

A. Cruise Narrative: AR01

A.1. Highlights

WHP Cruise Summary Information

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WHP Cruise and Data Information

Instructions: Click on any item to locate primary reference(s) or use navigation tools above. Shaded items not available at time of most recent update

Station locations for AR01: Lee/Bitterman

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NOAA: National Oceanic and Atmospheric Administration Ocean and Atmospheric Research Laboratories

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ELECTRONIC ACCESS TO DATA LISTED IN THIS REPORT

The data presented in this report is available on the World Wide Web (WWW) at the following sites:

For further information regarding the data sets contact: Ms. Betty E. Huss Data Manager, OACES/GCC at: U.S. Dept. of Commerce NOAA/AOML/OCD 4301 Rickenbacker Causeway Miami, Florida 33149-1026 Telephone: (305) 361-4395 Email address: huss@aoml.noaa.gov

LIST OF PARTICIPANTS: Leg1

LIST OF PARTICIPANTS: Leg2

The Chief Survey Technician aboard the R/V RONALD BROWN for the cruise was Jonathan Shannahoff.

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A.2. Cruise Summary

CHEMICAL AND HYDROGRAPHIC MEASUREMENTS ON A CLIMATE AND GLOBAL CHANGE CRUISE ALONG 24° N IN THE ATLANTIC OCEAN WOCE SECTION AR01 DURING JANUARY-FEBRUARY, 1998

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ABSTRACT

This document contains data and metadata from a zonal cruise along nominally 24.5°N in the Atlantic Ocean from Las Palmas, Canary Islands in Spain to Miami, Florida. The cruise took place from January 23 to February 24, 1998 aboard the NOAA Ship RONALD H. BROWN under auspices of the National Oceanic and Atmospheric Administration (NOAA). This report presents the analytical and quality control procedures performed during the cruise and bottle data from the cruise. The research was sponsored by the NOAA Climate and Global Change Program under: (i) The Ocean- Atmosphere Carbon Exchange Study (OACES); and (ii) the World Ocean Circulation Experiment (WOCE) repeat hydrography program. Samples were taken from up to 36 depths at 130 stations. The data presented in this report includes the analyses of water samples for: salinity, nutrients, total dissolved inorganic carbon dioxide (DIC), fugacity of carbon dioxide (fCO₂), total alkalinity (TA), pH, total organic carbon (TOC), total nitrogen (TN), total phosphorus (TP), chlorofluorocarbons, and stable carbon isotopic ratio of DIC $(^{13}C^{12}C)$. Basic hydrographic parameters, pressure, CTD salinity, temperature and the calculated potential temperature, and potential density are included as well.

List of Principal Investigators

A.3. INTRODUCTION

Since the world's oceans have a large capacity to sequester heat and carbon dioxide it is imperative that the oceans are studied in a comprehensive fashion to elucidate changes in the Earth's climate. An overall goal of the research is to observe and model the ocean sufficiently well to understand quantitatively how the ocean effects present climate, and how the ocean might change under a changing atmosphere. Thus, a longterm objective is to provide reliable predictions of climate change and associated regional implications on time scales ranging from seasons to centuries. Current predictions are uncertain, in part, because of poor understanding of source and sink patterns of greenhouse gases like carbon dioxide and the role of the ocean in mitigating or changing the timing of regional patterns associated with warmer climate.

This cruise was designed to support research sponsored by the National Oceanic and Atmospheric Administration (NOAA) Climate and Global Change Program under: (i) the Ocean-Atmosphere Carbon Exchange Study (OACES); and (ii) the World Ocean Circulation Experiment (WOCE) repeat hydrography program. The second leg of the cruise was conducted aboard the NOAA Ship RONALD H. BROWN from January 23 to February 24, 1998. The OACES objective of the cruise was to determine the fluxes of $CO₂$ in the North Atlantic during the winter. A baseline of total carbon inventory in this region was established such that the uptake rate of atmospheric $CO₂$ can be determined in future cruises. The objective of the WOCE (repeat) hydrography component was to understand the general circulation of the global ocean well enough to be able to model its present state and predict its evolution. The data presented in this report includes: hydrography, nutrients, total dissolved inorganic carbon dioxide (DIC), fugacity/partial pressure of carbon dioxide ($fCO₂/pCO₂$) 1, total alkalinity (TA), pH, total organic carbon (TOC), total nitrogen (TN), total phosphorus (TP), chlorofluorocarbons, and stable carbon isotopic ratio of DIC $(^{13}C/^{12}C)$.

[Detailed information of the CTD operations can be found in NOAA Data Report, ERL](#page-53-0) PMEL-68 (McTaggart et al, 1999).¹

A.4. DESCRIPTION OF STUDY AREA

A total of 130 full water column CTD stations were occupied, complete with water samples analyzed for salinity, oxygen and chlorofluorocarbon (CFC) content. A large amount of high quality measurements of all the carbonate parameters including underway surface water $pCO₂$ and nutrients were also made.

The majority of the data were collected along 24.5°N from 23.5°W to 69°W. Completing the transatlantic section were data collected along a NE-SW dogleg off the coast of

 $\frac{1}{1}$ The fCO₂ takes into account the non-ideality of CO₂ gas and is the thermodynamic quantity mostly used in calculations. It is approximately 0.4 to 0.6 % lower than the corresponding pCO₂. In this report we used theterms interchangeably. However, all reported values are fugacity values.

Africa, and along a second, short, zonal section along 26.5°N off the coast of Abaco Island from 69°W to 77°W, jogging north along 27°N in the Straits of Florida to 80°W. The cruise track and station locations are presented i[n Figure 1 a](#page-45-0)n[d Table 1. T](#page-25-0)he leg 1 followed this same trackline in the opposite direction, deploying XBTs to sample the temperature in the upper 750 m, and collecting underway $pCO₂$.

B. DATA COLLECTION AND ANALYTICAL METHODS

One hundred and thirty CTD (Conductivity-Temperature- Depth) hydrographic stations were occupied to collect discrete water samples and hydrographic data. A CTD/Rosette unit with a Seabird-911 CTD instrument equipped with 36, specially designed 10-L samples bottles was utilized for these casts. These bottles have the same outer dimensions as standard Niskin bottles, but are modified to reduce chlorofluorocarbon sample contamination. Water samples were collected for salinity, oxygen, nutrients, chlorofluorocarbons, ${}^{13}C/{}^{12}C$, as well as carbon related parameters including total dissolved inorganic $CO₂$ (DIC), discrete fugacity of $CO₂$ (fCO₂), total alkalinity (TA), pH, total organic carbon (TOC), total nitrogen (TN), and total phosphorus (TP) on all casts during the cruise using these modified ioNiskinls style bottles. In the data tables the missing values are assigned a value of -9.0. The WOCE quality control flags have been listed in Appendix A. All the parameters plotted versus depth are shown i[n Figure 2.](#page-46-0) Detailed information on individual data collection, and analysis procedures may be found in the following method sections.

B.1. HYDROGRAPHIC METHODS

B.1.1. CTD AND HYDROGRAPHIC OPERATIONS

Description of Measurement Techniques and Calibrations

CTD and in situ O2

Depth profiles were obtained with a Seabird 911 plus CTD, deck unit, and rosette pylon. The CTD included dual temperature sensors, dual conductivity sensors, two Beckman oxygen sensors, one Paroscientific pressure transducer, and two pumps to decrease the response time. Thirty-six 10-l "Niskin" bottles were mounted on the frame, along with the CTD, pinger, Lowered Acoustic Doppler Current Profiler (LADCP), and LADCP external battery pack. The bottles were specially designed to reduce chlorofluorocarbon contamination. These bottles have the same outer dimensions as standard 10-l "Niskin" bottles, but use a modified end-cap design to minimize the contact of the water sample with the end-cap O-rings after closing. The O-rings used in these water sample bottles were vacuum-baked prior to the first station. Stainless steel springs covered with a nylon powder coat were substituted for the internal elastic tubing standardly used to close "Niskin" bottles. Seabird software was used to acquire, plot, and process the CTD data on PC's. Raw data were stored on VHS tapes, PC hard drives, and SyQuest drives. Typically each cast sampled to within 10 meters of the sea floor as indicated by the pinger signal. The CTD/O₂ data were processed and calibrated following Seabird recommendations (CTD Data Acquisition Software and Technical Notes, Sea-Bird Electronics, Inc., 1808 - 136th Place NE, Bellevue, Washington 98005). Exceptional items are noted below. Details can be found i[n NOAA Data Report, ERL PMEL-68](#page-59-0) (McTaggart et al, 1999).

Pre- and post-cruise pressure, temperature, and conductivity sensor calibrations were performed at Sea-Bird Electronics, Inc. in Bellevue, Washington. Secondary sensor pair T1075 and C1347 were selected for final data reduction for all stations.

The oxygen sensor was calibrated by using the pre- and post-cruise laboratory calibration. Secondary oxygen data from sensor s/n 353 was retained for stations 1-32 and 34; primary oxygen data from sensor s/n 381 was retained for stations 33 and 35- 130.

Post-cruise calibrations were applied to CTD data associated with bottle data using the PMEL program CALBOT. WOCE quality flags were appended to bottle data records using the PMEL program FLAG. Quality flags were determined by plotting the absolute value of sample residuals versus pressure and selecting a cutoff value for bad flags. Values which were 2.8 standard deviations from the mean were considered bad. Of the 4313 sample salinities, 0.4% were flagged as bad and 3.6% were flagged as questionable. Of the 4130 sample oxygens, 1.2% were flagged as bad and 4.9% were flagged as questionable.

Measurement of Currents

A hull-mounted RD Instruments 150 kHz narrowband acoustic Doppler current profiler (ADCP) operated continuously during the cruise. Velocity data, averaged in earth coordinates using gyrocompass heading, were logged in three-minute (approximately 180 pings) ensembles using RDI Data Acquisition Software (DAS) version 2.48. Vertical bin size was 8 meters. The center of the first bin was located at 16 meters. Range varied from 200 to 400 meters, depending primarily on sea state. A user exit program (UE4, provided by Eric Firing, U. Hawaii) was used to interface navigation and heading equipment. Position was logged at the beginning and end of each ensemble from a Trimble Centurion P-code GPS receiver (estimated position accuracy of 5 - 10 meters). Mean gyrocompass corrections for each ensemble were recorded from an Ashtech 3DF GPS attitude determination system; 3DF array orientation was calibrated using P-code GPS and ADCP bottom track comparison. These data are used in post-processing to calculate mean ship velocity to reference ensemble means, and to compensate for dynamic gyrocompass errors. Estimated errors for an ensemble are 1-2 cm/s for relative velocity and 3-4 cm/s for ship speed errors due to position inaccuracy; errors induced by heading inaccuracies are reduced to less than 1 cm/s using GPS heading data. This total error of 4-6 cm/s over a three minute ensemble is reduced further by averaging during postprocessing; the fifteen minute averages commonly used represent an average over five kilometers at cruising speed, and should be accurate to 1-3 cm/s. The ADCP data will be available through internet address http://ilikai.soest.hawaii.edu/ sadcp/woce.html

On-station velocity profiles were obtained using a RDI 150 kHz Narrowband ADCP (Lowered or LADCP) mounted looking downward from the CTD frame. This technique measures and records velocity shear profiles extending 150 to 350 meters below the instrument approximately once per second. In postprocessing, the individual shear profiles are averaged by depth to produce a full-depth shear profile, which is integrated to estimate the depth dependent (baroclinic) component of the velocity field. The depthindependent (barotropic) component of velocity can be recovered if positions at the start and end of the cast are known; positions were logged on this cruise using a Trimble Centurion P-code GPS receiver, accurate to 5 - 10 meters. Readers are advised to refer to Fischer and Visbeck (1993) for a full explanation of methods and standard processing procedures. The LADCP data will be available through internet address: http://www.nodc.noaa.gov/ General/NODC-About/NODC-overview.html#services

Salinity Analyses

A Guildline 8400B autosal was used for the salinity analysis with batch P125 standard water. The autosal room was maintained at 22°C, and the autosal was set at 24°C. A total of 4380 samples were measured and 37 of them were rejected.

Oxygen Technique

An automatic titration system was used for the oxygen analysis with the Carpenter modification of the Winkler method using a photometric determined endpoint. Reagents for the Carpenter method titration were mixed by the AOML/OCD Group of George Berberian as specified in Friederich's MBARI Technical Report #91-6 (Friederich et al, 1991). Apparent oxygen utilization (AOU) is defined as O_2 measured- O_2 sat., where O_2 sat. is the saturation value at potential temperature and salinity of the sample determined according to Weiss (1970). A total of 4310 samples were measured and 52 of them were rejected.

B.1.2. NUTRIENT ANALYSIS METHODS

Sampling and analytical methods

Nutrient samples were collected from 10-L "Niskin" bottles in acid washed 25-ml linear polyethylene bottles after three complete seawater rinses and analyzed within 1 hour of sample collection. Measurements were made in a temperature-controlled laboratory (20 \pm 2 ^oC). Concentrations of nitrite (NO₂), nitrate (NO₃), phosphate (PO₄³) and silicic acid (H4SiO4) were determined using an Alpkem Flow Solution Auto-Analyzer aboard the ship. The following analytical methods were employed:

Nitrate and Nitrite:

Nitrite was determined by diazotizing with sulfanilamide and coupling with N-1 naphthyl ethylenediamine dihydrochloride to form an azo dye. The color produced is measured at 540 nm (Zhang et al., 1997a). Samples for nitrate analysis were passed through a home made cadmium column (Zhang et al., 2000), which reduced nitrate to nitrite and the resulting nitrite concentration was then determined as described above. Nitrate concentrations were determined from the difference of nitrate + nitrite and nitrite.

Phosphate:

Phosphate in the samples was determined by reacting with molybdenum (VI) and antimony (III) in an acidic medium to form an antimonyphosphomolybdate complex at room temperature. This complex was subsequently reduced with ascorbic acid to form a blue complex and the absorbance was measured at 710 nm (Grasshoff et al. ,1983). A total of 4306 samples were measured and 1248 of them were rejected.

Silicic Acid:

Silicic acid in the sample was analyzed by reacting the aliquote with molybdate in a acidic solution to form ß-molybdosilicic acid . The ß-molybdosilicic acid was then reduced by ascorbic acid to form molybdenum blue (Zhang et al., 1997b). The absorbance of the molybdenum blue was measured at 660 nm.

Calibration and standards:

Stock standard solutions were prepared by dissolving high purity standard materials $(KNO₃$, NaNO₂, KH₂PO₄ and Na₂SiF₆) in deionized water. Working standards were freshly made at each station by diluting the stock solutions in low nutrient seawater. The low nutrient seawater used for the preparation of working standards, determination of blank, and wash between samples was filtered seawater obtained from the surface of the Gulf Stream. Standardizations were performed prior to each sample run with working standard solutions. Two or three replicate samples were collected from the "Niskin" bottle sampled at deepest depth at each cast. The relative standard deviation from the results of these replicate samples were used to estimate the overall precision obtained by the sampling and analytical procedures. The precisions of these samples were 0.04 µmol/kg for nitrate, 0.01 µmol/kg for phosphate and 0.1 µmol/kg for silicic acid.

B.2. CARBON PARAMETERS

B.2.1. TOTAL DISSOLVED INORGANIC CARBON (DIC)

The DIC analytical equipment was set up in a seagoing laboratory van. The analysis was done by coulometry with two analytical systems (PMEL-1 and PMEL-2) used simultaneously on the cruise. Each system consisted of a coulometer (UIC, Inc.) coupled with a SOMMA (Single Operator Multiparameter Metabolic Analyzer) inlet system developed by Kenneth Johnson (Johnson et al., 1985,1987,1993; Johnson, 1992) formerly of Brookhaven National Laboratory (BNL). In the coulometric analysis of DIC, all carbonate species are converted to $CO₂$ (gas) by addition of excess hydrogen ion (acid) to the seawater sample, and the evolved $CO₂$ gas is swept into the titration cell of the coulometer with compressed nitrogen, where it reacts quantitatively with a proprietary reagent based on ethanolamine to generate hydrogen ions. These are subsequently titrated with coulometrically generated OH -. $CO₂$ is thus measured by integrating the total charge required to achieve this.

The coulometers were calibrated by injecting aliquots of pure $CO₂$ (99.995%) by means of an 8-port valve outfitted with two sample loops that had been calibrated at BNL (Wilke, 1993). The $CO₂$ gas volumes bracketed the amount of $CO₂$ extracted from the water samples for the two PMEL systems. All DIC values were corrected for dilution by 0.2 ml of $HgCl₂$ used for sample preservation. The total water volume was 540 ml. The correction factor used for dilution was 1.00037. The instruments were calibrated at the beginning, middle, and end of each coulometer cell solution with a set of the gas loop injections. The coulometer cell solution was replaced after 25 mg of carbon was titrated, typically after 9-12 hours of continuous use. Sample titration times were 9-16 minutes.

Certified Reference Materials (CRMs), consisting of poisoned, filtered, and UV irradiated seawater supplied by Dr. A. Dickson of Scripps Institution of Oceanography (SIO), were run on each cell. The results were close to the values determined manometrically by Dr. Charles D. Keeling at SIO as shown below. The CRM results have been presented i[n Figure](#page-51-0) 3 an[d Table](#page-26-0) 2. The overall accuracy and precision for the CRMs on both instruments combined was -0.1 +/-2.1 (n=125). DIC data reported for this cruise have been corrected to the Batch 40 CRM value by adding the difference between the certified value and the mean shipboard CRM value (certified value shipboard analyses) on a per instrument/per leg basis.

Av. value of CRMs run on PMEL-1: 1987.3 ± 2.0 µmol/kg (n = 59) Av. value of CRMs run on PMEL-2: 1984.6 ± 1.2 µmol/kg (n = 66) Manometric value [SIO reference material batch #40] was 1985.8±0.7 µmol/kg (n=10)

Samples were drawn from the "Niskin" bottles into cleaned, precombusted 500-ml Pyrex bottles using Tygon tubing according to procedures outlined in the Handbook of Methods for $CO₂$ Analysis (DOE, 1994). Bottles were rinsed once and filled from the bottom, overflowing half a volume. Care was taken not to entrain any bubbles. The tube was pinched off and withdrawn, creating a 5-ml headspace, and 0.2 ml of saturated HgCl₂ solution was added as a preservative. The sample bottles were sealed with glass stoppers lightly covered with Apiezon-L grease, and were stored at room temperature for a maximum of 12 hours prior to analysis.

Replicate seawater samples were taken from both the surface and 1000 m "Niskin" sample bottles and run at different times during the cell. The first replicate of the surface water was used at the start of the cell with fresh coulometer solution, the second surface water replicate in the middle of the cell after about 12 mg of C were titrated. The first one of the 1000 m replicates was run at the end of the cell after about 25 mg of C were titrated, while the second one of the 1000 replicate samples was run using a new coulometer cell solution. No systematic difference between the replicates was observed.

As example, the 1000m replicate samples run on both PMEL1 and PMEL2 combined had a standard deviation of 1.3 µmol/kg for 32 sets of duplicates, and the results of the surface replicates yielded a standard deviation of 0.9 µmol/kg for 98 sets of duplicates. The deviation is very similar to that observed for the CRMs and suggest no strong dependency of results with amount of carbon titrated for a particular cell. The results of the duplicate samples have been presented i[n Figure 4 a](#page-52-0)n[d Table 3.](#page-28-0)

Calculations Calculation of the amount of $CO₂$ injected was according to the Department of Energy (DOE) $CO₂$ handbook [DOE, 1994]. The gas loops yielded a calibration factor for the instrument defined as:

Cal. Factor =
$$
\frac{\text{calculated moles of CO}_2 \text{ injected from gas loop}}{\text{actual moles of CO}_2 \text{ injected}}
$$

The concentration of $CO₂$ ([CO₂]) in the samples were determined according to:

$$
[CO2] = Cal factor * \frac{(Counts - Blank * Run Time) * K µmol/count}{pipe}
$$
 (2)

where "Counts" is 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 of the solution, "Run Time" is the length of coulometric titration (in minutes), and K is the conversion factor from counts to µmol which is dependent on the slope and intercept relation between instrument response and charge. For a unit with Ecal slope of 1 and intercept of 0, the constant is $2.0728 * 10^{-4}$.

The pipette volume was determined by taking aliquots at known temperature of distilled water from the volumes prior to, during, and after the cruise. The weights with the appropriate densities were used to determine the volume of the syringes and pipette.

Calculation of pipette volumes, density, and final $CO₂$ concentration were performed according to procedures outlined in the DOE $CO₂$ handbook (DOE, 1994).

B.2.2. FUGACITY OF CO₂ (fCO₂)

Gas Chromatographic (GC) Method A total of 1463 discrete fCO₂ samples from 130 stations were taken and analyzed on the cruise using an analysis system based on gas chromatography (Neill et al., 1997). Sampling from the "Niskin" bottles occurred immediately after O_2 samples were drawn. Samples were drawn into 120 ml Pyrex septum bottles after rinsing the bottles several times. On the final fill water was drawn into the bottom of the bottle and overflowed at least one half volume. A Teflon lined septum was crimp sealed on the bottle ensuring that no headspace was present.

Prior to analysis 5-ml water was withdrawn and replaced with a headspace of known $CO₂$ concentration that was expected to closely match that of the water. The remaining water and headspace were equilibrated by rotating the bottles for at least 40 minutes in a constant temperature bath at 20 \degree C. The fCO₂ of the headspace was measured in a flame ionization detector (FID) after quantitative conversion of the $CO₂$ to methane. The analyses were referenced against a series of six gas standards with the following mole fractions: 198.09, 348.16, 977.79, 508.35, 1479.46, 717.4. The standards, which were run after each dozen samples, bracketed most of the concentrations measured in the water column. The precision of the $fCO₂$ measurements was estimated at 0.86% of the signal based on 89 replicate samples (see [Table 4\).](#page-29-0) The $fCO₂$ measurements had a data gap mid- cruise because of a catastrophic instrument failure caused by water being injected onto the column and catalyst. Good, full water column, coverage was obtained at the Eastern and Western side of the basin.

The surface water measurements showed that the water undersaturated for most of the transect except at the boundaries. The undersaturation reaches its greatest value of -45 to - 50 µatm between 60 and 75° E. The fCO₂ in the deep water showed a strong trend with lower concentrations in the West due to better ventilation of the Western half of the basin.

B.2.3. TOTAL ALKALINITY (TA)

Seawater samples were drawn from the "Niskin" bottles with a 40-cm length of silicon tubing. One end of the tubing was fit over the petcock of the "Niskin" bottle and the other end was inserted into the bottom of a 500-ml Corning glass-stoppered sample bottle. The sample bottle was rinsed three times with approximately 300 ml of seawater. The sample bottle was slowly filled from the bottom. Once filled, the sample bottles were kept in a constant water bath at 25°C for half-hour before analysis.

The titration system used to determine TA consisted of a Metrohm 665 Dosimat titrator and an Orion 720A pH meter controlled by a personal computer (Millero et al., 1993). The acid titrant, in a water-jacketed burette, and the seawater sample, in a waterjacketed cell, were kept at 25±0.1°C with a Neslab constant-temperature bath. The plexiglass water-jacketed cells were similar to those used by Bradshaw et al. (1988), except that a larger volume (200 ml) was used to increase the precision. The cells had fill and drain valves with zero dead-volume to increase the reproducibility of the cell volume.

The HCl solutions used throughout the cruise were made, standardized, and stored in 500-ml glass bottles in the laboratory for use at sea. The 0.2489 M HCl solutions (Batch 9601) were prepared by dilution of concentrated HCl in 0.45 M NaCl to yield an ionic strength equivalent to that of average seawater (0.7 M). The acid was independently standardized using a coulometric technique (Taylor and Smith, 1959; Marinenko and Taylor, 1968) by the University of Miami and by Dr. Dickson of Scripps Institution of Oceanography (SIO). The two standardization techniques agreed to +/-0.0001 N.

The volume of HCl delivered to the cell is traditionally assumed to have a small uncertainty (Dickson, 1981) and is equated with the digital output of the titrator.

Calibrations of the Dosimat burettes with Milli Q water at 25°C indicated that the systems deliver 3.000 ml (the value for a titration of seawater) to a precision of 0.0004 ml. This uncertainty resulted in an error of 0.4 µmol/kg in TA.

The titrators were calibrated in the laboratory before the cruise. Certified standard Reference Material (CRM) Batch 40 prepared by Dr. Dickson was used at sea to monitor the performance of the titrators. All TA data have been corrected based on CRM values for each cell and each leg (se[e Table 5\) \(](#page-32-0)Millero et al, 2000).

Carbonate parameters of surface waters indicate the occurrence of upwelling near the African coast. The surface carbonate parameters are consistent with those collected during the WOCE (World Ocean Circulation Experiment) 1992 cruise that sampled stations along the same latitude (24°N). Both studies yield values for normalized TA (TA*35/S) of 2291 \pm 6 µmol kg⁻¹. The values of TA for the deep water are in good agreement $(\pm 3.8 \text{ \mu} \text{mol/kg})$. Crossover comparison with OACES 1993 study also showed good agreement $(\pm 3 \mu)$ µmol/kg in TA). The pH is on average 0.004 higher than those made on the 1993 cruise.

Kitack Lee from AOML/OCD calculated total alkalinity (TA) from spectroscopic pH (25°C) and coulometric total dissolved inorganic carbon (DIC) using the carbonic acid dissociation constants of Mehrbach et al. (1973) as refit by Dickson and Millero (1987). A value of 1.2 μ mol kg⁻¹ has been subtracted from calculated TA values because calculated values are 1.2 μ mol kg⁻¹ higher than measured values.

B.2.4. pH

Seawater samples were drawn from the "Niskin" bottles with a 20-cm length of silicon tubing. One end of the tubing was fit over the petcock of the "Niskin" bottle and the other end was attached over the opening of a 10-cm glass spectrophotometric cell. The spectrophotometric cell was rinsed three to four times with a total volume of approximately 200 ml of seawater; the Teflon endcaps were also rinsed and then used to seal a sample of seawater in the glass cell. While drawing the sample, care was taken to make sure that no air bubbles were trapped within the cell. The sample cells were kept in a waterbath at 25°C for a half an hour before analysis.

Seawater pH was measured using the spectrophotometric procedure (Byrne, 1987) and the indicator calibration of Clayton and Byrne (1993). The indicator was an 8.0-mM solution of Kodak m-cresol purple sodium salt $(C_{21}H_{17}O_5)$ in MilliQ water. The absorbance ratio of the concentrated indicator solution (RI = 578A/434A) was 0.95. All absorbance ratio measurements were obtained in the thermostatted (25.0±0.05°C) cell compartments of HP 8453 UV-visible Diode Array Spectrophotometers. Measurements of pH were taken at 25°C on the total hydrogen ion concentration ($[H+]$ _T) scale, in mol/kg solution, and converted to seawater scale ($[H+]_{SW}$). The overall precision of the pH measurements obtained from the duplicate samples was ±0.0006. A total of 1997 samples were measured and 24 of them were rejected.

B.2.5. TOTAL ORGANIC CARBON, TOTAL NITROGEN AND TOTAL PHOSPHORUS

Total Organic Carbon Analyses TOC samples were analyzed by a high-temperature combustion (HTC) method using custom made instruments. Samples were analyzed with a furnace divided into two temperature zones (Hansell and Peltzer, 1998; Carlson et al., 1999). Ultra high purity $O₂$ flowed through the instrument at 175 ml/min. Samples were acidified (10 µl of 85% H3PO4 per 10 ml of sample) and sparged with $CO₂$ free oxygen for at least 10 minutes to remove inorganic carbon. One hundred µl of sample was injected manually through a septumless port into the quartz combustion tube packed with Pt gauze (Aldrich), 7% Pt on alumina catalyst (Shimadzu), Sulfix (Wako Pure Chemical Industries, Inc.) and CuO wire (Leeman Labs). The Pt gauze and Pt beads were heated to 800°C in the upper zone while the remaining packing material was heated to 600°C in the lower zone. The resulting $CO₂$ flowed through two water traps and a final copper halide trap then detected with a LiCor 6252 $CO₂$ analyzer. The signal was integrated with chromatographic software (Dynamax Macintegrator I version 1.3; Rainin Inst.).

Extensive conditioning of the combustion tube was essential to minimize the machine blank. The system blank (<10 µM) was assessed daily with ampoulated low carbon waters (LCW). The system response was standardized daily with a four point calibration curve of glucose solution in LCW. Deep Sargasso Sea water (>2000 m), which had been acidified and ampoulated, served as a daily reference material. Analyzing low carbon water and reference deep seawater several times a day allowed us to assess the system stability from run-to-run and day-to-day, ensuring confidence in our analysis. Both the low carbon and the deep Sargasso Sea references waters are part of an international certified reference material program for marine DOC measurement, run by the laboratory of Dr. Hansell. As such, the TOC analyses from the 24°N line are referenced to the international community of DOC laboratories using the CRM's.

Total Nitrogen Analyses Concentrations of TN (total nitrogen, or the sum or organic and inorganic N) were determined by high temperature combustion and detection of the nitric oxide produced. Samples had been collected into 60 ml polyethylene bottles for frozen storage until analysis in the shore laboratory. In the high temperature system, a •ls quartz combustion tube was held at 900°C in the upper zone and 800-900°C in the lower zone of a 2-zone Thermcraft tube furnace. The combustion tube has a 12 cm head space, 2-3 screens of pure Pt (52 mesh), an 8 cm bed of 7% Pt on alumina (Shimadzu, Inc.), and a 10 cm bed of quartz beads. 100 µl injections of seawater were made into the combustion tube by syringe through a septum. The carrier gas (UHP oxygen) flowed at a rate of 200 ml/min. Recovery of known standards (glycine, urea, EDTA, etc.) was >90%. Detection of NO was done with an Antek Model 7020 chemiluminescence detector.

Oxygen flow through the ozone generator was 28 ml/min. Standardization was performed daily with potassium nitrate in Milli-Q water. Q water was used as the system blank, and it was assumed to have zero N content. The system blank was normally <1 µM. Low nutrient sea water, collected at the surface of the Sargasso Sea, was used as

a reference material for daily use. The coefficient of variation in low nutrient surface water (4-5 µM TN) was 3-4%, while in deep water (>20 µM TN) it was 1%. Data acquisition was performed on a Dynamax Macintegrator I version 1.3, produced by Rainin Instruments.

Total Phosphorus Analyses Concentrations of TP (total phosphorus; organic plus inorganic P) were determined by UV photo-oxidation. Samples had been stored frozen in 60 ml polyethylene bottles until shore based analysis. A 6 ml aliquot was removed from each sample bottle and placed in a 20 ml fused quartz tube equipped with a Pyrex ground stopper (Quartz Scientific, Inc.). One hundred µl of 30% hydrogen peroxide was added to each tube and placed in a homemade irradiation unit (2 hours). The irradiation unit contained a 1200 W UV lamp (Hanovia) protected by a quartz jacket. A 2-tiered aluminum tube holder (40 tubes total) fitted around the lamp and held the samples 7 cm from the lamp. A fan placed at the bottom of the unit blew air across the samples for cooling. A hinged aluminum cylinder, open at the top and bottom, was fitted around the samples to keep stray UV light from leaving the system. This entire unit was placed in a fume hood, the front of which was covered with a black curtain while in use (again to collect stray UV light).

After irradiation, aliquots of the samples that had not been oxidized, and the photooxidized aliquots, were analyzed for phosphate using a colorimetric method on a Technicon Autoanalyzer II (Knap et al. 1997). Daily calibration was achieved from 4 point calibration curves using $KH₂PO₄$. Low nutrient seawater (Sargasso Sea surface water) was always processed with the samples as a daily quality control measure. Coefficients of variation for the measurement was X and X% for shallow and deep water samples.

B.2.6. 13 C/12 C OF DISSOLVED INORGANIC CARBON

Shipboard Sample Collection Methods Samples were collected in pre-washed and baked (450ºC) 500 ml ground glass- stoppered bottles using the following method. A length of Tygon tubing was attached to the "Niskin" bottle or seawater line and flushed for a few seconds. The end of the tubing was then placed at the bottom of the upright sample bottle and the bottle was filled, then overflowed with an amount equal to its volume if "Niskin" water volume permitted, otherwise with at least half its volume. Flow was stopped as the Tygon tubing was removed from the top of the bottle to avoid any splashing in the top. Using a syringe or turkey baster, 10 to 20 ml were withdrawn off the top of the sample to lower the water level to approximately 1 ml below the neck of the bottle, avoiding backwash of water from the turkey baster into the sample. The ground glass joint of the bottle was wiped dry with Kimwipes. Then 100 µl of a saturated HgC $I₂$ solution (per 250 ml of seawater) was injected beneath the surface of the sample using an Eppendorf pipet. The ground-glass stopper, which had been pre-greased with Apiezon M grease, was then inserted straight into the bottle without twisting. If any air streaks in the grease seal were visible, the stopper was removed, cleaned, and regreased, and the bottle was resealed. Clips (if required for the bottle neck-type) were

placed on the necks of the bottles, and two heavy rubber bands were placed around the stopper and bottle to prevent leakage. The sample bottle was then inverted a couple of times to mix the $HqCl₂$ throughout the sample.

Laboratory Methods $CO₂$ is extracted from the DIC seawater sample using a modification of the helium stripping technique described by Kroopnick (1974) as described in Quay et al (1992). The stripper is comprised of a glass tube with a stainless steel fitting and silicone-greased glass stopcock at the bottom (which connects to the He line), a glass frit which the He passes through, and a stainless steel fitting containing a 3-layer silicone rubber septum at the top. Approximately 1 ml phosphoric acid is injected into the stripper and bubbled with He for 10 minutes. The gas is then evacuated out of the stripper and the stripper is weighed. Then 80 to 125 ml of the sample is drawn into the stripper and it is weighed again to calculate the weight of water analyzed. A stainless steel needle pierces the septum and connects the stripper to the extraction line, which has been evacuated and filled with helium. The sample is stripped with 99.997% pure He at a flow rate of 200 ml/min for 20 minutes. Water is trapped out in two glass traps submerged in Dewars containing a slush mixture of dry ice and isopropanol at -70 $\mathrm{^{\circ}C}$. CO₂ is collected at -196 $\mathrm{^{\circ}C}$ in glass loop traps submerged in liquid N_2 . The δ^{13} C is then measured on a Finnigan MAT 251 mass spectrometer. The efficiency of the extraction method is 100 \pm 0.5 percent based on gravimetrically prepared Na₂CO₃ standards. The precision of the ¹³C/¹²C analysis is \pm 0.02‰ based on a replicate analysis of standards and seawater samples.

B.2.7. CHLOROFLUOROCARBONS (CFC)

As described above specially designed 10-l water sample bottles were used on the cruise to reduce CFC contamination.

Samples for the analysis of dissolved CFC-11, CFC-12 and CFC-113 were drawn from approximately 1700 of the 4300 water samples collected during the expedition. Samples for carbon tetrachloride (CC I_4 or CFC-10) analysis were drawn from approximately 430 samples. When taken, water samples for CFC analysis were usually the first samples drawn from the 10-l bottles. Care was taken to co-ordinate the sampling of CFCs with other samples to minimize the time between the initial opening of each bottle and the completion of sample drawing. In most cases, dissolved oxygen, $fCO₂$, total $CO₂$, alkalinity and pH samples were collected within several minutes of the initial opening of each bottle. To minimize contact with air, the CFC samples were drawn directly through the stopcocks of the 10-l bottles into 100-ml precision glass syringes equipped with 2 way metal stopcocks. The syringes were immersed in a holding tank of clean surface seawater until analyzed.

To reduce the possibility of contamination from high levels of CFCs frequently present in the air inside research vessels, the CFC extraction/analysis system and syringe holding tank were housed in a modified 20' laboratory van on the aft deck of the ship.

For air sampling, a 100 meter length of 3/8" OD Dekaron tubing was run from the CFC lab van to the bow of the ship. A flow of air was drawn through this line into the CFC van using an Air Cadet pump. The air was compressed in the pump, with the downstream pressure held at 1.5 atm using a back-pressure regulator. A tee allowed a flow (100 cc min^{-1}) of the compressed air to be directed to the gas sample valves, while the bulk flow of the air (>7 l min⁻¹) was vented through the back pressure regulator. Air samples were only analyzed when the relative wind direction was within 60 degrees of the bow of the ship to reduce the possibility of shipboard contamination. The Air Cadet pump was run for at least 60 minutes prior to analyzing each batch of air samples to insure that the air inlet lines and pump were thoroughly flushed

Concentrations of CFC-11, CFC-12 and CFC-113 in air samples, seawater and gas standards on the cruise were measured by shipboard electron capture gas chromatography (EC-GC), using techniques similar to those described by Bullister and Weiss (1988). For seawater analyses, a 30-ml aliquot of seawater from the glass syringe was transferred into the glass sparging chamber. The dissolved CFCs in the seawater sample were extracted by passing a supply of CFC-free purge gas through the sparging chamber for a period of 4 minutes at 70 cc min⁻¹. Water vapor was removed from the purge gas during passage through an 18 cm long x 3/8 inch diameter glass tube packed with the desiccant magnesium perchlorate. The sample gases were concentrated on a cold-trap consisting of a 1/8 inch OD stainless steel tube with an about 7 cm section packed tightly with Porapak N (60-80 mesh). To cool the trap, isopropanol cooled by a Neslab Cryocool refrigeration system was forced from a reservoir beneath the trap to a level above the packing with a stream of compressed nitrogen. After quickly bringing the isopropanol to the top of the trap, a low flow of nitrogen was bubbled through the bath to reduce gradients and maintained a temperature of –20°C. After 4 minutes of purging the seawater sample, the sparging chamber was closed and the trap was held open for an additional 1 minute to allow nitrous oxide $(N₂0)$ to pass through the trap and thereby minimize its interference with CFC-12. The trap was isolated, the cold isopropanol in the bath was drained, and the trap was heated electrically to 125°C. The sample gases held in the trap were then injected onto a precolumn (30 cm of 1/8 inch O.D. stainless steel tubing packed with 80- 100 mesh Porasil C, held at 90°C), for the initial separation of the CFCs and other rapidly eluting gases from the more slowly eluting compounds. The CFCs then passed into the main analytical column (about 183 cm of 1/8 inch OD stainless steel tubing packed with Carbograph 1AC, 80-100 mesh, held at 90°C) for final separation, and into the EC detector for quantification.

The analysis of carbon tetrachloride was made on a separate, but nearly identical apparatus to the electron capture-gas chromatography system used in the analysis of CFC-11, CFC-12 and CFC-113 (Bullister and Weiss, 1988). Samples were drawn in the same type of syringes used for the CFC analysis. In the CCI4 system, the sample injection port was flushed with 30-40 ml of sample before injecting sample into a calibrated loop (about 30 ml). After filling, an additional 30 ml of water was pushed through the loop and allowed to overflow. For analysis, a valve was switched and the water sample held in the loop was pushed into the stripper with the same $CCI₄$ free nitrogen that was used to strip the sample. The gases removed from the sample were dried while passing through an ~18 cm x 3/8 inch OD tube of magnesium perchlorate and concentrated on a trap packed with four inches of Porapak N and held at -30°C during trapping. At the conclusion of stripping, the trap was heated electrically and the contents swept onto the precolumn (0.53mm I. D. x 30 meters, DB624 capillary column, 45°C)) with clean nitrogen. The desired gases passed on to the main analytical column (0.53mm I. D. x 30 meters, DB624 capillary column, 45°C), before the precolumn vented the later peaks. All other aspects of the analysis were the same as the CFC analysis.

Both of the analytical systems were calibrated frequently using a standard gas of known CFC composition. Gas sample loops of known volume were thoroughly flushed with standard gas and injected into the system. The temperature and pressure was recorded so that the amount of gas injected could be calculated. The procedures used to transfer the standard gas to the trap, precolumn, main chromatographic column and EC detector were similar to those used for analyzing water samples. Two sizes of gas sample loops were present in the CFC analytical system, while four calibrated sample loops were used in the $CCI₄$ system. Multiple injections of these loop volumes could be made to allow the system to be calibrated over a relatively wide range of concentrations. Air samples and system blanks (injections of loops of CFC-free gas) were injected and analyzed in a similar manner. The typical analysis time for a seawater, air, standard or blank sample was 12 minutes on the CFC system and 20 minutes on the CCI4 system.

Concentrations of the CFC's and $CCl₄$ in air, seawater samples and gas standards are reported relative to the SIO93 calibration scale (Cunnold, et. al., 1994). Concentrations in air and standard gas are reported in units of mole fraction CFC in dry gas, and are typically in the parts-per-trillion (ppt) range. Dissolved CFC and $CCl₄$ concentrations are given in units of picomoles per kg seawater (pmol kg^{-1}). CFC and CCl₄ concentrations in air and seawater samples were determined by fitting their chromatographic peak areas to multi-point calibration curves, generated by injecting multiple sample loops of gas from a working standard (PMEL cylinder 33790 for CFC-11, CFC-12 and CFC-113; PMEL cylinder 33780 for CCI₄) into the analytical instrument. The concentrations of CFC-11 and CFC-12 in this working standard were calibrated before and after the cruise versus a primary standard (36743) (Bullister, 1984). No measurable drift in the concentrations of CFC-11 and CFC-12 in the working standard could be detected during this interval. Full range calibration curves were run at intervals of 3 days during the cruise. Single injections of a fixed volume of standard gas at one atmosphere were run much more18 frequently (at intervals of 1 to 2 hours) to monitor short term changes in detector sensitivity.

Extremely low $(<0.01$ pmol kg⁻¹) CFC concentrations were measured in deep water (>3000 meters) in the Eastern Basin of the North Atlantic between 25 ºW and 45 ºW along this section. Based on the median of CFC concentration measurements in the deep water of this region, which is believed to be nearly CFC-free, blank corrections of 0.003 to 0.015 pmol kg⁻¹ for CFC-11, 0.006 to 0.007 pmol kg⁻¹ for CFC-12 and 0.006 to 0.011 pmol kq^{-1} for CFC-113 have been applied to the data set. If the measured CFC

concentration for a sample is very low, subtracting a blank can result in a very small negative number reported (se[e Figure 2\).](#page-50-0) No blank corrections were required for the $CCl₄$ data.

On this expedition, we estimate precision (1 standard deviation) of 1% or 0.005 pmol kg⁻¹ (whichever is greater) for dissolved CFC-11, 2% or 0.005 pmol kq^{-1} (whichever is greater) for dissolved CFC-12 measurements (see listing of replicate samples given in [Table 6\),](#page-33-0) 4.4% or 0.002 pmol kg⁻¹ for CFC-113 and 1.4% or 0.006 pmol kg⁻¹ for CCl₄ [\(Table 7\).](#page-35-0) The results of the CFC air measurements are reported i[n Tables 8 a](#page-38-0)[nd 9.](#page-41-0)

A number of water samples had clearly anomalous concentrations relative to adjacent samples for one or more of the trace gases. These anomalous samples appeared to occur more or less randomly during the cruise, and were not clearly associated with other features in the water column (e.g. elevated oxygen concentrations, salinity or temperature features, etc.). This suggests that the high values were due to individual, isolated low- level CFC contamination events. Measured concentrations for these samples are included in this report, but are given a quality flag of either 3 (questionable measurement) or 4 (bad measurement). A total of 4 analyses of CFC-11, 8 analyses of CFC-12, 3 analyses of CFC-113 and 2 analyses of $CCl₄$ were assigned a flag of 3. A total of 9 analyses of CFC-11, 8 analyses of CFC-12, 18 analyses of CFC-113 and 4 analyses of $CCl₄$ were assigned a value of 4.

B.3. UNDERWAY MEASUREMENT METHODS

B.3.1. UNDERWAY fCO2

Underway $pCO₂$ system version 2.5 (analogous to those described in Ho et al. 1997, and Feely et al. 1998) was used to determine the $pCO₂$ of surface water and overlaying air on a continuous basis (Keeling 1965, Wanninkhof and Thoning 1993). When in operation, seawater is drawn from the uncontaminated seawater intake from the bow intake approximately 6 meters below the water line to a 30-l shower head equilibrator located in the main laboratory, where the headspace and seawater reach equilibrium on a short time scale. At specific times during an hourly cycle, the content of the headspace is measured by an infrared $CO₂$ analyzer. Uncontaminated air from the marine boundary layer is drawn continuously from the bow mast to the underway $pCO₂$ system. At a designated time, air is analyzed by a the infrared $CO₂$ analyzer, otherwise the air is bled off through a vent .

The $CO₂$ measurements are made by a Li-Cor differential, non-dispersive, infrared (NDIR) $CO₂$ analyzer (model 6251), and the result is based on the difference in absorption of infrared (IR) radiation passing through two gas cells. The reference cell is continuously flushed with a gas of known $CO₂$ concentration using the lowest concentration of three reference gas standards. During the hourly cycle the sample cell is flushed with one of three reference gas standards, marine boundary layer air, or headspace gas from the equilibrator.

The data may be downloaded at this web site or: http://www.aoml.noaa.gov/ocd/oaces/1998data.html

C. ACKNOWLEDGMENTS

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TABLE 1. Station locations

STN	Cast	Lat (°N)	Long (°W)	Date	STN	Cast	Lat (°N)	Long (°W)	Date
46		24.500	41.633	2/4/1998	111		26.500	76.083	2/20/1998
47	1	24.500	42.183	2/4/1998	112	1	26.500	76.200	2/21/1998
48		24.500	42.733	2/4/1998	113	1	26.483	76.300	2/21/1998
49	1	24.500	43.284	2/4/1998	114	1	26.505	76.422	2/21/1998
50		24.500	43.473	2/5/1998	115	1	26.500	76.517	2/21/1998
51	1	24.500	44.386	2/5/1998	116	1	26.500	76.617	2/21/1998
52		24.500	44.934	2/5/1998	117	1	26.500	76.683	2/22/1998
53	1	24.500	45.484	2/5/1998	118	1	26.499	76.753	2/22/1998
54	1	24.500	46.034	2/5/1998	119	1	26.500	76.784	2/22/1998
55		24.500	46.584	2/6/1998	120	1	26.500	76.816	2/22/1998
56	1	24.500	47.134	2/6/1998	121	1	26.520	76.901	2/22/1998
57	1	24.501	47.684	2/6/1998	122	1	27.001	79.200	2/23/1998
58		24.500	48.234	2/6/1998	123	1	27.002	79.283	2/23/1998
59	1	24.500	48.782	2/7/1998	124	1	27.001	79.381	2/23/1998
60	1	24.500	49.333	2/7/1998	125	1	27.038	79.481	2/23/1998
61		24.491	49.883	2/7/1998	126	1	27.013	79.605	2/23/1998
62	1	24.501	50.433	2/8/1998	127	1	27.020	79.674	2/23/1998
63	1	24.501	50.984	2/8/1998	128	1	27.002	79.788	2/23/1998
64		24.501	51.533	2/8/1998	129	1	27.006	79.857	2/23/1998
65	1	24.500	51.149	2/9/1998	130	1	26.999	79.937	2/23/1998

TABLE 1. Station locations (continued)

TABLE 2 Results of the certified reference material, CRM (Assigned value by SIO 40 = (1985.8 ± 0.7) mmol/kg) Coulometer: PMEL-1

Date	GMT (h:min)	Year Day	DIC (mmol/kg)	Date	GMT (h:min)	Year Day	DIC (mmol/kg)
24-Jan-98	16:02	24	1987.0	24-Jan-98	15:19	24	1985.3
25-Jan-98	0:41	25	1981.2	25-Jan-98	1:02	25	1985.7
25-Jan-98	4:47	25	1987.0	25-Jan-98	12:58	25	1986.7
25-Jan-98	15:19	25	1986.7	25-Jan-98	23:54	25	1986.6
26-Jan-98	4:29	26	1987.9	26-Jan-98	11:18	26	1985.9
26-Jan-98	18:48	26	1987.3	26-Jan-98	22:56	26	1985.0
27-Jan-98	7:36	27	1987.1	27-Jan-98	11:22	27	1986.6
27-Jan-98	21:31	27	1987.9	27-Jan-98	23:46	27	1984.7
28-Jan-98	9:37	28	1985.9	28-Jan-98	12:28	28	1985.7
28-Jan-98	22:19	28	1985.6	28-Jan-98	21:53	28	1984.8
29-Jan-98	9:02	29	1988.1	29-Jan-98	8:57	29	1984.2
29-Jan-98	23:31	29	1986.4	29-Jan-98	23:35	29	1985.1
30-Jan-98	22:36	30	1986.6	30-Jan-98	12:19	30	1985.4
31-Jan-98	22:11	31	1985.8	30-Jan-98	23:14	30	1983.8
1-Feb-98	9:06	32	1985.1	31-Jan-98	11:51	31	1983.9
2-Feb-98	6:16	33	1986.2	1-Feb-98	4:27	32	1984.1
2-Feb-98	21:23	33	1985.5	1-Feb-98	18:18	32	1984.7

TABLE 2 Results of the certified reference material, CRM (Assigned value by SIO 40 = (1985.8 ± 0.7) mmol/kg) Coulometer: PMEL-1

TABLE 3. Dissolved inorganic carbon duplicates

STA	BTL	Pres	DIC	Stdev	STA	BTL	Pres	DIC	Stdev
NO	NO	(db)	umol/kg		NO	NO	(db)	umol/kg	
1	9	$\overline{2}$	2119.7	0.26	67	36	5	2050.1	1.62
3	20	$\overline{2}$	2103.9	0.33	68	36	$\overline{4}$	2056.2	0.03
$\overline{\mathbf{4}}$	22	$\overline{\mathbf{4}}$	2100.8	0.47	69	36	$\overline{4}$	2060.2	0.25
5	$\overline{7}$	995	2209.6	1.75	70	18	1000	2195.2	0.91
5	27	3	2105.0	0.47	70	36	5	2056.3	1.32
$\overline{6}$	30	$\overline{3}$	2096.4	0.12	71	36	6	2046.5	0.43
7	31	3	2096.4	0.95	72	36	4	2046.1	0.08
$\boldsymbol{9}$	32	$\overline{\mathbf{4}}$	2097.8	1.27	73	17	1000	2195.1	0.01
11	16	1001	2205.0	0.23	73	36	4	2044.4	0.23
12	36	4	2098.4	0.95	74	36	7	2033.7	1.69
13	17	1001	2212.5	0.69	75	36	5	2041.7	0.27
13	35	4	2099.4	1.70	76	36	6	2038.2	0.99
14	32	3	2100.1	0.98	77	36	5	2037.6	1.61
15	17	1000	2209.1	0.82	78	36	$\overline{7}$	2035.3	0.39
15	36	4	2086.9	0.81	79	36	5	2035.2	0.38
18	36	$\overline{\mathbf{4}}$	2100.1	1.52	80	36	6	2023.7	0.07
19	18	1000	2212.8	0.44	81	36	$\overline{\mathcal{A}}$	2016.1	0.76
19	36	5	2101.0	0.41	82	36	$\overline{4}$	2036.6	0.48
20	36	6	2099.1	0.06	83	36	$\overline{4}$	2041.5	0.26
21	19	1000	2207.9	0.16	84	36	6	2036.9	1.46
21	36	6	2098.6	0.08	85	36	$\overline{4}$	2017.7	0.16
22	36	$\overline{\mathbf{4}}$	2096.7	0.45	86	17	999	2202.1	0.01
23	36	5	2098.3	1.67	86	36	4	2018.4	0.79
24	36	3	2096.2	0.18	87	36	5	2028.5	0.73
25	36	$\overline{\mathbf{4}}$	2099.6	1.14	88	36	5	2032.7	0.72
26	36	6	2098.6	0.98	89	17	1001	2179.8	1.17
30	18	1000	2200.1	1.39	90	16	1001	2186.1	0.71
31	18	1000	2200.6	1.88	90	36	4	2037.9	0.34
32	36	6	2101.8	0.42	94	36	$\overline{4}$	2034.8	0.33
36	36	5	2094.6	0.13	95	36	4	2035.4	0.54
37	20	1002	2200.4	0.40	98	36	$\overline{4}$	2043.1	0.89
38	36	4	2090.6	0.35	99	36	5	2042.8	0.93
40	36	4	2087.9	0.84	101	18	1001	2191.6	1.88
41	19	999	2200.8	0.45	101	36	4	2042.2	0.96
41	36	6	2085.0	0.76	102	18	999	2187.3	0.54
42	36	3	2076.3	0.84	102	36	5	2047.7	0.18
43	17	1000	2195.0	1.90	106	36	$\overline{4}$	2041.5	0.79
43	36	$\overline{\mathbf{4}}$	2080.1	0.86	107	36	4	2041.6	0.11
46	36	$\overline{\mathbf{4}}$	2081.0	0.83	110	36	4	2037.3	0.85
49	20	997	2194.9	1.15	111	36	4	2039.0	0.06
50	36	5	2077.0	0.01	112	18	999	2190.4	1.20
51	19	1001	2193.5	0.78	113	36	3	2040.1	1.11
51	36	5	2073.1	0.37	114	36	4	2040.5	1.41
53	18	1001	2197.6	1.10	117	36	3	2036.4	0.49
55	36	5	2073.1	0.33	118	15	999	2185.3	1.56
56	36	5	2075.5	0.07	121	18	5	2023.1	0.45

TABLE 3. Dissolved inorganic carbon duplicates (continued)

TABLE 4. Replicate pCO2 analyses

TABLE 4. Replicate pCO2 analyses (continued)

TABLE 4. Replicate pCO2 analyses (continued)

TABLE 5. Correction factors applied to raw data based upon carbonate parameters for Certified Reference Materials

a. Three slightly different correction factors were applied to cell 2 due to the change in volume from a broken piston.

b. The weighted average was used

TAcorr = TAsample x C.F. (TA) pHcorr = pHsample + C.F.(pH)

TABLE 6. Replicate dissolved CFC-11 and CFC-12 analyses

TABLE 7. Replicate dissolved CFC-113 and CCl4 analyses

TABLE 7. Replicate dissolved CFC-113 and CCl4 analyses (continued)

STN NO	BTL NO	CFC-113 pmol/kg	CFC-113 Stdev	CCI4 pmol/kg	CCI4 Stdev	STN NO	BTL NO	CFC-113 pmol/kg	CFC-113 Stdev	CCI4 pmol/kg	CC _{I4} Stdev
54	4	0.001	0.002	-9.000	-9.000	114	13	0.055	0.001	-9.000	-9.000
54	16	0.005	0.001	-9.000	-9.000	114	24	0.059	0.001	-9.000	-9.000
54	28	0.031	0.004	-9.000	-9.000	116	8	0.021	0.007	-9.000	-9.000
54	34	0.182	0.025	-9.000	-9.000	116	10	-9.000	-9.000	0.996	0.002
56	23	0.010	0.006	-9.000	-9.000	116	16	0.052	0.001	-9.000	-9.000
56	27	-9.000	-9.000	0.451	0.012	116	26	0.030	0.001	-9.000	-9.000
58		0.002	0.003	-9.000	-9.000	118	4	-9.000	-9.000	1.128	0.026
58	14	0.008	0.002	-9.000	-9.000	118	10	0.049	0.017	-9.000	-9.000
58	23	0.020	0.000	-9.000	-9.000	118	12	0.058	0.007	-9.000	-9.000
58	32	0.081	0.003	-9.000	-9.000	118	22	0.033	0.002	-9.000	-9.000
60	2	0.002	0.001	-9.000	-9.000	120	16	0.017	0.005	-9.000	-9.000
60	5	-9.000	-9.000	0.130	0.008	120	20	0.045	0.035	0.429	0.015
60	16	0.007	0.001	-9.000	-9.000	125	8	-9.000	-9.000	0.270	0.008
60	26	0.035	0.003	-9.000	-9.000	125	22	0.145	0.003	-9.000	-9.000
60	33	-9.000	-9.000	1.077	0.017	129	7	0.136	0.003	-9.000	-9.000
62	$\overline{2}$	0.006	0.001	-9.000	-9.000	130	6	-9.000	-9.000	2.107	0.021

TABLE 7. Replicate dissolved CFC-113 and CCl4 analyses (continued)

TABLE 8. CFC air measurements

Date	GMT	Latitude	Longitude	CFC-11	CFC-12		CCI4
(hhmm)	(°N)	(°W)	(ppt)	(ppt)	(ppt)	(ppt)	
6-Feb-98	1257	24.500	47.134	-9.000	-9.000	-9.000	93.088
7-Feb-98	1224	24.500	49.333	262.958	538.920	79.104	-9.000
7-Feb-98	1234	24.500	49.333	261.579	540.095	80.068	-9.000
7-Feb-98	1244	24.500	49.333	261.338	538.346	79.588	-9.000
7-Feb-98	1314	24.500	49.333	265.800	540.404	81.139	-9.000
7-Feb-98	1324	24.500	49.333	262.774	539.189	79.657	-9.000
7-Feb-98	1334	24.500	49.333	262.934	539.476	79.559	-9.000
7-Feb-98	1531	24.500	49.461	258.404	531.774	78.156	-9.000
8-Feb-98	1914	24.501	51.533	261.171	537.612	80.509	-9.000
8-Feb-98	1924	24.500	51.533	262.143	538.129	79.696	-9.000
8-Feb-98	1934	24.499	51.546	265.034	538.779	80.208	-9.000
8-Feb-98	2004	24.500	51.636	262.012	536.424	80.017	-9.000
8-Feb-98	2014	24.500	51.636	261.953	537.730	79.940	-9.000
8-Feb-98	2024	24.499	51.699	263.807	538.928	79.901	-9.000
8-Feb-98	2056	24.501	51.533	-9.000	-9.000	-9.000	95.090
8-Feb-98	2116	24.501	51.533	-9.000	-9.000	-9.000	93.306
8-Feb-98	2156	24.501	51.533	-9.000	-9.000	-9.000	93.817
8-Feb-98	2216	24.501	51.533	-9.000	-9.000	-9.000	91.694
9-Feb-98	2244	24.502	53.784	261.719	537.661	81.545	-9.000
9-Feb-98	2254	24.504	53.851	262.597	539.557	80.872	-9.000
9-Feb-98	2304	24.504	53.880	261.726	537.667	79.912	-9.000
9-Feb-98	2324	24.503	53.956	264.344	541.163	80.720	-9.000
9-Feb-98	2334	24.502	53.987	262.269	536.927	80.020	-9.000
9-Feb-98	2344	24.502	53.987	262.205	536.721	80.565	-9.000
10-Feb-98	2032	24.500	55.933	-9.000	-9.000	-9.000	94.388
10-Feb-98	2052	24.500	55.933	-9.000	-9.000	-9.000	93.208
10-Feb-98	2112	24.500	55.933	-9.000	-9.000	-9.000	92.775
10-Feb-98	2132	24.500	55.933	-9.000	-9.000	-9.000	91.823
11-Feb-98	339	24.500	56.667	-9.000	-9.000	-9.000	94.978
11-Feb-98	359	24.500	56.667	-9.000	-9.000	-9.000	95.100
11-Feb-98	439	24.500	56.667	-9.000	-9.000	-9.000	93.361
11-Feb-98	459	24.500	56.667	-9.000	-9.000	-9.000	94.658
11-Feb-98	2204	24.500	58.134	-9.000	-9.000	-9.000	96.657
11-Feb-98	2224	24.500	58.134	-9.000	-9.000	-9.000	96.483
11-Feb-98	2244	24.500	58.134	-9.000	-9.000	-9.000	96.476
13-Feb-98	115	24.500	61.067	262.315	536.445	81.119	-9.000
13-Feb-98	125	24.500	61.067	262.475	538.298	82.255	-9.000
13-Feb-98	135	24.500	61.067	261.623	538.645	80.140	-9.000
13-Feb-98	155	24.506	61.071	261.686	538.295	79.729	-9.000
13-Feb-98	205	24.505	61.105	262.698	538.700	80.228	-9.000
13-Feb-98	215	24.505	61.105	261.676	536.758	79.115	-9.000
13-Feb-98	229	24.500	61.801	-9.000	-9.000	-9.000	93.299
13-Feb-98	249	24.500	61.801	-9.000	-9.000	-9.000	94.033
13-Feb-98	329	24.500	61.801	-9.000	-9.000	-9.000	94.533
13-Feb-98	349	24.500	61.801	-9.000	-9.000	-9.000	95.347
14-Feb-98	1944	24.500	65.468	262.707	539.047	80.631	-9.000
14-Feb-98	1954	24.500	65.467	262.465	538.199	81.209	-9.000

TABLE 8. CFC air measurements (continued)

Date	GMT	Latitude	Longitude	CFC-11	CFC-12	CFC-113	CCI4
(hhmm)	(°N)	(°W)	(ppt)	(ppt)	(ppt)	(ppt)	
14-Feb-98	2004	24.501	65.467	262.275	536.354	80.125	-9.000
14-Feb-98	2024	24.500	65.467	262.132	536.824	80.285	-9.000
14-Feb-98	2034	24.501	65.467	262.028	537.808	80.243	-9.000
14-Feb-98	2044	24.501	65.467	262.004	537.114	80.121	-9.000
16-Feb-98	146	24.504	68.440	262.523	540.348	80.763	-9.000
16-Feb-98	156	24.503	68.544	263.901	539.621	81.137	-9.000
16-Feb-98	206	24.502	68.562	261.984	538.864	79.805	-9.000
16-Feb-98	226	24.498	68.666	263.276	540.683	79.877	-9.000
16-Feb-98	236	24.498	68.684	263.034	541.216	79.900	-9.000
16-Feb-98	246	24.498	68.684	263.002	541.274	80.052	-9.000
16-Feb-98	250	24.500	69.133	-9.000	-9.000	-9.000	94.950
16-Feb-98	310	24.500	69.133	-9.000	-9.000	-9.000	95.214
16-Feb-98	330	24.500	69.133	-9.000	-9.000	-9.000	93.795
19-Feb-98	25	26.500	73.216	262.293	538.847	80.539	-9.000
19-Feb-98	35	26.500	73.217	262.142	538.710	80.844	-9.000
19-Feb-98	45	26.500	73.217	261.824	539.329	80.451	-9.000
19-Feb-98	55	26.501	73.309	262.074	540.199	80.325	-9.000
19-Feb-98	110	26.500	73.583	-9.000	-9.000	-9.000	96.505
19-Feb-98	130	26.500	73.583	-9.000	-9.000	-9.000	96.064
19-Feb-98	150	26.500	73.583	-9.000	-9.000	-9.000	95.901
19-Feb-98	210	26.500	73.583	-9.000	-9.000	-9.000	94.810
20-Feb-98	1324	26.500	75.500	-9.000	-9.000	-9.000	96.687
20-Feb-98	1344	26.500	75.500	-9.000	-9.000	-9.000	95.869
20-Feb-98	1424	26.500	75.500	-9.000	-9.000	-9.000	95.886
20-Feb-98	1444	26.500	75.500	-9.000	-9.000	-9.000	95.399
20-Feb-98	2333	26.500	75.900	-9.000	-9.000	-9.000	96.398
20-Feb-98	2353	26.500	75.900	-9.000	-9.000	-9.000	95.629
21-Feb-98	1549	26.510	76.427	262.483	540.744	80.515	-9.000
21-Feb-98	1559	26.510	76.428	262.273	539.635	80.446	-9.000
21-Feb-98	1609	26.511	76.428	262.793	541.135	80.816	-9.000
21-Feb-98	1629	26.514	76.431	262.827	538.937	79.301	-9.000
21-Feb-98	1639	26.516	76.434	263.024	538.655	78.736	-9.000
21-Feb-98	1649	26.508	76.482	262.900	538.355	79.284	-9.000
22-Feb-98	108	26.500	76.617	261.254	537.878	79.587	-9.000
22-Feb-98	152	26.500	76.683	260.123	536.113	78.455	-9.000
22-Feb-98	234	26.500	76.683	-9.000	-9.000	-9.000	96.873
22-Feb-98	254	26.500	76.683	-9.000	-9.000	-9.000	96.657
23-Feb-98	237	26.111	78.494	264.570	540.167	81.155	-9.000
23-Feb-98	247	26.111	78.494	264.310	539.409	80.459	-9.000
23-Feb-98	257	26.163	78.587	262.826	539.090	79.707	-9.000
23-Feb-98	307	26.168	78.606	262.319	538.885	79.498	-9.000
23-Feb-98	337	26.171	78.731	262.246	539.018	79.676	-9.000
23-Feb-98	539	27.001	79.200	-9.000	-9.000	-9.000	93.798
23-Feb-98	559	27.001	79.200	-9.000	-9.000	-9.000	93.073
23-Feb-98	619	27.001	79.200	-9.000	-9.000	-9.000	93.724
23-Feb-98	1401	27.038	79.481	-9.000	-9.000	-9.000	97.231
23-Feb-98	1421	27.038	79.481	-9.000	-9.000	-9.000	96.196

TABLE 8. CFC air measurements (continued)

TABLE 8. CFC air measurements (continued)

TABLE 9. CFC air values (interpolated to station locations)

TABLE 9. CFC air values (interpolated to station locations, continued)

TABLE 9. CFC air values (interpolated to station locations, continued)

TABLE 9. CFC air values (interpolated to station locations, continued)

 Figure 1. Cruise track for the Atlantic Ocean cruise AR01 in January and February 1998

Figure 2. All parameters measured vs. depth

Chemical and Hydrographic Measurements (NOAA Data Report OAR AOML-41)

Figure 2. All the data vs. depth (continued)

Chemical and Hydrographic Measurements (NOAA Data Report OAR AOML-41)

Figure 2. All the data vs. depth (continued)

Figure 2. All the data vs. depth (continued)

Figure 2. All the data vs. depth (continued)

Figure 3. The results of the CRM measurements

5.0 4.5 \square Surface o 1000 m 4.0 3.5 Δ DIC (μ mol/kg)
 Δ 2.5
 Δ 2.0 \circ \circ \circ \circ \Box \mathbf{p}_{\square} \Box \circ \Box \circ \Box Ω \circ \Box \circ \Box \Box \circ _o \circ $\frac{0}{\Box}$ \Box 1.5 \Box o d^o \Box \Box ጭ \circ \Box \Box^\square 曾 Ω Ω \circ □品 1.0 \circ \Box \Box \circ D_{\square} \square \Box □ p $\neg p^{\circ}$ \Box 0.5 m \Box_{\Box} \Box math> ₽ \Box 머머 \circ B^{\square} O □ ባ \Box \Box 0.0 20 40 60 80 $\overline{0}$ 100 120 140 Station

Figure 4. The results of the DIC duplicates during the course of the cruise

NOAA Data Report ERL PMEL-68

CTD/O2 **measurements collected on a Climate and Global Change cruise along 24°N in the Atlantic Ocean (WOCE Section A6) during January–February 1998**

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CTD Data Summary

CTD/O₂ measurements collected on a Climate and Global Change cruise along 24°N in the Atlantic Ocean (WOCE Section A6) during January–February 1998

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Abstract.

Summaries of $CTD/O₂$ measurements and hydrographic data acquired on a Climate and Global Change cruise during the winter of 1998 aboard the NOAA ship *Ronald H. Brown* are presented. The majority of these data were collected along 24.5°N from 23.5°W to 69°W. Completing the transatlantic section are data collected along a NE–SW dogleg off the coast of Africa, and along a second, short, zonal section along 26.5°N off the coast of Abaco Island from 69°W to 77°W, jogging north along 27°N in the Straits of Florida to 80°W. Data acquisition and processing systems are described and calibration procedures are documented. Station location, meteorological conditions, $CTD/O₂$ summary data listings, profiles, and potential temperature-salinity diagrams are included for each cast. Section plots of oceanographic variables and hydrographic data listings are also given.

1. Introduction

The NOAA Office of Global Programs (OGP) sponsors the Atlantic Climate Change Program (ACCP)and the Ocean-Atmosphere Carbon Exchange Study (OACES) as elements under the Climate and Global Change Program. The long-term objective of the Climate and Global Change Program is to provide reliable predictions of climate change and associated regional implications on time scales ranging from seasons to centuries. Large uncertainties in current predictions include the sources and sinks of greenhouse gases like carbon dioxide and the role of the ocean in mitigating or changing the timing of regional patterns associated with warmer climate. Hydrographic and direct velocity measurements collected during this cruise will help to quantify the water masses and determine the meridional overturning circulation responsible for the redistribution of heat, fresh water, and carbon in the center of the subtropical gyre and estimate the remineralization component of the $CO₂$ increase in order to quantify the anthropogenic $CO₂$ burden.

The 24°N transatlantic section has been previously occupied in 1957, 1981, and 1992, revealing long-term variability in mid-depth temperature, salinity, and oxygen. This new data set extends this time series through a time when relatively large mid-depth changes due to decadal variations in the air-sea interaction for Labrador Sea Water formation have already been observed. In addition, this data set complements those from other seasons, allowing for investigation into seasonal variations in fluxes of mass, heat, and freshwater.

CTD/O2 stations were occupied during leg 2. Stations were spaced roughly 55–85 km apart across the basin, closer near the coastlines. Full water column $CTD/O₂$ profiles were collected at all stations and Lowered Acoustic Doppler Current Profiler (ADCP) measurements were taken on all but five stations prior to station 85. Underway salinity, temperature, shipboard ADCP, and carbon partial pressures were taken along the cruise track. Water samples were analyzed for a suite of natural and anthropogenic tracers including salinity, dissolved oxygen, inorganic nutrients, CFCs, dissolved inorganic carbon, total alkalinity, pH , $pCO₂$ dissolved organic carbon, and carbon isotopes[. Figure 1 sh](#page-75-0)ows station locations. [Table 1 p](#page-69-0)rovides a summary of cast information.

Leg 2 stations began with a NE–SW dogleg off the coast of Africa from station 1 at $28^{\circ}N$, 15°W in 130 m of water to station 22 at 24.5°N, 23.5°W in nearly 5000 m of water. Stations continued westward in a long zonal section along 24.5°N from station 22 to station 89 at 69°W across the Mid-Atlantic Ridge. The trackline jogged northwestward and stations were occupied along 26.5° N from 71° W at station 94 to 79° W at station 121. The remaining stations, 122–130, were along 27°N across the Straits of Florida. Leg 1 followed this same trackline in the opposite direction, deploying only XBTs to sample the temperature in the upper 750 m.

2. Standards and Pre-Cruise Calibrations

The CTD/O₂ system is a real-time data acquisition system with the data from a Sea-Bird Electronics, Inc. (SBE) 9plus underwater unit transmitted via a conducting cable to a SBE 11plus deck unit. The serial data from the underwater unit is sent to the deck unit in RS-232 NRZ format. The deck unit decodes the serial data and sends it to a personal computer for display and storage in a disk file using Sea-Bird SEASOFT software. The SBE 911plus system transmits data from primary and auxiliary sensors in the form of binary number equivalents of the frequency or voltage outputs from those sensors. These are referred to as the raw data. The calculations required to convert raw data to engineering units are performed by software.

The SBE 911 plus system is electrically and mechanically compatible with standard unmodified rosette water samplers made by General Oceanics (GO), including the 1016 36-position sampler, which was used for all stations on this cruise. A modem and rosette interface allows the 911 plus system to control the operation of the rosette directly without interrupting the flow of data from the CTD.

The SBE 9plus underwater unit is configured with dual standard modular temperature (SBE 3) and conductivity (SBE 4) sensors which are mounted near the lower end cap. The conductivity cell entrance is co-planar with the tip of the temperature sensor probe. The pressure sensor is mounted inside the underwater unit main housing. A centrifugal pump module flushes water through sensor tubing at a constant rate independent of the CTD 's motion to improve dynamic performance. A dissolved oxygen sensor is added to the pumped sensor configuration following the temperature-conductivity (TC) pair.

2.1 Conductivity

The flow-through conductivity-sensing element is a glass tube (cell) with three platinum electrodes. The resistance measured between the center electrode and end electrode pair is determined by the cell geometry and the specific conductance of the fluid within the cell, and controls the out-put frequency of a Wien Bridge circuit. The sensor has a frequency out-put of approximately 3 to 12 kHz corresponding to conductivity from 0 to 7 Siemens/meter (0 to 70 mmho/cm). The SBE 4 has a typical accuracy/stability of ±0.0003 S/m/month and resolution of 0.00004 S/m at 24 samples per second.

Pre-cruise sensor calibrations were performed at Sea-Bird Electronics, Inc. in Bellevue, Washington. The following coefficients were entered into SEASOFT using software module SEACON:

Conductivity calibration certificates show an equation containing the appropriate pressure-dependent correction term to account for the effect of hydrostatic loading (pressure) on the conductivity cell:

C (S /m)=(*g* + *h f* ² + *if* ³ + *j f* ⁴)/[10(1 + *ctcor* * *t* + *cpcor* * *p*)]

where *g ,h ,i ,j ,ctcor* ,and *cpcor* are the calibration coefficients above, *f* is the instrument frequency (kHz), *t* is the water temperature (degrees Celsius), and is the water pressure (dbar). SEASOFT automatically implements this equation.

2.2 Temperature

The temperature-sensing element is a glass-coated thermistor bead, pressure-protected by a stainless steel tube. The sensor output frequency ranges from approximately 5 to 13 kHz corresponding to temperature from –5 to 35°C. The output frequency is inversely proportional to the square root of the thermistor resistance which controls the

output of a patented Wien Bridge circuit. The thermistor resistance is exponentially related to temperature. The SBE 3 thermometer has a typical accuracy/stability of ±0.004°C per year and resolution of 0.0003°C at 24 samples per second. The SBE 3 thermometer has a fast response time of 0.070 seconds.

Pre-cruise sensor calibrations were performed at Sea-Bird Electronics, Inc. in Bellevue, Washington. The following coefficients were entered into SEASOFT using software module SEACON:

Temperature (ITS-90)is computed according to

 $T(C) = 1 / g + h [\ln(fO/f)] + i [\ln^2(fO/f)] + j [\ln^3(fO/f)] - 273.15$

where *g*, *h*, *i*, *j*, and *f*0 are the calibration coefficients above and *f* is the instrument frequency (kHz). SEASOFT automatically implements this equation and converts between ITS-90 and IPTS-68 temperature scales as desired.

2.3 Pressure

The Paroscientific series 4000 Digiquartz high pressure transducer uses a quartz crystal resonator whose frequency of oscillation varies with pressure induced stress measuring changes in pressure as small as 0.01 parts per million with an absolute range of 0 to 10,000 psia (0 to 6885 dbar). Repeatability, hysteresis, and pressure conformance are 0.005%FS. The nominal pressure frequency (0 to full scale) is 34 to 38 kHz. The nominal tem perature frequency is 172 kHz $+50$ ppm/ \degree C.

Pre-cruise sensor calibrations were performed at Sea-Bird Electronics, Inc. in Bellevue, Washington. The following coefficients were entered into SEASOFT using software module SEACON:

Pressure coefficients are first formulated into

$$
c = c1 + c2 * U + c3 * U2
$$

d = d1 + d2 * U

$$
t0 = t1 + t2 * U + t3 * U2 + t4 * U3
$$

where *U* is temperature in degrees Celsius. Then pressure is computed according to

$$
P(psia) = c*[1 - (t02/t2)] * {1 - d[1 - (t02/t2)]}
$$

where *t* is pressure period (μ s). SEASOFT automatically implements this equation.

2.4 Oxygen

The SBE 13 dissolved oxygen sensor uses a Beckman polarographic element. Oxygen sensors determine the dissolved oxygen concentration by counting the number of oxygen molecules per second (flux) that diffuse through a membrane. By knowing the flux of oxygen and the geometry of the diffusion path the concentration of oxygen can be computed. The permeability of the membrane to oxygen is a function of temperature and ambient pressure. The interface electronics outputs voltages proportional to membrane current (oxygen current)and membrane temperature (oxygen temperature). Oxygen temperature is used for internal temperature compensation. Initial computation of dissolved oxygen in engineering units is done in the software. The range for dissolved oxygen is 0 to 650 µmol/kg; nominal accuracy is 4 µmol/kg; resolution is 0.4 µmol/kg. Response times are roughly 2 s at 25°C and 5 s at 0°C.

The following oxygen calibrations were entered into SEASOFT using SEACON:

The use of these constants in linear equations of the form $I = mV + b$ and $T = kV + c$ will yield sensor membrane current and temperature (with a maximum error of about 0.5°C) as a function of sensor output voltage.

3. Data Acquisition

CTD/O2 measurements were made using a SBE 9plus CTD with dual sensor configuration. Each set of sensors included a temperature, conductivity, and dissolved oxygen sensor. The sets were placed as mirror images to each other mounted low on the CTD main housing with the intakes approximately 6–8 inches apart. The TC pairs were monitored for calibration drift and shifts by examining the differences between the two pairs on each CTD and comparing CTD salinities with bottle salinity measurements.

AOML's SBE 9plus CTD/O₂ s/n 09P10779-0363 (sampling rate 24 Hz) was mounted in a 36-position frame and employed as the primary package. Auxiliary sensors included an LADCP and Benthos altimeter. Water samples were collected using a GO 36-bottle rosette and 10-liter Nisken bottles. The primary package was used for all casts during this cruise.

The package entered the water from the starboard side of the ship and was held within 10 m of the surface for 1 minute in order to activate the pump. The package was lowered at a rate of 30 m/min to 50 m, 45 m/min to 200 m, and 60 m/min generally to within 10 m of the bottom, slowing gradually on the approach. The position of the package relative to the bottom was monitored by the ship 's Precision Depth Recorder (PDR)and the altimeter. A bottom depth was estimated from bathymetric charts and the PDR ran during the bottom 1000 m of the cast[. Figure 2 s](#page-76-0)hows the pressures of bottle closures during the upcast.

Upon completion of the cast, sensors were flushed repeatedly and stored with a dilute Triton-X solution in the plumbing. Nisken bottles were then sampled for various water properties detailed in the introduction. Sample protocols conformed to those specified by the WOCE Hydrographic Programme.

A SBE 11plus deck unit received the data signal from the CTD. The analog data stream was recorded onto video cassette tape as a backup. Digitized data were forwarded to a personal computer equipped with SEASOFT acquisition and processing software version 4.230. Preliminary temperature, salinity, and oxygen profiles were displayed in real time. Raw data files were archived to Syquest tapes.

3.1 Data Acquisition Problems

All of the three oxygen sensors employed during this cruise were problematic owing to the age of the modules. Oxygen sensor s/n 364 associated with the primary TC pair was replaced with oxygen sensor s/n 381 prior to station 33. S/n 364 had drifted more than 15 µmol/kg from its calibration and was exhibiting numerous shifts in oxygen current throughout the water column. Redundant oxygen sensor s/n 353 associated with the secondary TC pair was removed prior to station 45 in an effort to conserve its usefulness in case primary oxygen sensor s/n 381 failed later in the cruise. Also, secondary sensor s/n 353 was exhibiting multiple shifts in oxygen current at varying depths and thought to be more difficult to calibrate. Primary sensor s/n 381 was better behaved although much noisier.

There was no primary oxygen data from sensor s/n 381 collected for station 34 owing to a poor connection of the dissolved oxygen module.

3.2 Salinity Analyses

Bottle salinity analyses were performed in the ship's temperature-controlled salinity laboratory using two Guildline Model 8400B inductive autosalinometers, and a dedicated personal computer. Software allowed the user to standardize the autosal, and perform a second standardization using a fresher standard (30 PSS) for a linearity check. IAPSO Standard Seawater batch #133 was used as the primary standard. IAPSO Standard Seawater batch #305 was used as the second, fresher standard. The autosalinometer in use was standardized before each cast of samples were analyzed, or every 36 samples. The software limits set required that each successive reading be within ± 0.002 PSS or the program would reject that reading and seek another. Stable room temperature and high performance of the autosalinometers allowed these limits to be so strictly set.

Duplicate samples usually taken from the deepest bottle on each cast were analyzed on a subsequent day. Bottle salinities were compared with preliminary CTD salinities to aid in the identification of leaking bottles as well as to monitor the CTD conductivity cells' performance and drift. The expected precision of the autosalinometer with an accomplished operator is 0.001 PSS, with an accuracy of 0.003. The standard deviation of the duplicate differences is 0.0003 PSS. This value is far below the expected precision.

Calibrated CTD salinities replace missing bottle salinities in the hydrographic data listing and are indicated by an asterisk.

4. At Sea Processing

SEASOFT consists of modular menu driven routines for acquisition, display, processing, and archiving of oceanographic data acquired with SBE equipment and is designed to work with an IBM or compatible personal computer. Raw data are acquired from the instruments and are stored unmodified. The conversion module DATCNV uses the instrument configuration and pre-cruise calibration coefficients to create a converted engineering unit data file that is operated on by all SEASOFT post processing modules. The following is the SEASOFT processing module sequence and specifications used in the reduction of $CTD/O₂$ data from this cruise:

- DATCNV converted the raw data to pressure, temperature, conductivity, oxygen current, and oxygen temperature; and computed salinity, the time rate of change of oxygen current, and preliminary oxygen. DATCNV also extracted bottle information where scans were marked with the bottle confirm bit during acquisition.
- ROSSUM created a summary of the bottle data. Bottle position, date, and time were automatically output. Pressure, temperature, conductivity, salinity, oxygen current, oxygen temperature, time rate of change of oxygen current, and preliminary oxygen values were averaged over a 2-s interval (48 scans) from 5 to 3 s prior to the confirm bit in order to avoid spikes in conductivity and oxygen current owing to minor incompatibilities between the SBE 911plus CTD/O₂ system and GO 1016 rosette. ROSSUM computed potential temperature and sigma-theta.
- WILDEDIT marked extreme outliers in the data files. The first pass of WILDEDIT obtained an accurate estimate of the true standard deviation of the data. The data were read in blocks of 200 scans. Data greater than two standard deviations were flagged. The second pass computed a standard deviation over the same 200 scans excluding the flagged values. Values greater than 16 standard deviations were marked bad.
- SPLIT removed decreasing pressure records from the data files leaving only the downcast.
- FILTER performed a low pass filter on pressure with a time constant of 0.15 s. In order to produce zero phase (no time shift) the filter first runs forward through the file and then runs backward through the file.

Measurements can be misaligned due to the inherent time delay of the sensor response, the water transit time delay in the pumped plumbing line, and the sensors being physically misaligned in depth. ALIGNCTD aligns conductivity, temperature, and oxygen in time relative to pressure to ensure that all calculations were made using measurements from the same parcel of water minimizing salinity spiking and density errors. Primary conductivity was not advanced in ALIGNCTD because it is done in the factory setting of the 11plus deck unit. Secondary conductivity,

however, is not advanced in the deck unit and so was advanced 0.073 s in ALIGNCTD. Because SBE 3 temperature sensor response is fast (0.06 s), it was not necessary to advance temperature relative to pressure. Oxygen sensors s/n 364 and s/n 353 were advanced 3.0 s in ALIGNCTD; s/n 381 was not advanced in the software.

- CELLTM used a recursive filter to remove conductivity cell thermal mass effects from measured conductivity. Both conductivity cells were epoxy coated and therefore the thermal anomaly amplitude (alpha) and the time constant (1/beta) were 0.03 and 9.0 respectively for each sensor.
- DERIVE was used to recompute doxc/dt and oxygen with a time window size of 2.0 seconds.
- LOOPEDIT marked scans where the CTD was moving less than a minimum velocity of 0.25 m/s or travelling backwards due to ship roll.
- BINAVG averaged the data into 1-dbar pressure bins starting at 1 dbar with no surface bin. The center value of the first bin was set equal to the bin size. The bin minimum and maximum values are the center value \pm half the bin size. Scans with pressures greater than the minimum and less than or equal to the maximum were averaged.Scans were interpolated so that a data record exists every decibar. The number of points averaged in each bin was added to the variables listed in the data file.
- DERIVE recomputed salinity.
- STRIP removed scan number; and salinity, time rate of change of oxygen current, and preliminary oxygen computed in DATCNV from the data files.
- TRANS converted the data file format from binary to ASCII format.

In addition to the Seasoft processing modules, several PMEL programs were used to further reduce the CTD/O 2 data:

Because the pump does not turn on until 60 seconds after the CTD package is in the water, measurements of near-surface conductivity and oxygen values are inaccurate. FILLSFC was used to copy the first good value of salinity, potential temperature, oxygen, and oxygen current back to the surface. FILLSFC then back-calculated temperature and conductivity, and zeroed the time rate of change of oxygen current for those records. Filled salinities ranged from 3 to 9dbar, usually 5 dbar. There were only 7 stations where surface potential temperatures had to be filled in 1–2 dbar. Filled oxygens also ranged from 3 to 9 dbar, usually 5 dbar. WOCE flags for the affected parameters were changed to "7" for extrapolation.

- DESPIKE1 removed spikes from primary oxygen current and primary oxygen temperature data.DESPIKE1 also removed spikes from primary salinity data. Data were linearly interpolated over despiked records and the associated WOCE flags were changed to "6" for interpolation. Conductivity was backcalculated, and potential temperature and sigma-theta were recomputed for the interpolated records.
- DESPIKE2 removed spikes from secondary data in the same fashion as DESPIKE1.

Package slowdowns and reversals owing to ship roll can move mixed water in tow to in front of the CTD sensors and create artificial density inversions and other artifacts. In addition to SEASOFT module LOOPEDIT, PMEL program DELOOP computed values of density locally referenced between every 1 dbar of pressure to compute $N^2 = (-g/\rho)(d\rho/dz)$ and linearly interpolated measured parameters over those records where $N^2 \leq -1.0e$. 05 s^2 . WOCE flags were changed to "6" for interpolation and derived variables were recomputed over interpolated intervals.

- FILTDOC applied a median filter of width 5 dbar to the time rate of change in oxygen current.
- FIX353 added a positive shift to secondary oxygen current (s/n 353) at user selected depths, usually deeper than 3500 dbar, and recomputed oxygen. This shift was applied to stations 16–44 to correct an odd but persistent behavior of the aged oxygen module.
- FIX381 added a negative shift to primary oxygen current (s/n 381) at user selected depths, usually around 2900 dbar, and recomputed oxygen. This shift was applied to stations 50–118 to correct an odd but persistent behavior of the aged oxygen module.

5. Post-Cruise Calibrations

Post-cruise sensor calibrations were done at Sea-Bird Electronics, Inc. during March and May 1998.Secondary sensor pair T1075 and C1347 were selected for final data reduction for all stations for two reasons based on post-cruise temperature calibration information. First, T1075 has a drift of 0.3e –03°C/year with an uncertainty of 0.3e –03°C based on five calibrations between August 1996 and May 1998, whereas T1701 has a drift of 1.5e–03°C/year with an uncertainty of -0.4e –03°C based on seven calibrations between May 1996 and May 1998.Second,T1075 was determined by Sea-Bird to have no pressure correction, whereas T1701 has a pressure correction of - 1.4e–03°C/5000 dbar.

Secondary oxygen data from sensor s/n 353 was retained for stations 1-32 and 34; primary oxygen data from sensor s/n 381 was retained for stations 33 and 35–130.

Post-cruise calibrations were applied to CTD data associated with bottle data using PMEL program CALBOT. WOCE quality flags were appended to bottle data records using PMEL program FLAG. Quality flags were determined by plotting the absolute value of sample residuals versus pressure and selecting a cutoff value for bad flags. The value of 2.8 standard deviations of the remaining residuals was the cutoff for questionable flags. Of the 4313 sample salinities, 0.4% were flagged as bad and 3.6% were flagged as questionable. Of the 4130 sample oxygens, 1.2% were flagged as bad and 4.9% were flagged as question able.

5.1 Conductivity

Conductivity slope and bias, along with a linear pressure term (modified beta), were computed by a least-squares minimization of CTD and bottle conductivity differences. The function minimized was

$$
BC - m \cdot CC - b - \beta \cdot CP
$$

where *BC* is bottle conductivity (S/m), *CC* is pre-cruise calibrated CTD conductivity (S/m), CP is the CTD pressure (dbar), *m* is the conductivity slope, *b* is the bias (S/m), and β is a linear pressure term (S/m/dbar). The final CTD conductivity (S/m) is

$$
m * CC + b + \beta * CP
$$

The slope term *m* is a fourth-order polynomial function of station number to allow the entire cruise to be fit at once with a smoothly-varying station-dependent slope correction. For sensor C1347 a series of fits were made, each fit throwing out bottle values for locations having a residual between CTD and bottle conductivity greater than three standard deviations. This procedure was repeated with the remaining bottle values until no more bottle values were thrown out.

For C1347, the slope correction ranged from 0.99993647 to 0.99998722, the bias applied was –1.3e-04 S/m, and the beta term was –1.41e –08 S/m/ dbar. Of 4313 bottles, the percentage of bottles retained in the fit was 75.65 with a standard deviation of 1.144e –04 S/m. PMEL program CALCTD applied these calibrations.

CTD-bottle conductivity differences are plotted against station number to show the [stability of the calibrated CTD conductivities relative to the bottle conductivities \(Fig. 3,](#page-77-0) upper panel). CTD-bottle conductivity differences are plotted against pressure to show the tight fit below 500 m and the increasing scatter above 500 m (Fig. 3, lower panel).

5.2 Temperature

The pre-cruise calibration of T1075 is the mean of the two post-cruise calibrations, and is within 0.05e -03° C of the overall drift trajectory over the duration of the cruise as determined by the calibration history of the sensor. Therefore, the pre-cruise calibration was used in the final processing. The pressure correction for this sensor was determined by Sea-Bird to be zero. However, a bias of –0.6e –03°C was applied to temperature data in program CALCTD to account for the effect of viscous heating on SBE 3 sensors. An adjustment of $-0.6e -03^{\circ}$ C results in errors of no more than $\pm 0.15e$ –03°C from this effect for the full range of oceanographic temperature and salinity.

5.3 Oxygen

In situ oxygen samples collected during $CTD/O₂$ profiles are used for postmeasurement calibration. Because the dissolved oxygen sensor has an obvious hysteresis, PMEL program OXDWNP replaced up-profile water sample data with corresponding processe[d \(see section 4\) d](#page-62-0)own-profile $CTD/O₂$ data at common pressure levels. Oxygen saturation values were computed according to Benson and Krausse (1984) in units of μ mol/kg.

The algorithm used for converting oxygen sensor current and probe temperature measurements to oxygen as described by Owens and Millard (1985) requires a nonlinear least squares regression technique in order to determine the best-fit coefficients of the model for oxygen sensor behavior to the water sample observations. WHOI program OXFITMR uses Numerical Recipes (Press et al.,1986) Fortran routines MRQMIN, MRQCOF, GAUSSJ, and COVSRT to perform non-linear least squares regression using the Levenberg-Marquardt method. A Fortran subroutine FOXY describes the oxygen model with the derivatives of the model with respect to six coefficients in the following order: oxygen current slope, temperature correction, pressure correction, weight, oxygen current bias, and oxygen current lag.

Program OXFITMR reads the data for a group of stations. The data are edited to remove spurious points where values are less than zero or greater than 1.2 times the saturation value. The routine varies the six (or fewer) parameters of the model in such a way as to produce the minimum sum of squares in the difference between the calibration oxygens and the computed values. Individual differences between the calibration oxygens and the computed oxygen values (residuals) are then compared with the standard deviation of the residuals. Any residual exceeding an edit factor of 2.8 standard deviations is rejected. A factor of 2.8 will have a 0.5% chance of rejecting a valid oxygen value for a normally distributed set of residuals. The iterative fitting process is continued until none of the data fail the edit criteria. The best fit to the oxygen probe model coefficients is then determined. Coefficients were applied using program CA 381 or CA 353 for plotting in Matlab.

By plotting the oxygen residuals versus station, appropriate station groupings for further refinements of fitting are obtained by looking for abrupt station-to-station changes in the residuals. For each grouping, two sets of coefficients were determined, one fitting bottles \leq 2500 dbar and a second fitting bottles \geq 2000 dbar. Pressure correction, weight, and lag coefficients were fixed within a reasonable range (noted by asterisks in Table 2) from output of full water column group fits. The two sets of coefficients were blended at 2250 dbar using a pair of hyperbolic tangent functions with 250-dbar decay scales. Final coefficients were applied to downcast data using PMEL program CA C381 and CALC3532. Calibrated oxygens were extracted from the calibrated profiles by pressure to create the final bottle file using CALBOT.

CTD-bottle oxygen differences are plotted against station number to show the stability of the calibrated CTD oxygens [relative to the bottle oxygens \(Fig. 4, upper panel\).](#page-78-0) Note [that the residuals \(Table 2 a](#page-72-0)nd Fig. 4) are near the nominal WOCE standard accuracy of 0.5% for discrete oxygen titrations. CTD-bottle oxygen differences are plotted against pressure to show the tight fit below 1200 m and the increasing scatter above 1200 [m \(Fig. 4, lower panel\).](#page-78-0)

6. Data Presentation

PMEL program 24N EPIC converted finalized CTD/ $O₂$ data files into EPIC format (Soreide *et al.* ,1995); and computed ITS-90 temperature, ITS-90 potential temperature, and dynamic height. EPIC data files contain a WOCE quality flag parameter associated with pressure, temperature, CTD salinity, and CTD oxygen. Quality flag definitions can be found in the WOCE Operations Manual (1994).

The final calibrated data in EPIC format were used to produce the plots and listings that follow. The majority of the plots were produced using Plot Plus Scientific Graphics System (Denbo, 1992). Vertical sections of potential temperature, CTD salinity, potential density, and CTD oxygen are contoured with pressure as the vertical axis and latitude as the horizontal axis (Figs. $5 - 8$). Nominal vertical exaggerations are 1000:1 below 1000 dbar (lower panels) and 2500:1 above 1000 dbar (upper panels). Plots and summary listings of the $CTD/O₂$ data follow for each cast. Hydrographic bottle data at discrete depths are listed in the final section.

The hydrographic listings presented include two-digit WOCE quality flags. The numeric digits are associated with bottle salinity and bottle oxygen. Quality flag definitions can be found in the WOCE Operations Manual (1994).

7. Participating Institutions/Personnel [See NOAA data report 0AR AOML-41](#page-3-0)

8. Acknowledgments

The assistance of the officers, crew, and survey technician Jonathan Shannahoff of the NOAA ship *Ronald H. Brown* is gratefully acknowledged. Gregg Thomas provided very high quality sample salinities and analysis documentation. This cruise was sponsored by NOAA 's Office of Global Programs.

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TABLES

Table 1: CTD cast summary

Table 2a: Shallow water column station groupings for CTD oxygen algorithm parameters.

* Fixed parameter from full water column fit of all bottles (sensor 353) or each grouping (sensor 381).

Table 2b: Deep water column station groupings for CTD oxygen algorithm parameters.

* Fixed parameter from full water column fit of all bottles (sensor 353) or each grouping (sensor 381).

Table 3: We ather condition code used to describe each set of CTD measurements.

Table 4: Sea state code used to describe each set of CTD measurements.

Table 5: Visibility code used to describe each set of CTD measurements.

All CTD and Hydrographic Data can be obtained by contacting K.E. McTaggart at kem@pmel.noaa.gov.

WOCE Section AR01 CTD/O2 Measurements (NOAA Data Report ERL PMEL-68) McTaggart et al.

Figure 1: CTD station locations made on the R/V *Ronald H. Brown* from January ²⁴ to February 23, 1998.

Figure 2: Pressures of bottle closures at each station.

Figure 3: Calibrated CTD-bottle conductivity differences plotted against station number (upper panel). Calibrated CTD-bottle conductivity differences plotted against pressure (lower panel).

Figure 4: Calibrated CTD-bottle oxygen differences plotted against station number (upper panel). Calibrated CTD-bottle oxygen differences plotted against pressure (lower panel).

Figure 5: Potential temperature (◦C) sections. Contour intervals are 0.1 from 1–2◦C, 0.2 from 2–3◦C, 0.5 from $3-5^{\circ}\text{C}$, and 1 from $5-35^{\circ}\text{C}$.

Figure 6: Salinity (PSS-78) sections. Contour intervals are 0.01 from 34–35, 0.05 from 35–35.1, and 0.1 from 35.1–38.

Figure 7: Potential density (kg/m³) sections. Sigma-theta contour intervals are 0.5 from 22–26, 0.2 from 26–26.4, and 0.1 from 26.5–27.4. Sigma-2 contour intervals are 0.1 from 36.5–36.9, 0.05 from 36.9–37, and 0.01 from 37–37.05. Sigma-4 contour intervals are 0.02 from 45.82–48.

Figure 8: CTD oxygen (μ mol/kg) sections. Contour intervals are 10 from 100–300 μ mol/kg in the upper panel; 10 from 100–250 μ mol/kg, and 5 from 250–300 μ mol/kg in the lower panel.

