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CARBON DIOXIDE, HYDROGRAPHIC, AND CHEMICAL DATA OBTAINED DURING THE R/V *MAURICE EWING* CRUISE IN THE ATLANTIC OCEAN (WOCE SECTION A17, 4 JANUARY–21 MARCH 1994)

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ABBREVIATIONS AND ACRONYMS

A/D	analog-to-digital
bhp	brake horsepower
BNL	Brookhaven National Laboratory
^{14}C	radiocarbon
CALFAC	calibration factor
CDIAC	Carbon Dioxide Information Analysis Center
CFC	chlorofluorocarbon
CICYT	Comisión Interministerial de Ciencia y Tecnología
CNRS	Centre de la Recherche Scientifique
CO_2	carbon dioxide
CRM	certified reference material
CSIC	Consejo Superior de Investigaciones Cientificas, Spain
CSP	carbon system variable
CTD	conductivity, temperature, and depth sensor
DIC	dissolved inorganic carbon
DOE	U.S. Department of Energy
fCO_2	fugacity of CO_2
IFREMER	Institut Français de Recherche pour L'Exploitation de la Mer
IIM.CSIC	Instituto de Investigaciones Marinas, CSIC, Vigo, Spain
INSU	Institut National des Sciences de l'Univers
I/O	input/output
JGOFS	Joint Global Ocean Flux Study
LDEO	Lamont-Doherty Earth Observatory
LMCE	Laboratoire de Modélisation du Climate et de l' Environnement
LODYC	Laboratoire d'Océanographie Dynamique et de Climatologie
LPO	Laboratoire de Physique des Océans
NBS	National Bureau of Standards
NDP	numeric data package
NMFS	National Marine Fisheries Service
NOAA	National Oceanic and Atmospheric Administration
NODC	National Oceanographic Data Center
NSF	National Science Foundation
ORNL	Oak Ridge National Laboratory
pCO_2	partial pressure of CO_2
PNEDC	Programme National d'Etude de la Dynamique du Climat
PNNL	Pacific National Laboratory

QA	quality assurance
QC	quality control
RB	Rio de Janeiro, Brazil
R/V	research vessel
SFB	Sonderforschungsbereich
SIO	Scripps Institution of Oceanography
SOMMA	single-operator multi-parameter metabolic analyzer
SSS	seawater substandard
TALK	total alkalinity
TCO_2	total carbon dioxide
TD	to-deliver
VFC	voltage-to-frequency converter
WHOI	Woods Hole Oceanographic Institution
WHP	WOCE Hydrographic Program
WOCE	World Ocean Circulation Experiment

ABSTRACT

Ríos, A., K. M. Johnson, X. A. Álvarez-Salgado, L. Arlen, A. Billant, L. S. Bingler, P. Branellec, C. G. Castro, D. W. Chipman, G. Rosón, and D. W. R. Wallace. 2005. Carbon Dioxide, Hydrographic, and Chemical Data Obtained During the R/V *Maurice Ewing* Cruise in the Atlantic Ocean (WOCE Section A17, 4 January–21 March 1994), ed. A. Kozyr. ORNL/CDIAC-148, NDP-084. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee, 39 pp.

This documentation discusses the procedures and methods used to measure total carbon dioxide (TCO_2), total alkalinity (TALK), and pH at hydrographic stations during the R/V *Maurice Ewing* cruise in the South Atlantic Ocean on the A17 WOCE section. Conducted as part of the World Ocean Circulation Experiment (WOCE), this cruise was also a part of the French WOCE program consisting of three expeditions (CITHER 1, 2, and 3) focused on the South Atlantic Ocean. The A17 section was occupied during the CITHER 2 expedition, which began in Montevideo, Uruguay, on January 4, 1994 and finished in Cayenne, French Guyana, on March 21, 1994. During this period the ship stopped in Salvador de Bahia and Recife, Brazil, to take on supplies and exchange personnel. Upon completion of the cruise the ship transited to Fort de France, Martinique. Instructions for accessing the data are provided.

TCO_2 was measured using a single-operator multiparameter metabolic analyzer (SOMMA) coupled to a coulometer for extracting and detecting CO_2 from seawater samples. The overall precision and accuracy of the TCO_2 analyses was ±1.6 µmol/kg. A second carbon system variable, TALK, was determined by potentiometric titration with an overall precision of ±1.7 µmol/kg. During the A17 cruise the carbon system was overdetermined because a third carbonate system variable, pH, was also measured potentiometrically with an overall precision of ±0.003. The underway partial pressure of CO_2 (pCO_2) in surface waters was also continuously measured along the cruise track.

A comparison of A17 TALK with recent data in the South Atlantic Ocean confirms that A17 TALK data need a downward correction of 8 µmol/kg that was integrated in the CDIAC database. The internal consistency study carried out among the four carbon system variables led us to adjust the pH measurements by stations in order to eliminate the difference between TCO_2 measured and TCO_2 calculated from pH and TALK.

The R/V *Maurice Ewing* A17 data set is available free of charge as a numeric data package (NDP) from the Carbon Dioxide Information Analysis Center. The NDP consists of three oceanographic data files, one FORTRAN 77 data retrieval routine file, and this printed documentation, which describes the contents and format of all files as well as the procedures and methods used to obtain the data.

Keywords: carbon dioxide, TCO_2, total alkalinity, pH, partial pressure of CO_2, carbon cycle, coulometry, potentiometry, hydrographic measurements, World Ocean Circulation Experiment, meridional section, South Atlantic Ocean.

1. BACKGROUND INFORMATION

The World Ocean Circulation Experiment–World Hydrographic Program (WOCE-WHP) was a major component of the World Climate Research Program. The primary goal of WOCE was to understand the general circulation of the global ocean well enough to be able to model its present state and predict its evolution in relation to long-term changes in the atmosphere. The need for carbon system measurements arose from the serious concern over the rising atmospheric concentrations of carbon dioxide (CO_2). Increasing atmospheric CO_2 may intensify the earth's natural greenhouse effect and alter the global climate.

Although CO_2-related measurements—specifically, total CO_2 (TCO_2), total alkalinity (TALK), partial pressure of CO_2 (pCO_2), and pH—were not official WOCE measurements, a coordinated effort was supported as a core component of the Joint Global Ocean Flux Study (JGOFS). This effort received support in the United States from the U.S. Department of Energy (DOE), the National Oceanic and Atmospheric Administration (NOAA), and the National Science Foundation (NSF), and in Spain from the Comisión Interministerial de Ciencia y Tecnología (CICYT), for WOCE cruises through 1998 to measure the global spatial and temporal distributions of CO_2 and related parameters. Goals were to estimate the meridional transport of inorganic carbon in a manner analogous to oceanic heat transport (Bryden and Hall 1980; Roemmich and Wunsch 1985; Brewer et al. 1989; Holfort et al. 1998; Alvarez et al. 2003; Rosón et al. 2003), and to build a database suitable for carbon-cycle modeling and the estimation of anthropogenic CO_2 increase in the oceans. To obtain a reliable database, Wanninkhof et al. (2003) made a comparison of inorganic carbon system parameters measured in the Atlantic Ocean from 1990 to 1998, recommending small adjustments for consistency among other cruises in the zone. The CO_2 survey took advantage of the sampling opportunities provided by the WOCE cruises during this period, and the final data set covered on the order of 23,000 stations. Wallace (2002) reviewed the goals, conduct, and initial findings of the global CO_2 survey, and recently Sabine et al. (2004) estimated a global oceanic anthropogenic CO_2 sink between 1800 and 1994.

This report discusses results of the research vessel (R/V) *Maurice Ewing* expedition along the WOCE Section A17, from 4 January to 21 March, 1994 (Fig. 1.1). The cruise, designated as CITHER2_1–2, was a part of the French WOCE program consisting of three expeditions focusing on the South Atlantic Ocean: CITHER 1 (1993), 2 (1994), and 3 (1995). TCO_2 analysis personnel and support for this expedition were from Brookhaven National Laboratory (BNL), Lamont-Doherty Earth Observation (LDEO), and Battelle Pacific Northwest National Laboratory (PNNL). Analyses of TALK, pH, and nutrients were performed by Spanish scientists from the Consejo Superior de Investigaciones Cientificas (CSIC), Instituto de Investigaciones Marinas of Vigo. The hydrographic work was carried out by French scientists under the direction of Laurent Mémery Laboratoire d'Océanographie Dynamique et de Climatologie (LODYC), University of Pierre et Marie Curie, Paris, France.

The A17 section work will yield a map of the large-scale three-dimensional distribution of temperature, salinity, and chemical constituents, including the carbon system variables. This map will be combined with the results of the remaining French WOCE South Atlantic sections (A6, A7, A13, and A14) and the other South Atlantic WOCE sections measured by CO_2 survey participants (A8, A9, A10, and A11) to provide an extensive reference data set. Knowledge of the measured variables and their initial conditions allow determination of heat and water transports as well as carbon transport and elucidate regional sources and sinks of carbon and fossil fuel carbon. Studies estimating the carbon transport and establishing the anthropogenic CO_2 sources and sinks based on these data have already appeared in the literature (Holfort et al. 1998; Ríos et al. 2003). An understanding of anthropogenic CO_2 uptake and transports contributes to the understanding of processes relevant to climate change. The South Atlantic A17 section was especially relevant to CO_2 transport because it focused on the western boundary sections and currents, and provided a description of the water masses and their meridional evolution between 50°S and 10°N (Mémery et al. 2000).

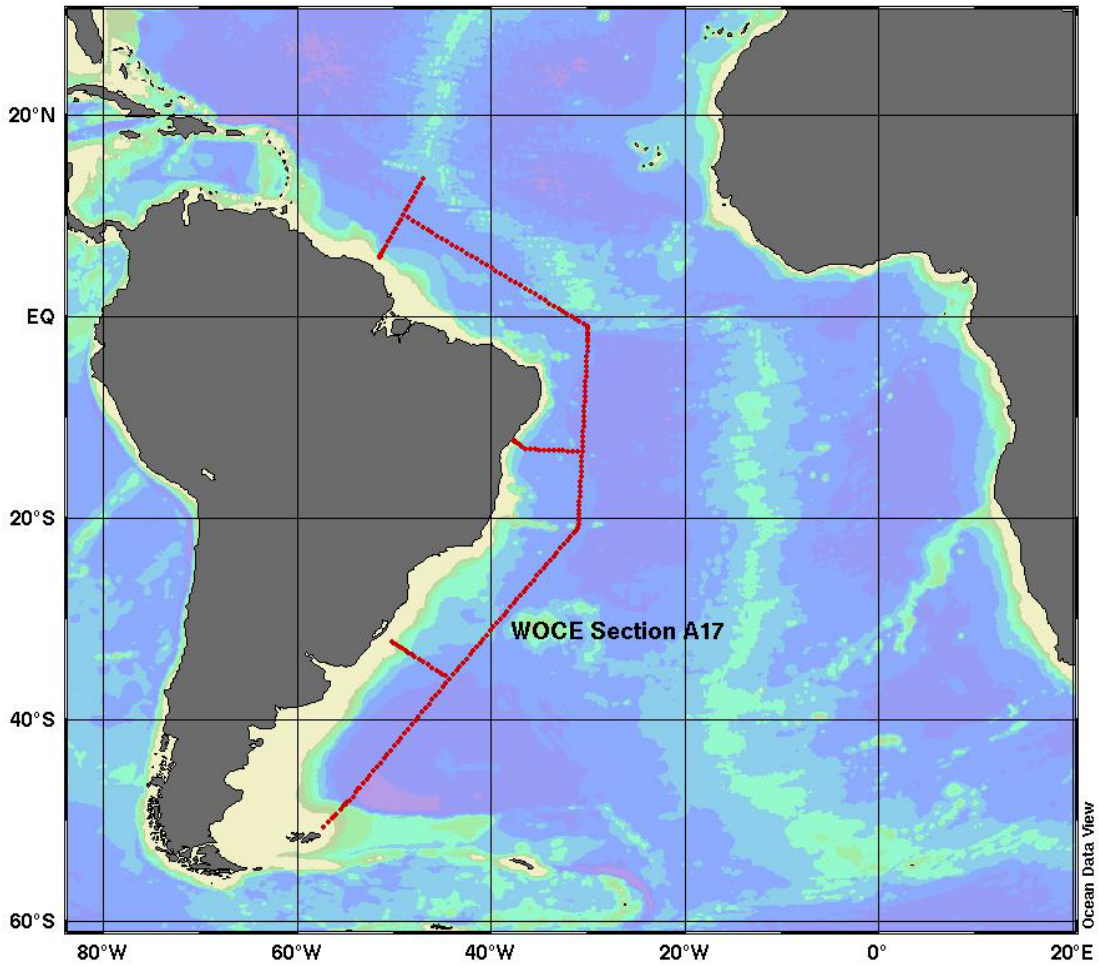

Fig. 1.1. Cuise track during the R/V *Maurice Ewing* Atlantic Ocean survey expedition along WOCE section A17.

The work aboard the R/V *Maurice Ewing* was supported by the Institut Français de Recherche pour L'Exploitation de la Mer (IFREMER; Grant 210161), the Institut National des Sciences de l'Univers (INSU), and the Centre de la Recherche Scientifique (CNRS), in the framework of the Programme National d'Etude de la Dynamique du Climat (PNEDC) and its WOCE/France subprogram. The carbon dioxide and nutrients work was supported by DOE (DE-ACO2-76CH00016) and CICYT (Grant ANT93-1156-E). We would like to thank the master, officers, and crew of R/V *Maurice Ewing* and all the participants on the cruise CITHER-2. Special thanks go to M. Arhan, coordinator of the WOCE-France program CITHER, and L. Mémery, chief scientist of cruise CITHER 2. The authors are also especially grateful to the Sonderforschungsbereich 460 (SFB) at the University of Kiel (Dr. F. Schott, Leader), funded by the Deutsche Forschungsgemeinschaft, for their support and assistance in completing the written documentation.

2. DESCRIPTION OF THE EXPEDITION

2.1 R/V *Maurice Ewing*: Technical Details and History

The R/V *Maurice Ewing* is a research vessel owned by the National Science Foundation (USA) and operated by the Lamont-Doherty Earth Observatory (LDEO) of Columbia University. It is classified by the America Bureau of Shipping as an A-1 and Baltic Ice Class IA ship. It was originally constructed as a seismic vessel in 1983, but it was acquired by Columbia in 1989, modified, and outfitted for tasks required of a general-purpose oceanographic research vessel. The vessel does, however, incorporate extensive and unique geophysical capabilities into its hardware; these include a Syntrak 480-24 seismic recording system, hydrophones, and sound source arrays. The vessel operates in the Atlantic, Indian, and Pacific Oceans. Table 2.1 provides a detailed description of the ship.

Table 2.1. Specifications of R/V *Maurice Ewing*

US NODC code	3230
Basic dimensions:	
Gross registered tonnage	1978
Overall length	73.0 m
Beam	14.10 m
Draught (maximum)	5.30 m
Fuel capacity	604 m^3
Service speed	11.0 kn
Maximum speed	13.5 kn
Freeboard to working deck	2.5 m
Personnel	Crew: 22; scientists: 28
Main engine (s)	4 × Diesel El at 5200 bhp at 1200 rpm
Range	17,000 mi
Maximum cruise duration	60 days
Nautical equipment	Integrated navigation system with radar, loran, SatNav; 3- and 12-kHz echosounders (hull-mounted) for scientific research; geological sonar; 4 oceanographic winches carrying 6,000 m of 9/16-in. 3 × 19, 0.68-in. coaxial cable, 0.322-in. CTD wire, or ¼-in. 3 × 19 wire. Hull-mounted Atlas deep ocean multibeam swath bottom mapping system and electronic data processing equipment (SUN computer). Ship has 35-ton- capacity gantry, 4-ton-capacity crane, and other winches for instruments or sampling
Science quarters	Dark room, 465 m^3 of cargo storage space, 65 m^2 of wet laboratory space, 208 m^2 of dry laboratory space, 30 m^2 of free working deck area, science office, vehicle staging room, and a small amount of container space

2.2 R/V *Maurice Ewing* A17 Cruise Information

Ship Name	*Maurice Ewing*
EXPOCODE	3230CITHER2_1-2
WOCE section	A17
Ports of call	Montevideo, Uruguay; Salvador de Bahia and Recife, Brazil; Cayenne, French Guyana
Dates	January 4–March 21, 1994
Funding support	CITHER cruise: INSU, CNRS, PNEDC, France
	TCO_2: DOE
	Alkalinity, pH, and nutrients: CICYT, Spain
Chief scientist	Dr. Laurent Mémery, LODYC, Paris, France

Parameters measured, institution, and responsible investigators

Parameter	Institution	Responsible Personnel
CTD, salinity, XBT	LODYC	L. Mémery, M. Arhan, H. Mércier
Nutrients	IIM.CSIC	X. Alvarez-Salgado, C. G. Castro
Oxygen	LPO	H. Mércier
CFCs	LODYC	L. Mémery
Tritium, He, ^{14}C	LMCE	P. Jean Baptiste
TCO_2	BNL/PNNL	L. Bingler, L. Arlen
Total alkalinity, pH	IIM.CSIC	A. F. Ríos, G. Rosón
Underway pCO_2	LDEO	D. Chipman
Brazilian observer	RB	J. A. Fontainha

Participating institutions

BNL	Brookhaven National Laboratory
IIM.CSIC	Instituto de Investigaciones Marinas, CSIC, Vigo, Spain
LDEO	Lamont-Doherty Earth Observatory
LMCE	Laboratoire de Modélisation du Climate et de l' Environnement
LODYC	Laboratoire d' Oceanographie Dynamique et de Climatologie
LPO	Laboratoire de Physique des Océans
PNNL	Pacific Northwest National Laboratory
RB	Rio de Janeiro, Brazil

2.3 Brief Cruise Summary

The analytical team for the A17 section CO_2 measurements was put together as part of the Global CO_2 Survey conducted during WOCE from 1990 to 1998. The A17 section covered the Argentine and Brazil deep basins from the tip of South America to the equator. The cruise took place during the height of the CO_2 survey and was completed with the cooperation of an international group of scientists from the United States, Spain, and France.

Although the cruise took place aboard a U.S. ship, the R/V *Maurice Ewing*, the A17 section was a part of a three-year-long French hydrographic expedition (CITHER) in the South Atlantic. In order to make the TCO_2 measurements on A17, four U.S. institutions had to combine forces to complete the work. The single-operator multi-parameter metabolic analyzer (SOMMA) and coulometer analytical system came from the Lamont-Doherty Earth Observatory (LDEO) at Columbia University; the TCO_2 group leader L. Bingler was from Battelle's Pacific Northwest Laboratory (PNNL); the assistant TCO_2 analyst L. Arlen came from the NOAA's National Marine Fisheries Service (NMFS) Laboratory in Sandy Hook, New Jersey. The training and financial support of the analysts was carried out at and provided by BNL. In addition, PNNL paid for a barometer, which was installed in the LDEO system, and supported the production of a revised instrument manual for the SOMMA-coulometer systems. The TALK was measured by A. F. Ríos and G. Rosón of CSIC, Instituto de Investigaciones Marinas of Vigo, Spain. The latter group also measured pH, so that as a result of the A17 cooperative scientific effort, the carbonate system was overdetermined. Underway pCO_2 was also measured by David Chipman, who installed the pCO_2 equipment in Montevideo, just before the start of the expedition.

The *Maurice Ewing* departed Montevideo on January 4, 1994, and headed generally south in direction of the Falkland Islands, where measurements for the main section were to begin just to the north of the islands. On the way measurements for two test stations were taken. Measurements for the main south-north section were started on January 10 beginning on the Falklands Plateau, with station intervals normally of 30 nm decreasing to 9 nm depending upon the topography. The station work was interrupted by a storm for a day during the period of January 14–15. On January 21 the ship turned northwest toward Brazil and then east to sample the Porto Alegre western boundary section, work which was completed on January 26. A storm and problems with the CTD wire and rosette interrupted the work for two days, but by January 31 the ship reached the Vema channel between the Argentine and Brazil basins, thereafter moving northward to continue the A17 section until February 10, when work at station 115 was completed. The ship then transited to Salvador de Bahia, Brazil, making two additional test stations before arriving in port on February 13. In Salvador de Bahia, French CTD and hydrographic personnel were exchanged. The CO_2 and nutrients measurement groups remained on board, however.

The *Maurice Ewing* departed Salvador de Bahia on February 17, 1994, and commenced sampling the Salvador western boundary section. However, difficulties were again experienced with the CTD and rosette, so that the completion of measurements for the latter section was delayed by two days. Due to these problems a decision was made to transit to Recife to pick up the expert Jean Pierre Gouillou, arriving from France, who was tasked with repairing the CTD and performing the software modification. The personnel transfer was completed during the period February 24–26, and the ship continued with the station samplings. With the removal of the first 500 m of the CTD wire, the CTD and rosette were restored to function, and after February 28 no additional problems were noted. By March 14 the main north-south section had been completed (station no. 210), and by March 15 the last section sampling between the Mid-Atlantic Ridge and Cayenne had begun, with sampling for the last station of the cruise (no. 235) taken just out from Cayenne on March 20. Some of the scientific personnel disembarked in Cayenne on March 21, 1994, whereupon the ship left immediately for Fort de France, Martinique, where the remainder of the scientific and crew disembarked.

A SOMMA (S/N 007) with CO_2 detected by coulometry was used to determine TCO_2 on the A17 section. TALK was determined by potentiometric titration using an automatic potentiometric titrator, Titrino Metrohm, with separate glass and reference electrodes. The pH was determined potentiometrically using a Metrohm Model 654 pH meter, a combination glass electrode, and National Bureau of Standards

(NBS) buffers for standardization. The CO_2 samples from more than 50% of the 235 CTD stations occupied during the A17 cruise were always drawn in conjunction with tracer samples (CFCs, tritium, etc.) and the standard WOCE variables (salinity, oxygen, temperature, and nutrients). As on previous cruises, not all stations could be sampled for TCO_2 and TALK because of the time required for analysis of the samples (see Table 3.1 for inorganic carbon sample distribution). However, pH and the WOCE standard variables were measured on all samples.

3. DESCRIPTION OF VARIABLES AND METHODS

3.1 Hydrographic Measurements

Water samples were collected using a 32-position rosette with 8-L Niskin bottles developed at the Laboratoire de Physique des Océans, IFREMER, Brest, France. The rosette was equipped with a Neil-Brown Mark-III CTD-O_2 (see Brown and Morrison 1978). In order to check the pressure measurements and temperature of the CTD on board, inverse thermometers and pressuremeters, type SIS, were mounted in the Niskin bottles to be fired at the bottom. The signal of the CTD was transmitted to the hydrographic data acquisition system of the LPO. This new system, created around a UNIX work station, allowed the user to see in real time the vertical profiles of the variables measured and calculated in order to check the quality of the signal transmitted by the CTD. The set of data transmitted by the CTD with a cadence of 32 cycles per second was recorded on a diskette. After each station, the data profiles were plotted vs pressure following the procedure of Billant (1985).

At the end of each cast, a full suite of water samples were drawn in the following order: CFCs, helium, oxygen, TCO_2, TALK, pH, nutrients, tritium, and salinity.

During the cruise 6778 samples were analyzed for salinity within 1–2 days of collection using a Guildline PORTASAL salinometer that was calibrated with standard seawater (Batch P123, K15 = 0.99994) produced at Wormley and dated June 10, 1993. The temperature of the thermostat was fixed at 21ºC until station 134, and at 22ºC from stations 135 to 235. The precision of the salinity determination was ±0.002 from 181 pairs of samples taken from two rosette sampling bottles closed at the same depth. The accuracy of the bottle salinity data was ±0.001.

Dissolved oxygen was determined by Winkler titration after the technique of Culberson and Huang (1987). The operational conditions and the analytical method, including the calculation of oxygen concentrations, followed the standard WOCE procedure and recommendations given by Culberson et al. (1991) in the WOCE Manual of Operations and Methods. Appropriate corrections for sample density, blanks, and volumetric expansion have been included. The precision of the analyses was ±0.78 µmol/kg from 196 pairs of samples taken from two rosette sampling bottles closed at the same depth. In total, 6756 oxygen analyses were completed during the A17 section.

The nutrients nitrate, nitrite, phosphate, and silicate were determined on every bottle closed on the A17 section by segmented flow analysis with a Technicon II Autoanalyzer. The combined nitrate and nitrite were determined after reduction of nitrate to nitrite in a Cd-Cu column according to the procedure of Mouriño and Fraga (1985). The method was calibrated by diluting concentrated primary standards of dried salts (KNO_3, KH_2PO_4, and SiF_6Na_2) dissolved in Milli-Q water with aged, filtered, and low-nutrient seawater and analyzing these substandards for each run of samples analyzed on the autoanalyzer. Phosphate was determined according to the procedure of Hansen and Grasshoff (1983) as modified by Alvarez-Salgado et al. (1992). The accuracy of the method was ±0.01 µmol/kg. Silicate was determined according to Hansen and Grasshoff (1983) using ascorbic acid as the reducing agent. The accuracy of the method was ±0.25 µmol/kg. Quality control and consistency of nutrient measurements can be seen in Groupe CITHER-2 (1996).

Table 3.1 summarizes the carbonate system variables measured on WOCE Section A17.

Table 3.1. Number of stations and samples analyzed for carbonate system variables on WOCE section A17

Parameter	Total stations on a section	No. of stations sampled for carbonate system	% of total stations sampled	CSP samples analyzed		
				Discrete	CRM[a]	Total
TCO_2	235	142	60	2,904	163	3,067
TALK	235	89	38	2,458	146	2,604
pH	235	235	100	5,756	1	5,757
Total				11,118	310	11,428

[a]Certified reference material.

3.2 Total CO_2 Measurements

As on previous cruises, TCO_2 was determined using an automated SOMMA dynamic headspace sample processor (S/N 007) with coulometric detection of the CO_2 extracted from acidified samples. A description of the SOMMA-coulometry system and its calibration can be found in Johnson et al. 1987; Johnson and Wallace 1992; and Johnson et al. 1993. Further details concerning the coulometric titration can be found in Huffman (1977) and Johnson et al. (1985). The methods used for discrete TCO_2 on WOCE sections have been extensively dealt with in previous reports (Johnson et al. 1998a) and only need to be briefly summarized.

Seawater samples were collected in 300-mL ground-glass stoppered bottles and poisoned with 100 µL of a 100% saturated solution of $HgCl_2$ to prevent biological alterations. Prior to analyses, the samples were stored in the dark and thermally equilibrated to within 2–3°C of the thermostatted SOMMA system (sample pipette and sample bath), which was kept at a constant temperature of approximately 20°C. The analysis of the TCO_2 samples was usually completed within 14 h of collection (see DOE 1994). Duplicate samples were usually collected on each cast at the surface and from the bottom waters and analyzed within the run of cast samples from which they originated. Following standard procedure, certified reference material (CRM) was routinely analyzed during the sample analyses (approximately one CRM for every 30 samples) according to DOE (1994). The CRMs were supplied by Dr. Andrew Dickson of the Scripps Institution of Oceanography, and the A17 cruise analysts were supplied with batch 18. The certified values for batch 18 were S = 35.298 and TCO_2 = 2115.15 µmol/kg. The CRM TCO_2 concentration was determined by vacuum-extraction and manometry in the laboratory of C. D. Keeling at Scripps Institution of Oceanography (SIO).

The SOMMA injected an accurately known volume of seawater from an automated to-deliver (TD) pipette into a stripping chamber. Following acidification of the seawater and continuous gas extraction, the resultant CO_2 was dried and coulometrically titrated on a model 5011 UIC coulometer with a maximum titration current of 50 mA in the counts mode [the number of pulses or counts generated by the coulometer's voltage-to-frequency converter (VFC) during the titration was displayed]. In the coulometer cell, the acid (hydroxyethylcarbamic acid) formed from the reaction of CO_2 and ethanolamine was titrated coulometrically (electrolytic generation of OH^-) with photometric endpoint detection. The product of the time and the current passed through the cell during the titration (charge in Coulombs) was related by Faraday's constant to the number of moles of OH^- generated and thus to the moles of CO_2, which reacted with ethanolamine to form the acid. The age of each titration cell was logged from its birth (time that electrical current is applied to the cell) until its death (time when the current is turned off). The age was measured in minutes from birth (chronological age) and in mgC titrated since birth (carbon age).

The system was controlled with an IBM-compatible PC equipped with two RS232 serial ports (coulometer and barometer), a 24-line digital input/output (I/O) card (solid state relays and valves), and an analog-to-digital (A/D) card (temperature, conductivity, and pressure sensors). The cards were manufactured by Real Time Devices (State College, PA 16803). The SOMMA temperature sensors (model LM34CH, National Semiconductor, Santa Clara, CA), with a voltage output of 10 mV/°F, were calibrated against thermistors certified to 0.02°F prior to the cruise using a certified mercury thermometer. These sensors monitored the temperature of SOMMA components, including the pipette, gas sample loops, and the coulometer cell. The SOMMA software was written in GWBASIC Version 3.20 (Microsoft Corp., Redmond, WA), and the instruments were driven from an options menu appearing on the PC monitor. With the coulometer operated in the counts mode, conversions and calculations were made using the SOMMA software rather than having the programs and the constants hardwired into the coulometer circuitry.

The SOMMA-coulometry systems were calibrated with pure CO_2. The calibration hardware consisted of an eight-port gas sampling valve (GSV) with two sample loops of known volume (determined gravimetrically by the method of Wilke et al. 1993) connected to the calibration gas through an isolation valve with the vent side of the GSV plumbed to a barometer. When a gas loop was filled with CO_2 at known temperature and pressure, the mass (moles) of CO_2 contained therein was calculated, and the ratio of the calculated mass to that determined coulometrically was the calibration factor (CALFAC). The CALFAC was used to correct the subsequent sample titrations for small departures from 100% recoveries (DOE 1994). The standard operating procedure was to make gas calibrations daily for each newly born titration cell (normally, one cell per day). Normally, two or three sequential gas calibrations were run per cell between the carbon ages of 3–9 mgC with the last CALFAC used for calculation of TCO_2 if it was consistent with the preceding CALFAC (i.e., agreement to ±0.1% or better). The mean CALFAC and the standard deviation of the mean are shown in Table 3.2. The CALFAC for system 007 remained very stable throughout the A17 section (the change in TCO_2 concentration due to change in CALFAC was 0.05% or 1.0 µmol/kg) over the period November 1993 through March 1994. The mean carbon age for the mean CALFAC shown in Table 3.2 was 8.9 ± 5.1 mgC titrated (N = 73).

The "to-deliver" volume (V_{cal}) of the sample pipettes was determined (calibrated) gravimetrically in November 1993 prior to the cruise. The calibration was checked periodically (for A17, once weekly) by collecting aliquots of deionized water dispensed from the pipette into preweighed serum bottles. The serum bottles were crimp-sealed and weighed immediately during the on-shore laboratory calibrations, or returned to shore where they were reweighed on a model R300S (Sartorius, Göttingen, Germany) balance as soon as possible. The apparent weight (g) of water collected (W_{air}) was corrected to the mass in vacuo (M_{vac}) and the calibrated TD pipette volume (V_{cal}) was calculated by dividing M_{vac} by the density of the calibration fluid at the calibration temperature (t_{cal}). For A17, V_{cal} was 28.9315 ± 0.0033 mL at a t_{cal} of 19.81°C (N = 47). The sample volume (V_t) at the pipette temperature was calculated for all A17 samples from the expression

$$V_t = V_{cal}\,[1 + a_v\,(t - t_{cal})] \quad , \tag{3.1}$$

where a_v is the coefficient of volumetric expansion for Pyrex-type glass (1×10^{-5}/°C), and t is the temperature of the pipette at the time of a measurement. The mean pipette temperature or analytical temperature (t) on the A17 section was 19.70 ± 0.29°C.

The factory-calibrated coulometer was electronically calibrated independently in the laboratory in November 1993, prior to the cruise as described in Johnson et al. (1993, 1996) and DOE (1994); and the terms INT_{ec} and $SLOPE_{ec}$ were obtained and entered into the software for system 007. The micromoles of carbon titrated (M), whether extracted from water samples or the gas loops, was

$$M = [\text{Counts} / 4824.45 - (Blank \times T_t) - (INT_{ec} \times T_i)] / SLOPE_{ec} \quad , \tag{3.2}$$

where 4824.45 (counts/μmol) is a scaling factor obtained from the factory calibration, T_t is the length of the titration in minutes, *Blank* is the system blank in μmol/min, INT_{ec} is the intercept from electronic calibration in μmol/min, T_i is the time in minutes during the titration where current flow was continuous, and $SLOPE_{ec}$ is the slope from electronic calibration. Note that the slope obtained from the electronic calibration procedure applied for the entire length of the titration, but the intercept correction applied only for the period of continuous current flow (usually 3–4 min) because the intercept can only be calculated from calibrated levels of current flowing continuously. The coulometer electronic calibration should not change over the duration of the cruise—shown for earlier cruises although not without some exceptions (Johnson et al. 1998b)—and system 007 was not electronically recalibrated during the A17 section. The electronic and gas calibration coefficients for system 007 are summarized in Table 3.2.

Table 3.2. Electronic calibration and mean gas calibration coefficients for system 007 coulometer on WOCE section A17

Period	$SLOPE_{ec}$	INT_{ec} (μmol/min)	CALFAC (n)	St. Dev.	Rel. st. dev. (%)
Nov. 1993	0.994635	0.000840	1.005434 (2)	0.000230	0.02
A17 section	0.994635	0.000840	1.005049 (73)	0.000466	0.05

For water samples, the discrete TCO_2 concentration in μmol/kg was calculated from

$$TCO_2 = M \times CALFAC \times [1 / (V_t \times \rho)] \times d_{Hg} \quad , \tag{3.3}$$

where ρ is the density of sea water in g/mL at the measurement temperature and sample salinity calculated from the equation of state given by Millero and Poisson (1981), and d_{Hg} is the correction for sample dilution with bichloride solution (for A17 d_{Hg} = 1.000333).

Quality control and quality assurance (QC-QA) were assessed from the results of the 163 CRM analyses made during the A17 section. The mean and standard deviation of the differences between the measured and the certified TCO_2 (measured – certified) are given in Table 3.3, and the temporal distribution of the differences is plotted in Fig. 3.1.

Table 3.3. Mean analytical difference (ΔTCO_2 = measured – certified) and the standard deviation of the differences between measured and certified TCO_2 on WOCE section A17

System	ΔTCO_2 (μmol / kg)	± St. dev. (μmol / kg)	N
0.7	0.26	1.64	163

The overall accuracy of the CRM analyses was better than 1 μmol/kg on system 007 for the A17 section. The precision of the CRM determination is the standard deviation of the differences between the measured and certified CRM TCO_2 (± 1.64 μmol/kg, N = 163). The outlier results are summarized in Table 3.4. Because six of the CRMs analyzed on A17 were considered to be outliers—meaning that the analytical difference (ΔTCO_2) between the measured and certified TCO_2 exceeded ±5.0 μmol/kg (measured – certified)—these data are not included in Table 3.4.

Throughout the WOCE work, care was taken to titrate a limited number of samples in each coulometer cell to avoid excessive cell carbon ages and coulometer-cell-solution exhaustion or failure. In actual practice, this has meant that, on average, no cell was used to titrate more than a single 36-bottle station (a cell age of ≈35 mgC titrated), and experience has confirmed this practice (Johnson et al. 1998b). This convention was not followed on the A17 section because, at this point in the program, experimental

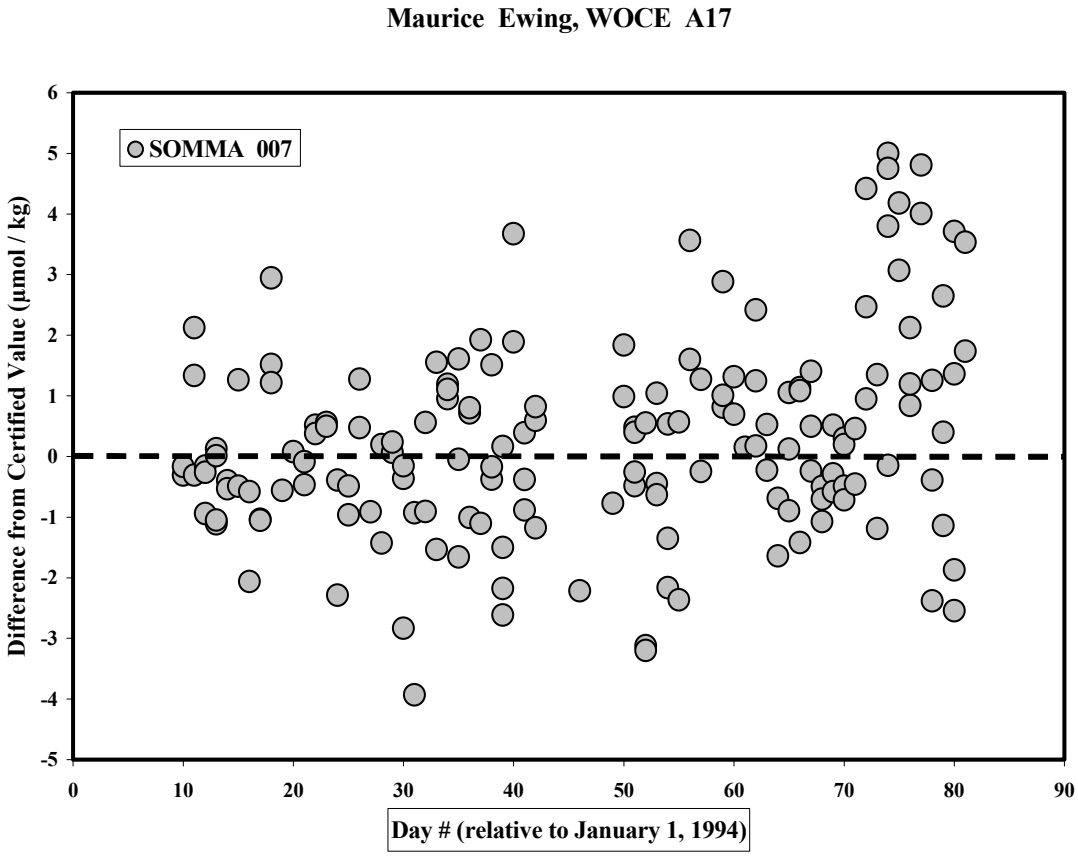

Fig. 3.1. Temporal distribution of differences between measured and certified TCO_2 for CRM analyzed on SOMMA-coulometry system 007 during WOCE section A17. The differences were calculated by subtracting the certified TCO_2 from the measured TCO_2.

evidence was needed concerning the actual lifetime of the cells. Hence, the A17 cells were run so that their carbon ages (mgC titrated) routinely exceeded the 35 mgC limit by factors of 1.5–2.5. Based on thousands of CRM analyses made during the CO_2 survey and an overall precision of ±1.6 µmol/kg for the coulometric determination of TCO_2, an empirical definition of "cell failure" was proposed. Failure was defined as two successive CRM analyses with a difference >5 µmol/kg on a cell whose carbon age exceeded 35 mgC. The 5 µmol/kg limit was chosen because it was equivalent to three standard deviations in precision. These "failures" have been designated as outliers (see Table 3.4). Table 3.4 indicates that two of the A17 cells (on 2.9 and 3.17) exhibited outliers, but that the second CRM analysis at a later carbon age with these cells was accurate. Hence, the sample data obtained with them were not flagged. For "failed" cells (2.24, 3.19, and 3.22), a quality flag of 3—the WHPO questionable measurement flag—was assigned to those samples analyzed between the carbon age at the time of the last accurate CRM analysis and the carbon age at failure or cell death. However, based on WHPO criteria, the flagged measurements could be correct but may be open to interpretation; we have no direct evidence that they are not correct. The data shown in Table 3.4 also suggest that the original decision to set a conservative limit on cell lifetimes of 35 mgC was sound because failures or outliers become more frequent after 35 mgC.

The second phase of the QC-QA procedure was an assessment of precision, which is presented in Table 3.5. The single-system precision was determined from samples with duplicates analyzed on system 007. Single-system precision has been assessed in Table 3.5 as "between-sample" precision (σ_{bs}),

Table 3.4. History and disposition of cells exhibiting unsatisfactory or outlier analytical differences (ΔTCO_2 = measured − certified) for CRM analyzed on WOCE section A17

Date	CRM no.	Carbon age (mgC)	ΔTCO_2 (µmol / kg)	Comments
2.7.94	595	30.3	−8.19	Cell terminated
2.9.94	596	34.4	+11.47	CRM OK at 53.2 mgC; no sample data flagged
2.24.94	261	59.4	−6.99	Sample data flagged between 40 and 71 mgC
3.17.94	140	64.8	+7.12	CRM OK at 86.8 mgC; no sample data flagged
3.19.94	47	92.3	+6.46	Sample data flagged between 73 and 92 mgC
3.22.94	441	65.9	+5.91	Sample data flagged between 45 and 71 mgC

Table 3.5. Precision of the discrete TCO_2 analyses on WOCE section A17

Mean absolute difference		
σ_{bs} (µmol / kg)	± St. dev. (µmol / kg)	K
Single-system precision		
0.73	1.02	226

which is the mean absolute difference between duplicates (N = 2) drawn from the same Niskin bottle, where K is the number of samples with duplicates analyzed.

Although the single-system sample precision (±0.73 µmol/kg) was excellent, it cannot be taken as the precision of the TCO_2 determination for the A17 section for two reasons unique to this cruise:

1. During section A17, the replicate samples were always analyzed one right after the other. On other WOCE sections, replicate analyses were spaced such that the interval between replicates was >3 but <12 h. This was done to provide a measure of drift (change in system response) during a sequence of sample analyses on the assumption that drift would be reflected in the single-system precision by an increase in the imprecision of the duplicate analyses. Running the duplicates in sequence eliminated the possibility of detecting drift, and sample precision consequently was probably overestimated.

2. An evaluation of the samples for which duplicates were taken indicated that 10 duplicate pairs exhibited very poor precision (absolute difference between replicates from 7 to 280 µmol/kg). These samples were flagged when the data set was submitted, and they are not included in the precision given in Table 3.5. Further study indicated that 9 of the 10 pairs originated from the surface rosette sample bottle (stations 8, 13, 25, 51, 61, 155, 177, 188, and 230) from 0 to 5 m, and that only one pair originated from a deep bottle (5334 m at station 157). If the flagged results were used to calculate precision, then σ_{bs} was 3.34 ± 18.70 µmol/kg (K = 115) for the rosette surface bottle duplicates and 0.82 ± 1.41 µmol/kg (K = 121) for the nonsurface bottle duplicates. These data suggested that the observed imprecision did not lay with the TCO_2 measurement system. The cause was probably due to an occasional but undetected mechanical problem with the rosette, especially when the rosette bottles were closed at or near the surface. Alternatively,

the on-deck sampling procedure at the rosette could have caused the degassing of CO_2 into the Niskin bottle headspace during the time it took to draw the duplicate samples.

For the above reasons, the precision of the TCO_2 determination on the A17 section was taken to be the standard deviation of the CRM differences (measured − certified) or ±1.64 µmol/kg (Table 3.3) instead of the single-system precision of ±1.02 µmol/kg given in Table 3.5.

The final step in the QC-QA procedure was the ship-to-shore comparison. Here, sample duplicates (commonly called the "Keeling samples") were analyzed in real time at sea by continuous gas extraction/coulometry and later, after storage, on shore by vacuum extraction/manometry. The Keeling samples were collected in specially provided, threaded 500-mL glass bottles with 4 mL of headspace volume, poisoned with 100 µL of a saturated $HgCl_2$ solution, and then sealed airtight with a greased ground-glass stopper that was secured to the bottle with a threaded plastic screw cap. The cap was bored out to fit over the top of the stopper and mated to the bottle threads. The airtight seal was made by gently tightening the cap until a secure seal between the stopper and bottle was attained. Overtightening caused the bottles to break immediately or during transit so that considerable care and practice were required to prepare a sample that would survive the journey back to SIO. The manometric analyses for 21 samples collected from 14 stations during section A17 were completed by December 1994 in the SIO laboratory of C. D. Keeling. The results of the comparison are given in Table 3.6. The mean ship-to-shore analytical difference (ship − shore) and the standard deviation of the differences was −0.09 ± 1.50 µmol/kg (N = 21). This was the best agreement between the ship and shore duplicate sample analyses made by any measurement group with or without BNL-supported equipment during the entire CO_2 survey. Prior to and subsequent to the A17 section, the ship-to-shore comparisons had and have consistently yielded slightly lower TCO_2 values (≅2 µmol/kg) for samples analyzed in real time aboard ship compared to the reference analyses made at SIO (Wallace 2002).

Table 3.6 is particularly useful in view of the problems with surface bottle precision, which suggested the possibility of mechanical or chemical problems during rosette sampling during the A17 section. Inspection of the data in the table indicates excellent agreement between surface sample duplicates analyzed on ship and on shore and indicates that the incidence of poor precision, for whatever reason, probably did not compromise the accuracy of the A17 TCO_2 data. Indeed, Tables 3.3, 3.5, and 3.6 show that the TCO_2 data set for the A17 section was internally consistent and highly accurate and precise with respect to the both the CRM, the seawater duplicate samples, and the ship-to-shore comparison seawater samples. Hence, no correction for CRM differences has been applied to the data, and the TCO_2 data clearly met survey criterion for accuracy (≤4 µmol/kg) and precision. The reader is also referred to a recent assessment of TCO_2 data quality in the Atlantic Ocean resulting from comparisons of TCO_2 analyzes from crossover points sampled by different cruises between 1990 and 1998 (Wanninkhof et al. 2003).

3.3 Total Alkalinity Measurements

TALK was determined with a Titrino Metrohm automatic potentiometric titrator using separate glass working and reference electrodes. Potentiometric titrations were carried out in a covered but not completely closed (headspace present) titration flask to a final pH of 4.4 as described by Pérez and Fraga (1987a). The electrodes were standardized using an NBS buffer of pH 7.413, checked using an NBS buffer of 4.008, and acclimated in a seawater solution buffered to a pH of 4.4. To determine the systematic errors produced by variations of the electrode residual liquid-junction potential, titration curves were performed each week in CO_2-free seawater acidified to pH 4.0 with hydrochloric acid as described by Culberson (1981). The titration curves were linearized, and the inverse slope was taken to represent the apparent hydrogen ion activity coefficient. The decimal logarithm difference (ranging from 0.01 to 0.06) between the apparent activity coefficients of the electrode and those given by Mehrbach

Table 3.6. TCO_2 difference (ship − shore) between duplicate seawater samples analyzed in real time by coulometry (ship) and onshore by manometry at SIO

Station	Date	Niskin no.	Depth (m)	TCO_2 ship (µmol/kg)	TCO_2 shore (µmol/kg)	ΔTCO_2 Ship − shore (µmol/kg)
12	12.01.94	14	3036.0	2260.57	2260.48	0.09
30	18.01.94	13	3048.0	2212.28	2217.38	−5.10
30	18.01.94	32	2.0[a]	2026.70	2027.72	−1.02
63	29.01.94	10	3060.0	2209.41	2209.67	−0.26
63	29.01.94	32	4.0	2032.91	2034.28	−1.37
93	06.02.94	12	2674.0	2174.51	2173.42	1.09
93	06.02.94	32	5.0	2062.76	2062.25	0.51
114	11.02.94	13	3044.0	2185.21	2184.92	0.29
114	11.02.94	32	0.0	2059.69	2059.25	0.44
145	25.02.94	14	3051.0	2180.87	2181.92	−1.05
163	03.03.94	12	3248.0	2183.38	2180.82	2.56
163	03.03.94	32	0.0	2003.62	2001.88	1.74
179	08.03.94	32	0.0	2019.41	2018.74	0.67
191	10.03.94	11	3049.0	2174.76	2174.80	−0.04
204	13.03.94	32	0.0	2021.11	2021.04	0.07
210	15.03.94	32	0.0	2020.76	2019.84	0.92
215	16.03.94	11	3051.0	2181.42	2180.43	0.99
215	16.03.94	32	0.0	2025.57	2025.71	−0.14
223	19.03.94	32	5.0	2020.16	2021.35	−1.19
228	20.03.94	6	3061.0	2179.78	2179.40	0.38
228	20.03.94	32	0.0	2018.21	2019.70	−1.49
Mean						−0.09
St. dev.						±1.50[b]
N						21

[a]The surface samples are usually the mean of two analyses. The SIO results are always mean of two analyses.

[b]The precision of the method was ±1.64 µmol/kg.

et al. (1973) at the same salinity and temperature with their electrode was the pH difference added to the final pH of the sample alkalinity titration to make our results equivalent with theirs using the constants of Mehrbach et al. (1973). During the cruise, the TALK of 146 CRMs from batch 18 was determined by this method. The TALK for batch 18 was not known at the time of the cruise because it was not measured during the original TCO_2 certification. Subsequently, TALK was measured at SIO on archived samples from batch 18 with the value TALK = 2297.77 µmol/kg. The mean and standard deviation of the differences between the measured and the certified TALK (measured − certified) are given in Table 3.7, and the temporal distribution of the differences is plotted in Fig. 3.2.

Table 3.7. Mean analytical difference (ΔTALK = measured – certified) and standard deviation of differences between measured and certified TALK on WOCE section A17

Mean ΔTALK (µmol/kg)	± St. dev. (µmol/kg)	N
+2.13	1.72	146

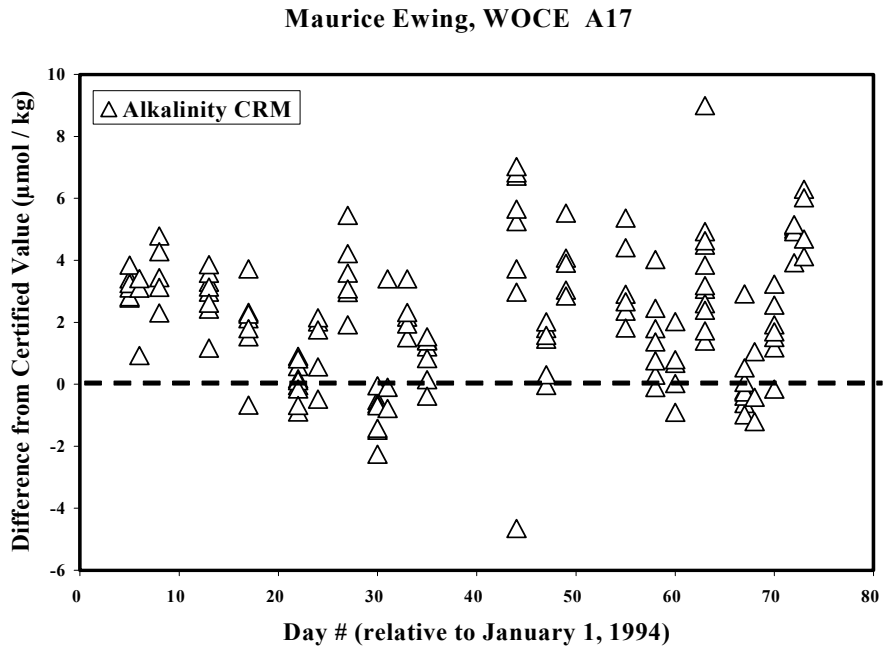

Fig. 3.2. Temporal distribution of differences between measured and certified TALK for CRM analyzed during WOCE section A17. The differences were calculated by subtracting the certified TALK from the measured TALK.

The precision of the method was assessed from 59 pairs of samples taken from two rosette sampling bottles closed at the same depth. The mean difference or precision of the TALK determination was 1.2 ± 1.1 µmol/kg, or approximately ±0.1%.

The TALK values were checked with CRMs and according to the data presented in Fig. 3.2 and Table 3.7, the mean analytical difference between measured and certified CRM was 2.1 ± 1.7 µmol/kg. Normally, the correction of 2 µmol/kg should be applied to the TALK values measured on WOCE A17 section. On the other hand, in the comparison of carbon system variables measured in the Atlantic Ocean, Wanninkhof et al. (2003) showed a deviation of –7 µmol/kg with respect to A09 in the crossover analysis, but the multiple-parameter linear regression suggested that the TALK data were 5–6 µmol/kg higher compared with data from other cruises in the tropical and southern regions. Wanninkhof et al. (2003) argued that the internal consistency suggested that the TALK was higher by 8 µmol/kg; therefore, a decrease in TALK of 6 µmol/kg would bring the values in better agreement. However, because a decrease was suggested for A09, the bias between A17 and A09 remains of the same magnitude. Taking into account that the offset of 6 µmol/kg is the recommended correction, no adjustment was recommended.

In order to clarify this apparent offset, a comparison of A17 TALK data was made with WOCE A14 data obtained during the CITHER-3 cruise carried out in January and February 1995 in the eastern South Atlantic, and with recent cruises carried out following approximately the same line A17 (FICARAM II and FICARAM IV) in March and April 2001 and 2002, respectively. Figure 3.3 shows the comparison of

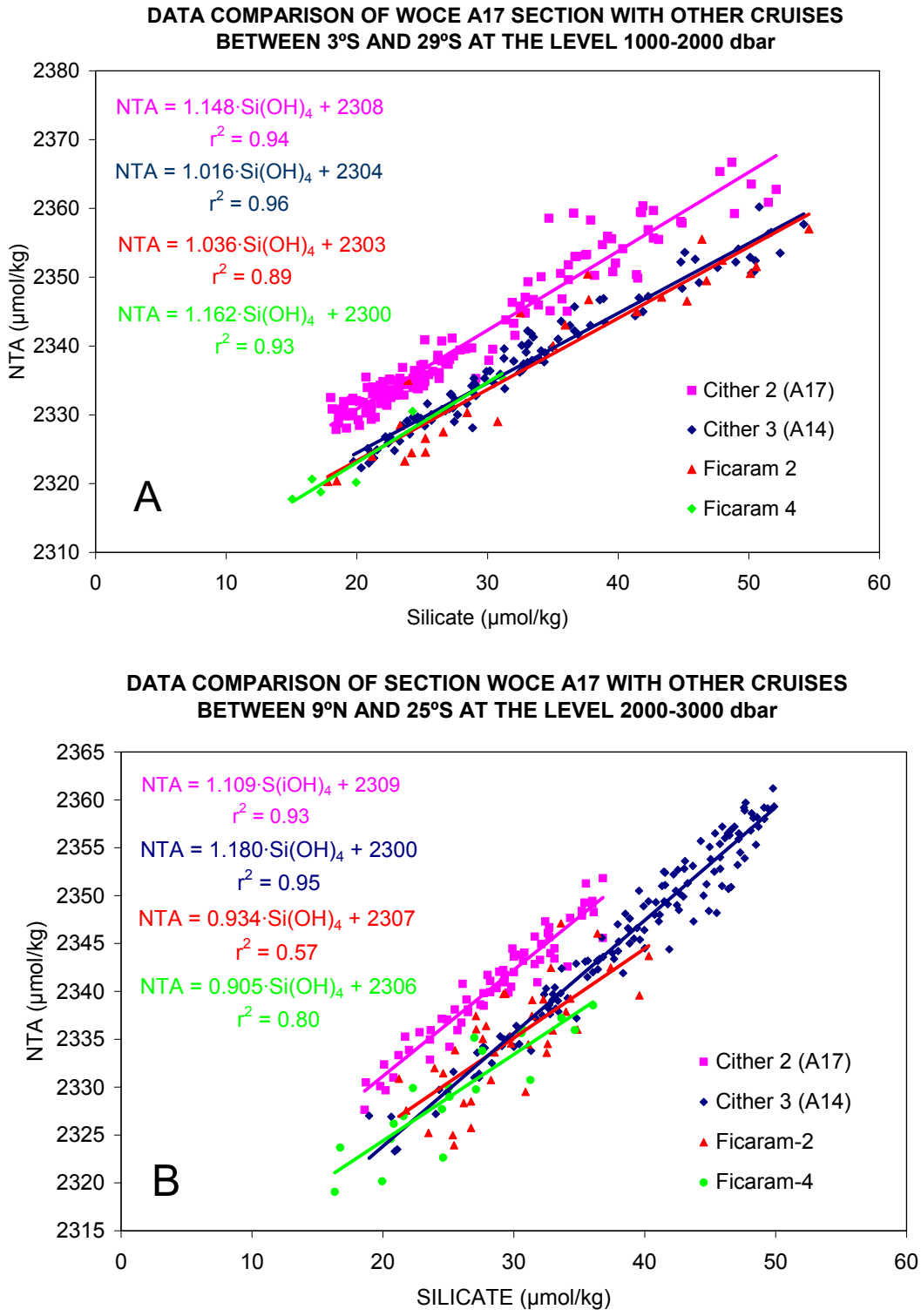

Fig. 3.3. Relationship between normalized TALK (NTA) and silicate, both in µmol/kg, for the cruises CITHER-2, CITHER-3, FICARAM-2, and FICARAM-4. (A) Between 3ºS and 29ºS at 1000–2000 dbar. (B) Between 9ºN and 25ºS at 2000–3000 dbar.

the normalized TALK (NTA) data with regard to the silicate content among the four cruises. The upper graph presents the data comparison corresponding to the zone between 3ºS and 29ºS at 1000–2000 dbar. The lower graph exhibits the same kind of comparison but along the latitude 9ºN to 25ºS at 2000–3000 dbar. In both cases, the slopes NTA vs silicate of the three cruises CITHER-3, FICARAM-2 and FICARAM-4 are coincident, and the slope NTA vs silicate for CITHER-2 is higher and parallel to the others. Taking a concentration of silicate of 30 µmol/kg, we find a difference of 8.0 ± 0.6 µmol/kg in the zone 3ºS–29ºS and 7.7 ± 1.1 µmol/kg in the zone 9ºN–25ºS.

The comparison made with recent cruises is coincident with the internal consistency made by Wanninkhof et al. (2003) that suggested that A17 TALK was higher by 8 µmol/kg. Therefore, a downward correction of 8 µmol/kg was applied to all the TALK values.

3.4 pH Measurements

For pH measurements, a Metrohm 654 pH meter with a Metrohm 6.0233.100 combination glass electrode was used. The pH electrode was standardized in the same way as the alkalinity electrodes [NBS buffer at pH 7.413 to calibrate, NBS buffer at pH 4.008 to check calibration according to Pérez and Fraga (1987b), acclimatization in a pH 4.4 seawater buffer]. The latter was made up in 1 kg of CO_2-free seawater with 4.0846 g of $C_8H_5KO_4$ and 1.52568 g of $B_4O_7Na_2$-$10H_20$ (borax). The temperature measurement for each pH sample was done with a Pt-100 probe, and pH values were normalized to 15°C. Changes in electrode response were corrected in the same manner as for alkalinity using titration curves generated at the end of the cruise in seawater (S = 34.655) with HCl at 25.7°C. The resulting correction factor for pH was 0.026 ± 0.001, which was added to the pH analyses. The precision of the pH determination was assessed from 186 pairs of samples collected from two rosette bottles closed at the same depth in the same way as for TALK. The precision of the determination was 0.002 ± 0.003.

3.5 Underway pCO_2 Measurements

Surface pCO_2 was measured continuously using a shower-type equilibrator with detection of CO_2 by an infrared analyzer according to a design and techniques reported by Broecker and Takahashi (1966). Partial pressures of CO_2 in the surface seawater have been computed from the CO_2 concentration measured in dried equilibrated air in the following manner. The pressure of equilibration, reduced by the vapor pressure of water (computed at the equilibrator temperature) was applied to the CO_2 concentration to yield the pCO_2 at equilibrator temperature. This value was then adjusted to the sea surface temperature using the relationship given by Takahashi et al. (1993) and expressed in units of microatmospheres (µatm). The R/V *Maurice Ewing* was not equipped with a thermosalinograph at the time of this cruise. Surface temperature was measured by means of a pair of thermistors attached to the keel. These thermistors were calibrated in place against a thermometer traceable to NIST. The resolution of the device used to read the thermistor was 0.1ºC. These data will likely be combined with other surface pCO_2 data from the Atlantic Ocean to form a separate report and will not be discussed further here.

3.6 Internal Consistency Checks

The pH values have a good precision, as shown by the reproducibility (0.002 ± 0.003) of the 186 pairs of samples collected from two rosette bottles closed at the same depth. During the cruise, surface seawater stored in 25-L plastic containers was used as pH "quasi-steady" seawater sub-standard (SSS). At each station, the pH of this SSS was measured before and after each series of samples, but samples of CRM were not analyzed. Therefore, the pH data could be displaced with respect to one station to other. The

internal consistency comparison made in Wanninkhof et al. (2003) between measured and calculated (from TALK and pH) TCO_2 showed a bias. They suspect that the calculation involving pH is the culprit.

Consequently, to correct the deviations of pH between stations, we carried out an internal consistency check using the CRM-referenced TCO_2 and TALK data and the fugacity of CO_2 (fCO_2) in surface waters. The first step to check if there is an offset is to compare the variations of fCO_2 (calculated – measured) in surface waters (ΔfCO_2) with the variations of the average TCO_2 (calculated – measured) of water column data (ΔTCO_2). Figure 3.4 shows a negative and significant correlation ($r^2 = 0.39$) between ΔfCO_2 and ΔTCO_2, which means that there is a pH bias between stations.

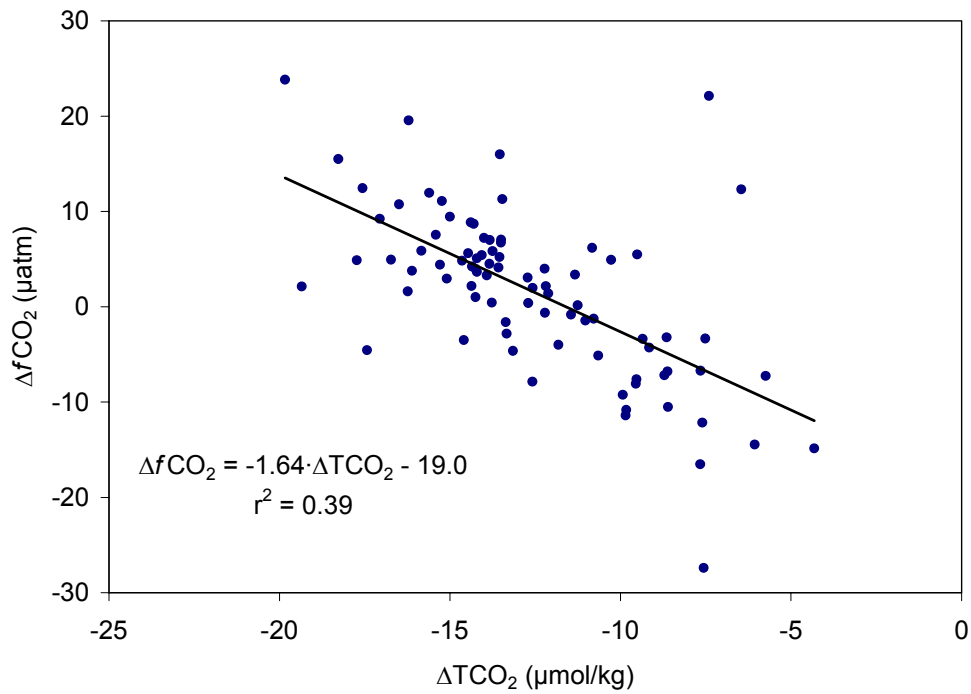

Fig. 3.4. Relationship between variations of fCO_2 (calculated – measured) in surface waters (ΔfCO_2) and variations of the average TCO_2 (calculated – measured) of water column data (ΔTCO_2).

The correction of pH was made using the surface data of calculated pH from measured fCO_2 and TCO_2. In all cases the dissociation constants of Mehrbach et al. (1973) as modified by Lueker et al. (2000) were used. After pH values were corrected, the relationship between variations of fCO_2 (calculated – measured) and variations of the average TCO_2 (calculated – measured) did not show any correlation ($r^2 = 0.002$), indicating that the bias had disappeared.

Once pH values were corrected, TCO_2 was calculated from pH and TALK and compared with the measured TCO_2. Figure 3.5 is a plot of the coulometrically measured TCO_2 vs TCO_2 derived from the TALK and pH measurements made on the A17 section. This plot shows a high regression ($r^2 = 0.997$; $p < 0.0001$) with an average error of the estimate of ±2.8 µmol/kg and a slope very close to unit (1.0088 ± 0.0011). The average difference between calculated and measured TCO_2 during the cruise was 4.3 ± 2.9 µmol/kg.

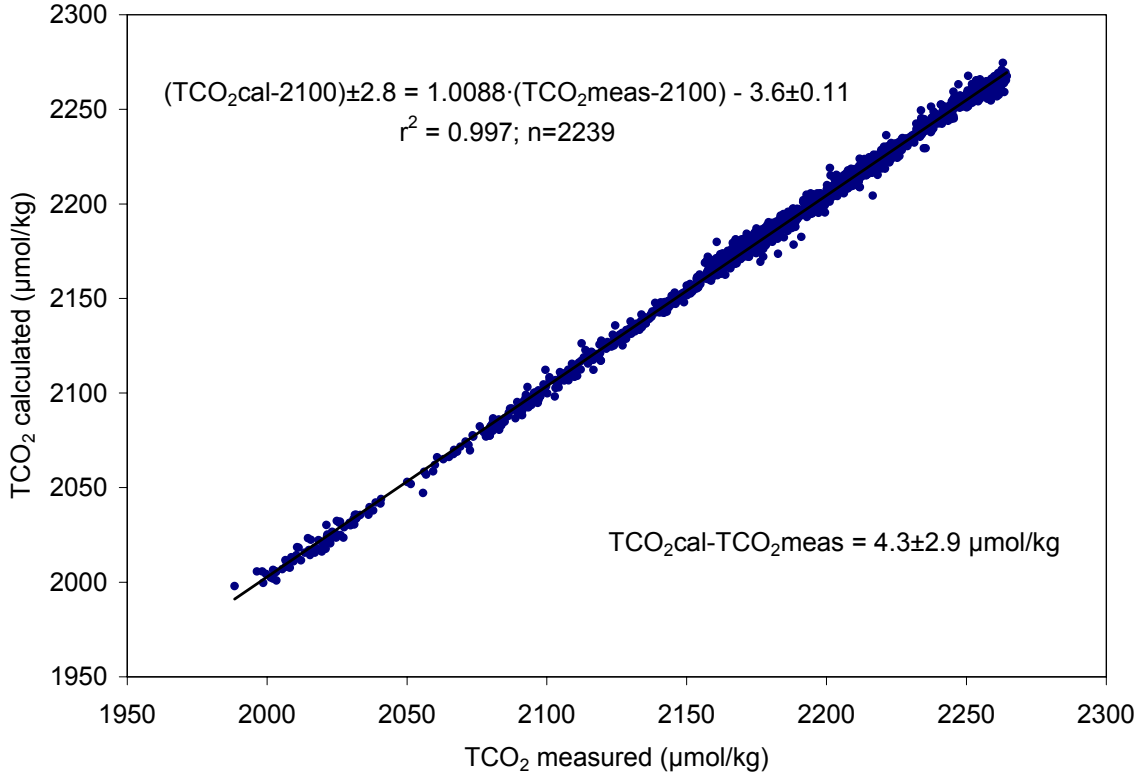

Fig. 3.5. Relationship between measured and calculated TCO_2 from TALK and pH using the dissociation constants given by Lueker et al. (2000).

Figure 3.6 compares the fCO_2 underway measured and fCO_2 calculated from surface TALK and pH data waters obtained during the A17 cruise. There is a high regression ($r^2 = 0.992$, $p < 0.0001$) with an average error of the estimate of ±3.1 µatm and a slope close to unity (1.0055 ± 0.0066). The average difference between calculated and measured pCO_2 was –2.1 ± 3.1 µatm.

After the TALK and pH corrections, the regressions between both measured and calculated TCO_2 and fCO_2 are higher ($r^2 = 0.997$, $r^2 = 0.992$, respectively) than those obtained by Ríos and Pérez (1999) using the original dissociation constants of Mehrbach et al. (1973) [$r^2 = 0.990$, $r^2 = 0.966$, respectively]. Also, their slopes are closer to unity in both cases (1.00088 vs 1.024 for TCO_2 and 1.0055 vs 0.899 for fCO_2), and the average error of their estimates decreases from ±4.4 to ±2.8 µmol/kg for TCO_2 and from ±6 to ±3.1 µatm for fCO_2.

3.7 Recommendations

In the light of the comparison of the TALK data with other cruises and the analysis of the internal consistency among the four variables of carbon system measured during the A17 section, we would suggest to apply the following corrections for the data in the CDIAC database:

1. According to the comparison between TALK measured on A17 and recent cruises (CITHER-3, FICARAM-2, and FICARAM-3), a downward correction of 8 µmol/kg is proposed for TALK.
2. Based on the internal consistency check carried out among the four carbon system variables, we propose to modify the pH measurements adding by stations the values gathered in Table 3.8.

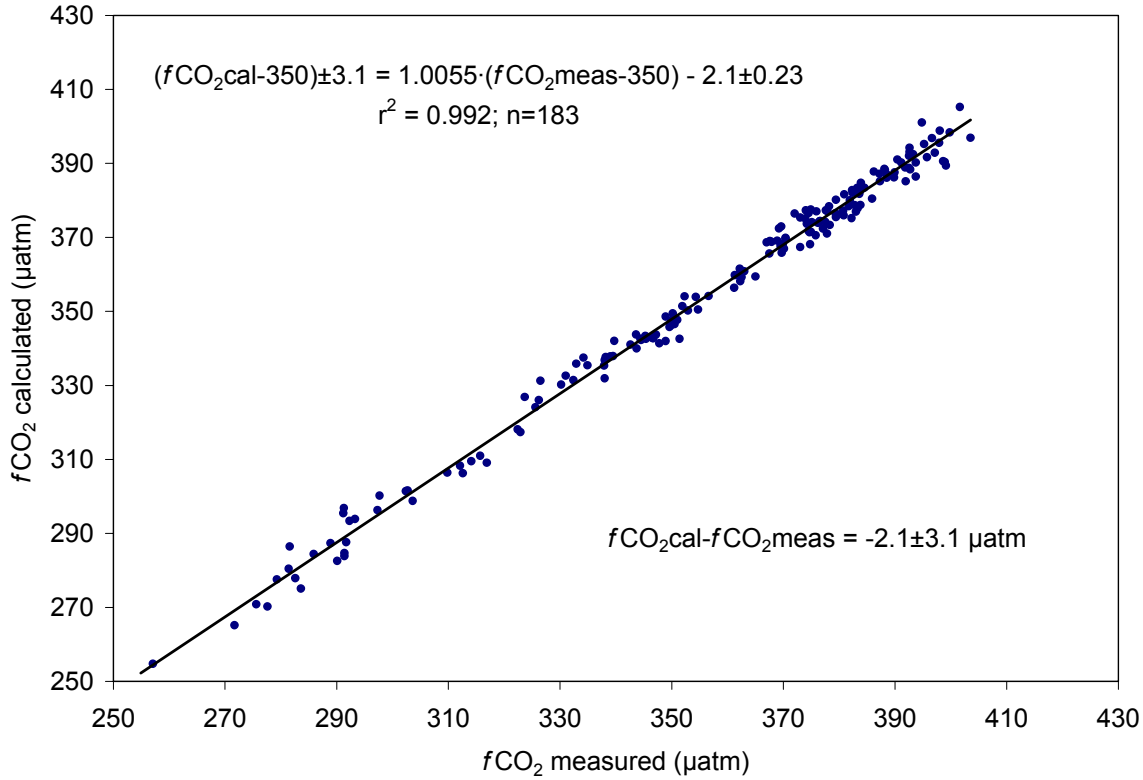

Fig. 3.6. Relationship between fCO_2 measured and fCO_2 calculated from TALK and pH using the dissociation constants given by Lueker et al. (2000).

Table 3.8. Recommended corrections for pH values measured during the WOCE section 17

Station	ΔpH	Station	ΔpH	Station	ΔpH	Station	ΔpH	Station	ΔpH
3	0.003	49	0.007	95	–0.007	143	0.001	189	0.005
4	0.013	50	0.012	96	–0.003	144	0.001	190	0.005
5	0.011	51	0.009	97	–0.007	145	0.011	191	0.007
6	0.003	52	0.003	98	–0.007	146	–0.007	192	0.007
7	0.018	53	0.003	99	–0.006	147	0.007	193	0.003
8	0.006	54	0.007	100	–0.007	148	0.007	194	0.007
9	0.033	55	0.003	101	–0.009	149	0.005	195	–0.001
10	0.023	56	0.003	102	–0.001	150	–0.003	196	–0.005
11	0.028	57	0.013	103	–0.011	151	–0.007	197	–0.001
12	0.013	58	0.003	104	–0.011	152	–0.007	198	0.011
13	0.013	59	0.003	105	–0.012	153	–0.007	199	0.009
14	0.003	60	0.011	106	–0.009	154	–0.005	200	0.009
15	0.017	61	0.017	107	–0.009	155	–0.007	201	0.009
16	0.013	62	0.011	108	–0.002	156	–0.007	202	0.009
17	0.019	63	0.005	109	–0.009	157	0.003	203	0.009
18	0.019	64	0.011	110	–0.009	158	0.003	204	0.009
19	0.011	65	0.011	111	–0.007	159	0.003	205	0.009

Table 3.8 (continued)

Station	ΔpH	Station	ΔpH	Station	ΔpH	Station	ΔpH	Station	ΔpH
20	0.009	66	0.011	112	–0.009	160	0.003	206	0.009
21	0.023	67	0.015	113	–0.009	161	0.007	207	0.007
22	0.021	68	0.017	114	–0.003	162	0.007	208	0.007
23	0.017	69	0.007	115	–0.005	163	0.001	209	0.007
24	0.011	70	0.007	118	0.008	164	0.003	210	0.007
25	–0.002	71	0.003	119	0.008	165	–0.003	212	–0.003
26	0.005	72	0.005	120	0.015	166	0.011	213	0.003
27	0.017	73	0.001	121	0.003	167	0.001	214	0.003
28	0.015	74	0.003	122	0.015	168	0.001	215	–0.001
29	0.017	75	–0.005	123	0.003	169	0.003	216	0.003
30	0.019	76	0.003	124	0.015	170	0.003	217	0.003
31	0.013	77	0.003	125	0.003	171	0.001	218	–0.007
32	0.003	78	0.006	126	–0.001	172	–0.007	219	0.003
33	0.009	79	0.001	127	0.003	173	–0.009	220	0.009
34	0.009	80	0.001	128	0.003	174	–0.007	221	0.003
35	–0.001	81	0.001	129	0.003	175	–0.001	222	0.003
36	0.011	82	–0.005	130	0.003	176	0.002	223	0.006
37	0.013	83	0.001	131	0.005	177	0.007	224	0.003
38	0.003	84	–0.009	132	0.003	178	0.007	225	0.003
39	0.003	85	–0.009	133	0.003	179	0.013	226	0.001
40	–0.007	86	–0.009	134	0.003	180	0.007	227	0.003
41	0.003	87	–0.014	135	–0.005	181	0.007	228	0.007
42	0.003	88	–0.009	136	0.003	182	–0.003	229	0.003
43	0.003	89	–0.009	137	0.003	183	–0.003	230	0.006
44	–0.011	90	–0.007	138	0.003	184	–0.011	231	0.003
45	–0.007	91	–0.015	139	0.003	185	–0.006	232	0.008
46	0.005	92	–0.007	140	0.009	186	–0.009	233	0.003
47	0.011	93	–0.001	141	0.003	187	–0.001	234	0.003
48	0.007	94	0.003	142	0.003	188	0.005	235	0.003

4. HOW TO OBTAIN THE DATA AND DOCUMENTATION

This database (NDP-084) 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. (This is built in to 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/ndp084/
ftp> dir
ftp> mget (files)
ftp> quit

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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