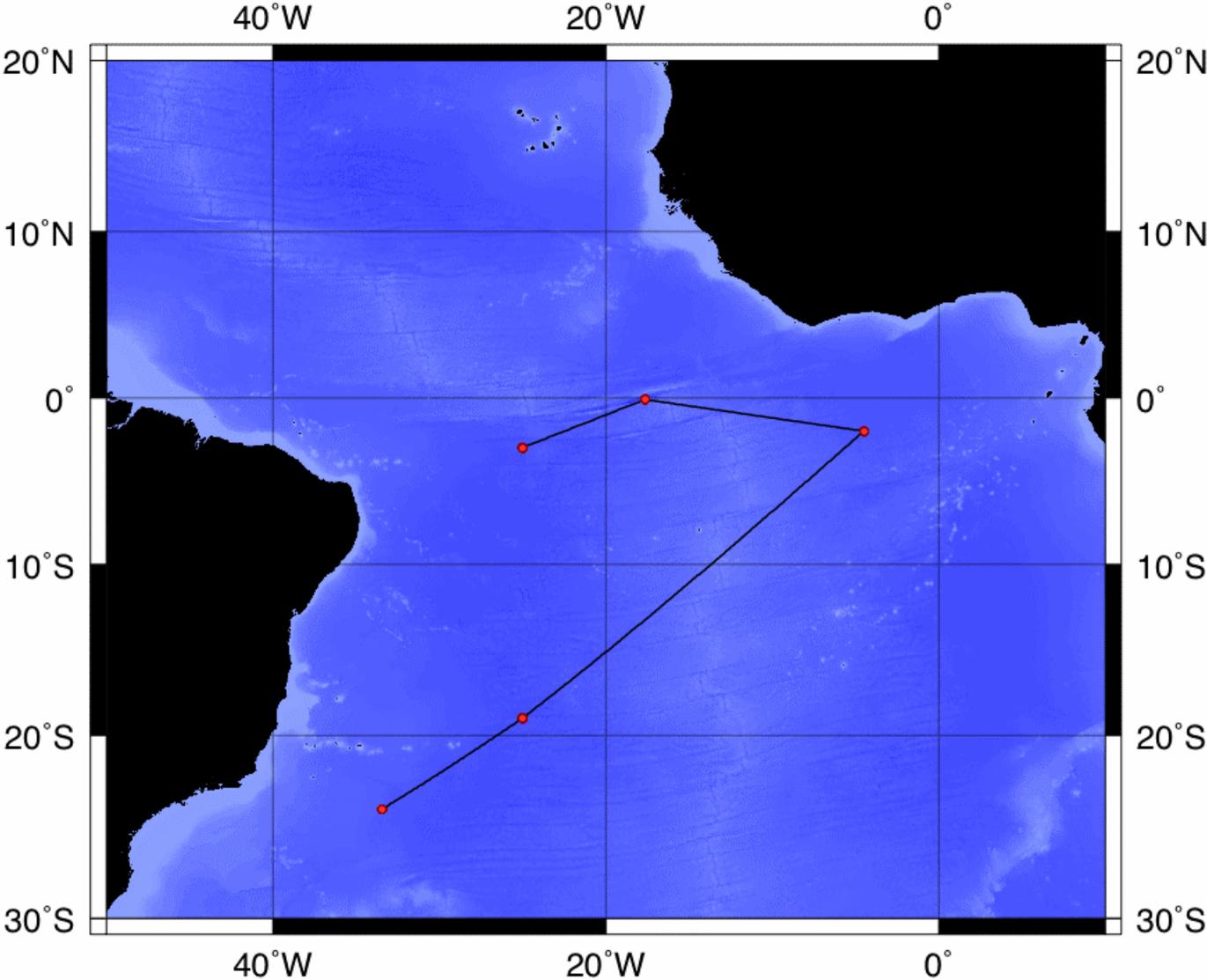
Shaded sections are not relevant to this cruise or were not available when this report was compiled

<b>Cruise Summary Information</b>	<b>Hydrographic Measurements</b>
<a href="#">Description of Scientific Program</a>	<b>CTD Data:</b>
<a href="#">Geographic Boundaries</a>	<a href="#">Acquisition</a>
<a href="#">Cruise Track (Figure):</a> <a href="#">PI</a> <a href="#">CCHDO</a>	<a href="#">Processing</a>
<a href="#">Description of Stations</a>	<a href="#">Calibration</a>
<a href="#">Description of Parameters Sampled</a>	<a href="#">Temperature</a> <a href="#">Pressure</a>
<a href="#">Bottle Depth Distributions (Figure)</a>	<a href="#">Salinities</a> <a href="#">Oxygens</a>
<a href="#">Floats and Drifters Deployed</a>	<b>Bottle Data</b>
<a href="#">Moorings Deployed or Recovered</a>	<a href="#">Salinity</a>
	<a href="#">Oxygen</a>
<a href="#">Principal Investigators</a>	<a href="#">Nutrients</a>
<a href="#">Cruise Participants</a>	<a href="#">Carbon System Parameters</a>
	<a href="#">CFCs</a>
<a href="#">Problems and Goals Not Achieved</a>	<a href="#">Helium / Tritium</a>
<a href="#">Other Incidents of Note</a>	<a href="#">Radiocarbon</a>
<b>Underway Data Information</b>	<b>References</b>
<a href="#">Navigation</a> <a href="#">Bathymetry</a>	<a href="#">Nutrients</a>
<a href="#">Acoustic Doppler Current Profiler (ADCP)</a>	<a href="#">CFCs</a>
<a href="#">Thermosalinograph</a>	<a href="#">Carbon System Parameters</a>
<a href="#">XBT and/or XCTD</a>	
<a href="#">Meteorological Observations</a>	
<a href="#">Atmospheric Chemistry Data</a>	
<b>Data Processing Notes</b>	<b>Acknowledgments</b>

**Station Locations • AR21 Leg 1 • 1991 • Atwood • *R/V Malcolm Baldrige***



**Station Locations • AR21 Leg 2 • 1991 • Pszenny • *R/V Malcolm Baldrige***



NOAA Data Report ERL AOML-24



**HYDROGRAPHIC, CARBON DIOXIDE, NUTRIENT, AND PRODUCTIVITY  
MEASUREMENTS FROM THE SOUTH ATLANTIC DURING JULY AND  
AUGUST OF 1991**

**Evan B. Forde  
James C. Hendee  
Rik Wanninkhof**

Atlantic Oceanographic and Meteorological Laboratory  
Miami, Florida  
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**UNITED STATES  
DEPARTMENT OF COMMERCE**

**Ronald H. Brown  
Secretary**

NATIONAL OCEANIC AND  
ATMOSPHERIC ADMINISTRATION

B. James Baker  
Under Secretary for Oceans and  
Atmosphere/Administrator

Environmental Research  
Laboratories

Alan R. Thomas  
Director

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### REMOTE ACCESS TO DATA LISTED IN THIS REPORT

The data presented in this report is available on a computerized Remote Bulletin Board System (RBBS) or via Internet FTP. For more detailed information, or for more information regarding electronic access to the individual data sets contact:

Mr. James C. Hendee Data Manager, OACES  
at: U. S. Dept. of Commerce  
NOAA/AOML/OCD 4301 Rickenbacker  
Causeway Miami, Florida 33149-1026

Telephone: 305-361-4396 Internet address:  
Hendee@ocean.aoml.erl.gov

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## LEG 2

Chief Scientist: Dr. Alex Pszenny AOML

<b>Analyst</b>	<b>Data Type</b>	<b>Affiliation</b>
Lloyd Moore	Nutrients	AOML
James McElroy	Productivity	AOML
Rik Wanninkhof	fCO <sub>2</sub> Discrete	AOML
	fCO <sub>2</sub> Underway	
	TCO <sub>2</sub>	
Tom Lantry	fCO <sub>2</sub> Discrete	AOML
	fCO <sub>2</sub> Underway	
	TCO <sub>2</sub>	

## DATA REDUCTION

<b>Data Type</b>	<b>Affiliation</b>	
Cindy Moore	DOC	RSMAS
Jia-Zhong Zhang	TALK	RSMAS
Hua Chen	Discrete fCO <sub>2</sub>	CIMAS/AOML
Rik Wanninkhof	Discrete fCO <sub>2</sub>	AOML
Rik Wanninkhof	TCO <sub>2</sub>	AOML
Tom Lantry	TCO <sub>2</sub>	AOML
Rik Wanninkhof	Underway fCO <sub>2</sub>	AOML
Doug Wilson	Underway fCO <sub>2</sub>	AOML
Betty Huss	Underway fCO <sub>2</sub>	AOML
Jim McElroy	Productivity	AOML
Raleigh Hood	Productivity	RSMAS
Garry Hitchcock	Productivity	RSMAS
Doug Wilson	CTD	AOML
Doug Wilson	Salinity	AOML
Doug Wilson	Oxygen	AOML
Dennis Frazel	Nutrients	AOML
Lloyd Moore	Nutrients	AOML
George Berberian	Nutrients	AOML

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**HYDROGRAPHIC, CARBON DIOXIDE, NUTRIENT, AND PRODUCTIVITY  
MEASUREMENTS FROM THE SOUTH ATLANTIC DURING JULY AND AUGUST OF 1991**

Ryan B. Forde, James C. Hendee and Rik Wanninkhof  
Atlantic Oceanographic and Meteorological Laboratory  
Miami, Florida 33169

**ABSTRACT**

From July 11 to September 2, 1991, the National Oceanic and Atmospheric Administration's (NOAA) Carbon Dioxide (CO<sub>2</sub>) and Radiatively Important Trace Species (RITS) programs participated in an oceanographic research cruise conducted aboard the NOAA ship MALCOLM BALDRIGE. This report presents the research from that cruise that was conducted for the CO<sub>2</sub> program, which has recently been renamed the Ocean-Atmosphere Carbon Exchange Study (OACES). During Leg 1 of this cruise, (Fortaleza, Brazil to Montevideo, Uruguay), 33 CTD hydrographic casts and 17 Go-Flo™ hydrographic (productivity) casts were conducted. Samples were also collected while underway on Leg 1, for the determination of the fugacity of CO<sub>2</sub> (fCO<sub>2</sub>) of the air and surface water. Leg 2, (Montevideo, Uruguay-Fortaleza, Brazil), collected 21 days of underway fCO<sub>2</sub> measurements, conducted five CTD hydrographic casts and nine Go-Flo™ hydrographic (productivity) casts. This report contains tables\* of the following data: hydrography from each CTD cast at the bottle trip depths, (including salinity, oxygen and nutrients), discrete carbon parameters, underway carbon parameter values, and data from productivity casts. Descriptions of the sampling techniques and analytical methods used in the collection and processing of these data are also presented in this report.

KEY WORDS: alkalinity, CO<sub>2</sub> carbon dioxide, chlorophyll, CTD, dissolved organic carbon, hydrography, nutrients, productivity, salinity, sigma-theta, South Atlantic, temperature

\*Not included in this CCHDO update

## **1. INTRODUCTION**

Human activity is producing gases, most notably carbon dioxide (CO<sub>2</sub>), and other trace gases including chlorofluorocarbons, nitrous oxide and methane, which are being released into the atmosphere and causing more of the radiation being emitted by the earth to be absorbed. This increased absorption is resulting in a net warming of the earth's atmosphere and creating a phenomenon commonly known as the "Green House Effect". Only about half of all of the anthropogenic CO<sub>2</sub> that is released into the atmosphere each year remains there. The global ocean is thought by many to be the ultimate destination, or "sink" for the 'missing' CO<sub>2</sub>. The understanding of the absorption and storage properties of the oceans is therefore essential to assessing the potential for climatic change due to man's effect on the radiation balance of the atmosphere.

The National Oceanic and Atmospheric Administration's (NOAA) Carbon Dioxide (CO<sub>2</sub>) program and Radiatively Important Trace Species (FITS) programs participated in a multifaceted oceanographic research cruise conducted aboard the NOAA ship MALCOLM BALDRIGE from July 11 to September 2, 1991. The NOAA CO<sub>2</sub> program has been recently renamed and is now called Ocean-Atmosphere Carbon Exchange Study (OACES). The two primary objectives of the cruise were to: (1) assess the role of biomass burning emissions from surrounding continents in controlling the distribution of ozone in the tropical South Atlantic atmospheric boundary layer for the FITS program and (2) to measure and establish baseline values and determine source and sink regions of CO<sub>2</sub> in the equatorial and the South Atlantic Ocean for OACES. This report presents only the OACES-related data from that cruise. These data include: hydrography, nutrients, discrete carbon, underway carbon parameters and productivity data from both legs of the cruise.

### **1.1. DESCRIPTION OF STUDY AREA**

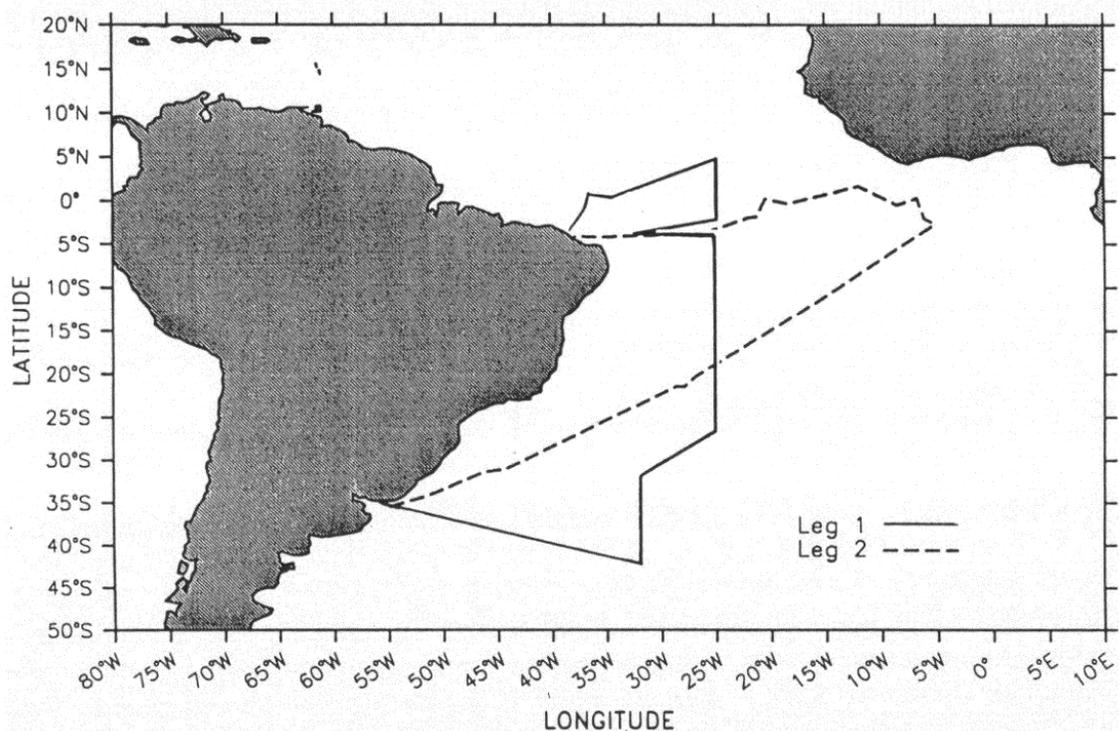
This study was conducted on two consecutive research cruise legs during 1991. Leg 1 sailed from Fortaleza, Brazil on July 11, 1991, proceeded NE to approximately 5°N and 25°W and then turned south and steamed along the 25°W line to 28°S. At 28°S, the track line turned SW to 32°W and continued South to 42°S before turning NW and ending in Montevideo, Uruguay on August 5, 1991. Leg 2 departed Montevideo, Uruguay on August 13, 1991 and proceeded NE to a point about 2°S and 4°W before subsequently steaming NW, and then SW ending in Fortaleza, Brazil on September 2, 1991. The cruise tracks for Legs 1 and 2 are shown on [Figure 1](#).

## **2. DATA COLLECTION AND ANALYTICAL METHODS**

Thirty-three CTD hydrographic stations on Leg 1, and five CTD hydrographic stations on Leg 2 were occupied to collect discrete water sample data. A CTD/rosette unit with a Neil Brown CTD instrument equipped with 24, 10-L Niskin™ bottles was utilized for these casts. Water samples were collected from the Niskin™ bottles for salinity, oxygen and nutrient measurements as well as carbon related parameters including total dissolved inorganic CO<sub>2</sub> (TCO<sub>2</sub>), fugacity of CO<sub>2</sub> (fCO<sub>2</sub>), total alkalinity (TALK) and Dissolved Organic Carbon (DOC). Continuous underway air and seawater surface samples for fugacity of CO<sub>2</sub> (fCO<sub>2</sub>) analysis were collected during both legs of the cruise. GoFlo™ hydrographic casts were also conducted on both legs for productivity measurements. These casts were made using 10-L Go-Flo™ bottles mounted on Kevlar™ hydrowire. Salinities and sea surface temperatures were also measured continuously during the entire cruise by a thermosalinograph. In most cases, if there was no bottle salinity value available for a given sample position, the electronically derived CTD value was used in calculations requiring a salinity measurement. More

detailed information on individual data collection, or analyses procedures may be found in the respective data sections.

### SOUTH ATLANTIC 1991 RITS/CO<sub>2</sub> CRUISE TRACKLINES



**Figure 1:** Study area and cruise track lines for NOAA Ship MALCOLM BALDRIGE.

## 2.1 HYDROGRAPHIC METHODS

### 2.1.1 CTD and Hydrographic Operations

All CTD operations were conducted using the same Neil Brown<sup>TM</sup> Instrument Systems Mark III CTD equipped with standard temperature and conductivity sensors, a Beckman<sup>TM</sup> polarographic dissolved oxygen sensor, and an auxiliary Seabird<sup>TM</sup> temperature sensor. Laboratory calibrations were performed, before and after the cruise, and were used in conjunction with Niskin<sup>TM</sup> bottle data, to calibrate the CTD data. Pressure and temperature data listed in this report are based on the post-cruise calibration. Temperature accuracy is estimated to be  $\pm .005^{\circ}\text{C}$ , and pressure accuracy to be  $\pm 5$  decibars.

#### Water sampling

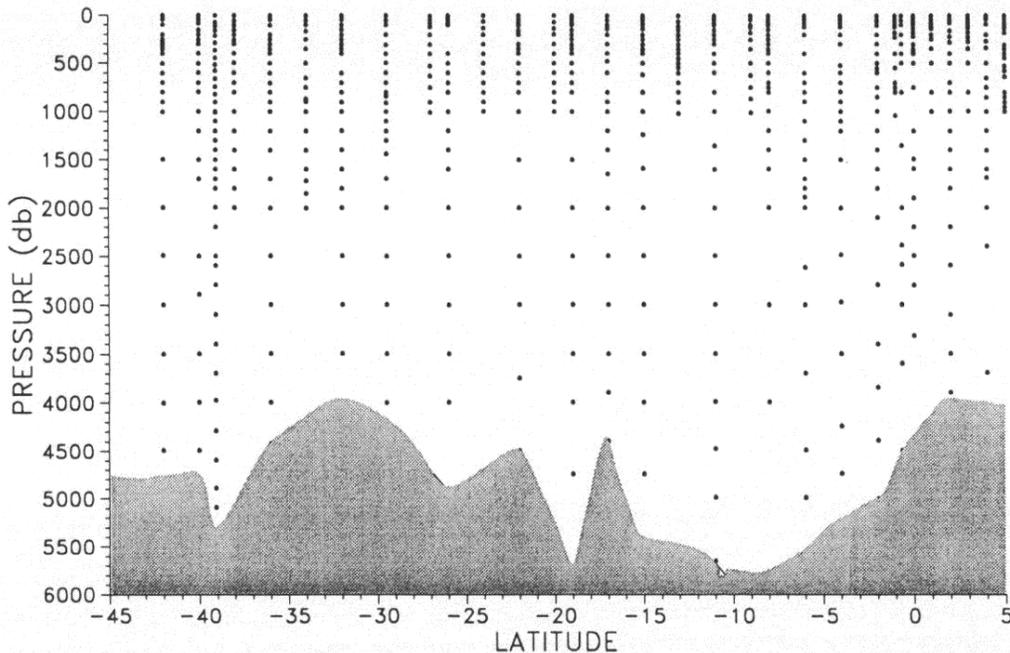
Water samples were collected in 10-L sampling bottles using a General Oceanics 24-place rosette system. Bottles were electronically fired during the upcast, with markers placed in the digital file for

use in determining exact bottle trip CTD values for calibration. Once on deck, aliquots were taken for laboratory analyses. Figure 2 shows the CTD cast bottle trip locations used for hydrographic and other discrete water sample measurements collected during Leg 1 of the cruise. More detailed information about the subsampling and analysis procedures for the various water property measurements may be found below.

### Oxygen

Dissolved oxygen samples were the first samples collected from 10-L Niskin™ bottles once the CTD unit was back on deck. The oxygen samples were collected, in 150-mL ground-glass stoppered sample bottles and were analyzed using the method described by Carpenter (1965), with computer-controlled colorimetric endpoint determination as described in Friederich, Sherman, and Codispoti (1984). Oxygen samples that have been collected and analyzed using the above methodology have a precision greater than one percent. Values are marked as questionable by italicizing them in the data tables for any of the following reasons: High or low photometric endpoints in the titration process due to improper light levels; possible contamination during processing (air bubbles seen in bottle, etc.); inexplicable large differences between bottle sample data values and apparently valid electronic CTD values.

### SOUTH ATLANTIC 1991 RITS/CO<sub>2</sub> CRUISE HYDROGRAPHIC AND DISCRETE CARBON DATA SAMPLE POSITIONS



**Figure 2:** Sampling positions for all Niskin™ Bottle derived data. The coarse smoothing grid for bottom topography causes sharp topographic features, such as the mid Atlantic Ridge at 0°N, to be eliminated.

## Salinity

Salinity samples were collected in 200-mL bottles. New caps were used for each sample. Bottle salinities were measured using a Guildline™ 8400 Autosol and P114 standard seawater in a temperature controlled van. Conductivity ratios were converted to salinities conforming to the PSS78 standard. Since CTD conductivity was relatively stable (except casts 32 and 33), bottle salinities that differed substantially from CTD salinity measurements are marked as questionable in the data tables.

## Temperature Density and Depth

Depth, Potential Temperature and Density (sigma-theta) values listed in the tables were calculated using standard Woods Hole Oceanographic Institute (W.H.O.I.) hydrographic subroutines. Depth is calculated from pressure using methods based on Saunders and Fofonoff (1976); density is determined by methods presented in F. Millero and A. Poisson (1981); and potential temperature referenced to zero pressure (theta) is calculated by integrating the adiabatic lapse rate using a fourth-order Runge-Kutta algorithm. Sigma-theta values, (ten meter averages), from the Leg 1 CTD casts are contoured and presented in [Figure 3](#).

### 2.1.2 Nutrient Analysis Methods

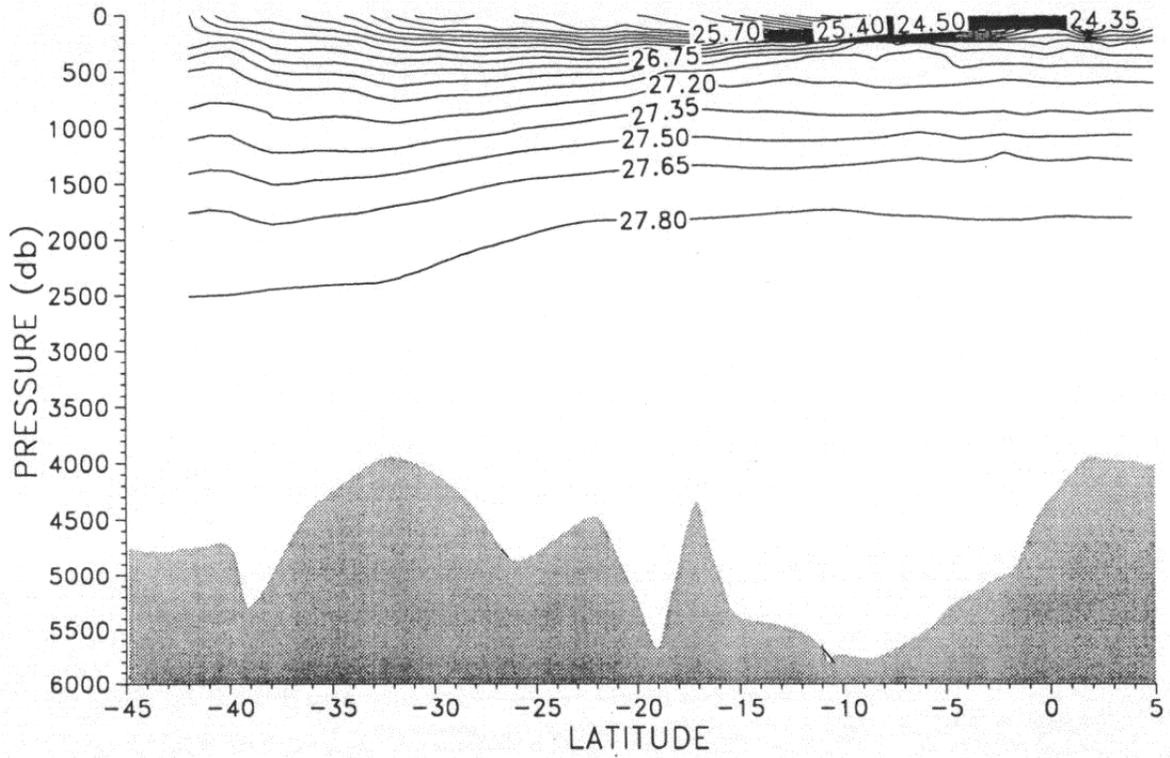
Nutrient samples were collected from 10-L Niskin bottles in aged 60-mL. linear polyethylene bottles after three complete seawater rinses and stored in the dark at 4°C until analysis was completed (within 24 hours of sample collection). Concentrations of dissolved inorganic nitrite (NO<sub>2</sub>), dissolved inorganic nitrate (NO<sub>3</sub>), and silicate (SiO<sub>4</sub>), reported in micromoles/liter, were determined using an AlpKem™ RFA/2 Auto-Analyzer aboard ship.

## Nitrates

The automated colorimetric procedures and methodologies used in the analysis of nitrite and nitrate are essentially similar to those described by Armstrong et al. (1967), with modifications described in Atlas et al. (1971). Standardizations were performed prior to each sample run with working solutions prepared aboard ship from pre-weighed "Baker Analyzed" reagent grade standards. Nitrite (NO<sub>2</sub>) was determined by diazotizing with sulfanilamide and coupling with N-1 naphthylethelendiamine dihydrochloride to form an azo dye. The color produced is proportional to the nitrite concentration. Samples for nitrate (NO<sub>3</sub>) analysis were passed through a copperized cadmium column, which reduces nitrate to nitrite and the resulting nitrite concentration was then determined as described above. The detection limits for nitrite and nitrate were 0.1 µmoles/L and 0.4 µmoles/L, respectively. The precision of duplicate standards measurements was ±0.25% at 8 µmoles/L for nitrite and ± 0.2% at 40 µmoles/L for nitrate. The accuracy for both analytes was assumed to be ±1 % since no absolute standards were available. Contoured nitrate values from Leg 1 of this study are presented in [Figure 4](#).

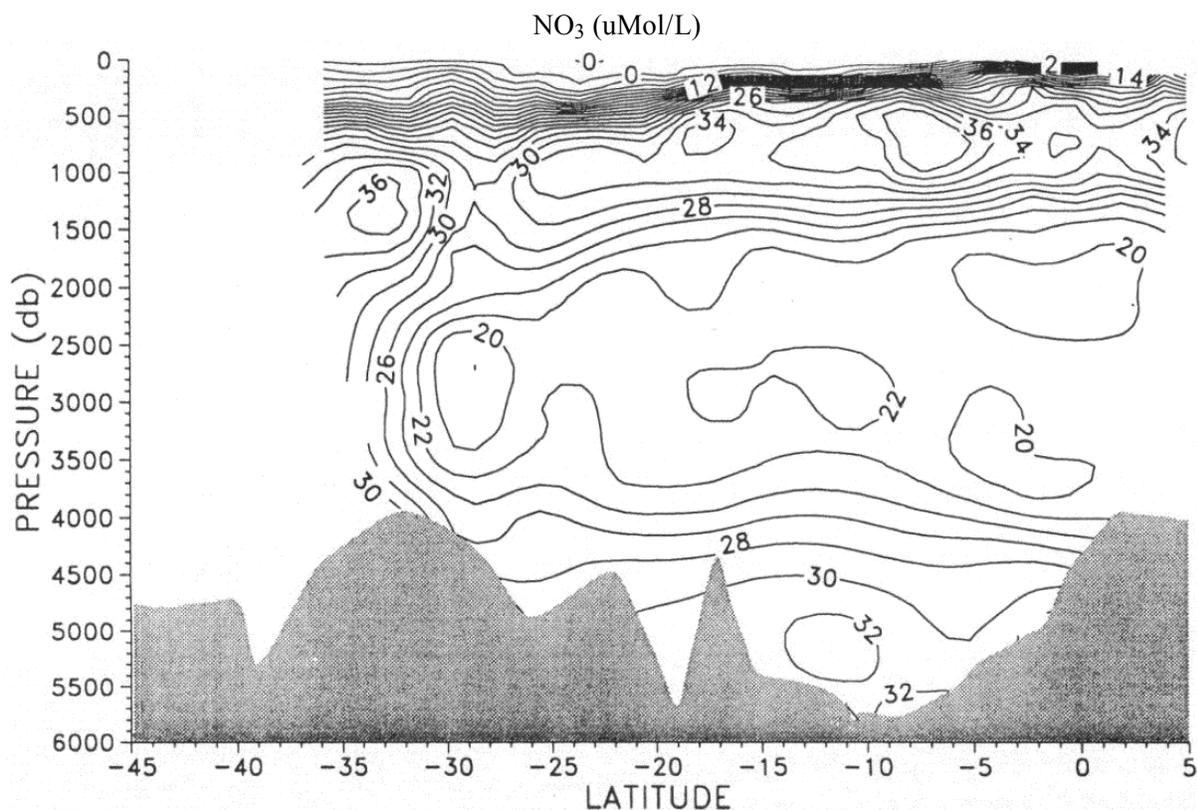
# SOUTH ATLANTIC 1991 RTS/CO<sub>2</sub> LEG 1

Sigma Theta



**Figure 3:** Potential density cross section utilizing 10 decibar averaged sigma-theta data from CTD stations on Leg 1. Contour interval = 0.15. See [Figure 2](#) caption for comment regarding bottom topography.

## SOUTH ATLANTIC 1991 RITS/CO<sub>2</sub> LEG 1



**Figure 4:** Nitrate data cross section for Leg 1. Contour interval = 2  $\mu\text{mol/L}$ . See [Figure 2](#) caption for comment regarding bottom topography.

### Silicates

The analytical procedures and methodologies used in the analysis of silicate are essentially similar to those described by Armstrong et al. (1967), with modifications described in Atlas et al. (1971). Silicate was determined from the reduction of silicomolybdate in acidic solution to molybdenum blue by ascorbic acid. The color produced is proportional to the concentration of silicate in the sample, with a detection limit of 0.4  $\mu\text{moles/L}$ . The precision of duplicate measurements was  $\pm 0.17\%$ , at 120  $\mu\text{moles/L}$  of silicate, with an assumed accuracy of  $\pm 1\%$ , since no absolute standards were available. [Figure 5](#) is a contour plot of the silicate values from Leg 1 of this cruise.

## 2.2 CARBON PARAMETERS

### 2.2.1 Total Dissolved Inorganic CO<sub>2</sub>

#### Sampling

Samples for dissolved inorganic CO<sub>2</sub> (TCO<sub>2</sub>) analysis were drawn from 10-L Niskin™ bottles into 500-mL Pyrex™ bottles using Tygon™ tubing. Bottles were rinsed once, and while being careful to not create bubbles, they were filled from the bottom until half of the bottles' volume had overflowed. The tube was pinched off and withdrawn, creating a 5-mL headspace volume. Each sample had 0.2 mL of a saturated HgCl<sub>2</sub> solution added to act as a sample preservative. The sample bottles were then sealed with glass stoppers lightly covered with Silastic™ grease. The samples were then stored in darkness at ambient (room) temperature for a maximum of two days prior to being analyzed.

#### Analysis

CO<sub>2</sub> analysis was performed by extracting the inorganic carbon in the sea water samples by acidification and subsequent displacement of the gaseous CO<sub>2</sub> into a coulometer cell. Two coulometers were used on the cruise. One was patterned after that of D. Chipman of Lamont-Doherty Earth Observatory (L.D.E.O.) and shall hereafter be referred to as the "Chipman" system; the other had a Single Operator Multiparameter Metabolic Analyzer (SOMMA) inlet system developed by K. Johnson of Brookhaven National Laboratories (B.N.L.) and shall be called the "Johnson" system.

The samples were introduced into the "Chipman" system by injecting a 23-mL aliquot from a 500-mL bottle with a glass syringe. A metal syringe guide/stopper assured that the injection volume was constant and reproducible. The temperature of the water remaining in the bottle was measured immediately after withdrawing the sample and was used to determine the density of the sample injected into the extraction tube. Subsequently, 1 mL of 10% phosphoric acid was injected into the extraction tube. The acid was purged with N<sub>2</sub> prior to use and stored in a bottle with CO<sub>2</sub>-free headspace. The CO<sub>2</sub> was extracted with ultra high purity N<sub>2</sub> which was run through a Malcosorb™ CO<sub>2</sub> scrubber. The evolved CO<sub>2</sub> gas went through a PFTE™ 0.2 micron filter to remove water droplets and aerosols and then titrated coulometrically using an UIC (model 5011) CO<sub>2</sub> coulometer. The gas stream was not dried prior to introduction into the cell. Sample analyses time was set to 20 minutes.

Prior to analysis on the automated "Johnson" system, each 500-mL sample bottle was inserted into a water bath at 20°C. Water from the bottle was displaced into a thermostatted pipette with a (500 ppm CO<sub>2</sub> in air) pressure gas. The water was then injected into an extraction chamber which contained 1 mL of 10% H<sub>3</sub>PO<sub>4</sub> solution which had been stripped of CO<sub>2</sub> prior to injection of the sample. The evolved gas was run through a condenser and a MgClO<sub>4</sub> drying column to dry the gas stream, and through an ORBO-53™ tube to remove volatile acids. Additional details concerning this system and procedures are presented in Johnson (1992), and Johnson et al. (1993).

Both the "Johnson" and "Chipman" coulometers were calibrated by injecting aliquots of pure CO<sub>2</sub> using an 8-port or 10-port valve with two sample loops of known volume. The CO<sub>2</sub> gas volumes bracketed the amount of CO<sub>2</sub> extracted from the water samples. The gas loops of the "Johnson" system were calibrated by weight with water at B.N.L. (Wilke et al., 1993). The gas loop volumes on the "Chipman" system were calibrated by alternating gas loop injections from the two gas sampling valves with the same coulometer using the "Johnson" loop volume as a reference. Liquid reference materials (RM's) consisting of bicarbonate in sodium chloride solution were supplied by A. Dickson of Scripps Institute of

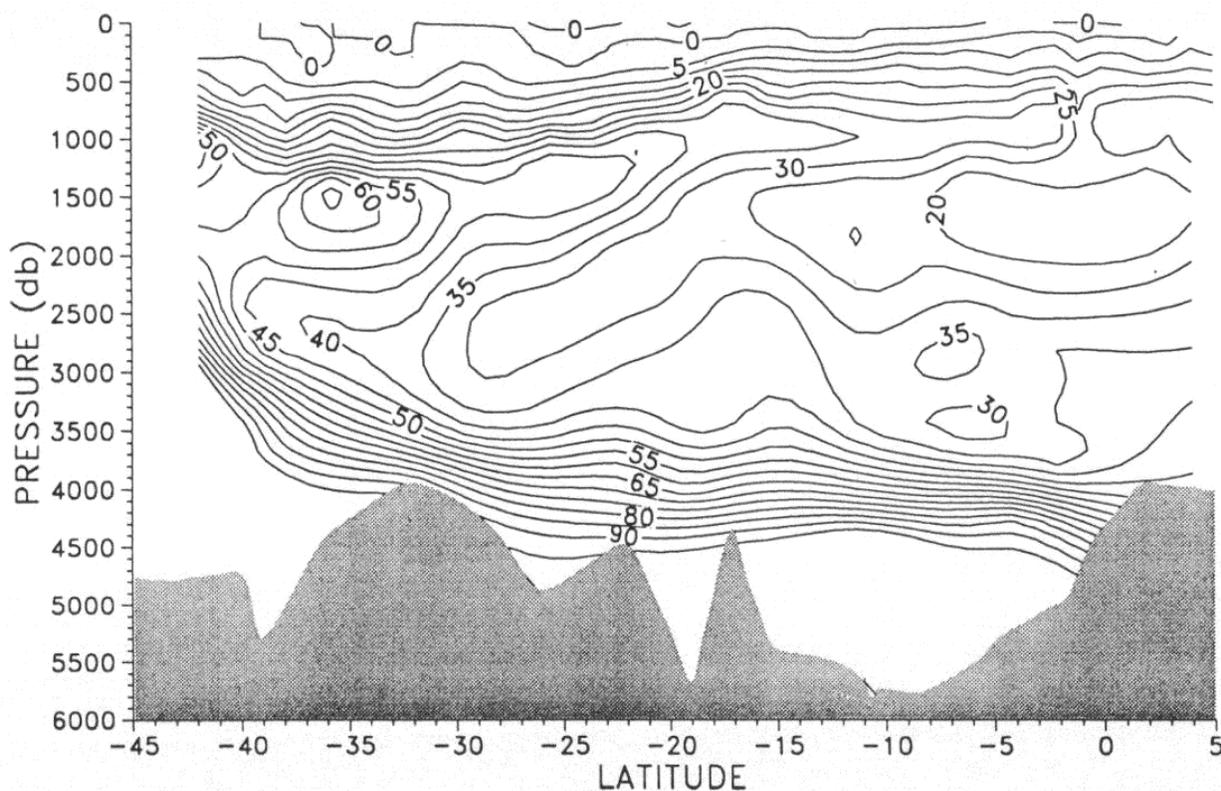
Oceanography (S.I.O.) and were run on each coulometer cell during the cruise. The results were close to the values determined manometrically by C.D. Keeling at S.I.O.

Av. value of RM's run on "Chipman"	2306.18 ± 1.47	n = 30
Av. value of RM's run on "Johnson"	2304.58 ± 1.50	n = 100
Manometric value [Dickson Batch #6]	2304.74 ± 0.94	n = 10

Note: All determinations, including replicates from the same bottle are pooled for the averages.

### SOUTH ATLANTIC 1991 RITS/CO<sub>2</sub> LEG 1

SI04 (uMol/L)



**Figure 5:** Silicate data cross section for Leg 1. Contour interval = 5  $\mu\text{mol/L}$ . See [Figure 2](#) caption for comment regarding bottom topography.

### Calculations

The instrument was calibrated three times for each cell solution with a set of gas loop injections. Calculation of the amount of CD<sub>2</sub> injected was determined according to methods described in the Department of Energy (DOE) CO<sub>2</sub> handbook (1991). The gas loops yielded a calibration factor for the instrument defined as:

Cal. factor =

$$\frac{\text{calculated moles of CO}_2 \text{ injected from gas loop}}{\text{measured moles of CO}_2 \text{ injected}}$$

The concentration of CO<sub>2</sub> ([CO<sub>2</sub>]) in the samples was determined according to:

[CO<sub>2</sub>] =

$$\frac{\text{Cal. factor} * (\text{Counts} - \text{Blank} * \text{Run Time} * 2.0728 * 10^{-4} \text{ } \mu\text{mol/count})}{\text{pipette volume} * \text{density of sample}}$$

where Counts is equal to the instrument reading at the end of the analysis; Blank is the counts/minute determined from blank runs performed at least once for each cell solution; Run Time is the minutes the sample is run;  $2.0728 * 10^{-4}$  is the conversion factor from counts to  $\mu\text{mol}$ . The pipette volume (or syringe volume) was determined by taking aliquots of distilled water at a known temperature from the volumes prior to, during, and after the cruise. No trend was observed in the change in volumes. Standard deviation in the series of measurements over three months was 0.03% of the total weight. The weights with the appropriate densities were used to determine the volume of the syringes and pipette. Calculations of pipette and syringe volumes, of densities, and of final CO<sub>2</sub> concentrations were all performed according to procedures outlined in the DOE CO<sub>2</sub> handbook (1991). All total CO<sub>2</sub> values are corrected for dilution by 0.2 mL of mercuric chloride solution assuming the solution is saturated with atmospheric CO<sub>2</sub> levels and total water volume is 540 mL yielding a correction factor of 1.00037. [Figure 6](#) shows a contour plot of the coulometer derived TCO<sub>2</sub> values from Leg 1 of this study.

## 2.2.2 Discrete fugacity of CO<sub>2</sub> (fCO<sub>2</sub>)

### Sampling

Samples were drawn from 10-L Niskin bottles into 500-mL Pyrex volumetric flasks using Tygon™ tubing. Bottles were rinsed once and while taking care not to entrain air bubbles, were filled from the bottom until half the bottles' volume overflowed. Five mL of water was then withdrawn with a pipette to create a small expansion volume. A saturated HgCl<sub>2</sub> solution, (0.2 mL), was added to the samples as a preservative. The sample bottles were then sealed with a screw cap containing a polyethylene liner and stored in darkness at room temperature for a maximum of two days prior to analysis.

### Discrete fCO<sub>2</sub> analyzer

The AOML discrete fCO<sub>2</sub> system is patterned after the design described in Chipman et al. (1993) and is discussed in detail in Wanninkhof and Thoning (1993). The major difference between the systems is that the AOML system uses a Licor (model 6262) non-dispersive infrared analyzer, while the Chipman et al. system utilizes a gas chromatograph with a flame ionization detector and a methanizer, which quantitatively converts CO<sub>2</sub> into CH<sub>4</sub> for analysis.

Samples are collected in 500-mL volumetric flasks and are brought to a temperature of  $20.00 \pm 0.02^\circ\text{C}$ , using a pre-bath at  $19\text{--}21^\circ\text{C}$  and a Neslab™ (model RT-220) controlled temperature bath. A 60-mL headspace is created in the flask by replacing the water using a compressed standard gas with a CO<sub>2</sub> mixing ratio close to the fCO<sub>2</sub> of the water. The headspace is circulated in a closed loop through the infrared analyzer (IR), which measures CO<sub>2</sub> and water vapor levels in the sample cell. The headspaces of

the two flasks are equilibrated simultaneously in channels A and B. While headspace from the flask in channel A goes through the IR analyzer, the headspace of the flask in channel B is recirculated in a closed loop. The sample in the A channel is equilibrated for 17 minutes while the air from the headspace of the flask flows through the IR analyzer. The sample in the B channel is circulated in a closed loop for 10 minutes and through the IR for 8 minutes. An expandable volume, consisting of a balloon, keeps the contents of the flasks at room pressure.

In order to maintain measurement accuracy and precision, a set of six gas standards is run through the system after every four to ten seawater samples. The standards have mixing ratios of 201.4, 354.1, 517.0, 804.5, 1012.2, and 1529 ppm, which bracket the  $f\text{CO}_2$  at 20°C ( $f\text{CO}_2$ , 20) values observed in the water column of the South Atlantic.

The determination of  $f\text{CO}_2$  in water from the discrete analyses involves several steps. The mixing ratio and detector response for the standards are normalized for temperature and pressure. The IR voltage output for samples are normalized with regard to pressure and are corrected for the presence of water vapor and converted to a mixing ratio. The mixing ratio in the headspace is converted to fugacity and corrected to fugacity of  $\text{CO}_2$  in the water sample prior to equilibration by accounting for change in total  $\text{CO}_2$  in water during the equilibration process (for details see, Wanninkhof and Thoning, 1993). The change in the  $f\text{CO}_2$  of water, ( $f\text{CO}_2\text{w}$ ), caused by the change in  $\text{TCO}_2$  is calculated using the constraint that total alkalinity (TAlk), remains constant during exchange of  $\text{CO}_2$  gas between the headspace and the water. The calculation is outlined in the appendix of Peng et al. (1987).

### **2.2.3 Methods for Potentiometric Total Alkalinity, $\text{TCO}_2$ and pH Measurements**

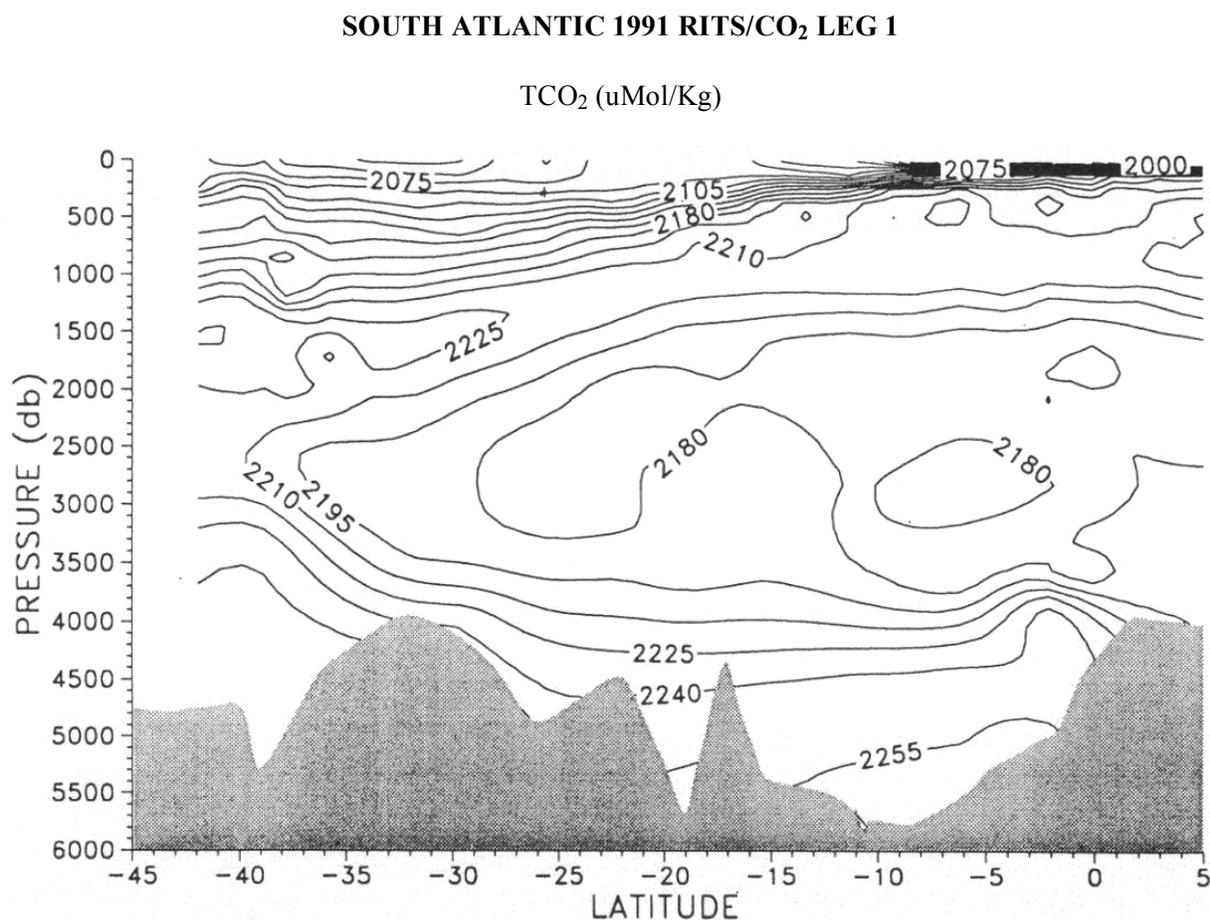
The total alkalinity and inorganic carbon (Dickson, 1981) in the water samples was determined during the cruise by making potentiometric titrations. The two systems used consisted of a Metrohm™ 615 titrator and Metrohm™ 605 pH meter that are operated by an Apple™ computer (Thurmond and Millero, 1982). The titration is done by adding HCl to the seawater past the carbonic acid end point. Seawater samples were contained in a water jacketed cell controlled to a constant temperature of 25°C with a Forma™ water bath. Due to the large number of samples to be measured, the titrations were not made over the entire pH range. This allowed a complete titration to be made in about 10 minutes. Unfortunately during the cruise the disk reader of the Apple™ computers failed and the titrations had to be run by hand.

The titrant solution was prepared from standard HCl and reagent grade NaCl. The 0.25 M HCl contained 0.45 M NaCl to yield an ionic strength equivalent to the seawater (0.7 M). The acid was standardized with weighed amounts of  $\text{Na}_2\text{CO}_3$  dissolved in 0.7 M NaCl solution in the laboratory. A blank titration was made to evaluate the residual alkalinity (14  $\mu\text{M}$ ) due to impurities in the NaCl. The normality of the acid was found to be  $0.2514 \pm 0.0001$  M). Measurements made in the laboratory after the cruise yielded the same concentration of the HCl.

The electrode system used to measure the emf of the sample during a titration consisted of a ROSS™ glass pH electrode and an Orion™ double junction reference electrode. The response of the electrodes were determined by HCl titration in 0.7 M NaCl solution. Electrodes with non-Nernstian behavior were discarded (slope larger than  $\pm 0.5$  mV of the theoretical slope). Three cells were used during the cruise (Cell 1, 2 and 3). They had volumes (V) and standard emf's, ( $E^*$ ), in seawater of  $V = 231.10 \pm 0.02$  cm<sup>3</sup>,  $238.99 \pm 0.02$  cm<sup>3</sup>,  $239.64 \pm 0.02$  cm<sup>3</sup>;  $E^* = 592, 585, 580$  mV ( $\pm 1$  mV), respectively.

The total alkalinity and total CO<sub>2</sub> were calculated from the volumes of acid added and the measured emf's using a least-squares Gran technique. A chemical model (Dickson, 1981) was used to determine the equivalence points on the titration curve.

The initial emf reading of the seawater solution before the titration began was used to determine the pH. The pH at 25°C was determined using the E\* calculated for each titration. The concentrations of H<sup>+</sup> are in mol/kg and are on the seawater scale ( $[H^+]_T = [H^+]_F + [HSO_4 + [HF]$ ). The electrodes were calibrated before going to sea by making titrations of 0.7 M NaCl with 0.25 M HCl (with 0.45 M NaCl) and TRIS buffer. The TRIS buffer was made up in the laboratory and calibrated with hydrogen electrode system before the cruise (Millero, 1986). The total seawater pH scale (Dickson, 1984) was used for all the measurements.



**Figure 6:** Dissolved inorganic carbon dioxide, TCO<sub>2</sub> (AOML value) cross section for Leg 1. Contour interval = 15  $\mu\text{mol/Kg}$ . See [Figure 2](#) caption for comment regarding bottom topography.

#### 2.2.4 Dissolved Organic Carbon Methods

A Shimadzu™ DOC-5000 Total Organic Carbon Analyzer with the ASI-5000™ Automated Sample Injector was purchased for use on this cruise. This is an automated DOC instrument utilizing high temperature catalytic combustion (680°C) and non-dispersive infrared detection. It was installed on the

ship and operated in NPOC mode (Non-purgable organic carbon) which means the "DOC" reported does not include volatile species. The only modification to the standard operating procedures for this commercial instrument was that "zero" (high-purity) oxygen was used instead of compressed air for the carrier stream.

The water column was sampled using Niskin™ water sampling bottles mounted on the 24 bottle rosette/CTD package that was described in the Hydrographic Methods section of this report. Samples for the DOC analysis were collected on deck in the 40-mL glass vials which fit the autosampler carousel. The samples were free-flowed from the Niskin™ bottle into the vial. Care was taken so that the inner surfaces of the vial and the water stream from the valve did not come into contact with any other surfaces. Each vial was filled and rinsed with sample three times, before being filled for analysis. The sample was immediately acidified to pH of 2 by addition of vacuum-distilled HCl, and sealed with Parafilm™ and a plastic snap ring. Sample levels were kept far enough below the top of the vial to insure that the water did not come into contact with the Parafilm™ during subsequent handling.

The samples were moved to the autosampler for immediate processing, or were stored at 4°C if a delay was necessary. The autosampler was set to purge each sample of inorganic carbon species by bubbling high purity oxygen through the sample for five minutes immediately before the analysis. The gas stream continued to be introduced during the analytical process, except when the water was being transferred to the instrument by the sipper. Samples and standards were run in replicate, (usually six per determination). Peak area for each replicate was recorded for later statistical handling.

Data calibrations on this cruise were produced by the standard addition method; three levels of known concentrations of KHP (Potassium Hydrogen Phthalate) were added to aliquots of a sample and the series run as if they were discrete samples. This procedure insures that matrix effects and artifacts due to handling of the samples are reflected in the calibrations. The single largest problem in calibrating the DOC instrument is evaluating the "instrument blank", the part of the reported signal which is NOT due to organic carbon. Low organic carbon water produced by redistillation of research grade distilled water over potassium permanganate, and batch UV-irradiated Gulf Steam seawater were run daily as samples to monitor this apparent blank (which was usually <4 µmol/L).

## 2.3 PRODUCTIVITY

### 2.3.1 Methods for Chlorophyll Measurements

Chlorophyll *a* concentrations were determined from duplicate 250-mL and 300-mL aliquots taken from a flow-through system and Go-Flo™ hydrographic casts respectively. The samples were filtered through Whatman GF/F filters which were then placed in 5 mL of a 40/60 (vol.:vol.) mixture of dimethyl sulfoxide (DMSO) :90% Acetone solution and placed in the dark for one hour. This is a modification of the Shoaf and Lium, (1976) and Burnison, (1980) procedure. The fluorescence of the DMSO/Acetone extracts were measured at sea with a Turner Designs™ fluorometer model 111. The fluorometer was calibrated at sea with Sigma chlorophyll *a*, following the method of Parsons et al., (1984).

Water was collected hourly from the seawater flow-through system for chlorophyll *a* analysis. The intake valve is located in the bow of the ship at about 3 m below the surface. The Go-Flo™ hydrographic casts for both chlorophyll *a* and production rate measurements were made using 10-L Go-Flo™ bottles mounted on Kevlar hydrowire. Six sampling depths were selected according to light levels. Seawater samples were collected at 100, 50, 30, 15, 6, and 1% of the incident surface irradiance ( $I_0$ ). Diffuse vertical attenuation coefficients ( $K$ ), in reciprocal meters, were estimated at all stations using a Secchi

disk and the relation  $K = 1.4/\text{Secchi depth}$ . Photosynthetically available radiation (PAR) was also measured with depth using a Lambda Instruments™ LI-190S  $4\pi$  spherical collector. Calculations for this measurement were done after each cast. All Go-Flo™ hydrocasts were performed within a three hour time window (between 7-10 am local), to help ensure uniform sampling conditions throughout the cruise. Contour plots of chlorophyll values from Leg 1 of this cruise are found in [Figure 7](#).

### 2.3.2 Methods for Productivity Measurements

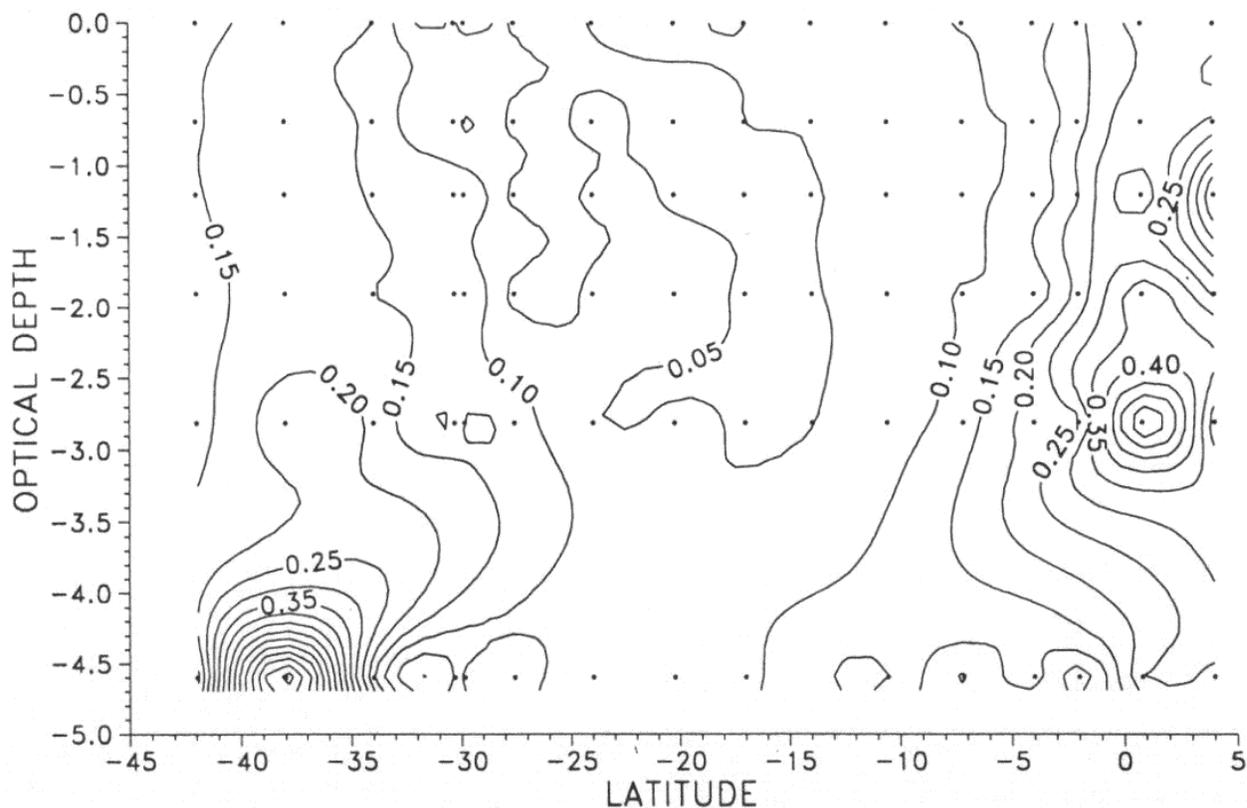
Productivity measurements were made using the Carbon method, as originally described by Steemann-Nielsen (1952), with modifications by Fitzwater et al. (1982) to minimize trace metal contamination. All materials were acid-cleaned in dilute (0.1 N) HCl, then rinsed with Milli-Q™ water. Incubation bottles were rinsed with the seawater sample prior to being filled. Samples were collected from the Go-Flo bottles in darkened 2-L acid-cleaned polycarbonate bottles. Approximately 250 mL of sample was transferred to each of three (two light, one dark) acid cleaned polycarbonate bottles and inoculated with 5  $\mu\text{Ci}$  of  $\text{NaH}^{14}\text{CO}_3$  with acid cleaned Eppendorf™ pipettes. The Amersham-Serlet™ isotope ( $^{14}\text{C}$ -bicarbonate) was prepared in a carrier solution of 0.3 g/L Baker Instra Analyzed™  $\text{NaHCO}_3$ . The three incubation bottles were then placed into small Plexiglas™ tubes that were wrapped with blue film, (#TS-51-xsr from Madico Inc.). The number of wraps were calibrated to simulate the 100, 50, 30, 15, 6, and 1% of the incident surface  $I_0$ , corresponding to optical depths listed in [Appendix C](#) of 0, -0.69, -1.20, -1.90, -2.81, and -4.60. The samples were incubated on deck for 24 hours in clear Plexiglas™ cylinders filled with circulating surface seawater. The samples were then taken to the lab where they were filtered, in darkness, through Whatman GF/F filters, and rinsed with filtered seawater without being exposed to air.

Filtrations were performed under a pressure differential of <50 mm Hg to minimize cell breakage (Goldman and Dennett, 1985). The filters were transferred to Nalgene™ scintillation bags, and acidified with 0.5N HCl. After one hour, a 3-mL aliquot of Universol™ (ICN radiochemicals) scintillation cocktail was added to each bag as described in Hitchcock (1986)

Isotope activity of the samples was measured aboard ship with a Tracor model 300 scintillation counter. Production rate ( $\text{mg C}/\text{m}^3/\text{h}^1$ ) was calculated from the mean value of the two light bottles minus the dark bottle activity. A contour plot of productivity measurements from Leg 1 of this cruise is presented in [Figure 8](#).

## SOUTH ATLANTIC 1991 RITS/CO<sub>2</sub> LEG 1

### CHLOROPHYLL A (Mg/M3)



**Figure 7:** Chlorophyll *a* cross section from Leg 1. Dots represent sample locations. Contour interval = 0.05 mg/m<sup>3</sup>.

## 2.4 UNDERWAY MEASUREMENT METHODS

### Sampling

During Legs 1 and 2 of the S. ATL-91 cruise, underway measurements of fugacity of CO<sub>2</sub> in surface seawater, (fCO<sub>2</sub>w), and air, (fCO<sub>2</sub>a) were performed with an automated system. The seawater intake was located in the ship's bow bubble, approximately 3 m below the water line. A thermosalinograph, which records temperature and salinity was placed in a shunt off the main seawater intake line, in the bow bubble as well. Since there was evidence of seawater being heated prior to its reaching the thermosalinograph, water temperature was acquired from a hull mounted probe used for acoustic Doppler current profile data reduction. On Leg 2, discrete samples were taken from the underway system at six-hour intervals and analyzed for TCO<sub>2</sub>, fCO<sub>2</sub>, and major nutrients in addition to the continuous fCO<sub>2</sub> measurements. Cruise tracks from Legs 1 and 2, with the range of fCO<sub>2</sub>w-fCO<sub>2</sub>a values represented by stick diagrams, are presented in [Figures 9](#) and [10](#).

### 2.4.1 Underway $f\text{CO}_2$ Measurements

The shipboard automated underway  $f\text{CO}_2$  system runs on an hourly cycle during which three gas standards, a headspace sample from the equilibrator, and an ambient air sample are analyzed. The equilibrator, which was designed by R. Weiss of S.I.O., is made from a large (58 cm H x 23 cm ID) Plexiglas™ chamber. The equilibrator has a shower head in the top through which surface seawater is forced at a rate of 20–30 L/min. The water spray through the 16-L head space and the turbulence created by the jets impinging on the surface of 8-L of water, cause the gases in water and headspace to equilibrate. A drain 20 cm from the bottom of the equilibrator discharges excess water from the system over the side of the ship. Air in the equilibrator head space is circulated with an Aircadet™ pump (model 7530–40) at 6 L/min in a closed loop through a mass flow meter (MFM) and back pressure regulator. During 23 minutes of each hour, 75 mL/min is teed off upstream of the back pressure regulator through a mass flow controller (MFC) and into the 12-mL sample cell of a Licor™ (model 6251) non-dispersive infrared analyzer. The air removed from the equilibrator through the IR analyzer is replaced with ambient air through an intake/vent line that runs to the outside of the ship. The introduction of the ambient air into the equilibrator chamber during sampling of the headspace results in an error in the determination of the equilibrated head space composition no greater than one micro atmosphere. The total time required to fully replace equilibrator air through the ambient air intake/vent line is 213 minutes. The headspace equilibration time, as determined by return to equilibrium after perturbation by adding nitrogen to the head space, is approximately 2.5 minutes. The intake/vent line also assures that the pressure in the head space of the equilibrator remains at atmospheric value.

During underway sampling operations ambient air is drawn through 100 m of 0.37 cm OD Dekoron™ tubing from the bow mast of the ship at a rate of 6 to 8 L/min. During 22 minutes of each hour, ambient air mixing ratios are measured in the IR analyzer by teeing off the air line at a flow rate of 75 mL/min. Compressed gas standards with nominal mixing ratios of 300, 350, and 400 ppm (parts per million by volume) flow through the IR analyzer for five minutes each hour at 75 mL/min for calibration. The 300 ppm standard flows continuously at 50 mL/min through the reference side of the IR analyzer (detector) as well. All reference tanks undergo a pre- and post-cruise calibration at CMDL against standards certified by the World Meteorological Organization (WMO).

The IR analyzer/detector's voltage output is measured once per second with a Keithley™ (model 195 A) digital multimeter; 1-minute averages are calculated and stored on the hard disk of an MS-DOS computer. The MFC's connected to the reference and sample inlet of the IR, the MFM's measurement of the intake rate of ambient air and recirculation rate of the headspace of the equilibrator, the back pressure in the air and equilibrated air lines, and two thermistors readings of the water temperature in the equilibrator are all logged at 1-minute intervals as well.

#### *$f\text{CO}_2$ Calculations*

The mixing ratios of ambient air and equilibrated headspace air are calculated by fitting a second-order polynomial fit through the response of the detector versus mixing ratio of the standards. Due to the need for sufficient time to flush the sample cell and lines leading to the IR from the previous gas, the first three minutes of each analysis run are not used in the calculations. The subsequent one-minute readings for each analysis are averaged, yielding one 19-minute average ambient air mixing ratio and one 20-minute average equilibrated headspace mixing ratio per hour. Typical standard deviations for air values are  $\pm 0.1$  ppm and for equilibrated headspace  $\pm 0.3$  ppm.

Mixing ratios of dried equilibrated headspace and air must be converted to fugacity of CO<sub>2</sub> in water and water saturated air in order to determine the driving force for the air-sea CO<sub>2</sub> flux. For ambient air, assuming 100% water vapor content, the conversion is:

$$f_{CO_2a} = X_{CO_2a} (P - p_{H_2O}) \exp(B_{11} + 2 \delta_{12}) P/RT \quad (1)$$

where  $p_{H_2O}$  is the water vapor pressure at the sea surface temperature, and  $P$  is the atmospheric pressure. The exponential term is the fugacity correction where  $B_{11}$  is the second virial coefficient of pure CO<sub>2</sub> ( $B_{11} = 1636.75 + 12.0408 T - 0.0327957 T^2 + 3.16528 \times 10^{-5} T^3$ ) and  $\delta_{12}$  ( $= 57.7 - 0.118 T$ ) is the correction for an air-CO<sub>2</sub> mixture (Weiss, 1974). The calculation for the fugacity in water includes an empirical temperature correction term for the increase of  $f_{CO_2}$  due to heating ( $df_{CO_2w}/dT = 4.23\% / ^\circ C$ . D. Chipman and T. Takahashi, personal communication), of the water from passing through the pump and through 5 cm ID PVC tubing within the ship. The water in the equilibrator is typically 0.3°C warmer than sea surface temperature. The fugacity in water is calculated according to:

$$f_{CO_2w} = x_{CO_2w} (P - p_{H_2Oeq}) (\exp[(T_{sw} - T_{eq}) 0.0428]) \exp(B_{11} + 2 \delta_{12}) P/RT \quad (2)$$

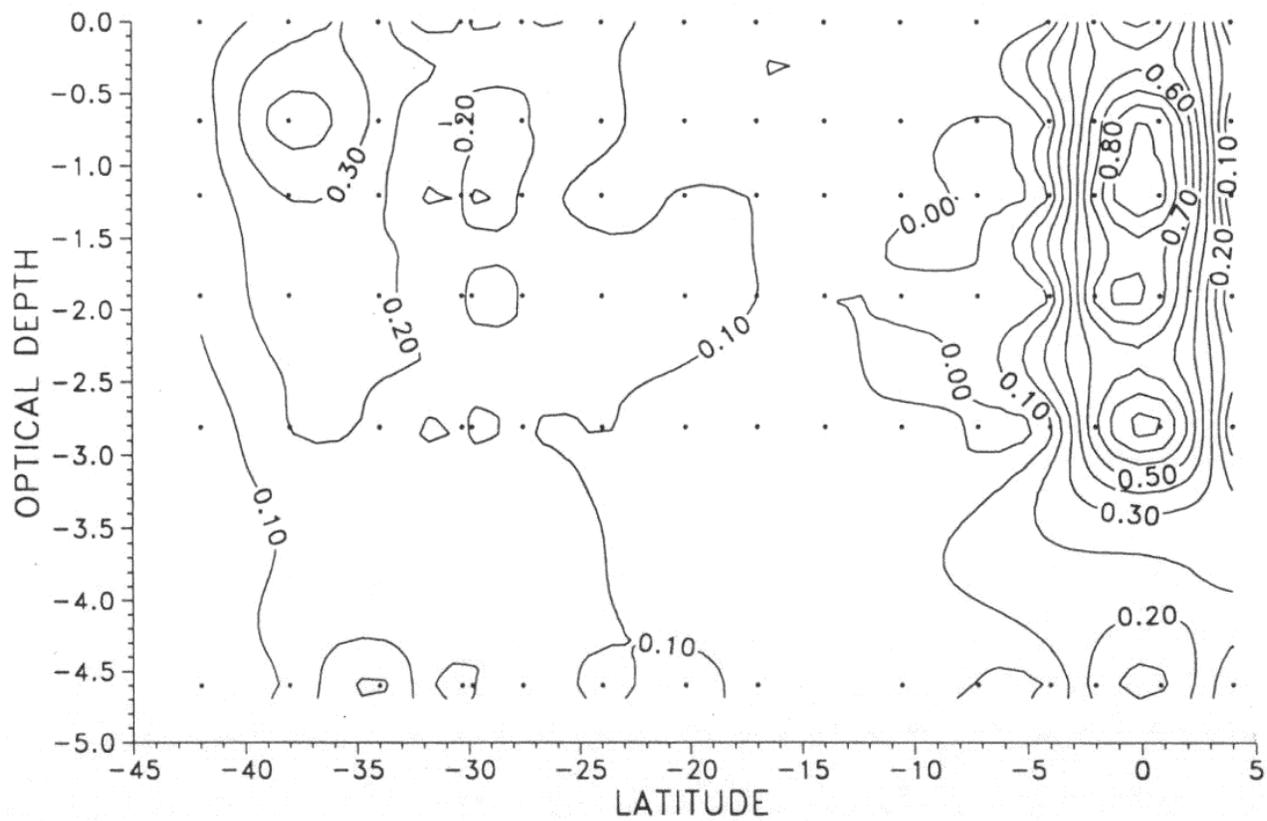
where  $p_{H_2Oeq}$  is the water vapor pressure at the temperature of the water in the equilibrator,  $T_{sw}$  is the temperature of the surface seawater,  $T_{eq}$  is the temperature of the water in the equilibrator.

### 3. ACKNOWLEDGMENTS

The dedication and assistance of the officers and crew of the NOAA ship MALCOLM BALDRIGE is gratefully appreciated and hereby acknowledged. The authors also thank Ms. Betty Huss for her expertise and efforts in the processing of the initial data sets. This research was supported by the climate and Global Change Program of NOAA.

SOUTH ATLANTIC 1991 RITS/CO<sub>2</sub> LEG 1

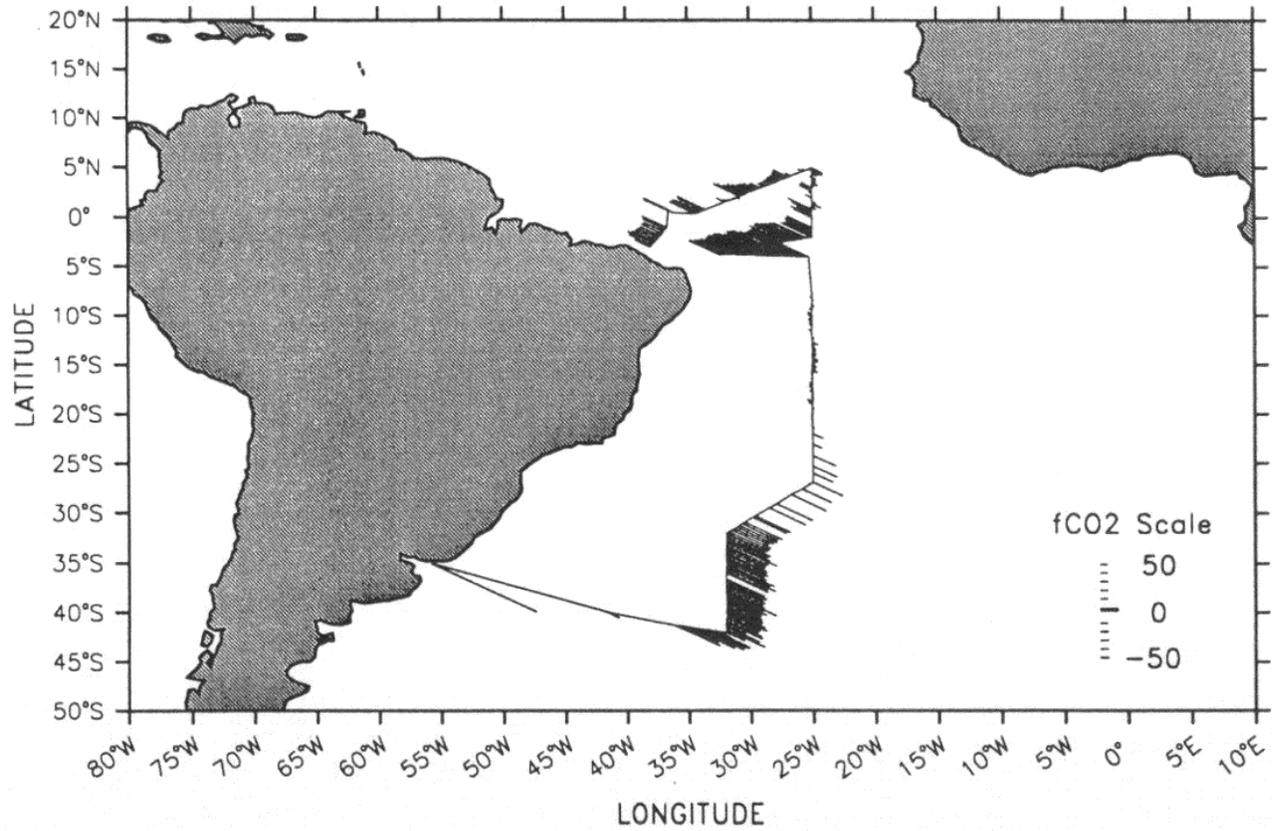
PRODUCTIVITY (mgC m<sup>-3</sup>h<sup>-1</sup>)



**Figure 8:** Productivity cross section from Leg 1. Dots represent sample locations. Contour interval = 0.1 mg C m<sup>-3</sup> h<sup>-1</sup>

# SOUTH ATLANTIC 1991 RITS/CO<sub>2</sub> LEG 1

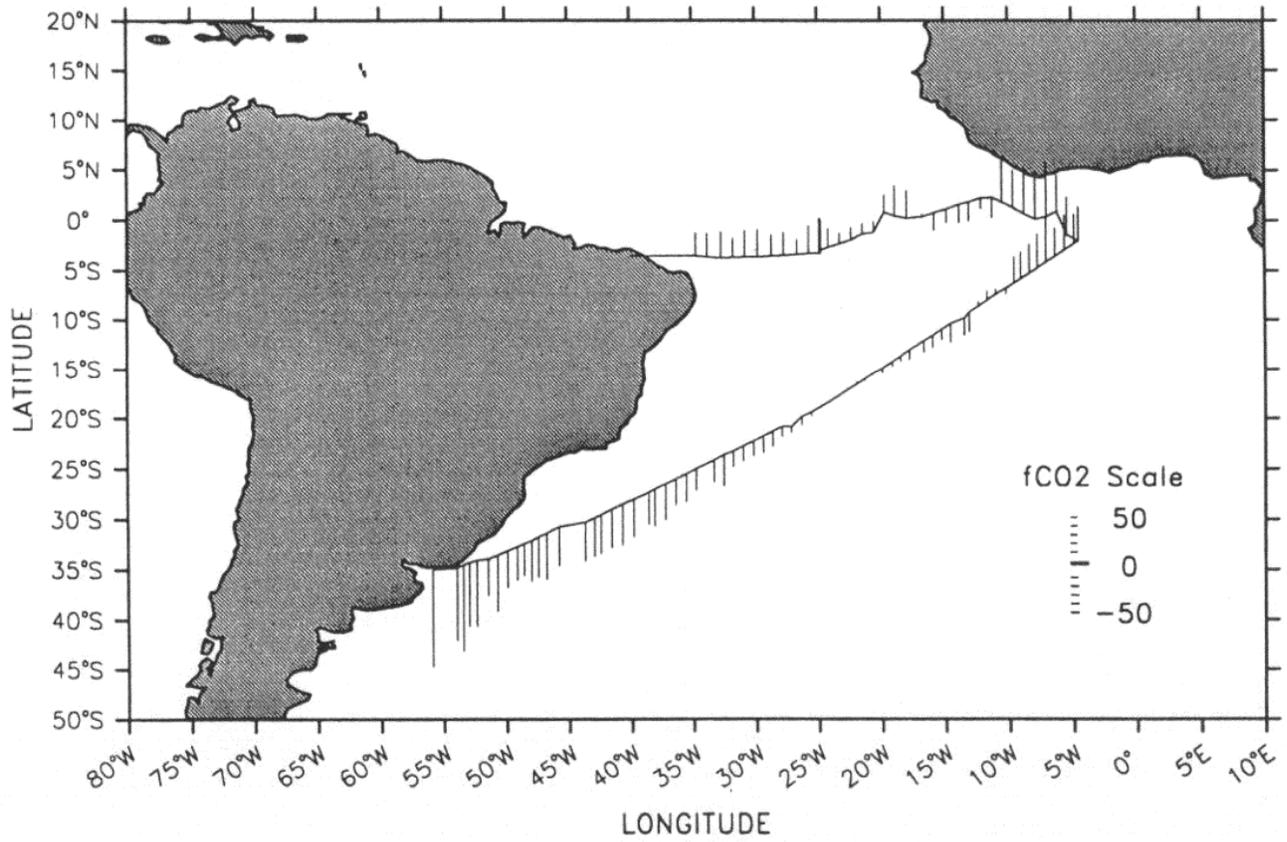
UNDERWAY fCO<sub>2</sub> (water - air) [uatm]



**Figure 9:** Underway fCO<sub>2</sub>(w-a) measurements from Leg 1. Stick height, above, or to the left of track line equals fCO<sub>2</sub>(w-a). Negative fCO<sub>2</sub>(w-a) values depict sinks and appear below, or to the right of the track line.

## SOUTH ATLANTIC 1991 RITS/CO<sub>2</sub> LEG 2

UNDERWAY fCO<sub>2</sub> (water - air) [uatm]



**Figure 10:** underway fCO<sub>2</sub>(w-a) measurements from Leg 2. Stick height above track line equals fCO<sub>2</sub>(w-a). Negative fCO<sub>2</sub>(w-a) values appear below the track line.

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## APPENDIX A: Index of Measurements and Units

### List of measurements

Column heading or abbreviation	Explanation
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#### *Hydrography, Appendix B*

TCO <sub>2</sub> (coul.)	dissolved inorganic carbon dioxide (coulometer)
TCO <sub>2</sub> (titr.)	dissolved inorganic carbon dioxide (titrated)
fCO <sub>2,20</sub>	fugacity of CO <sub>2</sub> at 20 degrees
TAlk	total alkalinity
calc.	means the value has been calculated
coul.	coulometer
DOC	dissolved organic carbon

#### *Productivity measurements, Appendix C*

OPT DEPTH	optical depth
PROD-RATE	organic carbon production rate
CARB-DAY	organic carbon production per day (= PROD_RATE*24)
CHLORO_A	chlorophyll
CHLOR_DAY	chlorophyll production per day
TOT-PIGS	chlorophyll + phaeopigments
INCUB-TIME	incubation time for productivity measurements

#### *Underway measurements, Appendix D*

Lat	latitude in decimal degrees
Lon	longitude in decimal degrees
XCO <sub>2,a</sub>	the volume fraction of CO <sub>2</sub> in air
XCO <sub>2,w</sub>	the volume fraction of CO <sub>2</sub> in equilibrator headspace
fCO <sub>2,w-a</sub>	fugacity of CO <sub>2</sub> (water value minus the air value)
SST	sea surface temperature
SST-Eq.T	sea surface Temperature-Equilibrators temperature
Sal (CTD)	salinity from CTD measurement at stations
Sal (TSG)	salinity measurement from thermosalinograph

## Hydrographic and Carbon System parameters, Appendix B

Parameter	Units	Unit spelled out
Depth	m	meters
Pres.	db	decibars
Temp.	°C	degrees centigrade
Pot. T.	°C	degrees centigrade
Salinity	(none)	salinity
Sigma theta	(none)	potential density
Oxygen	mL/L	milliliters per liter
NO <sub>2</sub>	umol/L	micro moles per liter
NO <sub>3</sub>	umol/L	micro moles per liter
SiO <sub>4</sub>	umol/L	micro moles per liter
TCO <sub>2</sub> (coul.)	umol/kg	micro moles per kilogram
fCO <sub>2</sub> (20 deg.)	uatm	micro atmospheres at 20°C
pH	(none)	
TAlk	uEq/Kg	micro equivalents per kilogram
TCO <sub>2</sub> (titr.)	umol/Kg	micro moles per kilogram
DOC	umol/L	micro moles per liter

## Productivity parameters, Appendix C

Parameter	Units	Unit spelled out
SALINITY	(none)	salinity
INCUB TIME	HRS	hours
DEPTH	m	meters
OPT DEPTH	(none)	optical depth
PROD-RATE	mgC/m <sup>3</sup> /h <sup>1</sup>	milligrams of carbon per m <sup>3</sup> per hr
CARB_DAY	mgC/m <sup>3</sup>	milligrams per cubic meter
CHLORO_A	mgC/m <sup>3</sup>	milligrams per cubic meter
CHLORO_DAY	mgC/m <sup>3</sup>	milligrams per cubic meter
TOT-PIGS	mgC/m <sup>3</sup>	milligrams per cubic meter

## Underway parameters, Appendix D

Parameter	Units	Unit spelled out
Lat	Dec. Deg.	decimal degrees
Lon	Dec. Deg.	decimal degrees
XCO <sub>2,a</sub>	ppm	parts per million
XCO <sub>2,W</sub>	ppm	parts per million
SST	deg. C	degrees centigrade
SST-Eq.T	deg. C	degrees centigrade
Sal (CTD)	none	
Pressure	mb	millibars
fCO <sub>2,w</sub>	uatm	microatmospheres
fCO <sub>2,w-a</sub>	uatm	microatmospheres

## DATA PROCESSING NOTES (Leg 1)

Date	Person	Data Type	Action	Summary
2000-01-11	Rik Wanninkhof	CTD	Submitted	needs reformatting
2000-05-06	Rik Wanninkhof	CTD	Status Update	Data are Public
				I did not realize that the data were in non-public status. Feel free to release it to the community at large (recognizing that not all data meets "WOCE specifications"). Don't hesitate to contact us if there are further questions.
2000-06-12	Danie Bartolacci	CTD	Website Updated:	data are public
2000-12-20	Heidi Buck	Cruise Report	Website Updated:	txt version online
2002-05-01	Danie Bartolacci	CTD/BTL/SUM	Update Needed:	Correct Data Status Fields
				Database does not reflect having BOT in. DOC is for CTD only. Correct database to indicate BOT is in and all params. WOCE fmt all files. Create SUM. Create exchg.
2002-10-17	Karla Uribe	CTD/SUM	Website Updated:	CTD converted to WOCE, unformatted SUM put online
				CTD was converted to WOCE format using the header information, documentation and sumfile. The original CTD zip contains a file called LOCATION.CSV which is a sumfile, I put a copy of that file on the website. That sumfile is still unformatted and it is required to finish testing the CTDs. The original CTD files contained 3 OXY values, the ML/L was selected to be put in the WOCE format which means those units must be converted before converting to exchange.
2002-10-30	Karla Uribe	SUM	Website Updated:	SUM created, Lat/Lon converted from decimal values
				Sumfile was created from a CSV file that was found in the CTD zip. Lat/Lon data was converted from decimal values. Sumfile in WOCE format.
2005-01-04	Robert Key	BTL	Status Update	Available for submission
				On the same page you have listed the 1991 M. Baldrige cruise. Under the data link there is no bottle data. These data are public and i have a copy of everything with WOCE flags added. I can provide a copy if you need it or alternately, it should be available from Kozyr at CDIAC.
2005-01-05	Robert Key	DEL13/DEL14	Submitted	Updated data files
				Here are the similar (to AR21_1993) files for AR21a (leg 1 and 2 separate). I also attach my README as well as the NOAA final report. Nutrients and oxygen from these early 90s NOAA cruises tend to be below WOCE standard. This cruise pre-dated development of CRMs for carbon, so final calibration on those data are not as accurate as we'd expect today.
2011-02-10	Dave Muus	CTD	Website Update	Exchange and NetCDF files online, sum corrected
				"Notes on Malcolm Baldrige cruise July 11 - Sept 2, 1991. Expocode 3175MB91 110210/dm  Section ID AR21 per Documentation file.  1. Summary file dated 20021029 failed sumchk test. WOCE SECT column was blank. Added AR21. LONGITUDE not Left Justified. Realigned longitude values. sumchk okay. Stations 1 - 31 plot on African continent. Original summary file (ar21_asu_replaced20021030.txt) shows longitudes negative - West not East. Changed longitudes from E to W.  2. WOCE format CTD files are named "CAST-0cc.CAL" where cc is CASTNO in summary file. Renamed CTD files to WOCE CTD filename format: AR21_a00ss.wct where ss is STNNBR.  3. First 9 casts had end-of-line "*" in wrong column for 2nd line. Corrected.  4. Removed "_1 _2" between EXPOCODE and WHP-ID to make EXPOCODE agree

with summary file.

5. NUMBER OBS. column not lined up properly. Moved one space to right.
6. Converted CTDOXY ML/L to UMOL/KG.
7. No bottom depth. Used 99999 in summary file to make exchange file, then changed summary file to -9 and exchange file bottom depth to -999.
8. No quality flags in original data set. Apparently all flags set to "2" in 2002-10-17 WOCE format CTD file. Left flags unchanged. Note caution in Documentation file re CTD Oxygen data.
9. Made Exchange and NetCDF format CTD files. Checked with Java OceanAtlas."

2011-03-10	Dave Muus	BTL	Website Update	Exchange and WOCE files online
Notes on AR21 Leg 1 bottle data EXPOCODE 3175MB91 110309/dm				
1. Original bottle data received from Bob Key as AR21a.leg1.Z on January 5, 2005.				
2. pH and DOC have no quality flags. Used flag 2 for pH and DOC values. Used PH_SWS and PH_TMP = 25 Degrees per README.AR21a.				
3. CASTNOs do not match Summary file cast numbers from CTD data and NOAA Data Report ERL AOML-24(dated April 1994) Bottle file has Station numbers: 8, 14, 20, 25, 30 and 32. Not on CTD file Summary file or Data Report. Changed bottle data file cast numbers from all "1"s to CTD and Data Report station and cast numbers. Data Report has Station 38 for casts 31, 32 and 33. CTD and AR21a.leg1.Z have casts 32 and 33 in Station 39. Station 38/31 is more than 1400km from casts 32 and 33. Casts 32 and 33 have same position and bottom depth. Used Station 39 for casts 32 and 33.				
4. Bottom depths in AR21a.leg1.Z file differ from bottom depths in Data Report. Used Data Report bottom depths to Summary file.				
5. Compared Summary File to Data Report and made following corrections assuming Data Report is correct:				
Station Cast 2 2 Changed Longitude from 36 10.80 W to 35 10.80 W 5 5 Changed longitude from 25 0.60 W to 25 0.00 W 9 8 Changed latitude from 0 0.60 S to 0 0.00 S 11 10 Changed latitude from 2 0.00 S to 1 59.40 S 11 10 Changed longitude from 24 0.00 S to 25 0.00 W 18 15 Changed latitude from 11. 0.00 S to 10 59.40 S 18 15 Changed longitude from 25 0.60 W go				

## DATA PROCESSING NOTES (Leg 2)

Event Date	Person	Date Type	Summary
2011-03-10	Muus, Dave	BTL	Exchange & WOCE files online Notes on AR21 Leg 2 bottle data EXPOCODE 3175MB91_2 110309/dm 1. Original bottle data received from Bob Key as AR21a.leg2.Z on January 5, 2005. 2. AR21a.leg2.Z has no ALKALI data. TALK are in NOAA Data Report ERL AOML-24(dated April 1994) but are calculated data (uEq/Kg) and were not used. 3. DELC13 have no quality flags. Used flag 2. 4. CASTNOs do not match Summary file cast numbers from CTD data and NOAA Data Report ERL AOML-24 (dated April 1994) Changed bottle data file cast numbers from all "1"s to Data Report cast numbers. 5. Bottom depths in AR21a.leg2.Z file differ from bottom depths in NOAA Data Report. Used Data Report values since they have better agreement with deepest bottle depths. For example, Station 4 deepest bottle is 5645m(5765db), Data Report bottom depth is 5908 and data file bottom depth is 3589m.
2011-03-22	Muus, Dave	BTL	Cast numbers changed Corrected WOCE format bottle file placed on line: Cast numbers changed from "1"s to Data Report cast numbers. Data reordered from surface to bottom.