

**CARBON DIOXIDE, HYDROGRAPHIC, AND CHEMICAL DATA OBTAINED DURING THE
R/V *RONALD H. BROWN* REPEAT HYDROGRAPHY CRUISE IN THE ATLANTIC OCEAN:
CLIVAR CO₂ SECTION A16S_2005
(11 JANUARY–24 FEBRUARY, 2005)**

Contributed by

R. Wanninkhof,¹ S.C. Doney,² E. Peltola,¹ R.D. Castle,¹ F.J. Millero,⁴ J.L. Bullister,³ D.A. Hansell,⁴
M.J. Warner,⁵ C. Langdon,⁴ G.C. Johnson,³ and C.W. Mordy³

¹Atlantic Oceanographic and Meteorological Laboratory, NOAA, Miami, FL

²Woods Hole Oceanographic Institution, Woods Hole, MA

³Pacific Marine Environmental Laboratory, NOAA, Seattle, WA

⁴Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, FL

⁵University of Washington, Seattle, WA

Prepared by

Alex Kozyr

Carbon Dioxide Information Analysis Center

Oak Ridge National Laboratory

Oak Ridge, Tennessee, USA

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OAK RIDGE NATIONAL LABORATORY

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ABBREVIATIONS AND ACRONYMS

AOML	Atlantic Oceanographic and Meteorological Laboratory
BNL	Brookhaven National Laboratory
CDIAC	Carbon Dioxide Information Analysis Center
CFC	chlorofluorocarbon
CLIVAR	Climate Variability (Program)
CO ₂	carbon dioxide
CRM	certified reference material
CTD	conductivity, temperature, and depth sensor
DOC	dissolved organic carbon
DOE	U.S. Department of Energy
EXPOCODE	expedition code
f CO ₂	fugacity of CO ₂
GCOS	Global Climate Observing System
GCRP	Global Change Research Program
GOOS	Global Ocean Observing System
JGOFS	Joint Global Ocean Flux Study
LADCP	Lowered acoustic Doppler current profiler
LDEO	Lamont-Doherty Earth Observatory
MLR	multilinear regression
NDP	numeric data package
NDIR	nondispersive infrared analyzer
NOAA	National Oceanic and Atmospheric Administration
NSF	National Science Foundation
ORNL	Oak Ridge National Laboratory
pCO ₂	partial pressure of CO ₂
PMEL	Pacific Marine Environmental Laboratory
QA	quality assurance
QC	quality control
RSMAS	Rosenstiel School of Marine and Atmospheric Science
R/V	research vessel
SIO	Scripps Institution of Oceanography
SOMMA	single-operator multi-parameter metabolic analyzer
SST	sea surface temperature
TALK	total alkalinity
TCO ₂	total inorganic carbon
UCI	University of California, Irvine
UW	University of Washington
WHP	WOCE Hydrographic Program
WOCE	World Ocean Circulation Experiment

ABSTRACT

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This report presents methods, and analytical and quality control procedures for salinity, oxygen, nutrient, inorganic carbon, organic carbon, chlorofluorocarbon (CFC), and bomb ¹⁴C system parameters performed during the A16S_2005 cruise, which took place from January 11 to February 24, 2005, aboard research vessel (R/V) *Ronald H. Brown* under the auspices of the National Oceanic and Atmospheric Administration (NOAA). The R/V *Ronald H. Brown* departed Punta Arenas, Chile, on January 11, 2005, and ended its cruise in Fortaleza, Brazil, on February 24, 2005. The research conducted was one of a series of repeat hydrography sections jointly funded by NOAA and the National Science Foundation as part of the CLIVAR/CO₂/repeat hydrography/tracer program. Samples were taken from 36 depths at 121 stations.

The data presented in this report include the analyses of water samples for total inorganic carbon (TCO₂), fugacity of CO₂ (*f*CO₂), total alkalinity (TALK), pH, dissolved organic carbon (DOC), CFC, ¹⁴C, hydrographic, and other chemical measurements.

The R/V *Ronald H. Brown* A16S_2005 data set is available free of charge as a numeric data package (NDP) from the Carbon Dioxide Information Analysis Center (CDIAC). The NDP consists of the oceanographic data files and this printed documentation, which describes the procedures and methods used to obtain the data.

Keywords: carbon dioxide, total CO₂, total alkalinity, pH, fugacity of CO₂, carbon cycle, coulometry, potentiometry, hydrographic measurements, CLIVAR, Atlantic Ocean

1. BACKGROUND INFORMATION

The cruise of research vessel (R/V) *Ronald H. Brown* along section A16S from Punta Arenas, Chile, to Fortaleza, Brazil, was the second in the National Oceanic and Atmospheric Administration (NOAA) - led contributions to a series of repeat hydrography cruises to measure decadal changes in circulation, heat and fresh water budgets, and carbon inventory in the ocean. The cruises repeat a subset of the World Ocean Circulation Experiment Hydrographic Program (WHP) and Joint Global Ocean Flux Study (JGOFS) lines occupied in each major ocean basin in the 1990s.

The WOCE/WHP program is driven by the need to monitor the increases in carbon dioxide (CO₂) in the ocean and provide the necessary data to support continuing model development that will lead to improved forecasting skills for oceans and global climate. During the 1990s, the WOCE/JGOFS survey provided a full-depth baseline data set against which to measure future changes. By integrating the scientific needs of programs requiring measurement of the full water column, major synergies and cost savings are achieved. These measurements are of importance both for major research programs, such as Climate Variability (CLIVAR) and the U.S. Global Climate Research Project (GCRP) Ocean Carbon and Climate Change Program (OCCC), and for operational activities such as the Global Ocean Observation System (GOOS) and the Global Climate Observing System (GCOS). As outlined in the program documentation, one component of a global observing system for the physical climate/CO₂ system should include periodic observations of hydrographic variables, CO₂ system parameters, and other tracers. The large-scale observation component of the OCCC program has a need for systematic observations of the invasion of anthropogenic carbon in the ocean that is superimposed on a variable natural background. The five topical areas addressed by the CO₂/CLIVAR repeat hydrography program are

1. carbon system studies;
2. heat and freshwater storage and flux studies;
3. deep and shallow water mass and ventilation studies;
4. calibration of autonomous sensors; and
5. data for model calibration.

A hydrographic survey consisting of a meridional lowered acoustic Doppler current profiler (LADCP)/conductivity, temperature, and depth (CTD)/rosette section in the western South Atlantic was carried out in January–February 2005 (see also Wanninkhof and Doney, 2005 for additional cruise details). The R/V *Ronald H. Brown* departed Punta Arenas, Chile on 11 January 2005. Starting from 60 deg. S, a total of 121 LADCP/CTD/Rosette stations were occupied (see Fig. 1.1) and 12 Argo floats and 11 drifters were deployed from 17 January–21 February. Up to thirty-six water samples and continuous LADCP, CTD, and bio-optical data were collected on each cast to within 20 m of the bottom. Station spacing was nominally 0.5 deg. of latitude except near the continental slope of South Georgia Island where a shorter station spacing was used to resolve boundary currents. Fewer than 36 discrete water samples were also collected on the shallow, continental slope stations as well as for some of the early stations due to heavy weather conditions. Salinity, dissolved oxygen, and nutrient samples were analyzed from every bottle sampled on the rosette. Other parameters from the bottles were sampled at a lower density. The cruise ended in Fortaleza, Brazil, on 24 February 2005.

This data report focuses on the measurements of total inorganic carbon or dissolved inorganic carbon (TCO₂ or DIC), fugacity of CO₂ (*f*CO₂), total alkalinity (TALK), pH, dissolved organic carbon (DOC), chlorofluorocarbons (CFC-11 and CFC-12), ¹⁴C, nitrate (NO₃), nitrite (NO₂), phosphate (PO₄), silicate (SiO₄), and dissolved oxygen (O₂).

The methodology, instrumentation, and standardization of these parameters improved significantly during the WOCE/JGOFS era. Notable developments include release of manuals detailing the analytical methods and operating protocols (DOE 1994). Certified reference materials (CRMs) are now available for

TCO₂ and TALK, which are run interspersed with samples to determine calibration offsets. For this cruise, the TALK and TCO₂ values were adjusted to account for the small difference between the CRMs run at sea and the certified value determined at Scripps Institution of Oceanography (SIO). The TCO₂ coulometers were calibrated daily by injecting aliquots of pure CO₂ (99.995%). The stability of each coulometer cell solution was confirmed with the analyses of several CRMs each day.

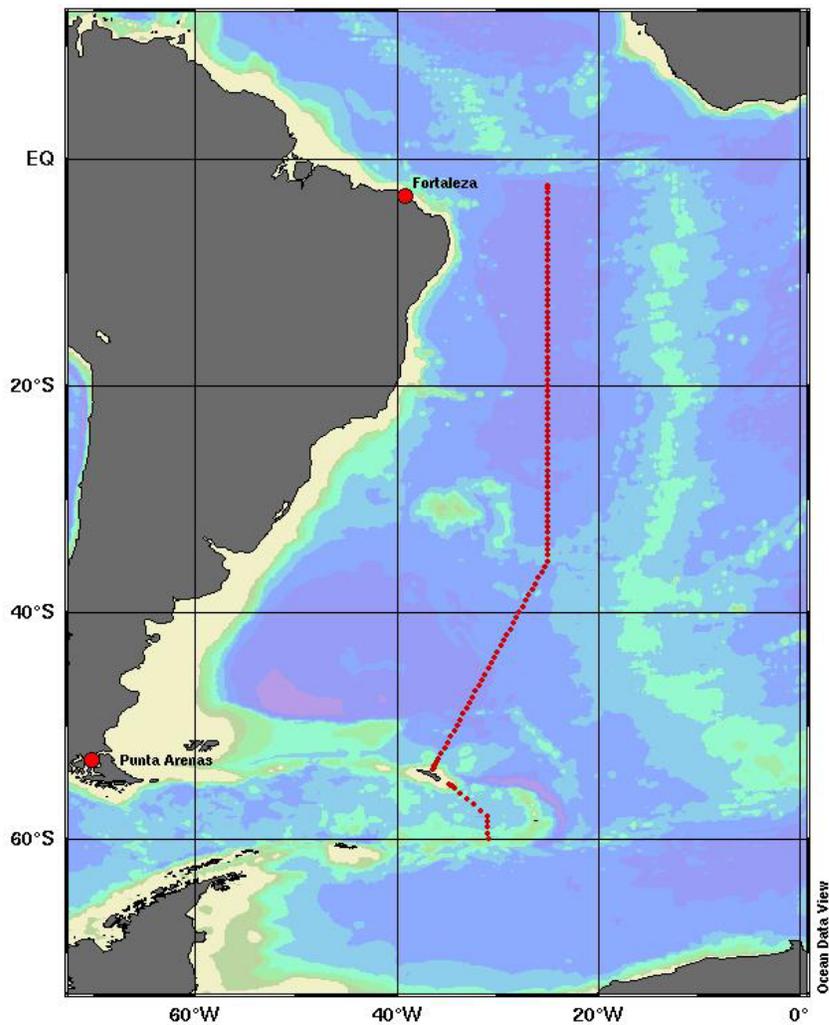


Fig. 1.1. Cruise track for the Atlantic Ocean A16S_2005 cruise in January–February 2005.

Instrumentation has improved in the last decade. Alkalinity measurements can be done with better precision through automation and close checks of the response of electrodes. Burettes are independently calibrated, and the preparation of titrant (hydrochloric acid) has undergone improved quality control and standardization (Millero et al. 1998). Measurement of pH is now done with extreme precision with spectrophotometric methods (Byrne and Breland 1989). The TCO₂ measurements are done by coulometry, a precise integrative method. During the A16S_2005 cruise two single-operator multiparameter metabolic analyzers (SOMMAs) (Johnson et al. 1999) were utilized for analyses, which facilitated a sample throughput of up to 80 samples per day. The *f*CO₂ measurements were done with an

equilibration system described in Wanninkhof and Thoning (1993). Oxygen measurements were performed by Winkler titrations (Carpenter 1965) with photometric endpoint detection (Friederich, Sherman, and Codispoti 1984).

The data underwent careful quality assurance and quality control (QA/QC) both during and after the cruise. The precision of the measurements was determined from duplicate sampling and comparison of data from deep water, where little variability is expected. Outliers in the data were flagged based on several methods utilizing prior knowledge of the trends and known relationships between parameters. Depth profiles for each parameter were scrutinized for outliers. When deviations were observed, other parameters were assessed to determine whether they showed deviations as well. Inorganic carbon system parameters were linked through physical and chemical properties. In particular, if two of the four carbon system parameters are measured, the other two can be calculated, provided that the silicate concentration, the phosphate concentration, the temperature, and the salinity of the sample are known. These so-called internal consistency calculations were used to assess the difference between calculated and measured values. When the difference between the measured TALK and the TALK calculated from TCO_2 and pH or $f\text{CO}_2$ exceeded $10 \mu\text{mol/kg}$, the three parameters were scrutinized and compared with other parameters to assess whether the datum should be labeled as questionable. Other techniques, described in detail below, include regional multi-linear regressions (MLR) between the inorganic carbon parameters and physical and chemical parameters known to correlate with them [for instance, $\text{TCO}_2 = f(\text{T}, \text{S}, \text{AOU}, \text{Si}, \text{PO}_4)$]. Again, the differences between measured and calculated parameters were inspected. Finally, the parameters were plotted against latitude for narrow depth intervals. Since changes along depth horizons are usually gradual, anomalies can be easily spotted and flagged.

This report describes procedures and methods for hydrographic measurement and the analytical procedures, calculations, and assessment of precision for nutrient, oxygen, TCO_2 , TALK, $f\text{CO}_2$, pH, CFCs, ^{14}C , and DOC measurements. A description of the QA/QC methods based on internal consistency of these parameters and the MLR technique is also provided.

2. DESCRIPTION OF THE EXPEDITION

2.1 R/V *Ronald H. Brown*: Technical Details and History

The NOAA ship R/V *Ronald H. Brown*, a state-of-the-art oceanographic and atmospheric research platform, is the largest vessel in the NOAA fleet. With its highly advanced instruments and sensors, R/V *Ronald H. Brown* travels worldwide supporting scientific studies to increase our understanding of the world's oceans and climate. Commissioned on July 19, 1997, in its home port of Charleston, South Carolina, *Ronald H. Brown* has sailed in the Pacific, Atlantic, and Indian Oceans. The ship was named in honor of former Secretary of Commerce Ronald H. Brown, who was killed in a plane crash on April 3, 1996, while on a trade mission to Bosnia. R/V *Ronald H. Brown* is operated by NOAA Marine and Aviation Operations and carries a complement of 6 NOAA Corps officers, 20 crew members, and a maximum of 33 scientists. Table 2.1 provides a detailed description of the ship.

Table 2.1. Specifications of R/V *Ronald H. Brown*

Designer	VT Halter Marine, Inc.
Builder	VT Halter Marine, Inc., Moss Point, Mississippi
Launched	May 30, 1996
Delivered	April 18, 1997
Commissioned	July, 19, 1997
Hull number	R104
Call letters	WTEC
Home port	Charleston, South Carolina
Length	83.5 m (274 ft)
Breadth (molded)	16.0 m (52.5 ft)
Draft, maximum	5.2 m (17.0 ft)
Depth to main deck	8 m (26.5 ft)
Displacement	3,250 tons
Maximum speed	15 kn (9 kn on one generator)
Cruise speed	12 kn
Range	11,300 nm at 12-kn speed plus 30 days on station
Total crew and scientists	58
Maximum cruise duration	60 days (45 day practical limit)
Science quarters	Main lab: 1,730 ft ² Electronics/computer lab: 720 ft ² Wet lab: 230 ft ² Hydro lab: 700 ft ² Biochemical lab: 720 ft ²

2.2 R/V *Ronald H. Brown* A16S_2005 Cruise Information

Ship name	<i>Ronald H. Brown</i>
EXPOCODE	33RO200501
CLIVAR section	A16S_2005
Ports of call	Punta Arenas, Chile; Fortaleza, Brazil
Dates	January 11– February 24, 2005
Funding support	NOAA, NSF
Chief scientists	Dr. Rik Wanninkhof, NOAA/AOML Dr. Scot Doney, WHOI

2.3 Parameters Measured, Institution, and Responsible Investigators

Parameter	Institution	Responsible Investigator
CTD	PMEL/AOML	G. Johnson/M. Baringer
ADCP/LADCP	UH/LDEO	E. Firing/A. Thurnherr
Salinity	PMEL	G. Johnson
Nutrients	UW/AOML	C. Mordy, J.-Z. Zhang
Dissolved Oxygen	RSMAS-UM	C. Langdon
CFCs	PMEL, UW	M. Warner, J. Bullister
Tritium, Helium	LDEO	P. Schlosser
TCO ₂	AOML, PMEL	R. Wanninkhof, R. Feely
Discrete pCO ₂	AOML	R. Wanninkhof
TALK, pH	RSMAS/UM	F. Millero
DOC	RSMAS/UM	D. Hansell
CDOM	UCSB	N. Nelson/C. Carlson
Underway pCO ₂	AOML	R. Wanninkhof
CO ₂ System Develop.	USF	R. Byrne
¹⁴ C, ¹³ C	WHOI	A. McNichol

2.4 Participating Institutions

PMEL	Pacific Marine Environmental Laboratory
AOML	Atlantic Oceanographic and Meteorological Laboratory
LDEO	Lamont-Doherty Earth Observatory
RSMAS/UM	Rosenstiel School of Marine and Atmospheric Science, University of Miami
UCSB	University of California at Santa Barbara
UH	University of Hawaii
USF	University of South Florida
WHOI	Woods Hole Oceanographic Institution
UW	University of Washington

3. DESCRIPTION OF VARIABLES AND METHODS

3.1 Hydrographic Measurements

Samples for CFCs, helium isotopes (^3He), oxygen (O_2), hydrochlorofluorocarbon (HCFCs), partial pressure of CO_2 ($p\text{CO}_2$), TCO_2 , hydrogen ion activities (pH), TALK, radiocarbon ($\Delta^{14}\text{C}$), tritium, DOC, chromophoric dissolved organic matter (CDOM), particulate inorganic/organic carbon (PIC/POC), salinity, and nutrients were drawn in this sequence from a CTD sampling package containing thirty-six 12-L Bullister bottles. A detailed descriptions of methods for the CTD data, LADCP data and biooptical data are given in Wanninkhof and Doney (2005). Oxygen, nutrient, and salinity samples were taken from all bottles. Oxygen draw temperature readings were commenced after station 25. For the other parameters, not all stations or all bottles were sampled. The stations at full degrees of latitude (odd numbered stations) were generally completely sampled for CFCs, TCO_2 , pH, and TALK, with partial sampling for DOC and CDOM. The half-degree stations were partially sampled for HCFC, PIC/POC, CFCs, TCO_2 , pH, and TALK. Discrete $p\text{CO}_2$ profiles were obtained at every two degrees. ^3He , $\Delta^{14}\text{C}$, and tritium were sampled at different intervals (primarily at full-latitude stations).

A total of 4174 bottle **salinity** samples were taken during the cruise, of which 127 were flagged as questionable and 3 as bad. Two samples were lost during analysis. Samples were drawn from the 12-L Bullister bottles into 250-mL Kimax borosilicate bottles. The bottles were rinsed at least three times before being filled to approximately 220 mL. A plastic insert and Nalgene cap were used to seal the sample in the bottle. At the conclusion of sampling, the time was noted and samples were placed into the salinometer lab so they could equilibrate to room temperature. Samples were analyzed after a period of at least 10 hours and typically not more than 24 hours from the time of sampling. Samples were run on a Guildline 8400B Laboratory Salinometer, serial number 60843. The salinometer had been last calibrated at Guildline in January of 2004. IAPSO Standard Seawater was used to standardize the instrument. The software used (ASALW) was developed at Scripps Institution of Oceanography. As per the instructions provided in the software, the cell was rinsed at least two times with sample at a relatively fast flow rate; the flow was adjusted to a slower rate for the final fill, and a reading was taken. The cell was drained and slowly filled for a second reading. If the two readings agreed within 0.00005, the values were accepted; otherwise, an additional reading was required. PSS-78 salinity (UNESCO, 1981) was calculated. Corrections were applied to the data for differences between beginning and ending standards.

Samples for dissolved **oxygen** analyses were drawn from 12-L Bullister bottles into calibrated 140-mL iodine titration flasks using Tygon tubing with silicone adapters that fit over the petcock to avoid contamination of DOC samples. Bottles were rinsed twice and filled from the bottom, then overflowed three volumes (care was taken to avoid entraining any bubbles). One-mL of MnCl_2 and one-mL of NaOH/NaI were added, then the flask was stoppered and shaken. Deionized water was added to the neck of each flask to create a water seal. The flasks were stored in the lab in plastic totes at room temperature for 1–2 hours before analysis. A total of 4659 samples were analyzed during the cruise, of which 37 samples were flagged as questionable and 4 as bad. Three samples were not reported. The whole-bottle titration technique of Carpenter (1965) was performed with modifications by Culberson et al. (1991), but with a more dilute solution of thiosulfate (10 g/L). Dissolved oxygen analyses were performed with a Monterey Bay Aquarium Research Institute (MBARI)-designed automated oxygen titrator using photometric end-point detection based on the absorption of 365-nm wavelength ultra-violet light. The titration of the samples and the data logging were controlled by a 386 PC running the oxygen program written by Gernot Friedrich (Friederich et al. 1984). Thiosulfate was dispensed by a Dosimat 665 fitted with a 5.0-mL burette. The autotitrator and Dosimat performed well.

Dissolved **nutrient** (phosphate, silicic acid, nitrate, and nitrite) samples were drawn in 40-mL HDPE Boston Round sample bottles that had been stored in 10% HCl and rinsed four to five times with sample before filling. A replicate was always drawn from the deep bottle for analysis on the subsequent

station. All samples were brought to room temperature prior to analysis. A separate analytical run was conducted at each station (except for the shallowest stations). An analytical run consisted of blanks and working standards, old working standards, deep water from the previous station, samples analyzed from deep to surface, replicate analysis of the four deep samples and any problem samples, and finally the working standards and blanks. The blanks were deionized water, and the standards were a “zero” standard in Low Nutrient Seawater (LNSW) and a high standard. Linearity of the autoanalyzer was checked every ten days, and corrections for non-linearity were applied during final data reduction.

All nutrients were measured using automated continuous flow analysis with a segmented flow and colorimetric detection. The four-channel autoanalyzer was customized using components from various systems. The major components were an Alpkem 301 sampler, two 24-channel Ismatek peristaltic pumps, four Thermo-Separation monochrometers, and custom software for digitally logging and processing the chromatographs. Glass coils and tubing from the Technicon Autoanalyzer II were used for analysis of phosphate, and micro-coils from Alpkem were used for the other three analyses. The detailed methods are described by Gordon et al. (1993). Because pump tubing destined for the cruise was lost in transit, some of the pump tube sizes suggested in the manual had to be modified. Pump tubes were changed four times during the expedition.

Silicic acid was analyzed using a modification of Armstrong et al. (1967). An acidic solution of ammonium molybdate was added to a seawater sample to produce silicomolybic acid. Oxalic acid was added to inhibit a secondary reaction with phosphate. Finally, the reduction with ascorbic acid formed the blue compound silicomolybdous acid. The color formation was detected using a 6-mm flowcell at 660 nm. The use of oxalic acid and ascorbic acid (instead of tartaric acid and stannous chloride as suggested by Gordon et al.) was to reduce the toxicity of our waste stream.

Nitrate and nitrite analyses were also modified from Armstrong et al. (1967). Nitrate was reduced to nitrite in a cadmium column, then formed into a red azo dye by complexing nitrite with sulfanilamide and N-1-naphthylethylenediamine. The color formation was detected using a 6-mm flow cell at 540 nm. The same technique was used to measure nitrite (excluding the reduction step), but the color formation was detected using a 10-mm flow cell at 540 nm.

Phosphate analysis was based on the technique of Bernhardt and Wilhelms (1967). An acidic solution of ammonium molybdate was added to the sample to produce phosphomolybdic acid, and this was reduced to the blue compound phosphomolybdous acid following the addition of hydrazine sulfate. The reaction was heated to 55°C to bring the reaction to completion, and color formation was detected using a 10-mm flow cell at 815 nm.

3.2 Total CO₂ Measurements

Samples for TCO₂ measurements were drawn according to procedures outlined in the *Handbook of Methods for CO₂ Analysis* (DOE 1994) from 12-L Bullister bottles into 540-mL Pyrex bottles using Tygon tubing with a silicone adapter on the petcock to avoid contamination of DOC samples. Bottles were rinsed and filled from the bottom, leaving 5 mL of headspace; care was taken not to entrain any bubbles. After 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.

TCO₂ samples were collected at every degree from all depths (typically 36 for standard deep water stations) with three replicate samples. Some samples were also collected at every half-degree. The replicate seawater samples were taken from the surface, 1000 m, and bottom Bullister bottles and run at different times during the cell. The first replicate of the bottom water was used at the start of the cell with fresh coulometer solution, and the first of the 1000-m replicates was run in the middle of the cell after about 12 mg of C were titrated. The second one of the bottom replicates was run at the end of the cell after about 25 mg of C were titrated. A new coulometer cell was started with the second of the 1000-m replicates and the first of the surface replicates. In the middle of this cell, the second of the surface

replicates was run and the first one of the surface duplicates of a partial station. The second of the partial station duplicates was run at the end of this cell. No systematic difference between the replicates was observed. There was no systematic dependency of results with an amount of carbon titrated for a particular cell. A total of 2482 samples for TCO₂ were collected and analyzed during the cruise.

The TCO₂ analytical equipment was set up in a seagoing laboratory van. The analysis was done by coulometry with two analytical systems (called AOML-1 and AOML-2) used simultaneously on the cruise. Each system consisted of a coulometer (UIC, Inc.) coupled with a single operator multi-parameter metabolic analyzer (SOMMA) inlet system developed by Kenneth Johnson (Johnson et al. 1985, 1987, 1993; Johnson 1992) now retired from Brookhaven National Laboratory (BNL). In the coulometric analysis of TCO₂, 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 pure air or compressed nitrogen, where it reacts quantitatively with a proprietary reagent based on ethanolamine to generate hydrogen ions. In this process, the solution changes from blue to colorless, which triggers a current through the cell and causes coulometrical generation of OH⁻ ions at the anode. The OH⁻ ions react with the H⁺, and the solution turns blue again. A beam of light is shone through the solution, and a photometric detector at the opposite side of the cell senses the change in transmission. Once the percent transmission reaches its original value, the coulometric titration is stopped, and the amount of CO₂ that enters the cell is determined by integrating the total charge during the titration.

The coulometers were calibrated by injecting aliquots of pure CO₂ (99.995%) by means of an 8-port valve outfitted with two sample loops with known gas volumes (AOML-1: 1.9951 mL at 25.05°C and 0.9807 mL at 25.10°C; AOML-2: 2.0018 mL at 25.09°C and 0.9949 mL at 25.06°C) bracketing the amount of CO₂ extracted from the water samples for the two AOML systems.

The stability of each coulometer cell solution was confirmed three different ways: the Certified Reference Material (CRM), Batch 66, supplied by Dr. A. Dickson of SIO, was measured at the beginning and the middle, gas loops in the beginning and at the end, and the duplicate samples at the beginning, middle, and end of each cell solution (Fig 3.1., Table3.1.). The coulometer cell solution was replaced after 25 mg of carbon was titrated, typically after 9–12 hours of continuous use.

The pipette volume was determined prior to the cruise by taking aliquots at known temperature of distilled water from the volumes. The weights with the appropriate densities were used to determine the volume of the pipettes (AOML1: 28.716 mL at 20.00°C, AOML2: 22.547 mL at 20.00°C).

Calculation of the amount of CO₂ injected was according to the CO₂ handbook (DOE 1994). The concentration of CO₂ ($[CO_2]$) in the samples was determined according to:

$$[CO_2] = Cal. factor * \frac{(Counts - Blank * Run Time) * K \mu mol/count}{pipette volume * density of sample}$$

where *Cal. Factor* is the calibration factor, *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 solution, *Run Time* is the length of coulometric titration (in minutes), and *K* is the conversion factor from counts to μ mol.

The instrument has a salinity sensor, but all TCO₂ values were recalculated to a molar weight (μ mol/kg) using density obtained from the CTD's salinity sensor. The TCO₂ values were corrected for dilution by 0.2 mL of HgCl₂ used for sample preservation. The total water volume of the sample bottles was 540 mL. The correction factor used for dilution was 1.00037. A correction was also applied for the offset from the CRM. This correction was applied for each cell using the CRM value obtained in the beginning of the cell. The results underwent initial quality control on the ship using property plots: TCO₂ vs. Depth, TCO₂ vs. Potential Temperature, TCO₂ vs. AOU, TCO₂ vs. NO₃, TCO₂ vs. SiO₃, TCO₂ vs. PO₄, TCO₂ vs. TALK, and TCO₂ vs. pH. Also contour plots of TCO₂ vs. LAT and Depth were used to analyze the quality of the data.

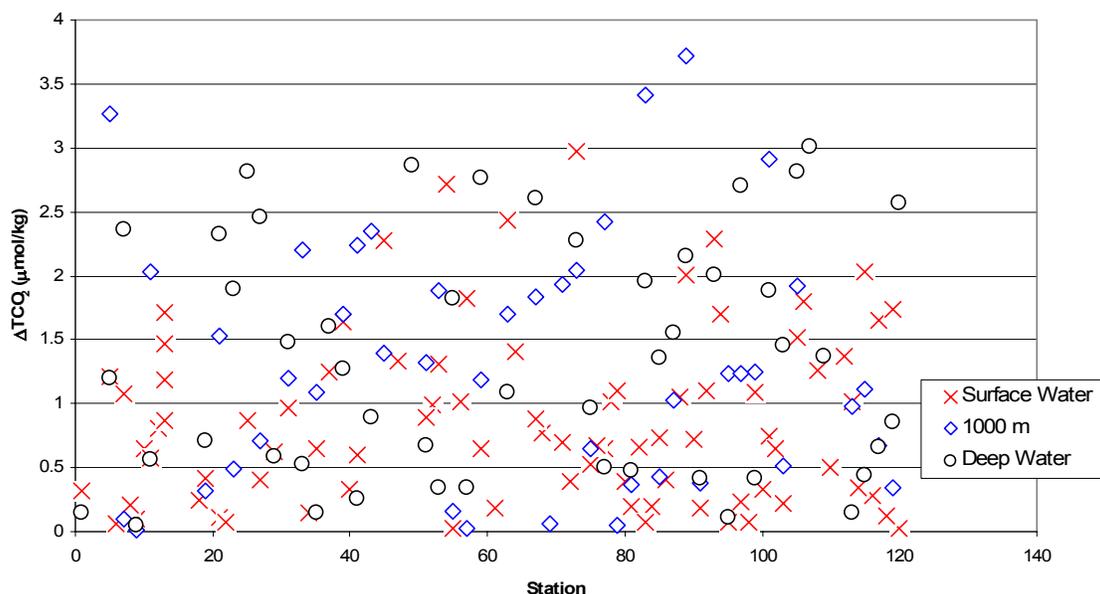


Fig. 3.1. Results of the duplicate TCO₂ samples collected during the R/V *Ronald H. Brown* cruise along the Atlantic Ocean section A16S_2005.

Table 3.1. TCO₂ duplicate measurement statistics

Measurement method	Avg.	Std. dev.	No.
Duplicate samples measured back-to-back	0.9	0.68	64
One duplicate measured at the beginning; one at the middle of the cell	1.0	0.82	62
One duplicate measured at the middle; one at the end of the cell	1.1	0.91	34
One duplicate measured at the beginning; one at the end of the cell	1.3	1.02	72
Duplicates run on the same instrument but on different cells	1.2	0.83	102
Duplicates run on different instruments			0
Duplicates measured at the beginning of the cell, but not back-to-back	1.3	0.89	6
Duplicates measured at the middle of the cell, but not back-to-back	0.6	0.63	12
Duplicates measured at the end of the cell, but not back-to-back	0.7	0.98	4
Total no. of measurements			356

The overall performance of the instruments was good during the cruise. The air purifier supplying carrier and pneumatic gas malfunctioned at station 24. Compressed tanks of ultra-high purity nitrogen gas were used thereon. At the same time, soda lime traps used to scrub any CO₂ from the carrier gas were removed from the air/N₂ line, since they developed cracks over time and also appeared to release CO₂ in pulses into the carrier. A coulometer was replaced during the test cast runs. It did not find an endpoint and did not stop counting. A number of pinch valves failed and were replaced; some cell caps began to leak, and some electrode leads broke. Finally, the Orbo tubes (filled with silica gel to absorb possible acid vapors) tended to break and leak and were not used after station 109 on either system.

Due to concerns about the large amount of water used for a TCO₂ sample and use of grease on the stoppers that could contaminate samples for dissolved organic matter (DOM), comparison tests were performed with samples drawn in 250-mL borosilicate bottles with ground glass stoppers stored under cold water with the regular sampling procedures outlined above. The results are shown in Table 3.2.

Table 3.2. Test results of different sample bottle sizes for TCO₂ measurements

Type	Bottle ²	RT ³	TCO ₂ μmol/kg	Bullister Bottle No	Volume (mL)	Average ⁴ μmol/kg
CRM ¹	213	14	1971.11			
bottle	A9	13	2122.29	9	500	
bottle	C9	13	2121.10	9	500	2121.69
bottle	S76	10	2119.95	9	250	
bottle	S77	12	2120.01	9	250	2119.98
bottle	S78	12	2120.28	10	250	
bottle	S79	11	2120.89	10	250	2120.58
bottle	A10	13	2121.04	10	500	
bottle	C10	12	2122.5	10	500	2121.77
bottle	A11	12	2121.37	11	500	
bottle	C11	14	2123.05	11	500	2122.21
CRM	213	15	1972.10			
bottle	S80	13	2120.74	11	250	
bottle	S81	19	2121.09	11	250	2120.915
bottle	S82	11	2120.51	12	250	
bottle	S83	17	2121.03	12	250	2120.77
bottle	A12	20	2126.01	12	500	
bottle	C12	20	2125.5	12	500	
bottle	A13	20	2128.34	13	500	
bottle	C13	17	2122.12	13	500	2122.12
bottle	S84	11	2120.61	13	250	
bottle	S85	11	2119.34	13	250	2119.97
bottle	S86	9	2119.26	14	250	
bottle	S87	9	2119.41	14	250	2119.33
bottle	A14	9	2120.74	14	500	
bottle	C14	9	2121.61	14	500	2121.17

¹CRM = 1969.57 μmol/kg;

²Bottles with prefix “S” are the 250-mL bottles; the others are the 540-mL bottles used during the cruise;

³RT: run time of the sample on the coulometer in minutes.

⁴Average: Average of duplicate large or duplicate small bottles taken from a particular Bullister bottle.

These tests and more ad-hoc tests at the beginning of the cruise showed a small but systematic difference between the small and large sample bottles: the average for large bottles was 2121.79 $\mu\text{mol/kg}$; for small bottles, 2120.26 $\mu\text{mol/kg}$; standard deviations were 0.37 and 0.55, respectively. The cause of the artifact is not clear, but the tests led to the decision to use the 500-mL greased stopper bottles for the entire cruise.

3.3 Discrete Fugacity of CO_2 Measurements

Samples for $f\text{CO}_2$ were drawn from 12-L Bullister bottles into 500-mL Pyrex™ volumetric flasks using Tygon™ tubing with a Silicone adapter over the petcock to avoid contamination of DOC samples. Bottles were rinsed twice, filled from the bottom, and overflowed half a volume while care was taken that no bubbles were entrained. About 5 mL of water was withdrawn by removing the pinched-off sampling tube from the neck of the flask to create a small expansion volume, then 0.2 mL of saturated mercuric chloride (HgCl_2) solution was added as a preservative. The sample bottles were sealed with a polyethylene-lined screw cap. The samples were stored upside down in coolers at room temperature for a maximum of 10 hours.

Thirty samples were drawn at every fourth station (at 2° intervals) for a total of 847 samples from 29 stations. In addition, samples were drawn in duplicate from the underway seawater line at 6-hour intervals between Punta Arenas and the start of the line at 60°S , 31°W .

The $f\text{CO}_2$ was measured on the A16S_2005 cruise at a constant temperature of 20°C by equilibrating a 500-mL water aliquot in a volumetric flask with a closed headspace. The headspace was circulated through a nondispersive infrared detector that measures both CO_2 and H_2O levels. The analytical instrumentation is detailed in Wanninkhof and Thoning (1993) and is similar to the setup used in the S.Atl-91 cruise that occupied the same cruise line from 43°S northward in 1991 (Forde et al. 1994). Discrete $f\text{CO}_2$ measurements were also made on the SAVE-5/HYDROS-4 cruises using a system developed by Chipman et al. (1993) that covered a similar track from 54°S to 2°N in 1989–1990 (SAVE 1992).

In short, in the system used on A16S_2005, a 500-mL water sample was equilibrated at ambient pressure with an 80-mL headspace in a volumetric flask held at a temperature of 20°C in a thermostatted bath. The headspace was circulated through a nondispersive infrared analyzer (NDIR), LICOR, model 6262. Upon equilibration, the circulation flow was stopped and 20 consecutive 1-second readings of H_2O content and CO_2 content in the cell were taken and averaged. The system was a dual-channel system where one equilibration occurs while circulating through the NDIR and a second flask was equilibrated offline. Once the first sample was analyzed, the second flask was switched in line with the NDIR and the residual air in the NDIR was equilibrated with the second flask content. The second equilibration phase through the NDIR took less time as a large part of the headspace was already equilibrated offline. The two-channel configuration decreases the total analysis time to about 20 minutes for two samples. An expandable volume in the circulation loop near the flasks consisting of a small deflated balloon kept the content of flasks at room pressure.

To account for instrument drift and to maintain measurement precision, a set of six gas standards was run through the system before and after every eight seawater samples. The standards of CO_2 in natural air were obtained from Scott-Marin and referenced against primary standards purchased from C.D. Keeling in 1991. The primary standards were on the WMO-78 scale. The mole fractions of the standards, which were run in the following sequence, were:

Tank number	Mole fraction
CA05989	378.71 ppm
CA05980	792.51 ppm
CA05984	1036.92 ppm
CA05940	1533.70 ppm
CA05988	593.64 ppm
CA05998	205.07 ppm

The standards were also used as the headspace gas for the equilibration. Since the mole fractions of the gases in the headspace prior to equilibration were known, the small perturbation of the $f\text{CO}_2$ in the water during the equilibration process could be quantitatively accounted for. The headspace gas was selected so that it is close to the anticipated water value, thereby minimizing the correction.

The determination of $f\text{CO}_2$ @20°C [$f\text{CO}_2(20)$] in water from the headspace measurement involved several steps. The infra-red (IR) detector response for the standards was normalized for temperature. The IR analyzer output of dry mole fraction of CO_2 ($x\text{CO}_2$) for samples was normalized to 1 atm pressure. The sample values were converted to the true mixing ratio based on a second-order polynomial fit between the instrument $x\text{CO}_2$ readout and the values of the three nearest concentrations of the compressed gas standards. The mixing ratio in the headspace was converted to a fugacity assuming 100% humidity and corrected to fugacity of CO_2 in the water sample prior to equilibration by accounting for change in total CO_2 in water during the equilibration process (for details see Wanninkhof and Thoning 1993). The change in $f\text{CO}_2(20)$ caused by the change in TCO_2 was calculated using the constraint that TALK remains constant during exchange of CO_2 gas between the headspace and the water. The calculation is outlined Peng et al. (1987).

Uncertainty based on duplicate sampling of the same Bullister bottle for $f\text{CO}_2$ analysis was determined on select stations of the cruise. The comparisons are presented In Table 3.3

Table 3.3. Comparison of duplicate discrete $f\text{CO}_2$ samples.

Station	Sample No.	$f\text{CO}_{2\text{av}}$	$\Delta f\text{CO}_2$	% difference
5	203	1093.8	3.0	0.3
5	209	1089.0	2.3	0.2
9	103	1087.3	1.5	0.1
9	105	1088.8	2.4	0.2
9	109	1081.6	2.7	0.2
21	135	572.7	0.4	0.07
49	121	838.0	0.4	0.05
65	121	756.1	5.6	0.7
93	124	1040.3	2.3	0.2

$f\text{CO}_{2\text{av}}$ = average of the duplicate samples.

$\Delta f\text{CO}_2$ = absolute difference between the duplicates

% difference = $\Delta f\text{CO}_2 / f\text{CO}_{2\text{av}} \times 100$

Measuring TCO_2 , TALK, and $f\text{CO}_2(20)$ on the cruise, offers an opportunity to assess the internal consistency of these inorganic carbon parameters. For the analyses, the apparent carbonate dissociation constants determined by Mehrbach (1973) as refitted by Dickson and Millero (1987) were used. An Excel program developed by D. Pierrot of RSMAS/University of Miami using the code developed by Lewis and Wallace (1998) facilitated the calculations. The average difference between measured alkalinity and that calculated using TCO_2 and $f\text{CO}_2(20)$ was $-2.03 \pm 4.91 \mu\text{mol/kg}$ ($n= 768$). The agreement was the best obtained to date and suggested an excellent data quality of these parameters. A compilation of the difference plotted versus depth is shown in Fig. 3.2.

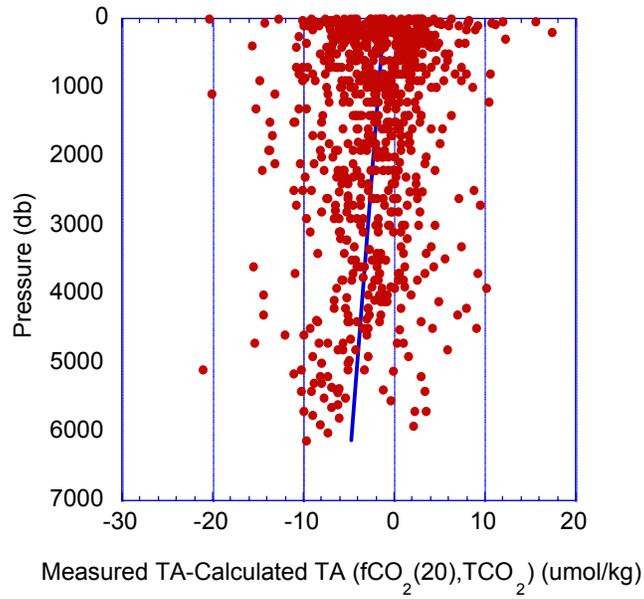


Fig. 3.2. Difference between measured TALK and that calculated from TCO_2 and $f\text{CO}_2(20)$ plotted versus depth.

The distribution of differences is presented in Fig. 3.3. The figure shows a near-normal distribution with a slight negative bias suggesting predominantly random errors.

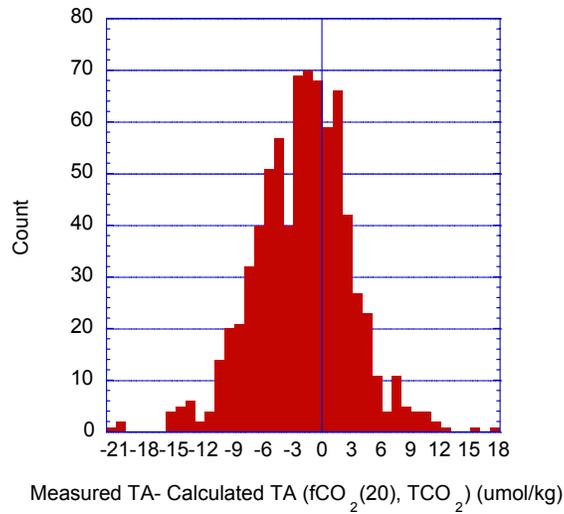


Fig. 3.3. Distribution of measured TALK – calculated TALK from TCO_2 and $f\text{CO}_2(20)$.

The A16S_2005 cruise overlapped with the A16N_2003a cruise from 6°S to 2.5°S and measurements of $f\text{CO}_2(20)$ were performed at 4°S and 6°S on both cruises. The depth profiles shown in Figs. 3.4 and 3.5 show excellent agreement between the observations at the two locations. For example, for the depth interval between 1800 and 3500 dB in the core of the North Atlantic deep water where $f\text{CO}_2(20)$ is quite constant, the average of the values of the two overlap stations are well within one standard deviation (9 μatm) of each other with no significant differences between the 2003 and 2005 data.

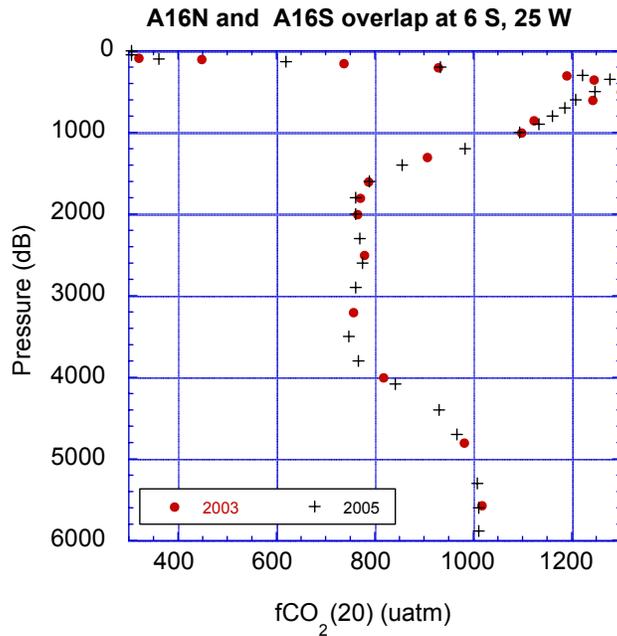


Fig. 3.4. Comparison of $f\text{CO}_2(20)$ data at 6°S for 2003 and 2005.

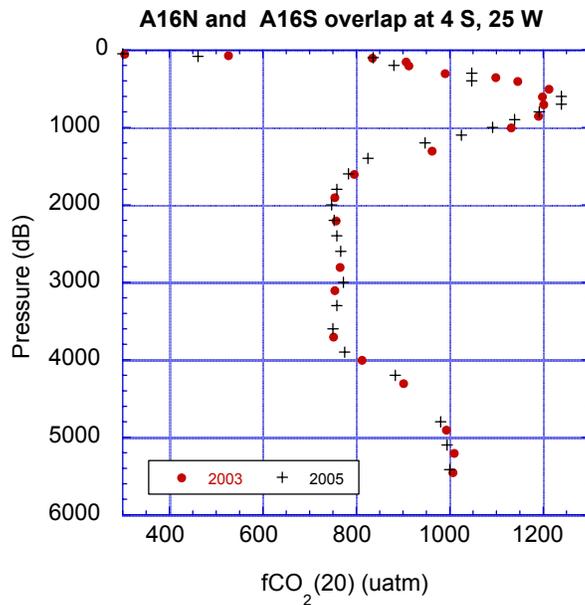


Fig. 3.5. Comparison of $f\text{CO}_2(20)$ data at 4°S for 2003 and 2005.

3.4 Total Alkalinity Measurements

Samples for total alkalinity measurements were drawn from 12-L Bullister bottles into 500-mL borosilicate flasks using silicone tubing fit over the petcock to avoid contamination of DOC samples. Bottles were rinsed a minimum of two times and filled from the bottom and a quarter of a volume was overflowed while taking care to avoid the entrainment of any bubbles. Approximately 15 mL of water was withdrawn from the flask by arresting the sample flow and removing the sampling tube, thus creating a small expansion volume and a reproducible headspace. The sample bottles were sealed at a ground glass joint with a glass stopper. The samples were stored at room temperature for a maximum of 7 hours. Thirty-six samples and three duplicates were drawn on odd number stations (at 1° intervals) for a total of 61 full stations. Typically, 9 depths were sampled with a duplicate at the surface at the 60 “half stations.” Periodically, multiple duplicate samples were drawn with a specific focus on photic zone and region of high DOC. The purpose was to determine the difference in TALK after filtration with a 0.45- μm nylon membrane filter. Additional underway samples were drawn in duplicate from the underway seawater line at 6-hour intervals between Punta Arenas, Chile, and the start of the line at 60°S, 31°W

The TALK was evaluated from the proton balance at the alkalinity equivalence point, $\text{pH}_{\text{equiv}} = 4.5$ at 25°C and zero ionic strength in 1 kg of sample. The method utilizes a multi-point hydrochloric acid titration of seawater according to the definition of total alkalinity (Dickson 1981).

The titration system consisted of a Metrohm 665 Dosimat titrator, an Orion 720A pH meter, and a custom-designed, plastic water-jacketed titration cell (Millero et al. 1993a). Both the seawater sample and acid titrant are temperature-equilibrated to a constant temperature of $25 \pm 0.1^\circ\text{C}$ with a water bath (Neslab, model RTE-17). The plastic water-jacketed cell is similar to the cells used by Bradshaw and Brewer (1988) except a larger volume (~200 mL) is employed to increase the precision. Each cell has a fill-and-drain valve, which increases the reproducibility of the volume of sample contained in the cell. The titration acidified seawater passed the carbonic acid endpoint by adding HCl stepwise through an injection tip into the cell. A typical titration recorded the (electro-magnetic field) EMF after the readings became stable (deviation less than 0.09 mV), and then enough acid was added to change the voltage a preassigned increment (13 mV). A full titration (~25 points) takes about 20 min. The electrodes used to measure the EMF of the sample during a titration consisted of a ROSS glass pH electrode (Orion, model 810100) and a double-junction Ag, AgCl reference electrode (Orion, model 900200).

A single 50-L batch of ~0.25-m HCl acid was prepared in 0.45-m NaCl by diluting concentrated HCl, AR Select, Mallinckrodt, to yield a total ionic strength similar to seawater of salinity 35.0 ($I \approx 0.7$ M). The acid was standardized by a coulometric technique (Marinenko and Taylor 1968, Taylor and Smith 1959) and verified with alkalinity titrations on seawater of known alkalinity. Furthermore, Andrew Dickson’s laboratory performed an independent determination of the acid molality on sub-samples. The calibrated molality of the acid used was 0.2434 ± 0.0001 m HCl. The acid was stored in 500-mL glass bottles sealed with Apiezon® L grease for use in the field.

The volumes of the cells used were determined to ± 0.03 mL in the laboratory by multiple titrations using seawater of known total alkalinity and CRM. Calibrations of the burette of the Dosimat with water at 25°C indicate that the systems deliver 3.000 mL (the approximate value for a titration of seawater) to a precision of ± 0.0004 mL, resulting in an error of ± 0.3 $\mu\text{mol/kg}$ in TALK and TCO_2 . The reproducibility and precision of measurements are checked using low nutrient surface seawater and CRM, Batch Nos. 59 and 66. CRMs were utilized to account for instrument drift and to maintain measurement precision. Duplicate analyses provide additional QA and were taken from same Bullister bottle.

The assigned values of the CRM provided by A. Dickson of SIO were:

Batch #59:	Total alkalinity: 2220.98 ± 0.58 $\mu\text{mol/kg}$	Salinity: 33.316
Batch #66:	Total alkalinity: 2193.27 ± 0.60 $\mu\text{mol/kg}$	Salinity: 32.962

An integrated program controlled the titration, data collection, and the calculation of the carbonate parameters (TALK, pH, and TCO_2) (Millero et al. 1993b). The program is patterned after those

developed by Dickson (1981), Johansson and Wedborg (1982), and DOE (1994). The program uses a Levenberg-Marquardt nonlinear least-squares algorithm to calculate the TALK and TCO₂ from the potentiometric titration data.

<u>CRM</u>	<u>Instrument 1</u>	<u>Instrument 2</u>
Total number of sets:	56	52
Number of sets used:	48	46
Standard deviation:	±3.5 µmol/kg	±2.7 µmol/kg

<u>Duplicates</u>	<u>Between Systems</u>	<u>Instrument 1</u>	<u>Instrument 2</u>
Total number of sets:	143	31	42
Number of sets used:	130	25	35
Standard deviation:	±2.9 µmol/kg	±1.6 µmol/kg	±1.3 µmol/kg

Note: Duplicate samples with differences three times larger than standard deviation were omitted from the analyses. The number omitted is the difference between the total number of sets and the sets used.

At the beginning of the cruise, a titration cell was swapped out for a spare cell because of a combination of instability in the electrodes and an air bubble consistently being trapped. One valve and a proximity switch were replaced without discernible downtime. Sporadically, a solenoid valve at the bottom of the titration cell would fail to engage or disengage, resulting in the loss of the sample or a failed titration due to a poor rinse or an air bubble. The titration cell on system showed some drift in CRM values on February 4, 2005; the titration cells recalibration values were used to correct this.

Communication problems between the software and the components of the TALK system were remedied with the replacement of cables and/or components. A Metrohm 665 Dosimat titrator and an Orion 720A pH meter were replaced. Computer instability resulted in the loss of one sample.

3.5 pH Measurements

Samples for pH measurements were drawn from 12-L Bullister bottles into 50-mL glass syringes using polycarbonate Luer-lock valves that fit in the petcock. Syringes were rinsed a minimum of three times and filled while care was taken to avoid the entrainment of any bubbles. A rubber band ensured positive pressure on the barrel of the syringe. The samples were stored at room temperature for a maximum of 7 hours. Thirty-six samples and 3 duplicates were drawn on odd-numbered stations (at 1° intervals) for a total of 61 full stations. At even-numbered stations, surface water and a duplicate were always taken; in addition, 5 to 20 other depths were also sampled, for a total of 60 half stations. Typically, nine depths were sampled with a duplicate at the surface for the half-stations. Underway samples were drawn in duplicate from the underway seawater line at 6-hour intervals between Punta Arenas, Chile, and the start of the line at 60°S, 31°W.

Measurements of the pH of seawater on the total hydrogen ion concentration pH scale (pH_t) were performed using the multi-wavelength spectrophotometric techniques of Clayton and Byrne (1993). Determination of the absorbance at several wavelengths eliminates the need to know the concentrations of indicator in the sample. Sulphonaphthalein indicators such as m-cresol purple (mCP), thymol blue, and cresol red are suitable for determining pH. The system is patterned after the standard operating procedure developed by DOE (1994) and utilizes mCP. This fully automated system performs discrete analysis of pH samples approximately every 12 minutes on a sample volume of 25 mL. A microprocessor-controlled syringe and sampling valve aspirates and injects the seawater sample into the 10-cm optical cell at a precisely controlled rate. The syringe rinses and primes the optical cell with 20 mL of sample and the software permits 5 minutes for temperature stabilization. A refrigerated circulating temperature bath (Neslab, model RTE-17) regulates the temperature of the sample at 25 ± 0.01°C. An Agilent 8453 UV/VIS spectrophotometer measures background absorbance of the sample. The automated syringe and sampling valves aspirates 4.90 mL seawater and 0.008 mL of indicator and injects the mixture into the

cell. After the software permits 5 min for temperature stabilization, a Guildline 9540 digital platinum resistance thermometer measures the temperature and the spectrophotometer acquires the absorbance at 434, 578, and 730 nm.

A concentrated solution of 2.0 mM of mCP (C₂₁H₁₈O₃S) dye of known pH_t = 7.91 and R = 1.625 at 25°C were used.

A precision of better than 0.001 pH is possible with care, specifically with regard to temperature equilibration and sample handling. Measurements made on duplicate samples, TRIS buffers, and CRM, Batch No. 59, validate the precision and accuracy. Duplicate analyses provide additional QA and were taken from same Bullister bottles. The pH_{sws} for the CRM was determined by spectrophotometric methods independently in the laboratory at RMSAS, University of Miami:

Batch #59:	pH _{sws} @ 25°C	7.9048 ± 0.0007 (n = 19)
	Salinity	33.316

The pH_t of the sample is perturbed by the addition of the indicator. The magnitude of this perturbation is a function of the difference between the seawater and indicator acidity. A correction factor applied for each batch of dye adjusts for this perturbation. For a 4.90-mL sample of seawater, 0.008 mL of mCP is added and the absorbance ratio is measured. From a second addition of mCP and a second absorbance ratio measurement, a change in the absorbance ratio per mL of added indicator is calculated. The value of the absorbance ratio (R_m) measured subsequent to the initial addition of the indicator was used to calculate R from:

$$R = R_m + (0.00095 - 0.00133 R_m) V_{ind} \quad (1)$$

where V_{ind} is the volume of mCP used. Clayton and Byrne (1993) calibrated the mCP indicator using TRIS buffers (Ramette et al. 1977) and the equations of Dickson (1993). These equations are used to calculate pH_t, the total scale in units of moles per kilogram of solution. The conversion of the pH_t (mol/kg_{H₂O}) to the seawater scale (mol/kg_{sol}) can be made using equations of Dickson and Millero (1987), Dickson and Riley (1979), and Dickson (1990).

CRM

Total number of sets:	136
Number of sets used:	124

CRM Batch #59:	7.9050 ± 0.0024 (pH _{sws} at 25°C)
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TRIS buffer

Total number of sets:	296
Number of sets used:	264

TRIS Buffer (0.04 m):	8.0935 ± 0.0019 (pH _t @ 25°C)
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Duplicates

Total number of sets:	291
Number of Sets used:	214

Standard deviation:	± 0.0019 (pH _{sws} @ 25°C)
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Note: The instrumental software automatically runs a duplicate analysis when the baseline absorbance at 730 nm is beyond a set threshold, thus a large number of duplicate results were omitted. Duplicate

samples with differences more than three times larger than the standard deviation were omitted from the analyses. The number omitted is the difference between the total number of sets and the sets used.

At the start of the cruise, the outflow from the optical cell leaked into the thermostat-equipped water jacket; this was repaired by replacing the tubing. Sporadically, samples drawn from the syringe entrained an air bubble because the valve was improperly opened, the tubing was pinched, or the syringe plunger was dry and became stuck in the barrel. Some syringes suffered from fatigue at the metal Luer-lock and this resulted in the sample being lost or the analysis failing. Occasionally the software lost communication with the microprocessor-controlled syringe pumps and paused analysis; the problem was resolved by following the steps outlined in the software to reestablish communication.

3.6 Dissolved Organic Carbon Measurements

Water samples were collected from the rosette. Samples collected from the surface to 250 meters were filtered using precombusted (500°C) GF/F inline filters as they were being collected from the Niskin bottle. At depths > 250 meters, the samples were collected without filtration. After collection, samples were frozen upright in 60-mL acid-cleaned high-density polypropylene bottles and remained cold until analysis. Prior to analysis, samples were returned to room temperature then acidified to pH < 2 with concentrated hydrochloric acid. Analysis was performed onshore using a Shimadzu TOC-V_{CSH} Total Organic Carbon Analyzer with the TNM-1 Total Nitrogen detector attached. Instrument conditions were as follows:

Combustion temperature	680 °C
Carrier gas	UHP Oxygen
Carrier flow rate	150 mL/min
Ozone generation gas	Zero Air from Whatman TOC Gas Generator
Ozone flow rate	500 mL/min
Sample sparge time	2.0 minutes
Minimum number of injections	3
Maximum number of injections	5
Number of washes	2
Standard deviation maximum	0.1000
CV maximum	2.00%
Injection volume	100 µL

The TOC system was calibrated using potassium hydrogen phthalate in Milli-Q water; the TN system was calibrated using potassium nitrate in Milli-Q water. System performance was verified daily using Consensus Reference Water distributed by the Dr. Hansell Laboratory. This reference water is water from deep in the Sargasso Sea that has been acidified and sealed in 10-mL ampoules, the concentration of which ($\approx 44 \mu\text{M C}$) has been determined by the consensus of up to six expert and independent laboratories. After verifying proper operation of the TOC/TN instrument, samples were set up on an auto sampler for analysis. The run started with a QW (Q Water) blank and a reference seawater analysis. Then six samples would be analyzed followed by another QW blank and reference seawater analysis. This sequence would be repeated until all samples for that run were analyzed. The run ended with a QW blank, reference water, and a non-acidified QW blank. This was done to verify that the hydrochloric acid used to acidify the samples was uncontaminated. QW blanks and reference water samples were used to evaluate system performance during the analytical run. If a problem was detected with the blanks or reference waters, the samples were reanalyzed.

3.7 Chlorofluorocarbon Measurements

Samples for the analysis of dissolved CFC-11, -12, -113, and carbon tetrachloride (CCl_4) were drawn from 2378 of the 4192 bottles collected during the expedition. Specially designed 12-L Bullister bottles were used on the cruise to reduce CFC contamination. These bottles have the same outer diameter 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 provided with standard Niskin bottles. When taken, water samples for CFC and carbon tetrachloride analysis were the first samples drawn from the Bullister bottles. Care was taken to coordinate 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, ^3He , and HCFC 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 Bullister bottles into 100-mL precision glass syringes equipped with two-way metal stopcocks. The syringes were immersed in a holding tank of clean surface seawater until analyzed.

Concentrations of CFC-11 and CFC-12 were measured by shipboard electron capture gas chromatography (EC-GC) using techniques modified from those described by Bullister and Weiss (1988). For seawater analyses, water was transferred from a glass syringe to a fixed volume chamber (~30 mL). The contents of the chamber were then injected into a glass-sparging chamber. The dissolved gases in the seawater sample were extracted by passing a supply of CFC-free purge gas through the sparging chamber for a period of 4 min at 70 mL/min. Water vapor was removed from the purge gas during passage through an 18-cm long, 3/8-in. diameter glass tube packed with the desiccant magnesium perchlorate. The sample gases were concentrated on a cold-trap consisting of a 1/8-in. outside diameter (OD) stainless steel tube with a ~10-cm section packed tightly with Porapak N (60–80 mesh). A vortex cooler, using compressed air at 100 psi, was used to cool the trap to approximately -20°C . After 4 min of purging, the trap was isolated, and the trap was heated electrically to $\sim 100^\circ\text{C}$. The sample gases held in the trap were then injected onto a precolumn (~25 cm of 1/8-in. OD stainless steel tubing packed with 80–100 mesh Porasil C, held at 70°C) for the initial separation of CFC-12, -11, and -113 from carbon tetrachloride. After the CFCs had passed from the pre-column into the main analytical column (~183 cm of 1/8-in. OD stainless steel tubing packed with Carbograph 1AC, 80–100 mesh, held at 70°C) of GC1 (a HP 5890 Series II gas chromatograph with an EC detector), a valve was used to direct the precolumn flow (and more slowly eluting carbon tetrachloride peak) to a second gas chromatograph (Shimadzu Mini II GC with ECD). For the first 52 stations, the chromatographic column in the Shimadzu GC was 1 m of 1/8-in. OD stainless steel tubing packed with 80–100 mesh Porasil C.

Both of the analytical systems were calibrated frequently, with frequency listed below, 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 were 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 used. 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 seawater, air, standard, or blank samples was ~11 min.

Concentrations of the seawater samples, and gas standards are reported relative to the SIO98 calibration scale. Dissolved CFC concentrations are given in units of picomoles per kilogram seawater (pmol/kg). CFC concentrations in 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 45191 for CFC-11, CFC-12, CFC-113, and CCl_4) into the analytical instrument. The response of the detector to the range of moles of CFC passing through the detector remained relatively constant during the cruise. Full-range calibration curves were run at intervals of 14

days during the cruise. These were supplemented with occasional injections of multiple aliquots of the standard gas at more frequent time intervals. Single injections of a fixed volume of standard gas at one atmosphere were run much more frequently (at intervals of ~90 minutes) to monitor short-term changes in detector sensitivity. The CFC-113 peak was often on a small bump on the baseline, resulting in a large dependence of the peak area on the choice of endpoints for integration. To provide better precision, the height of the peak was used instead. The precisions of measurements of the standard gas in the fixed volume ($n = 690$) were $\pm 0.67\%$ for CFC-12 and 0.59% for CFC-11.

The efficiency of the purging process was evaluated periodically by re-stripping high-concentration surface water samples and comparing the residual concentrations to initial values. These re-strip values ranged from approximately 1% for CFC-11 and CFC-12 in cold waters to values of $<1\%$ in warm waters. A fit of the re-strip efficiency as a function of temperature was applied to the final data set. The cold-water values have been applied to all values in the preliminary data set.

There were very few measurements of CFC-11 and CFC-12 concentrations less than 0.005 pmol/kg along A16S section.

Based on the analysis of 100 duplicate samples, the precisions (1 standard deviation) of 0.45% or 0.003 pmol/kg (whichever is greater) for dissolved CFC-11, and 0.78% or 0.004 pmol/kg for CFC-12 measurements was estimated.

A very small number of water samples had anomalously high CFC concentrations relative to adjacent samples. These samples occurred sporadically during the cruise and were not clearly associated with other features in the water column (e.g., anomalous dissolved oxygen, salinity, or temperature features). This suggests that these samples were probably contaminated with CFCs during the sampling or analysis processes. Measured concentrations for these anomalous samples are included in the data set, but are given a quality flag value of either 3 (questionable measurement) or 4 (bad measurement). A quality flag of 5 was assigned to samples drawn from the rosette but never analyzed due to various reasons (e.g., leaking stopcock, plunger jammed in syringe barrel). A total of 13 analyses of CFC-11 and 16 analyses of CFC-12 were assigned a quality flag "3." Four analyses of CFC-11 and 6 analyses of CFC-12 were assigned a quality flag "4." A total of 13 samples were given a quality flag "5" (sampled but not analyzed).

3.8 Underway pCO₂ (fCO₂) Measurements

The shipboard automated underway pCO₂ system was situated in the hydrographic laboratory. It ran on an hourly cycle during which 3 gas standards, 8 headspace samples from the equilibrator, and 3 ambient air samples were analyzed. The system consisted of an equilibrator where surface seawater from the bow intake was equilibrated with headspace, a valve box that contained the infrared analyzer, and an electronics box with a computer and interface boards that controlled valves and log sensors.

The equilibrator, designed by R. Weiss of SIO, is made from a 58 cm H \times 23 cm inside diameter (ID) cylindrical Plexiglas™ chamber. Surface seawater flows through a showerhead in the top at a rate of 10–13 L/min. The water spray through the 16-L headspace and the turbulence of the water streams impinging on the surface of 8 L of water cause the gases in water and headspace to equilibrate. Excess water flows through an outlet 20 cm from the bottom of the equilibrator into an over-the-side drain. Two vents in the top of the equilibrator ensure that the headspace remains at the measured laboratory pressure. Headspace gas circulates in a closed loop driven by a KNF pump at 200 mL/min. From the equilibrator, the gas passes through a condenser, a column of magnesium perchlorate, a mass flow meter (MFM), the 12 mL sample cell of a Licor™ Model 6251 non-dispersive infrared analyzer (IR), and back into the equilibrator headspace.

A second KNF pump draws marine air from an intake on the bow mast through ~100 m of 0.95 cm (3/8-in.) OD Dekoron™ tubing at a rate of 6–8 L/min. A filter of glass wool at the intake prevents particles from entering the gas stream. At designated times, the program diverts ~250 mL/min of air from this line into the Licor™ sample cell for analysis. Excess marine air and the two vent lines from the

equilibrator empty through an endcap into an open-ended PVC tube. This means that any air drawn into the equilibrator is marine air rather than lab air with elevated and variable CO₂ concentration.

Both sample streams (equilibrator headspace and marine air) are analyzed bone dry. They pass first through a cold trap (condensor) at 5°C and then through a column of magnesium perchlorate. Standard gases also run through the magnesium perchlorate.

A custom developed program run under LabView™ controls the system and graphically displays air and water mole-fraction of CO₂ (xCO₂) readings. The program logs the voltage and temperature of the infrared analyzer, water flow, gas flows, equilibrator temperature, and barometric pressure. It also logs temperature and salinity from a Seabird MicroTSG™ unit connected to the seawater line near the equilibrator. An RS-422 feed from the shipboard computing system (SCS) provides additional data including time, latitude, longitude, temperature, and salinity in the sea chest near the seawater intake, relative and absolute wind speed and direction, and fluorometer readings. The program writes all of this data to disk at the end of each measurement phase.

The details of instrumental design can be found in Wanninkhof and Thoning (1993), Ho et al. (1995), and Feely et al. (1998).

The system runs on an hourly cycle during which 3 standard gases, 3 marine air samples, and 8 surface water samples (from the equilibrator headspace) are analyzed on the schedule listed in Table 3.3. A Valco multi-port valve selects the gas to be analyzed. Each measurement phase starts by flowing either standard (at ~50mL/min), equilibrator headspace (at ~200mL/min), or marine air (at ~250mL/min) through the Licor. Fifteen seconds before the end of each phase, a solenoid valve stops the gas flow. Ten seconds later, the program logs all sensors and writes the data to disk.

Table 3.4. Hourly sampling cycle for the underway pCO₂ system (version 2.5).

Minutes after the Hour	Sample
4	Low standard
8	Mid standard
12	High standard
16.5	Water (= headspace of equilibrator)
21	Water
25.5	Water
30	Water
34	Air (marine air from the bow line)
38	Air
42	Air
46.5	Water
51	Water
55.5	Water
60	Water

The headspace equilibration time, as determined by return to equilibrium after perturbation by adding nitrogen to the headspace, was approximately 2.5 min. The transit time of water from the bow to the equilibrator was determined in 1998 by injecting a slug of dye into the intake and measuring the response on a fluorometer that is located in the hydrolab, close to the equilibrator. The response time,

defined as the time elapsed between peak concentration and the half peak level, $t_{1/2}$, was 1.45 min. This short time suggests little dispersion of the water during transit through the tubing.

The unit is standardized every hour with three compressed air standards containing known amounts of CO₂ gas in (natural) air. The standard gases were purchased from NOAA/CMDL in Boulder and are directly traceable to the World Meteorological Observatory (WMO) scale.

The standards used on the cruise were:

<u>Tank No</u>	<u>Mole Fraction CO₂ (ppm) (xCO₂)</u>
CC 71588	531.98
CA05344	411.42
CA05395	315.25

All xCO₂ values are reported in parts per million (ppm), and f CO₂ values are reported in micro atmospheres (μ atm).

The mixing ratios of ambient air and equilibrated headspace air are calculated by fitting a second-order polynomial through the hourly-averaged voltage response of the detector versus mixing ratios of the standards preceding and following the air and water samples. Mixing ratios of dried equilibrated headspace and air are converted to f CO₂ in surface seawater and water saturated air. For ambient air (a) and equilibrator headspace (eq), the f CO_{2a}, or f CO_{2eq} are calculated assuming 100% water vapor content:

$$f\text{CO}_{2a/\text{eq}} = x\text{CO}_{2a/\text{eq}}(P - p\text{H}_2\text{O}) \exp[(B_{11} + 2d_{12})P/RT]$$

where f CO_{2a/eq} is the fugacity in ambient air or equilibrator, p H₂O is the water vapor pressure at the sea surface temperature, P is the atmospheric pressure (in atm), T is the sea surface temperature (SST) or equilibrator temperature (in K), and R is the ideal gas constant (82.057 mL atm deg⁻¹ mol⁻¹). The exponential term is the fugacity correction where B_{11} is the second virial coefficient of pure CO₂:

$$B_{11} = -1636.75 + 12.0408T - 0.032795T^2 + 3.16528 \times 10^{-5}T^3$$

and

$$d_{12} = 57.7 - 0.118 T$$

where d_{12} is the correction for an air-CO₂ mixture in units of mL/mol (Weiss 1974).

The calculation for the fugacity at SST as measured by the thermosalinograph involves a temperature correction term for the increase of f CO₂ due to heating of the water from its passage through the pump and through 5-cm ID Teflon-sleeved stainless steel tubing within the ship. The water in the equilibrator is typically 0.2 to 0.3°C warmer than sea surface temperature. At the southern end of the transect when SST \approx 2–5°C, the difference was as much as 1°C. The empirical temperature correction from equilibrator temperature to SST is outlined in Weiss et al. (1982).

$$\text{dln}(f\text{CO}_2) = (t_{\text{eq}} - \text{SST}) \times [0.03107 - 2.7851 \times 10^{-4} t_{\text{eq}} - 1.839 \times 10^{-3} \ln(f\text{CO}_{2\text{eq}})]$$

where $\text{dln}(f\text{CO}_2)$ is the difference between the natural logarithm of the fugacity at t_{eq} and SST, and t_{eq} is the equilibrator temperature in °C.

The precision of the measurements is estimated at 0.2 ppm based on repetitive measurements of marine air. The accuracy of the air values is believed to be better than 0.5 ppm based on comparisons with flask samples on tests performed in 1995. Equilibrator headspace values are believed to be accurate to within 2 μ atm. The greater uncertainty is attributed to the equilibration efficiency. Outside the calibration

range of the standards, an accuracy of 5 ppm (μatm) is assigned based on laboratory tests where the calibrated IR output is compared with standards of known concentration outside the calibration range.

At the start of the cruise, from 1/14/05 17:04 (UTC) until 1/16/05 15:50 (UTC), problems with the electrical power caused the program to run out of sync and the equilibrator thermistor to give bad readings. Connecting the instrument to an uninterruptible power supply (UPS) eliminated the problem.

4. HOW TO OBTAIN THE DATA AND DOCUMENTATION

This database (NDP-087) is available free of charge from CDIAC. The complete documentation and data can be obtained from the CDIAC oceanographic web site (<http://cdiac.ornl.gov/oceans/doc.html>), through CDIAC's online ordering system (http://cdiac.ornl.gov/pns/how_order.html) or by contacting CDIAC.

The data are also available from CDIAC's anonymous file transfer protocol (FTP) area via the Internet. (Please note that your computer needs to have FTP software loaded on it. It is included in most newer operating systems.) Use the following commands to obtain the database:

```
ftp cdiac.ornl.gov or >ftp 160.91.18.18
Login: "anonymous" or "ftp"
Password: your e-mail address
ftp> cd pub/ndp087/
ftp> dir
ftp> mget (files)
ftp> quit
```

The full datasets from the cruise, including bottle and CTD data, can be found at the CLIVAR repeat hydrography website: http://ushydro.ucsd.edu/cruise_data_links.html

Contact information:

Carbon Dioxide Information Analysis Center
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, Tennessee 37831-6335
USA

Telephone: (865) 574-3645
Telefax: (865) 574-2232

E-mail: cdiac@ornl.gov
Internet: <http://cdiac.ornl.gov/>

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