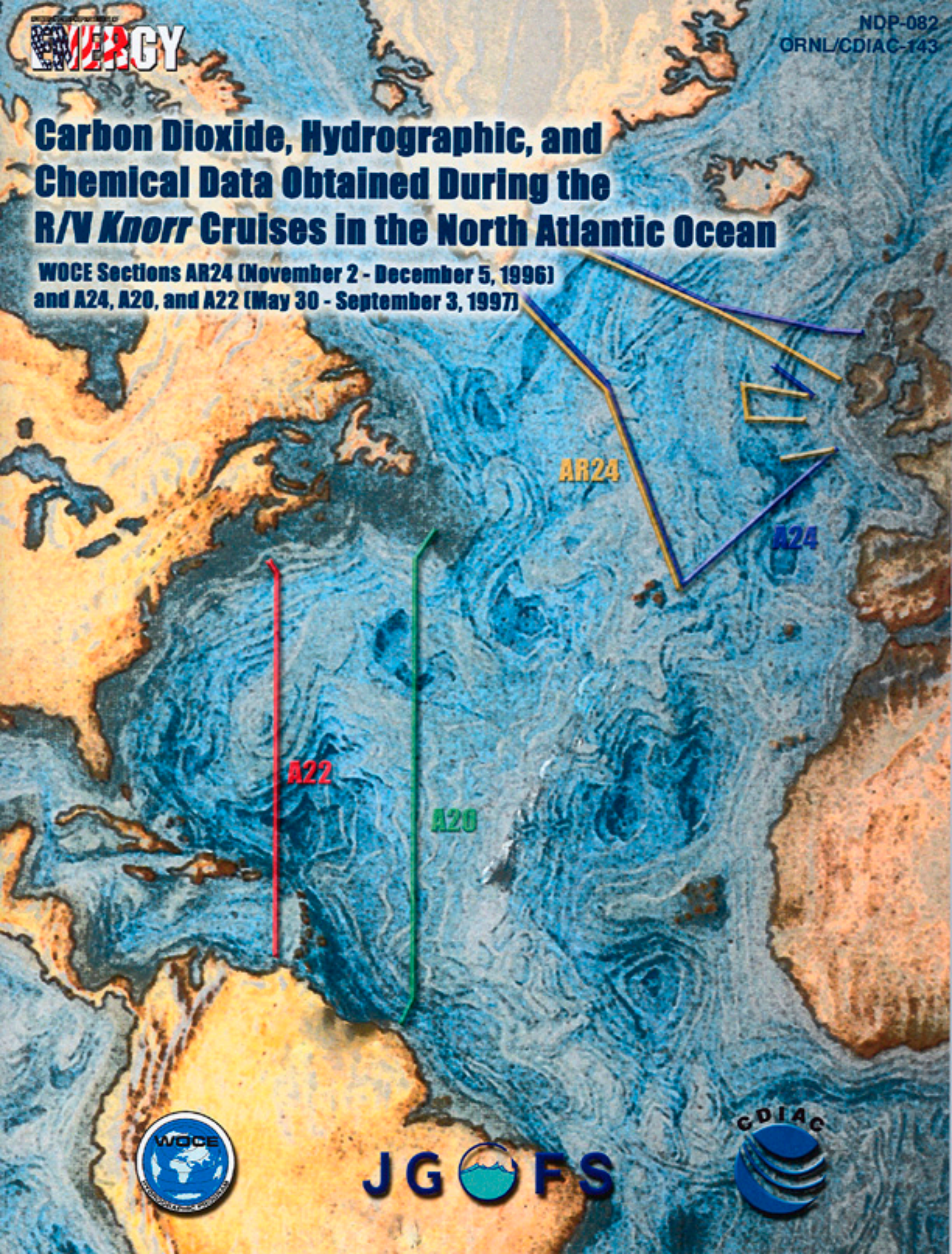
NDP-082
ORNL/CDIAC-143

Carbon Dioxide, Hydrographic, and Chemical Data Obtained During the R/V *Knorr* Cruises in the North Atlantic Ocean

WOCE Sections AR24 (November 2 - December 5, 1996) and A24, A20, and A22 (May 30 - September 3, 1997)



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CARBON DIOXIDE, HYDROGRAPHIC, AND CHEMICAL DATA OBTAINED DURING THE R/V *KNORR* CRUISES IN THE NORTH ATLANTIC OCEAN ON WOCE SECTIONS AR24 (NOVEMBER 2–DECEMBER 5, 1996) AND A24, A20, AND A22 (MAY 30–SEPTEMBER 3, 1997)

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Date Published: September 2003

Prepared for the
Climate Change Research Division
Office of Biological and Environmental Research
U.S. Department of Energy
Budget Activity Numbers KP 12 04 01 0 and KP 12 02 03 0

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UT-BATTELLE, LLC
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-00OR22725

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ACRONYMS

ACCE	Atlantic Circulation and Climate Change Experiment
A/D	analog-to-digital
ADCP	acoustic Doppler current profiler
ALACE	autonomous Lagrangian circulation explorer
BOD	biological oxygen demand
BNL	Brookhaven National Laboratory
^{14}C	radiocarbon
CALFAC	calibration factor
CDIAC	Carbon Dioxide Information Analysis Center
CFC	chlorofluorocarbon
CMDL	Climate Monitoring and Diagnostics Laboratory
CO_2	carbon dioxide
CTD	conductivity, temperature, and depth sensor
CRM	certified reference material
DOE	U.S. Department of Energy
emf	electro-magnetic fields
EXPOCODE	expedition code
FTP	file transfer protocol
GMT	Greenwich mean time
GPS	global positioning system
IAPSO	International Association for the Physical Sciences of the Ocean
I/O	input-output
IR	infrared
JGOFS	Joint Global Ocean Flux Study
kn	knots
LADCP	lower ADCP
LDEO	Lamont-Doherty Earth Observatory
MATS	Miami University alkalinity titration systems
NBIS	Neil Brown Instrument system
NDP	numeric data package
NOAA	National Oceanic and Atmospheric Administration
nm	nautical mile
NSF	National Science Foundation
ODF	Ocean Data Facility
ODV	Ocean Data View
ORNL	Oak Ridge National Laboratory
OSU	Oregon State University
PC	personal computer
PDF	Portable Document Format
PI	principal investigator
PU	Princeton University
QA	quality assurance
QC	quality control
R/V	research vessel
RSMAS	Rosenstiel School of Marine and Atmospheric Sciences
SIO	Scripps Institution of Oceanography
SOMMA	single-operator multiparameter metabolic analyzer
SSW	standard seawater
TALK	total alkalinity

TCO_2	total carbon dioxide
TD	to-deliver
UH	University of Hawaii
UM	University of Miami
UW	University of Washington
VFC	voltage to frequency converter
WHOI	Woods Hole Oceanographic Institution
WHPO	WOCE Hydrographic Program Office
WOCE	World Ocean Circulation Experiment
WHP	WOCE Hydrographic Program

ABSTRACT

Johnson K., R. Key, F. Millero, C. Sabine, D. Wallace, C. Winn, L. Arlen, K. Erickson, K. Friis, M. Galanter, J. Goen, R. Rotter, C. Thomas, R. Wilke, T. Takahashi, and S. Sutherland. 2003. *Carbon Dioxide, Hydrographic, and Chemical Data Obtained During the R/V Knorr Cruises in the North Atlantic Ocean on WOCE Sections AR24 (November 2–December 5, 1996) and A24, A20, and A22 (May 30–September 3, 1997)* A. Kozyr (ed.) ORNL/CDIAC-143, NDP-082. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee, 41 pp. doi: 10.3334/CDIAC/otg.ndp082

This documentation describes the procedures and methods used to measure total carbon dioxide (TCO_2) total alkalinity (TALK), and partial pressure of CO_2 (pCO_2) at hydrographic stations on the North Atlantic Ocean sections AR24, A24, A20, and A22 during the R/V *Knorr* Cruises 147-2, 151-2, 151-3, and 151-4 in 1996 and 1997. Conducted as part of the World Ocean Circulation Experiment (WOCE), the expeditions began at Woods Hole, Massachusetts, on October 24, 1996, and ended at Woods Hole on September 3, 1997. Instructions for accessing the data are provided.

A total of 5,614 water samples were analyzed for discrete TCO_2 using two single-operator multiparameter metabolic analyzers (SOMMAs) coupled to a coulometer for extracting and detecting CO_2. The overall accuracy of the TCO_2 determination was ± 1.59 µmol/kg. The TALK was determined in a total of 6,088 discrete samples on all sections by potentiometric titration using an automated titration system developed at the University of Miami. The accuracy of the TALK determination was ± 3 µmol/kg. A total of 2,465 discrete water samples were collected for determination of pCO_2 in seawater on sections A24, A20, and A22. The pCO_2 was measured by means of an equilibrator-IR system by scientists from Lamont-Doherty Earth Observatory. The precision of the measurements was estimated to be about ± 0.15%, based on the reproducibility of the replicate equilibrations on a single hydrographic station.

The North Atlantic data set is available as a numeric data package (NDP) from the Carbon Dioxide Information Analysis Center. The NDP consists of 12 ASCII data files, one Ocean Data View–formatted data file, a NDP-082 ASCII text file, a NDP-082 PDF 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; partial pressure of CO_2; coulometry; gas chromatography; World Ocean Circulation Experiment; North Atlantic Ocean; hydrographic measurements; carbon cycle.

1. BACKGROUND INFORMATION

The World Ocean Circulation Experiment (WOCE) Hydrographic Program (WHP) was a major component of the World Climate Research Program. The primary WOCE goal 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 impetus for the carbon system measurements arose from 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 [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 to make the carbon measurements 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) 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 the oceanic heat transport (Bryden and Hall 1980; Brewer, Goyet, and Drysen 1989; Holfort et al. 1998; Roemmich and Wunsch 1985) and to build a database suitable for carbon-cycle modeling and the estimation of anthropogenic CO_2 increase in the oceans. The CO_2 survey took advantage of the sampling opportunities provided by the WOCE cruises during this period, and the final data set was expected to cover on the order of 23,000 stations. Wallace (2002) recently reviewed the goals, conduct, and initial findings of the survey.

This report discusses the results of the research vessel (R/V) *Knorr* expedition along the WOCE Sections AR24, A24, A20, and A22 [cruises 147-2, 151-2, 151-3, and 151-4, respectively (Fig. 1)]. The latter three cruises not only were part of WOCE but also were a component of the Atlantic Circulation and Climate Change Experiment (ACCE). The ACCE was intended to improve the understanding of the entrainment and transformation of warm saline subtropical water into the subpolar North Atlantic waters, with special emphasis on sampling the North Atlantic Current region. This region plays an important role in the exchange of CO_2 between the subtropical and subpolar gyres. The exchange between these gyres affects the magnitude and direction of air-sea CO_2 exchange in the North Atlantic and is therefore an important factor in the global carbon cycle. By 1997 the goal of high-quality measurements of chemical and physical parameters had been completed in all of the major oceans except the North Atlantic. Hence the cruises documented here also represent the concluding phase of the DOE-sponsored Global CO_2 Survey.

The expedition (section AR24) started at Woods Hole, Massachusetts, USA, on October 24, 1996, with a transit to the Azores; the station work began on November 2, 1996. The 1997 cruises started from Ponta Delgada, Azores, on May 30, 1997, and ended in Woods Hole on September 3, 1997, after stops in Halifax, N.S., Canada, and Port of Spain, Trinidad. The large-scale three-dimensional distribution of temperature, salinity, and chemical constituents, including the carbonate system parameters measured on these cruises (TCO_2, and TALK on the AR24 section and TCO_2, TALK, and pCO_2 on A24, A20, and A22 sections), will be plotted using the data from these sections. Knowledge of these parameters and their initial conditions will enable researchers to determine heat and water transport, as well as carbon transport, which will contribute to the understanding of processes affecting climate change. The sections described in this report include WOCE Section A22, the only Caribbean transect of the WOCE program. In addition, the stations occupied on these cruises repeat some sections sampled during the International Geophysical Year during the 1950s. They also include measurements from the eastern subpolar gyre of source and overflow waters from the Labrador, Norwegian, Greenland, and Iceland Seas. They give good coverage of boundary currents, particularly the Deep Western Boundary Current; and repeating AR24 and A24 provides some insight into seasonal variation in the North Atlantic.

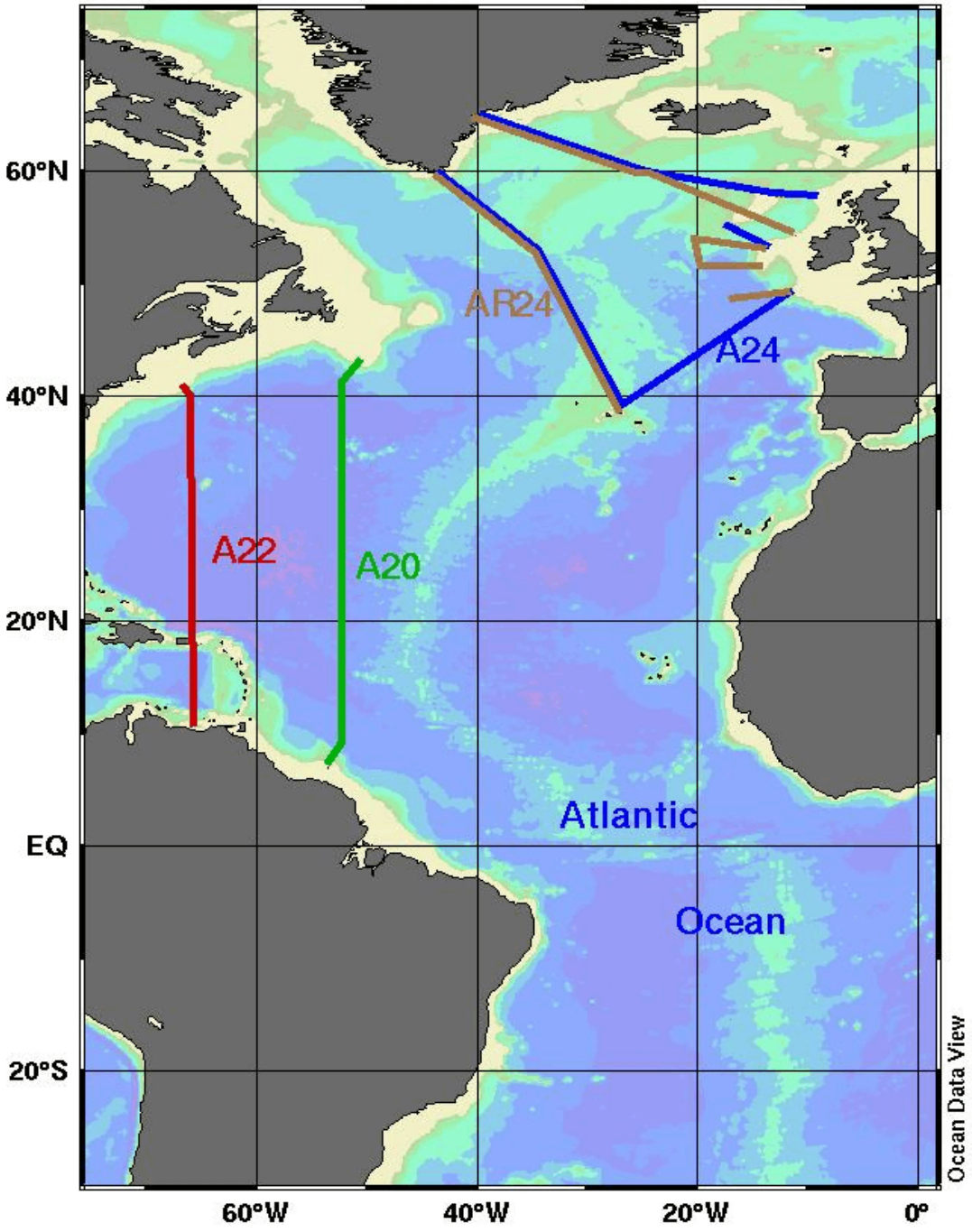

Fig. 1. **The cruise tracks during the North Atlantic survey expeditions along WOCE Sections AR24, A24, A20, and A22.**

This data documentation is the result of the cooperative efforts of chemical oceanographers from Brookhaven National Laboratory (BNL), the University of Hawaii (UH), Lamont-Doherty Earth Observatory (LDEO), and the University of Miami's Rosenstiel School of Atmospheric and Marine Science (RSMAS), U.S.A. The work aboard the R/V *Knorr* was supported by DOE under contract DE-ACO2-76CH00016 and DE-FG02-93ER61540. The authors are also especially grateful to the Sonderforschungsbereich 460 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 *Knorr:* Technical Details and History

The R/V *Knorr*, built in 1969 by the Defoe Shipbuilding Company in Bay City, Michigan, is owned by the U.S. Navy. It was turned over to the Woods Hole Oceanographic Institution (WHOI) in 1971 for operation under a charter agreement with the Office of Naval Research. It was named for E. R. Knorr, a hydrographic engineer and cartographer who in 1860 held the title of Senior Civilian and Chief Engineer Cartographer of the U.S. Navy Office. Its original length and beam were 245 and 46 ft, respectively. Beginning on February 6, 1989, it underwent a major midlife retrofit or "jumbo-izing" at the McDermott Shipyard in Amelia, Louisiana. A midsection was added to the ship to stretch its length by 34 ft, to 279 ft, and fore and aft azimuthing propulsion systems were added to make it one of the most maneuverable and stable ships in the oceanographic fleet. By the time it was returned to WHOI in late 1991, the retrofit had taken 32 months. The WOCE section P6 was the vessel's first scientific cruise after the retrofitting. The R/V *Knorr* was designed for a wide range of oceanographic operations and possesses antiroll tanks and a strengthened bow for duty in icy waters. Like its sister ship, the R/V *Melville*, it is used for ocean research and routinely carries scientists from many different countries. Table 1 provides a list of technical characteristics of the R/V *Knorr*.

Table 1. Technical characteristics of the R/V *Knorr*

Ship name:	R/V *Knorr*			
Call sign:	KCEJ			
Basic dimensions:				
Gross registered tonnage		2518 T	Displacement	2958 LT
Overall length		279 ft	Beam	46 ft
Draught (maximum)		16.5 ft	Service speed	12 kn
Maximum speed		14.5 kn	Minimum speed	0.1 kn
Main deck clear length		126 ft		
Personnel:				
	Crew	24		
	Scientists	34		
Main engine:	4 × Mak6M 322 = 4 × 1000 kW at 750 rpm			
Propulsion:	Twin lips diesel-electric, azimuthing stern thrusters, 1500 SHP			
Bow thruster:	Lips retractable azimuthing 900 SHP			
Fuel capacity:	160,500 gal			
Maximum cruise duration:	60 days (12,000 nm)			
Nautical equipment:	Integrated navigation system Potable water generator 2 instrument hangars Winches: 1 heavy-duty trawl with 30,000 ft of ½-in. wire 2 hydrographic, both with 30,000 ft of hydrowire Hydraulic cranes on the starboard side aft and midships Scientific storage space of 1,320 ft^2 Portable van space Machine shop Fume hoods Uninterruptible power supply Air conditioning Library/lounge 3680 ft^2 of laboratory space for multidisciplinary research			

2.2 The North Atlantic Ocean CO_2 Survey Cruises Information

2.2.1 WOCE Section AR24

Ship name:	R/V *Knorr*
Expocode	316N147-2
Cruise/Leg:	147-2/A24R
Ports of call:	Ponta Delgada, The Azores
Dates:	November 2, 1996–December 5, 1996
Funding support:	DOE, NSF
Chief scientist:	Dr. Mike McCartney, WHOI

Parameters measured, institution, and responsible investigators

Parameter	Institution	Responsible investigators
CTD[1], Salinity	WHOI	M. McCartney
Nutrients	WHOI	M. McCartney
Oxygen	WHOI	M. McCartney
CFCs[2]	SIO	R. Weiss
Tritium, helium	LDEO	P. Schlosser
TCO_2	UH/BNL	R. Rotter, C. Winn, K. M. Johnson
TALK	RSMAS	M. Galanter, J. Goen, F. Millero
Underway pCO_2	AOML	R. Wanninkhof
^{14}C	PU	R. Key, R. Rotter
ADCP[3]/LADCP[4]	UH	E. Firing

2.2.2 WOCE Section A24

Ship Name	R/V *Knorr*
Expocode	316N151-2
Cruise / Leg	151-2/A24
Ports of call	Ponta Delgado, St. Michael, Azores; Halifax, N.S., Canada
Dates	May 30, 1997–July 5, 1997
Funding support	DOE, NSF
Chief Scientist	Dr. Lynne Talley, SIO

Parameters measured, institution, and responsible investigators

Parameter	Institution	Responsible investigators
CTD, salinity	SIO	L. Talley, F. Delahoyde, C. Mattson
Nutrients	SIO/ODF	J. Swift, D. Masten, S. Becker
Oxygen	SIO/ODF	J. Swift, J. Boaz
CFCs	SIO	R. Weiss, F. Van Woy, M. Vollmer
Tritium, helium	LDEO	P. Schlosser, D. Smith, S. Khatiwala
TCO_2	BNL	D. Wallace, K. Johnson, L. Arlen
TALK	RSMAS	F. Millero, M. Galanter, J. Goen
pCO_2, discrete	LDEO	T. Takahashi, A. Wilson
Underway pCO_2	SIO	R. Weiss, F. Van Woy
^{14}C	PU	R. Key, R. Rotter
ADCP/LADCP	UH	E. Firing

2.2.3 WOCE Section A20

Ship name	R/V *Knorr*
Expocode	316N151_3
Cruise/leg	151-3/A20
Ports of call	Halifax, N.S, Canada, Port of Spain, Trinidad
Dates	July 17, 1997–August 10, 1997
Funding support	DOE, NSF
Chief scientist	Dr. Robert Pickart, WHOI

Parameters measured, institution, and responsible investigators

Parameter	Institution	Responsible investigators
CTD, salinity	WHOI	R. Pickart, M. Swartz
Nutrients	OSU	L. Gordon, J. Jennings, B. Sullivan
Oxygen	WHOI	R. Pickart
CFCs	LDEO	W. Smethie, E. Gorman, L. Baker, D. Chaky
Tritium, helium	WHOI	W. Jenkins, P. Landry, S. Birdwhiste
TCO_2	BNL	D. Wallace, R. Wilke, K. Erickson, K. M. Johnson
pCO_2, discrete	LDEO	T. Takahashi, J. Goddard
TALK	RSMAS	F. Millero, C. Sabine, C. Thomas
Underway pCO_2	SIO	R. Weiss
^{14}C	PU	R. Key, C. Sabine, C. Thomas
Bio-optics	LDEO	C. Knudson
Halocarbons	DU	R. Moore, P. Morneau, W. Groszko
ADCP/LADCP	WHOI	D. Torres
ALACE[5] floats	UW	D. Swift

2.2.4 WOCE Section A22

Ship name	*Knorr*
Expocode	315N151_4
Cruise/leg	151-4/A22)
Ports of call	Port of Spain, Trinidad; Woods Hole, MA, USA
Dates	August 15, 1997–September 3, 1997
CO_2 funding support	DOE, NSF
Chief scientist	Dr. Terrence Joyce, WHOI

Parameters measured, institution, and responsible investigators

Parameter	Institution	Responsible investigators
CTD, salinity	WHOI	T. Joyce, G. Knapp, L. Stein
Nutrients	OSU	L. Gordon, A. Ross, J. Arrington
Oxygen	WHOI	G. Knapp, D. Wellwood
CFCs	LDEO	W. Smethie, L. Baker, D. Chaky, E. Gorman, R. Swartz
Tritium, helium	WHOI	W. Jenkins, J. Curtis, P. Landry
TCO_2	BNL	D. Wallace, K. M. Johnson, K. Erickson
pCO_2, discrete	LDEO	T. Takahashi, A. Wilson
Underway pCO_2	SIO	R. Weiss
$14C$	PU	R. Key, C. Thomas, R. Rotter

ADCP, LADCP	WHOI	F. Bahr
Halocarbons	DU	W. Groszko
pALACE floats	UW	D. Swift
Observer	Venezuela	Antonio Perez-Aguirre

[1]CTD–conductivity, temperature, and depth sensor
[2]CFC–clorofluorocarbon
[3]ADCP–acoustic Doppler current profiler
[4]LADCP–lower ADCP
[5]ALACE–autonomous Lagrangian circulation explorer

Participating institutions

AOML	Atlantic Oceanographical and Meterological Laboratory
BNL	Brookhaven National Laboratory
LDEO	Lamont-Doherty Earth Observatory
UH	University of Hawaii
OSU	Oregon State University
PU	Princeton University
RSMAS	Rosensteil School of Marine and Atmospheric Science, University of Miami
SIO	Scripps Institution of Oceanography
SIO/ODF	Ocean Data Facility Scripps Institution of Oceanography
UW	University of Washington
WHOI	Woods Hole Oceanographic Institution
DU	Dalhousie University

2.3 Brief Cruise Summary

For the section AR24 (cruise 147-2), the TCO_2 and TALK systems were placed on board and set up on the R/V *Knorr* in Woods Hole, Massachusetts, during the period October 21–24, 1996, by the University of Miami TALK and the UH/BNL TCO_2 measurement groups. The systems were successfully tested, and the *Knorr* departed Woods Hole on October 24 for the Azores with Mike McCartney as chief scientist. C. Winn was the CO_2 group leader during the transit to the Azores and was present when one of the benches supporting one of the SOMMA-coulometer systems broke loose, threatening to destroy the analytical system. Fortunately, the analytical equipment suffered only minor damage, and the minor repairs required were completed by the time the ship was ready to begin the AR24 section. C. Winn left the ship in the Azores and was replaced by R. Rotter, A. Adams, and J. Tegeder, with R. Rotter serving as the group leader. The ship departed on the AR24 cruise from Ponta Delgada on November 1, 1996. The cruise track was, with minor deviations, basically a winter version of the two transoceanic A24 sections completed during the summer of 1997 (see Fig. 1).

During the AR24 section, the principal problem with the TCO_2 SOMMA systems Nos. 004 and 030 was the malfunctioning of the solenoid pinch valves used to dispense the sample. Some were damaged and ceased to work, while others were sensitive to power fluctuations and worked intermittently. Replacement valves were quickly consumed, so that SOMMA system No.30 became the primary system. As a consequence, the bulk of the sample TCO_2 analyses completed during the AR24 section (see Table 4 in Sect. 3.2) were made on system 030. These problems also resulted in the sampling of 10 fewer stations for TCO_2 than for TALK during the cruise, with most of the discrepancies occurring between November 14 and 20, 1996. After the concluding station 176 on December 2, 1996, the *Knorr* docked in South Hampton, United Kingdom, on December 3, 1996.

Following the AR24 section, the analytical systems were repaired and re-calibrated. They were then set up on the R/V *Knorr* in Woods Hole during the week of May 13–19, 1997, by the University of

Miami TALK and the BNL TCO_2 measurement groups. Three SOMMA-coulometer systems and three TALK titrators were set up for the three WOCE sections (A24, A20, and A22). In addition to the discrete TCO_2 systems (S/Ns 004 and 030), a third system (S/N 006) was set up for underway surface TCO_2 measurements. The equilibrator-infrared (IR) gas analyzer system for the determination of partial pressure of CO_2 (pCO_2) in discrete sea water samples was set up by the scientists from LDEO. The discrete TCO_2 systems were successfully calibrated using both CO_2 calibration gas and the certified reference material (CRM) on May 17, 1997, while the calibration of the underway system (006) was completed on May 30. The *Knorr* departed Woods Hole on May 20 (Leg 151_1) with Dr. Tom Rossby as chief scientist. The TALK group remained onboard to test the instruments on the "shake-down" transit from Woods Hole to the embarkation point for Leg 151-2, Ponta Delgada on the island of St. Michael, Azores.

Some 300 underway surface samples were drawn and analyzed for TALK during the shake-down cruise, but these data are not reported to the Carbon Dioxide Information Analysis Center (CDIAC). Greg Eischeid of WHOI completed the plumbing connections between the ship's underway intake and the underway SOMMA (006). After correcting some minor problems, he obtained the required flow of 1 L/min through the underway system. Problems with operating the underway pipette were also encountered, but they were eliminated by software changes coordinated through BNL, so that by the time the ship arrived in Ponta Delgada, the underway system was operational. The most serious problem with the discrete TCO_2 systems was that an erratic transmission reading with the system 030 coulometer made titrations impossible. This program was temporarily corrected by "jiggling" the voltage-to-frequency converter (VFC) and ensuring that all associated chips were properly seated. System 004 was tested successfully during the shake-down cruise, which ended on May 29, 1997, in Ponta Delgada.

K. M. Johnson departed JFK Airport in New York on May 27, 1997, for Ponta Delgada via Lisbon and arrived on May 28 in the Azores, where he joined L. Arlen, who was already in Ponta Delgada. The TALK and TCO_2 measurement groups moved onboard ship on May 29 and readied the systems for the following day, when the ship departed Ponta Delgada on section A24 with Dr. Lynne Talley as chief scientist. Sample analysis began on system 004 immediately, but the system 030 coulometer once again exhibited unstable erratic transmission readings and was immediately replaced with the back-up unit. Sample analysis with this unit began on May 31, 1997.

The cruise track for section A24 was basically rectangular, encompassing four separate sections (see Fig. 1) starting and ending in the Azores. The first section began at Terceira, Azores, proceeding northeastward toward the Goban Spur and crossing the Mediterranean Water/Labrador Sea Water mixing zone obliquely. Upon completion of the first section, the ship was diverted to Cork, Ireland, for an emergency exchange of crew members. The second section crossed the southern Rockall Trough, from Porcupine Bank to the southern end of the Rockall Bank. The third section crossed the northern part of the subpolar gyre, from the Hebrides to Rockall Bank, to Hatton Bank, to the Reykjanes Ridge and to Greenland near Angmassalik, crossing the Rockall Trough just north of the Anton Dohrn Seamount. Ice conditions at Greenland were favorable, and sampling was completed at stations well onto the shelf (average depth 500 m). After a transit southward to Cape Farewell, Greenland, the fourth section began at Cape Farewell and proceeded southeastward to the Charlie Gibbs Fracture Zone and then back to Terceira with the last Station on June 28, 1997. After a 6-day transit, the ship docked in Halifax, Nova Scotia, on July 5.

The weather remained uniformly good throughout Leg A24, and all carbonate measurement systems were operated essentially without major problems. Perhaps the biggest disappointment was the failure to rendezvous with the nearby R/V *Meteor* in early June for a social gathering. Some 153 hydrographic stations were occupied during A24. TCO_2 was measured on 92 of these stations and TALK was measured on 90. Therefore, roughly 60% of the stations occupied on this cruise were sampled for TALK and TCO_2. This proportion was somewhat higher than the 50% of stations sampled on typical WOCE cruises as a result of an accelerated frequency of sampling. The increased frequency was brought about by making the A24 station interval dependent on bathymetry, which often varied radically over distances much less than the proscribed WOCE station interval of 30 nm. The carbon group sampled as many stations as possible given the limits imposed by the length of time required for the TCO_2 and TALK determinations. In

addition, discrete surface samples were taken at most stations, and the underway system was operated continuously on Section A24. Originally the A24 section was scheduled to terminate in St. Johns, but because repairs were required, the *Knorr* put into Halifax on July 4, 1997. An attempt was made to arrange for a back-up coulometer or to repair the damaged coulometer before the next cruise. Unfortunately, this did not work out, and scientists were still left without a back-up coulometer for the coming cruises.

Because of the delay for repairs in Halifax, no direct handoff between CO_2 measurement crews was made. The TCO_2 relief team consisting of Rick Wilke and Ken Erickson arrived well after the first crew had left and just prior to the *Knorr's* departure on July 17, 1997, on section A20. However, Wilke had been briefed at BNL concerning the performance of the TCO_2 systems and possible problems due to de-powering of the ship during the repairs. The relief crew for TALK consisted of Chris Sabine and Carrie Thomas, who were also responsible for the ^{14}C samples.

The *Knorr* left Halifax bound for Port of Spain, Trinidad, on July 17, 1997, with Dr. Robert Pickart as chief scientist and 31 other scientists. From July 17 until August 10, 1997, except for a couple of dog legs across the shelf regions, the *Knorr* occupied a series of stations in a straight line from the Newfoundland Shelf to the Suriname Shelf along approximately 52º W (WOCE Section A20). This Section is also a part of the ACCE and one of two North Atlantic WOCE meridional long-lines (the second long-line, A22, was visited during the subsequent cruise). In the early days of the cruise, heavy fog off the Grand Banks made for slow going. Otherwise, the excellent weather experienced during the cruise allowed for the sampling of 95 hydrographic stations, which was more than planned. After the initial test station in 3000 m at 57º W, the ship steamed to the 1000-m isobath and the work commenced. During A20, the water masses sampled included the slopewaters, the Laborador Current, the Labrador Sea Water, the Deep Western Boundary Current, the Gulf Stream with a warm core ring, the Sargasso Sea, and finally, as the ship turned toward Trinidad, the North Brazil Current system. On the depths less than 1000 m, a 24-position conductivity, temperature, and depth (CTD) sensor was used, while for greater depths, a 36-position CTD was used. Hydographic station intervals ranged from 3 nm on the shelf, to 10–15 nm across the slopes, to 15–25 nm across the Gulf Steam and 40 nm in the Sargasso Sea. Other physical oceanographic tasks completed included the deployment of 11 floats and drifters and the deployment or recovery of 4 moorings. The TCO_2 systems 004 and 006 continued to operate well, but system 030 required the replacement of one pinch valve and a faulty isolation valve on July 19. Thereafter, this instrument functioned satisfactorily. The *Knorr* arrived in Port of Spain, Trinidad, on August 10, 1997.

K. Johnson left New York on August 12 to relieve R. Wilke of the TCO_2 measurement group, while K. Erickson and C. Thomas remained on board to continue the TCO_2 and TALK measurements for the next section A22.

The *Knorr* departed Port of Spain at 9 A.M. on August 15, and the first station was sampled only 12 hours out of port. Station 1 was a joint station with the R/V *Hermano Gines* from the EDIMAR Laboratory, Margarita, Venezuela, just outside the sill of the Cariaco Basin. Some joint nutrient samples were taken and analyzed aboard each ship. Then the *Knorr* began the Caribbean portion of the A22 transect, which ended with Station 23 on 300-m depth south of Puerto Rico on August 20, 1997. The *Knorr* jogged around the eastern end of the Island, and the transect was resumed north of Puerto Rico along approximately 66ºW and continued until Station 77 in 200 m of water on the shelf south of Cape Cod, Massachusetts, on September 2, 1997. Some 77 WOCE hydrostations were occupied during this leg. In addition, 10 floats and 9 drifters were deployed and one mooring was recovered. All of the carbon parameter instruments, including the underway SOMMA, functioned satisfactorily until the end of the cruise; and fortunately a back-up coulometer was never needed. The R/V *Knorr* docked in Woods Hole on September 3, where it was met by R. Wilke and E. Lewis from the BNL TCO_2 group who helped pack the equipment The entire TCO_2 measurement group with its equipment departed Woods Hole on the afternoon of September 4, 1997.

3. DESCRIPTION OF MEASUREMENTS AND METHODS

3.1 Hydrographic Measurements

During the cruises, the responsibility for the hydrographic data was divided between Scripps Institution of Oceanography (SIO) (section A24) and WHOI (sections AR24, A20, and A22). Hence the hydrography description is given in separate sections for SIO and WHOI operations and methods.

3.1.1 SIO/Ocean Data Facility Methods and Instrumentation (Section A24)

The SIO hydrographical procedures are described in detail by Lynne Talley in the chief scientist's cruise report for WOCE Section A24, which can be obtained on the WHPO web site at http://whpo.ucsd.edu/data/onetime/atlantic/a24/index.htm. Navigational data were logged automatically at 1-minute intervals on a Sun SPARC station. Underway bathymetry was acquired from the ship's SeaBeam system at 5-minute intervals. These data were merged with the navigation data to provide a time-series of underway position, course, speed, and bathymetry, which were used for all station positions, depths, and for bathymetry on vertical sections. A thermosalinograph (Falmouth Scientific Instruments) was mounted on the bow approximately 3 m below the surface for underway salinity.

The hydrographic casts were made with a 36-position 10-L rosette system belonging to the Ocean Data Facility (ODF) at SIO. This unit consisted of a 36-bottle frame, thirty-one 10-L Niskin bottles, a Neil Brown Instrument System (NBIS) Mark III CTD with dual conductivity and temperature sensors, transmissometer, LADCP, altimeter, and pinger. The rosette system was suspended from a three-conductor 0.322-inch electromechanical cable, and power to the CTD and pylon was provided through the cable from the ship. For the first 10 casts, a General Oceanics 1016 36-place pylon was used; thereafter a Sea Bird Electronics (SBE), 36-place pylon, and SBE 33 deck unit were used. The rosette was deployed from the starboard side hangar, and the port side Markey CTD winch was used throughout section A24. At the beginning of each station, the time, position, and bottom depth were logged; the sensors were powered; and control was transferred to the CTD acquisition and control system in the ship's laboratory and the CTD lowered to within 10 m of the bottom. The CTD provided real-time pressure, depth, temperature, salinity (conductivity), oxygen, and density, and these variables were used to select the sampling depths.

At the end of each cast, water samples (full suite) were drawn in the following order: chlorofluorocarbons (CFCs), helium, oxygen, pCO_2, TCO_2, TALK, tritium, nutrients, and salinity. However, only salinity, oxygen, and nutrients were measured at every station. A log was kept to document the sampling sequence and to note anomalies (e.g., leaks), and WHP quality flags were assigned to each sample using the analyzed bottle salinities, oxygen, and nutrients. No major problems with the CTD operation were experienced, and the original set of 31 Niskin bottles was used throughout section A24. At the end of the cruise, the CTD and the entire acquisition and control system were packed and shipped back to SIO.

The CTD was calibrated for pressure and temperature at the ODF calibration facility (La Jolla, California) in April 1997, prior to WOCE section A24. At sea, bottle salinity and oxygen were used to calibrate the conductivity and oxygen sensors, respectively, and the temperature calibration was checked with an SBE 35 laboratory-grade reference material. Further details concerning the pre- and post-cruise calibration of the CTD sensors can be found in the cruise report available from WHPO. ADCP and LADCP profiles were made throughout the section using the hull-mounted ADCP system permanently installed on the *Knorr* and the LADCP mounted vertically inside the rosette frame bottle rings. The quality of the shipboard ADCP to depths of 500 m was good throughout the cruise, as were the LADCP station profiles.

Bottle salinity samples were collected after three rinses in 200-mL Kimax high alumina borosilicate bottles, sealed, and determined after thermal equilibration, usually within 8 to 12 hours of collection.

Salinity was determined at 24°C on two Guildline Autosal Model 8400A salinometers located in a temperature-controlled laboratory (21.4–24.6°C). The salinometer was standardized with International Association for the Physical Sciences of the Ocean (IAPSO) standard seawater (SSW) batch P-127, using at least one fresh vial per cast. The accuracy of the determination was 0.002 relative to the SSW batch used. Salinity was then calculated for each sample (UNESCO 1981) and merged into the data base.

Bottle oxygen was determined by filling 125-mL iodine flasks to overflowing (3× bottle volume) with a draw tube after two bottle rinses. Sample temperature was measured immediately with a thermometer imbedded in the draw tube. The Winkler reagents were added, the flasks stoppered, and shaken upon stoppering and shaken again 20 minutes later to ensure that the dissolved oxygen was completely fixed. Oxygen was determined according to the technique of Carpenter (1965), incorporating the modifications of Culberson et. al (1991) within 4 hours of collection on an SIO-designed automated oxygen titrator using photometric endpoint detection at an ultraviolet wave length of 365 nm. Standards prepared from pre-weighed potassium iodate were run each time the automated titrator was used, and reagent blanks were determined by analyzing distilled water. The final oxygen results have been converted to µmol/kg. Conversion was done using the in-situ temperature, not the temperature of the sample from the Niskin bottles, because of a software failure. Bottle volumes were precalibrated at SIO. The precision of the analysis calculated from 57 replicate pairs (duplicates drawn from the same Niskin bottle) was ± 0.004 mL/L.

Phosphate, nitrate, nitrite, and silicate were determined on virtually every Niskin bottle closed from stations 1 through 153. The samples were collected in 45-mL high-density polypropylene, narrow-mouth, screw-capped centrifuge tubes that were rinsed with HCL and then rinsed three times with sample before filling. The samples were analyzed on an ODF-modified four-channel Technicon AutoAnalyzer II, usually within 1 hour of the cast, in a temperature-controlled laboratory. If the samples were stored for longer than 1 hour prior to analysis, they were stored at 4°C (no more than 4 hours). The Auto Analyzer instrumentation—which incorporates the method of Armstrong, Stearns, and Strickland (1967) for silicate, the method of Armstrong et al. (1967) as modified for nitrate and nitrite, and the method of Bernhardt and Wilhelms (1967) for phosphate—is described by Gordon and co-workers (Atlas et al. 1971; Hager et al. 1972; Gordon et al. 1992). Standards were analyzed at the beginning and end of each group of sample analyses with a set of secondary intermediate concentrations prepared by diluting pre-weighed primary standards. The primary standard for silicate was Na_2SiF_6; for nitrate, nitrite, and phosphate, KNO_3, $NaNO_2$, and KH_2PO_4 were used, respectively. Chemical purities ranged from 99.97% ($NaNO_3$) to 99.999% (KNO_3). Deep seawater was also used as a substandard. Some 3439 nutrient samples were analyzed during section A24.

3.1.2 WHOI Methods and Instrumentation (Sections AR24, A20, and A22)

Unless otherwise stated, procedures remain as in Section 3.1.1. The underway-Doppler speed log did not function during sampling of section A22, and the hull-mounted transducer had to be removed for repair. Otherwise, navigational and meteorological data were logged by the shipboard data acquisition system (dubbed Athena) at 1-minute intervals. These data include heading, time and date, geographic positioning system (GPS), wind speed and direction, sea surface temperature and conductivity, and additional meteorological data. A secondary suite of data calculated or derived from these data was also logged at 1-minute intervals. These files were also the source of event-specific data (e.g., station location). Underway salinity was calibrated with bottle salinity.

For the WHOI sections, the *Knorr* was outfitted with equipment belonging to WHOI. For details see the chief scientist's report for Sections A20 and A22 on the WHPO web site: http://whpo.ucsd.edu/data/onetime/atlantic/index.htm. The CTD used was a WHOI-modified NBIS Mark-III CTD with oxygen sensor, conductivity cell, LADCP, pressure transducer, temperature sensor, and pinger mounted on a 33-position 10-L Niskin bottle rosette frame. The AR24 section differed from the A20 and A22 sections and virtually all other CO_2 survey work because a 24-bottle rosette was used with 4-L sampling bottles, instead of the usual 10-L Niskin bottles, in order to reduce sampling time at the

rosette in late fall when seas were expected to be rougher. A General Oceanic-1016 pylon was used and was controlled using an SIO-furnished Surface Control Interface, a dedicated PC, and software provided by SIO/ODF. Temperature and pressure calibrations were performed at WHOI before section A20. The CTD was re-calibrated after its return to WHOI in December 1997. For details concerning the pre-cruise, at-sea, and post-cruise CTD calibrations, see the cruise report and Millard and Yang (1993).

Oxygen, nutrients, and salts were analyzed from virtually every Niskin bottle closed during the cruise. Bottle salinity samples were collected after two rinses in 8-ounce glass bottles. Then they were thermally equilibrated to 22°C and analyzed on a Guildline Autosal Model 8400B salinometer. The salinometer was standardized once a day using IAPSO SSW Batch P-131 (dated October 10, 1996). The accuracy was ± 0.002.

Bottle oxygen was determined by filling 15-mL brown glass tincture bottles. Oxygen was determined using a modified Winkler technique similar to that described by Strickland and Parsons (1972). The titration is automated using a PC controller and a Metrohm Model 665 Dosimat buret. The endpoint is determined amperometrically using a dual-plate platinum electrode, with a resolution of better than 0.001 mL. The accuracy of the method is 0.02 mL/L with a standard deviation of replicate samples of ± 0.005. Standardization of the thiosulphate titrant was done daily. No problems were noted during the cruises. This technique is described further by Knapp, Stalcup, and Stanley (1990).

The nutrient samples were collected in 30-mL high-density polypropylene bottles that were loaded directly into the autosampler tray. The bottles were soaked in 10% HCl every other day and rinsed three times with sample before filling. The samples were analyzed on the same SIO/ODF-modified four-channel Technicon AutoAnalyzer II used on A24, except that an Alpkem Model 303 autosampler was substituted for the ODF autosampler. The analytical methods are described in Gordon et al. (1994).

3.2 Total CO_2 Measurements

As on previous cruises, TCO_2 was determined using automated dynamic headspace sample processors (SOMMA) 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). A schematic diagram of the SOMMA analytical sequence may be found in earlier cruise reports (see Johnson et al. 1995,1996), and further details concerning the coulometric titration can be found in Huffman (1977) and Johnson, King, and Sieburth (1985). The methods used for discrete TCO_2 on WOCE sections have been extensively dealt with in previous reports (Johnson et al. 1998a) and need only be briefly summarized.

The AR24 section required modification of the usual sampling procedures. As noted in Section 3.1.2, 4-L sampling bottles were employed on the rosette, limiting the amount of sample available for the carbonate system analysts to one 500-mL bottle. Hence, the TCO_2 coulometric titration analysis had to be completed before the partially empty 500-mL bottle was passed to the TALK group for the potentiometric alkalinity titration. There was enough sample to complete both measurements, but not enough time or sample for TCO_2 replicate analyses from the same 500-mL sample bottle. The 4-L sampling bottles also made it impossible to draw duplicate samples from the same sampling bottle. Without duplicate samples from the hydrographic stations, standard measures of sample precision (DOE 1994; Johnson et al. 1998b) could not be completed on the AR24 section. Samples were poisoned with 100 µL of a 50% solution of $HgCl_2$ and analyzed for TCO_2 within 24 hours of collection (DOE 1994).

For sections A24, A20, A22, single or duplicate samples were collected in 300-mL biological oxygen demand (BOD) bottles, poisoned with 100 µL of a 50% solution of $HgCl_2$, and analyzed for TCO_2 within 24 hours of collection, according to standard operating procedures (DOE 1994). The samples were stored in a dark refrigerator at 4–6°C until approximately 1–2 hours before analysis, when they were removed and placed in a temperature bath at 18–20°C and thermally equilibrated. The SOMMA sample pipette and sample bath were also kept at approximately 20°C. Duplicate samples were usually collected on each cast at the surface and from the bottom waters. For some casts, three sets of duplicates were taken. The duplicates were analyzed within the run of cast samples from which they originated so that the time

elapsed between duplicate analyses was 3–12 hours. As per standard operating procedure (DOE 1994), CRM was routinely analyzed according to DOE (1994) guidelines. The CRM was supplied by Dr. Andrew Dickson of the SIO, and for the North Atlantic cruises, batches 33, 36, and 37 were used. The certified values for these batches were TCO_2 = 2009.85 µmol/kg @ salinity = 33.781 for batch 33; TCO_2 = 2050.21 µmol/kg @ salinity = 35.368 for batch 36; and TCO_2 = 2044.15 µmol/kg @ salinity = 34.983 for batch 37. The CRM TCO_2 concentration was determined by vacuum-extraction/manometry in the laboratory of C. D. Keeling at SIO.

An accurately known volume of seawater was injected from an automated to-deliver (TD) pipette into a stripping chamber. Following acidification, the resultant CO_2 from continuous gas extraction 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 VFC during the titration was displayed). In the coulometer cell, the acid (hydroxyethylcarbamic acid) formed from the reaction of CO_2 and ethanolamine is 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) is related by Faraday's constant to the number of moles of OH^- generated and thus to the moles of CO_2 that reacted with ethanolamine to form the acid. The age of each titration cell is 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 is measured in minutes from birth (chronological age) and in mgC titrated since birth (carbon age).

Each system was controlled with an IBM-compatible PC equipped with two RS232 serial ports (coulometer and barometer), a 24-line digital input/output card (solid state relays and valves), and an analog-to-digital card (temperature, conductivity, and pressure sensors). Real Time Devices (located in State College, PA 16803) manufactured the cards. 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 0.02ºF prior to the cruise using a certified mercury thermometer. These sensors monitored the temperature of SOMMA components, including the pipette, gas sample loops, and 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 coulometers operated in the counts mode, conversions and calculations were made using the SOMMA software rather than the programs and the constants hardwired into the coulometer circuitry.

The SOMMA-coulometry systems were calibrated with pure CO_2 (calibration gas) using hardware consisting of an 8-port gas sampling valve (GSV) with two sample loops of known volume [determined gravimetrically by the method of Wilke, Wallace, and Johnson (1993)] connected to the calibration gas through an isolation valve; the vent side of the GSV was 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 prepared titration cell [normally, one cell per day and three sequential calibrations per cell at a carbon age of 3–9 mgC (mean age @ 6 mgC), with the result of the third calibration taken as the CALFAC if it was consistent with the second (i.e., agreement to ± 0.1% or better)]. Daily gas calibrations were made on both systems throughout the cruises.

The "to-deliver" volume (V_{cal}) of the sample pipettes was determined (calibrated) gravimetrically prior to the cruise to ± 0.02% or better in October of 1996. The calibration was checked periodically during all cruises by collecting aliquots of deionized water dispensed from the pipette into pre-weighed 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 balance (Sartorius, Göttingen, Germany) as soon as possible. The apparent weight (g) of water collected (W_{air}) was corrected to the mass in vacuum (M_{vac}) with the "to-deliver" volume being M_{vac} divided by the density of the calibration fluid at the calibration temperature. After the AR24 section in 1996, the system pipettes were dismounted and replaced with chemically cleaned pipettes in March, 1997. For the 1997

sections, the calibration volumes (V_{cal}) at the calibration temperature (t_{cal}) of the sample pipettes were redetermined to ± 0.01% from a set of calibration samples taken on July 3, 1997, on board the *Knorr* at the completion of section A24 and were weighed on September 17. The TCO_2 pipette volumes for the four North Atlantic sections are summarized in Table 2.

Table 2. The "to-deliver" pipette volume (V_{cal}) and calibration temperature (t_{cal}) for the discrete SOMMA-Coulometer Systems (S/N 004 and 030) used on WOCE Section AR24 (1996) and Sections A24, A20, and A22 (1997)

Section	System S/N	V_{cal} (mL)	t_{cal} (°C)
AR24 (1996)	004	21.8927	19.91
A24/A20/A22 (1997)	004	21.2630	19.19
AR24 (1996)	030	21.3733	20.91
A24/A20/A22 (1997)	030	25.8544	19.52

The sample volume (V_t) at the pipette temperature was calculated from the expression:

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

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 on the AR24 section in 1996 was 20.32 ± 0.51°C (n = 948), and on the 1997 North Atlantic Sections it was 19.55 ± 0.52°C (n = 4666).

The factory-calibrated coulometers were electronically calibrated independently in the laboratory before 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 each system. The micromoles of carbon titrated (M), whether extracted from water samples or the gas loops, was

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

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 be calculated only from calibrated levels of current flowing continuously.

Unfortunately, the coulometer system 030, which was electronically calibrated prior to the AR24 cruise and again in March 1997, had to be replaced at the start of section A24 in May 1997. However, the replacement coulometer (S/N CBE-9010-V) was calibrated at the factory on March 20, 1997. Hence we assumed that the replacement coulometer was properly calibrated, and we entered the default calibration coefficients into the software ($SLOPE_{ec}$ = 1.0 and INT_{ec} = 0.0). The system 004 was also recalibrated in March 1997 following the AR24 cruise with nearly identical results to those obtained in October 1996, and it was not recalibrated during the 1997 WOCE sections. The electronic calibration coefficients, along with the mean gas calibration factors determined for the North Atlantic section discrete TCO_2 coulometers, are given in Table 3.

Table 3 illustrates an advantage of the independent laboratory electronic calibration procedure. The mean CALFAC for systems 004 and 030 using the laboratory-determined electronic calibration coefficients was approximately 1.0036 (or 99.64% recovery of the theoretical mass of CO_2 calibration gas measured coulometrically) vs 1.0053 (99.47% recovery) for the factory-calibrated coulometer. Hence, a small percentage (0.17%) of the less than 100% recovery for known masses of CO_2 coulometrically

Table 3. The electronic calibration and the mean gas calibration coefficients for the discrete TCO_2 systems on WOCE Section AR24 (1996) and Sections A24, A20, and A22 (1997)

Section	System S/N	$SLOPE_{ec}$	INT_{ec} µmol/min	CALFAC(n)	St. dev.	Rel. st. dev. (%)
AR24	004	0.999372	0.002528	1.003892(9)	0.000650	0.06
A20/A22/A24	004	0.998905	0.001466	1.003361(63)	0.000740	0.07
AR24	030	0.999306	0.003550	1.003780(26)	0.000497	0.05
A20/A22/A24	030[a]	1.000000	0.000000	1.005344(59)	0.001369	0.13

[a]Factory-calibrated coulometer installed at the beginning of the A24 section in May 1997.

titrated can be explained by a factory-calibration procedure that is apparently slightly less accurate than the laboratory calibration. This difference has been consistent throughout the CO_2 survey.

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

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

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 the AR24 section in 1996 dHg = 1.0002 and for the 1997 sections d_{Hg} = 1.000333).

One of the SOMMA-Coulometry Systems (S/N 004) was equipped with a conductance cell (Model SBE-4, Sea-Bird Electronics, Inc., Bellevue, WA) for the determination of salinity measurement as described by Johnson et al. (1993). Whenever possible SOMMA and CTD salinity were compared to identify mistrips or other anomalies, but the bottle salinity (furnished by the chief scientist) was used to calculate TCO_2.

Quality control-quality assurance (QC-QA) was assessed from the results of the 275 CRM analyses made using systems 004 and 030 during the four North Atlantic sections. These data are summarized in Table 4, and the temporal distribution of the differences is plotted in Fig. 2 for section AR24 (1996) and in Fig. 3 for sections A24, A20, and A24 (1997).

Table 4. The mean analytical difference (ΔTCO_2 = measured−certified) and the standard deviation of the differences between measured and certified TCO_2 on WOCE Sections AR24, A24, A20, and A22

Section	System S/N	Δ TCO_2 (µmol/kg)	St. dev. (µmol/kg)	n
AR24	004	1.42	2.10	16
AR24	030	1.54	1.88	49
Mean/total		**1.51**	**1.92**	**65**
A24	004	0.04	1.10	49
A20	004	0.23	1.20	42
A22	004	0.06	0.69	17
Mean/total		**0.10**	**1.08**	**108**
A24	030	0.79	1.00	48
A20	030	0.44	1.43	35
A22	030	0.26	1.22	19
Mean/total		**0.57**	**1.21**	**102**
Overall mean/total		**0.61**	**1.47**	**275**

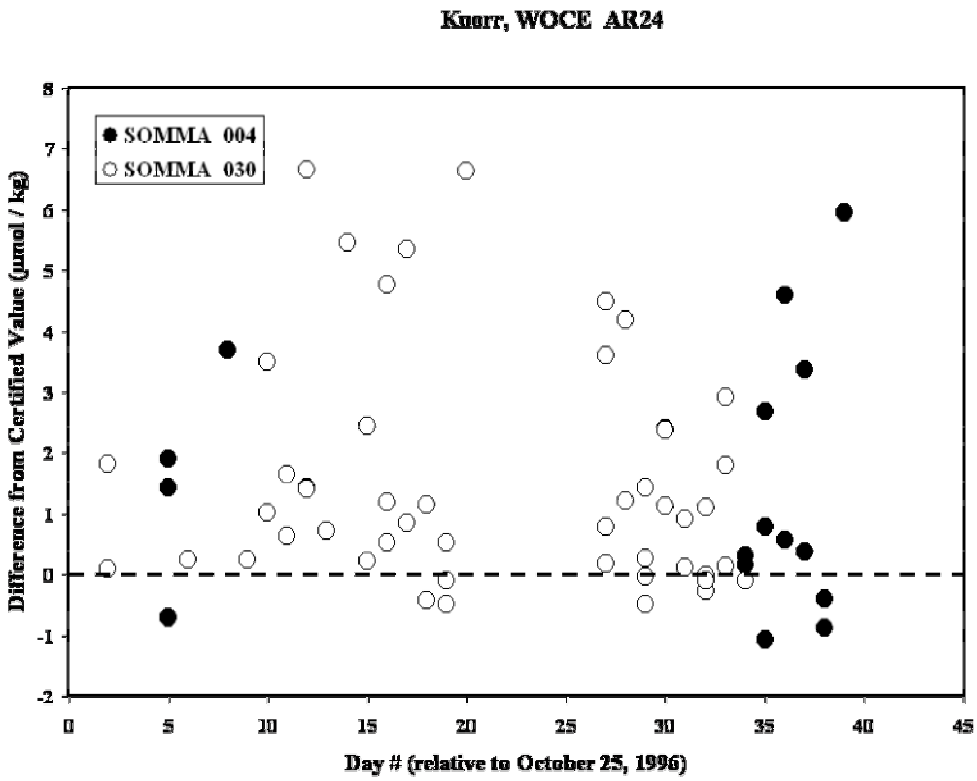

Fig. 2. The temporal distribution of differences between the measured and certified TCO_2 for CRM analyzed on SOMMA-coulometry systems 004 (closed circles) and 030 (open circles) during the WOCE North Atlantic Section AR24 in 1996. The differences were calculated by subtracting the certified TCO_2 from the measured TCO_2.

The overall accuracy of the CRM analyses was better than 1 µmol/kg on both systems for the four North Atlantic sections, with a combined overall mean difference of + 0.61 µmol/kg (n = 275). However, Table 4 shows that on the AR24 section (1996), the mean difference and the standard deviation of the differences were noticeably larger for both systems compared with the 1997 sections (A24/A20/A22). This may be due in part to mechanical problems experienced by the AR24 measurement group, operator procedures, and possibly the relatively short time available to service and re-calibrate the systems prior to the AR24 section. The latter was brought about by the fact that system 004 had been used in the Indian Ocean from 1994–1996 and was only returned to BNL for service, repair, and re-calibration in the fall of 1996. System 030, which was a newly built system returned to the laboratory after a test cruise in the North Atlantic, also was not returned until the summer of 1996. For the 1997 sections, both systems were available in the laboratory for servicing from January through May of 1997. Indeed, the 1997 WOCE sections represented the only opportunity during the CO_2 survey for the BNL measurement group to thoroughly service and test the systems, reagents, and analytical gases in the laboratory with real samples and CRM prior to shipment. As a result, the accuracy and precision of the CRM analyses made in 1997 (see Table 4) probably represent the highest quality possible for these systems under field conditions.

All CRM analyses made on the discrete systems (004 and 030) during the 1997 sections are reported in Table 4. However, for section AR24, two CRM analyses were classified as outliers and dropped from the data set. These were CRM No. 206 run on system 030 on November 23 (difference = +10.17 µmol/kg) at a cell carbon age of 39.5 mgC, and CRM No. 600 on system 030 on November

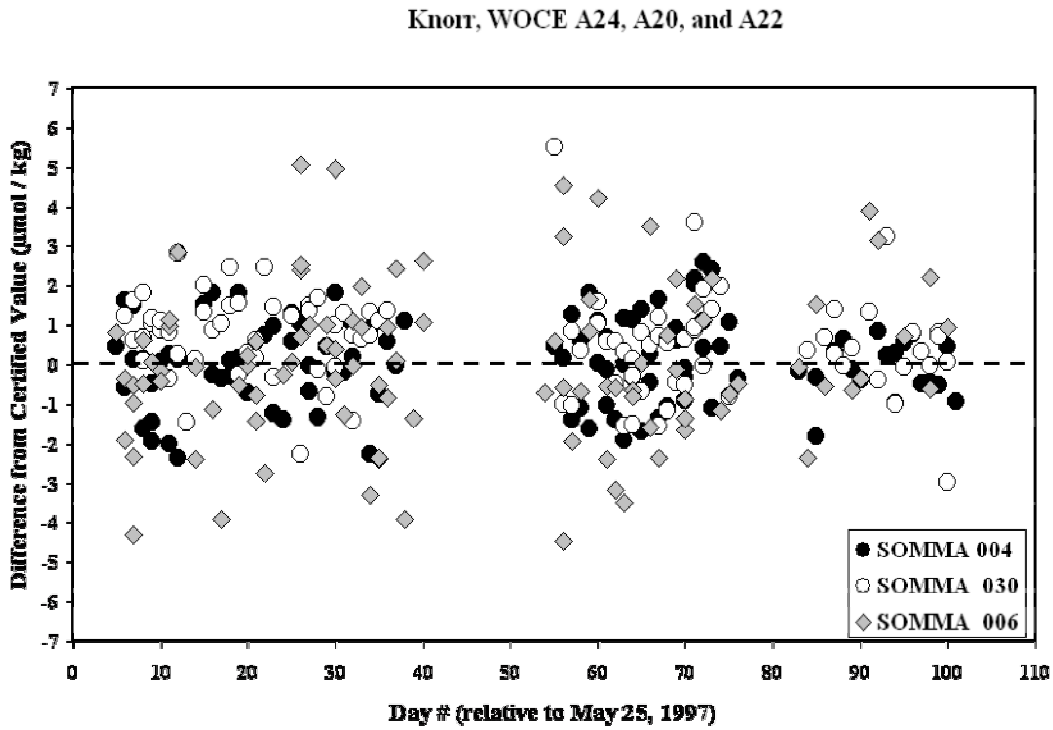

Fig. 3. The temporal distribution of differences among the measured and certified TCO_2 for CRM analyzed on SOMMA-coulometry systems 004 (closed circles) and 030 (open circles) and 006 (shaded diamonds) during the WOCE North Atlantic Sections A24, A20, and A22 in 1997. The differences were calculated by subtracting the certified TCO_2 from the measured TCO_2.

28 (difference = +7.99 µmol/kg) at a carbon age of 35.7 mgC. One CRM analysis (CRM No. 352) run on system 004 on December 1 is not included in the data set because the titration did not attain an endpoint.

The second phase of the QC-QA procedure was an assessment of precision. As described in the text, duplicate samples could not be taken during the AR24 section in 1996. Hence the only estimate of AR24 sample precision was the standard deviation of the differences between the measured and certified TCO_2 on both systems (see Table 4). Because differences from both systems have been combined, the CRM measurements are analogous to the sample duplicates analyzed on each system and should reflect both random and systemic error (bias). The decrease in precision for the CRM analyzed on the AR24 section in 1996 (±1.92 µmol/kg) compared with the CRM analyzed in 1997 (±1.20 µmol/kg) was consistent with the problems described for the 1996 leg. The good agreement in TCO_2 between systems in 1996 (see Table 4) suggests that analyzing duplicate seawater samples on each system, as was done in 1997, might have yielded a higher precision than the precision of the CRM differences. Nevertheless, without sample duplicates, the AR24 sample precision must be based on the CRM analyses. Hence the precision of the TCO_2 determination for the AR24 section in 1996 was ±1.92 µmol/kg (n = 65). Because procedures and performance varied from 1996 to 1997, separate estimates of sample precision were required for each year; the data for 1997 are given in Table 5.

By 1997 the deployment of two independent SOMMA systems side-by-side was routine, and the conventions employed for the estimation of precision in the earlier WOCE data reports are retained in Table 5. For sections A24, A20, and A22 in 1997, the single-system precision was determined from samples with duplicates analyzed on the same system (either 004 or 030). The sample precision was calculated using duplicates that were analyzed on both systems (004 and 030).

Table 5. Precision of the discrete TCO_2 analyses on WOCE Sections A24, A20, and A22

Section	Mean absolute difference			Pooled standard deviation			
	σ_{bs} (µmol/kg)	± St. dev.	K	S_p^2 (µmol/kg)	K	n	d.f.
Single-system precision							
A24	1.08	1.01	175	1.04	175	350	175
A20	0.95	1.14	84	1.04	84	168	84
A22	0.99	0.93	71	0.96	71	142	71
Sample precision							
All	1.76	1.41	56	1.59	61	122	61

Single-system and sample precision have been separately assessed in Table 5 as

- "between-sample" precision (σ_{bs}), which is the mean absolute difference between duplicates (n = 2) drawn from the same Niskin bottle; and
- the pooled standard deviation (S_p^2) calculated according to Youden (1951), where *K* was the number of samples with duplicates analyzed, *n* was the total number of replicates analyzed from *K* samples, and $n - K$ was the degrees of freedom (d.f.).

Single-system precision provided a measure of drift in system response during a sequence of sample analyses. This is because the time lapse between duplicate analyses on the same system using the same coulometer cell was deliberately kept at 3–12 hours, on the assumption that drift or change in response would be reflected in the single-system precision by an increase in the imprecision of the duplicate analyses. Sample precision, on the other hand, was measured because TCO_2 measurements were made on two separate systems, and an estimate of overall sample precision for the section (s), independent of which analytical system was used, was required. Sample precision is the most conservative estimate of precision, incorporating several sources of random or systematic (bias) error.

As on other sections in the Atlantic Ocean (e.g., A8 and A10) where SOMMA-coulometer systems have been run in parallel, the sample precision was slightly less than the single-system precision. This indicated that changes in system response during the coulometer cell lifetime in 1997 were clearly within the precision of the method (±1.59 µmol/kg), while the slight but consistent decrease in sample precision compared with single-system precision was probably due at least in part to a small bias between the 004 and 030 systems. Although the precision was equivalent for both systems, system 030 gave on average slightly higher results than system 004. For example, the mean ΔTCO_2 for system 004 CRM was +0.10 µmol/kg, but it was +0.57 µmol/kg for system 030 CRM (see Table 4); while the mean of the seawater samples (n = 56, Table 5) analyzed on 030 was +1.17 µmol/kg higher than the mean for the same samples analyzed on system 004. Hence the uniformly excellent single-system precision for 1997 cannot be used for sample precision, and analyzing duplicate replicates on each system remains the definitive measure of the overall precision of the 1997 data set and the TCO_2 calibration procedures. The two discrete systems should give the same result for the same sample, and the extent to which they differ is a measure of the overall precision of the data set obtained with two independent systems. For TCO_2 on the 1997 North Atlantic WOCE sections, the precision of the TCO_2 determination was ± 1.59 µmol/kg (K = 56).

The North Atlantic sample precision for all four sections in 1996 and 1997 (±1.92 and ±1.59 µmol/kg, respectively) is in good agreement with the published and unpublished sample precision for other WOCE sections where systems were run in parallel: AE1, 1991 (±1.65 µmol/kg); P6, 1992 (±1.65 µmol/kg); A10, 1993 (±1.92 µmol/kg); A8, 1994 (±1.17 µmol/kg); Indian Ocean, 1995 (±1.20 µmol/kg). During the 1997 North Atlantic sections, a limited number of duplicate samples (K = 6) were analyzed from two different Niskin bottles closed at the same depth, and the mean absolute difference and standard deviation was 0.77 ± 0.50 µmol/kg, which was consistent with earlier findings (e.g., Johnson et al. 1998a; Johnson

et al. 2001) that there were likely no significant analytical effects due to gas exchange with the overlying headspace of the Niskin bottles during sampling.

Tables 4 and 5 show an internally consistent data set of high quality with excellent accuracy (≤ 2.0 μmol/kg), high single-system precision (≤ ±1.0 μmol/kg), and a slightly higher imprecision for the sample precisions (±1.59–1.92 μmol/kg). Based on these data, the TCO_2 data clearly meet survey criteria for accuracy (≤ 4.0 μmol/kg) and precision, and as with previous data submissions, no correction for instrumental bias or CRM analytical differences has been applied to the TCO_2 data.

3.3 Total Alkalinity Measurements

TALK and pH were measured using an automated potentiometric titration system developed at the University of Miami (hereafter designated as MATS). MATS is described by Millero et al. (1993a). It consisted of two parts: a Metrohm model 665 Dosimat titrator and a pH meter (Orion, Model 720A) which are interfaced with a PC. A water-jacketed, fixed-volume (~200 mL), closed Plexiglass sample cell, of greater volume than but otherwise similar to those used by Bradshaw and Brewer (1988), was used to increase the precision of the measurements. The cell, titrant burette, and sample cell were theromstatted at 25 ±0.05°C using a constant temperature bath (Neslab, Model RTE 221). A Lab Windows/CVI program was used to run the titrators, record the volume of titrant added, and record the measured electromagnetic frequency (emf) of the electrodes through RS232 serial interfaces. The electrodes for measuring the emf during the titration consisted of a ROSS glass pH electrode (Orion, Model 810100) and a double-junction Ag/AgCl reference electrode (Orion, Model 900200).

Seawater samples were titrated by adding enough HCl to exceed the carbonic acid endpoint of the titration. During a typical titration, the emf readings were recorded until stable (±0.05 mV). Normally, at this point, a fixed volume of acid would be added; however, the MATS were designed to add enough acid to increase the voltage by a pre-assigned increment (13 mV). This was done to give an even distribution of data points over the course of a full titration, which consists of 25 data points and takes about 20 minutes. With two systems, approximately 7 hours was required to run a 31-bottle station cast. As noted in Sections 3.1 and 3.2, 4-L Niskin sampling bottles were employed on the rosette, which limited the amount of sample available for the carbonate system analysts to one 500-mL bottle. Hence there was not enough sample water to complete duplicate alkalinity analyses from the same bottle or to draw duplicate samples from the same sampling bottle.

The titrant (acid) used throughout the cruises was prepared, standardized, and stored in 500-mL borosilicate glass bottles for use in the field. A single 55-gal batch of 0.25-m HCl acid was prepared by dilution of concentrated HCl (AR Select Mallinckrodt). The acid was prepared in 0.45–m NaCl to yield a total ionic strength similar to that of seawater salinity 35.0 (I = ~0.7 M). The acid was standardized by coulometry (Taylor and Smith 1959; Marinenko and Taylor 1968). The acid molality was also checked by titration on seawaters with known alkalinities, and subsamples were sent to the laboratory of A. Dickson at SIO for an independent laboratory determination of the molality. The calibrated molality of the acid used for the North Atlantic WOCE Sections was 0.24892 ±0.00003 m HCl.

The consistency of the method was checked for each cast using low-nutrient surface seawater, and the accuracy of the method was checked by analyzing CRM Batches 33 (1996), 36, and 37 (1997) and comparing the analyzed values with the certified TALK in the same manner as for TCO_2 (see also Section 3.2 for batch data). The mean differences between at-sea measurements and the certified TALK values are given in Table 6. The TALK of each batch was also determined in the laboratory by weight titrations, which were found to agree with the certified values to ±2 μmol/kg. In addition, the pH of the CRM batches was determined in the laboratory spectrophotometrically according to the methods of Clayton and Byrne (1993) prior to the cruise. The at-sea titration pH measurements were also compared with the pre-cruise spectrophotometric values, and the reader is referred to Millero et al. (1999) for further details.

Table 6. The mean analytical difference between analyzed and certified TALK for the MATS on WOCE Section AR24 (1996), and Sections A24, A20, and A22 (1997)

Section	Cells	n	CRM TALK µmol/kg	Measured TALK µmol/kg	ΔTALK µmol/kg
AR24	2, 19, 17	59	2234.9	2233.3	−1.6
A24	2, 18, 12	148	2283.9	2283.3	−0.6
A20	2, 18, 12	96	2314.1	2217.1	3.0
A22	2, 12	65	2314.1	2215.4	1.3

The mean differences between the at-sea measurements and the certified TALK were within 3.0 µmol/kg (Table 6). Hence the measured and certified TALK were in good agreement. For pH and TCO_2, the corresponding results were 0.021 and 9 µmol/kg, respectively, with the larger deviation in pH attributable to the non-Nernstian behavior of the electrodes near a pH of 8 (Millero et al. 1993b).

The at-sea sample alkalinity titrations were corrected using the results for the CRM. For TALK, the CALFAC used to correct the at sea measurements was

$$CALFAC = CRM \text{ (certified value)/(at-sea value)} \quad ,$$

and for pH the CALFAC was

$$pH = pH \text{ (CRM) / pH (at-sea)} \quad .$$

Duplicate samples were usually taken for each station in the same manner as for TCO_2 (surface and deep) and analyzed to determine and monitor the precision of the MATS. The average difference between replicates was ±1.0, ±1.1, and ±1.1 µmol/kg for sections A24, A20, and A22, respectively, which demonstrated the high precision of the MATS throughout the study. A preliminary description of the major trends in the data and the behavior of alkalinity over time in the North Atlantic is given by Millero et al. (1999).

3.4 Discrete pCO_2 Measurements

The discrete measurements of pCO_2 were performed by the LDEO group on three of four sections of the North Atlantic survey. During the WOCE sections A24, A20, and A22, a total of 2,465 samples were analyzed onboard the R/V *Knorr* (1,103, 595, and 767 samples respectively). On the earlier WOCE section AR24, discrete pCO_2 was not measured.

An automated equilibrator-IR gas analyzer system was used during the expedition for the determination of partial pressure of CO_2 in the seawater samples. Its design is similar to that described by Chipman, Marra, and Takahashi (1993) with the exception that the gas chromatograph was replaced with an IR gas analyzer. The equilibrator-IR system is shown schematically in Fig. 4.

The system consists of a circulation pump plumbed to recirculate air in a closed system through porous plastic gas dispersers immersed in a 250-mL seawater sample. The seawater sample is contained in a 250-mL Pyrex reagent bottle with a standard taper-ground glass stopper that serves as an equilibration vessel. A Pyrex extension tube (~20 mL), which has a standard taper-ground glass male-joint to form an airtight seal with the reagent bottle, is connected to the mouth of the reagent bottle to provide an extra headspace to prevent seawater from entering the gas circulation line. Four sets of flasks and circulation pumps are used so that four water samples can be processed concurrently. Because the partial pressure of CO_2 is sensitive to temperature, the equilibration flasks are kept immersed in a water bath maintained at 20°C. The temperature at which the water sample is equilibrated with circulating gas is measured with a precision of ±0.01°C and is recorded.

An electrically driven Valco 10-port valve (the equilibrator selection valve in Fig. 4) is used to isolate each of the equilibrators during the initial equilibration. Manually operated 2-way and 3-way Whitey valves allow the headspace in each equilibrator to be filled with a calibration gas of known CO_2 concentration, creating a known initial condition for the headspace (about 40 mL) before equilibration. The equilibrator is open to the laboratory air through isolation coils attached to the low-pressure side of the equilibrator, keeping the total pressure of equilibration the same as the ambient atmospheric pressure. The atmospheric pressure is measured with a high-precision electronic barometer with an accuracy of better than 0.05% and is recorded. It takes about 20 minutes for each water sample to be thermally equilibrated with the constant-temperature water bath, and the headspace gas is recirculated through the water sample throughout the period to ensure CO_2 equilibration.

An electrically driven Valco 6-port valve (the sample selection valve in Fig. 4) is connected to the equilibrator selection valve and to the calibration gas selection valve. This allows selection of the gas sample to be analyzed for CO_2: the equilibrated sample gas or one of the four calibration gases. A 2-way normally-closed Skinner solenoid valve on the output of the calibration gas selection valve controls the flow of the calibration gases to the sample selection valve. It also provides a necessary second means of stopping the flow of the calibration gases to prevent their accidental loss in case of a control malfunction. The concentration of CO_2 in the gas equilibrated with the seawater sample is determined using an IR gas analyzer (LICOR Model 6125) in a flow-through mode. A 0.5-mL aliquot of equilibrated headspace gas, representing less than 1% of the circulating gas, is isolated using a gas pipette (attached to the sampling valve in Fig. 4) and swept with CO_2-free air (or pure nitrogen gas) flowing at a constant rate of about 50 mL/min. For low-pCO_2 samples, a 1-mL gas pipette (attached to the sampling valve) is used. The sample gas is passed through a permeation drying tube for the removal of water vapor and injected into the IR gas analyzer cell (about 7 mL in volume) filled previously with CO_2-free air. The displaced CO_2-free air is discharged out of the cell into the laboratory. The small volume of the gas sample ensures that all of the CO_2 from the gas pipette is found in the analyzer cell at the same time, so that the peak height is proportional to the amount of CO_2 present in the gas pipette. Drying of the sample gas avoids the effects of pressure-broadening of the CO_2 absorption spectra and of dilution caused by water vapor. The amount of CO_2 in the sampling pipette is a function of the loop volume, temperature, and pressure. The temperature is held constant and measured, and the pressure of the sample gas is same as the barometric pressure, which is measured with an accuracy of better than 0.05%. The peak height, which represents the number of moles of CO_2 in the sample gas, is calibrated every 1.5 hours using a quadratic equation fitted to three calibration gas mixtures (366.52, 788.8 and 1211.4 ppm mole fraction in dry air).

The analytical procedure begins with water samples being drawn from the 10-L Niskin bottles off a rosette directly into 250-mL Pyrex reagent bottles. These served as both sample containers and equilibration vessels. The samples were immediately inoculated with 100 µL of 50% saturated mercuric chloride solution, sealed airtight with ground glass stoppers to prevent biological modification of the pCO_2, and stored in the dark until analysis. Measurements were normally performed within 24 hours of sampling. A headspace of 3 to 5 mL was left above the water to allow for thermal expansion during storage. Prior to analysis, the sample flasks were brought to the water bath temperature of 20°C in the constant-temperature bath. The equilibrator headspace, including the extension tube and the gas circulation tubings, was filled with a calibration gas of known CO_2 concentration. The gas in the equilibrators, and in the tubing that connects them to the gas pipette loop, was recirculated continuously for about 20 minutes through a gas disperser immersed in the water. This provided a large surface area for gas exchange between the sample water and circulating gas, and equilibrium for CO_2 was attained in 15 min. The temperature of the bath water was assumed to be that of the sample water and was measured at the time of equilibration with a precision of ±0.01°C using a thermometer calibrated against a NIST-certified thermometer. This temperature is reported in the data tables as "TEMP_PCO2" and showed no variation at a limit of ±0.01ºC.

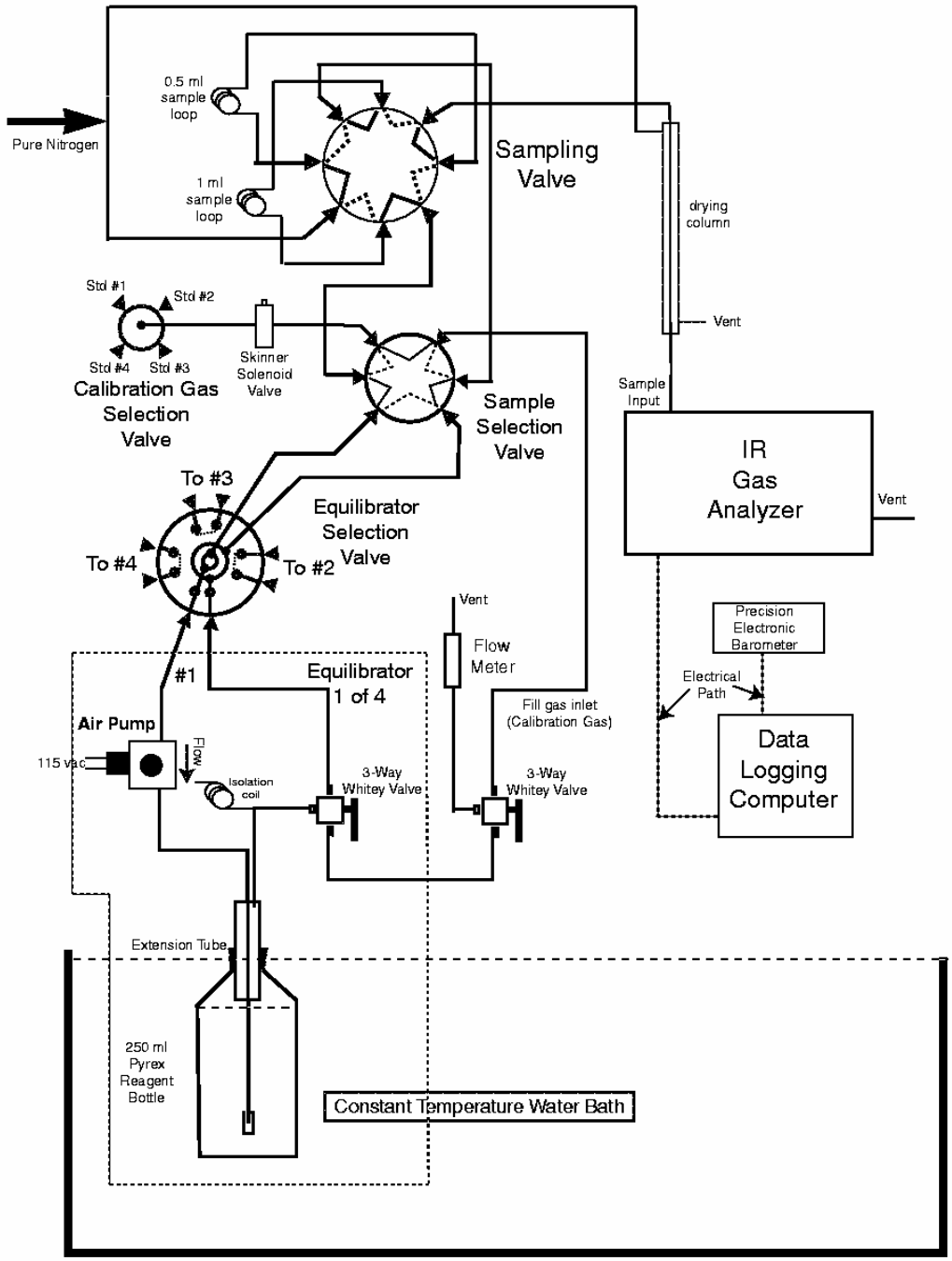

Fig. 4. Schematic diagram for one of the four equilibrator-IR systems used for the pCO2 determination in discrete seawater samples.

The equilibrated air samples were saturated with water vapor at the temperature of equilibration and had the same pCO_2 as the water. By injecting the air aliquot into the IR analyzer after the water vapor was removed, the concentration of CO_2 was measured. Therefore, the effect of water vapor must be taken into consideration for computing pCO_2 as follows:

$$pCO_2\ (\mu\text{atm}) = [C_{meas}\ (\text{ppm})] \times [\textit{total press. of equilibration}\ (\text{atm}) - \textit{water vapor press.}\ (\text{atm})]$$

where C_{meas} is the mole fraction concentration of CO_2 in dried equilibrated air. The total pressure of equilibrated air is measured by having the headspace in the equilibrator flask always at atmospheric pressure. The latter was measured with an electronic barometer at the time each equilibrated air sample was injected into the IR analyzer for CO_2 determination. The water vapor pressure was computed at the equilibration temperature, and salinity of the seawater. C_{meas} was determined by using a quadratic equation fit to three of the calibration gas mixtures.

The concentrations for standard gases used are traceable to the WMO reference scale through analysis in the laboratories of C. D. Keeling of SIO (La Jolla, California) and of Pieter P. Tans of NOAA/CMDL (Boulder, Colorado). The values of the standard gas mixtures used during this cruise were 366.52 ppm CO_2, 788.0 ppm CO_2, and 1211.4 ppm CO_2.

Corrections were made to account for the change in pCO_2 of the sample water due to the transfer of CO_2 between the water and circulating air during equilibration. We know the pCO_2 in equilibrated, perturbed water and the TCO_2 by coulometry before the equilibration. We can also calculate the change in TCO_2 in the water based on the change in pCO_2 between the post-equilibrium value and the known concentration in the pre-equilibrium condition. With the pre-equilibrium TCO_2 plus the perturbation in TCO_2 during equilibration, the post-equilibrium TCO_2 value was obtained. Using the post-equilibrium TCO_2 and measured pCO_2 values, TALK at the end of the equilibration was calculated, using the temperature, salinity, phosphate, and silicate data. Since the perturbation does NOT change the TALK, the pre-equilibrium pCO_2 from the pre-equilibrium TCO_2, the calculated TALK, and the temperature, salinity, etc., were calculated. This is the value that was reported as pCO_2, the pre-equilibrium calculated value. The magnitude of this correction is generally less than 2 μatm. Details of the computational scheme are presented in a DOE technical report by Takahashi, et al. (1998).

The pCO_2 values reported in this data set are expressed as micro-atmospheres at the temperature of equilibration. The precision of the pCO_2 measurement for a single hydrographic station was estimated to be about ±0.15% based on the reproducibility of replicate equilibrations. The station-to-station reproducibility was estimated to be about ±0.5%.

4. DATA CHECKS AND PROCESSING PERFORMED BY CDIAC

An important part of the numeric data packaging process at CDIAC involves the QA of data before distribution. Data received at CDIAC are rarely in a condition that would permit immediate distribution, regardless of the source. To guarantee data of the highest possible quality, CDIAC conducts extensive QA reviews that involve examining the data for completeness, reasonableness, and accuracy. The QA process is a critical component in the value-added concept of supplying accurate, usable data for researchers.

The following information summarizes the data processing and QA checks performed by CDIAC on the data obtained during the R/V *Knorr* cruise along WOCE Sections AR24, A24, A20, and A22 in the North Atlantic Ocean.

1. The final carbon-related data were provided to CDIAC by the ocean carbon measurement principal investigators listed in Section 2. The final hydrographic and chemical measurements and the station information files were provided by the WHPO after quality evaluation. A FORTRAN 90 retrieval code was written and used to merge and reformat all data files.

2. Every measured parameter for each station was plotted vs depth (pressure) to identify questionable data points using the Ocean Data View (ODV) software (Schlitzer 2001) Station Mode (Fig. 5).

3. Section plots for every parameter were generated using ODV's Section Mode in order to map a general distribution of each property along all North Atlantic Ocean sections (Fig. 6).

4. To identify "noisy" data and possible systematic, methodological errors, property-property plots were generated (Fig. 7) for all parameters, carefully examined, and compared with plots from previous expeditions in the North Atlantic.

5. All variables were checked for values exceeding physical limits, such as sampling depth values that are greater than the given bottom depths.

6. Dates, times, and coordinates were checked for bogus values (e.g., values of MONTH <1 or >12; DAY <1 or >31; YEAR <1996 or >1997; TIME <0000 or >2400; LATITUDE <7.000 or >67.000; LONGITUDE <-68.000 or >-8.000.

7. Station locations (latitudes and longitudes) and sampling times were examined for consistency with map and cruise information supplied by principal investigators.

8. The designation for missing values, given as −9.0 in the original files, was changed to −999.9 for consistency with other oceanographic data sets.

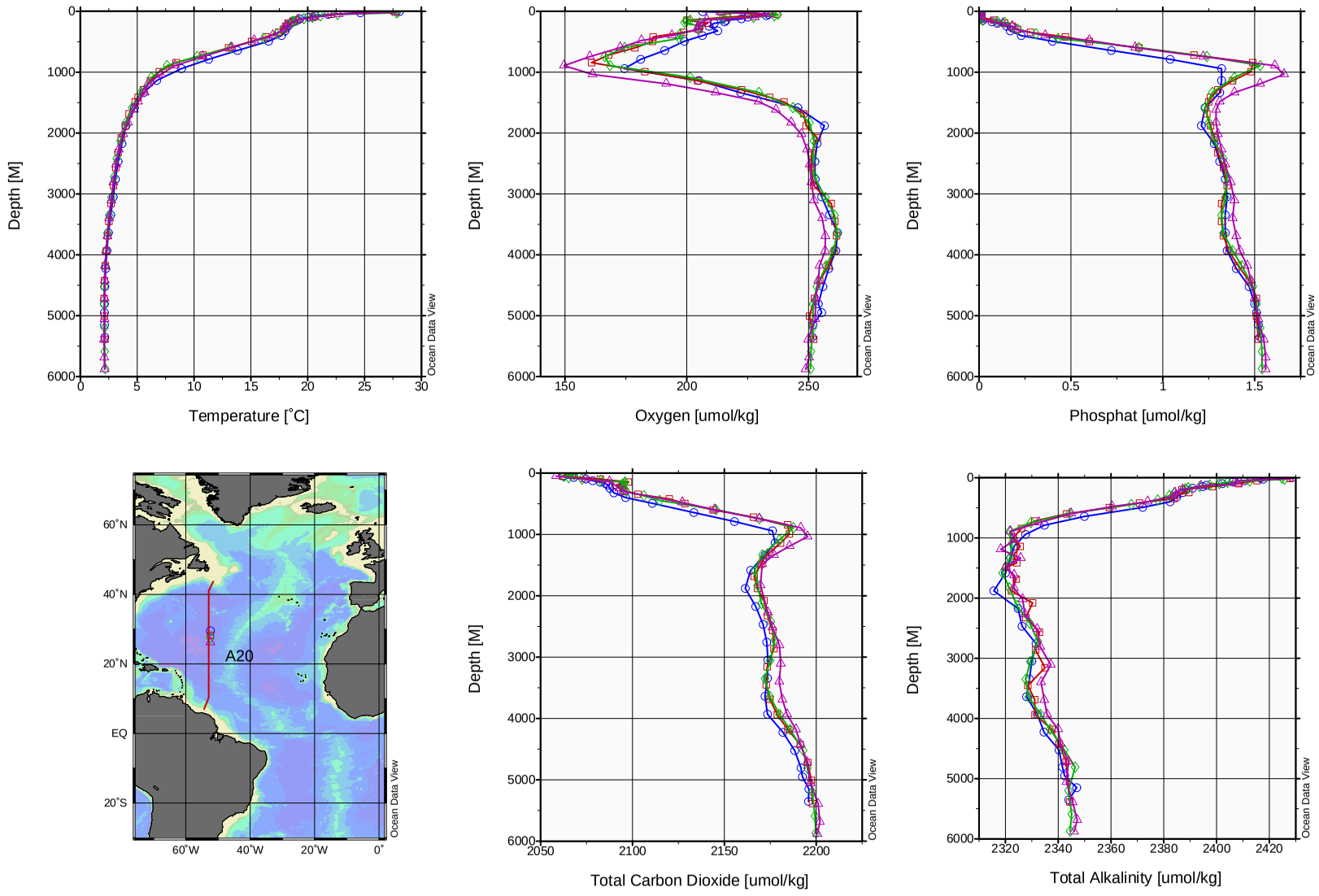

Fig. 5. Example of Ocean Data View station mode plot: Measurements vs depth for Stations 45–48 of Section A20.

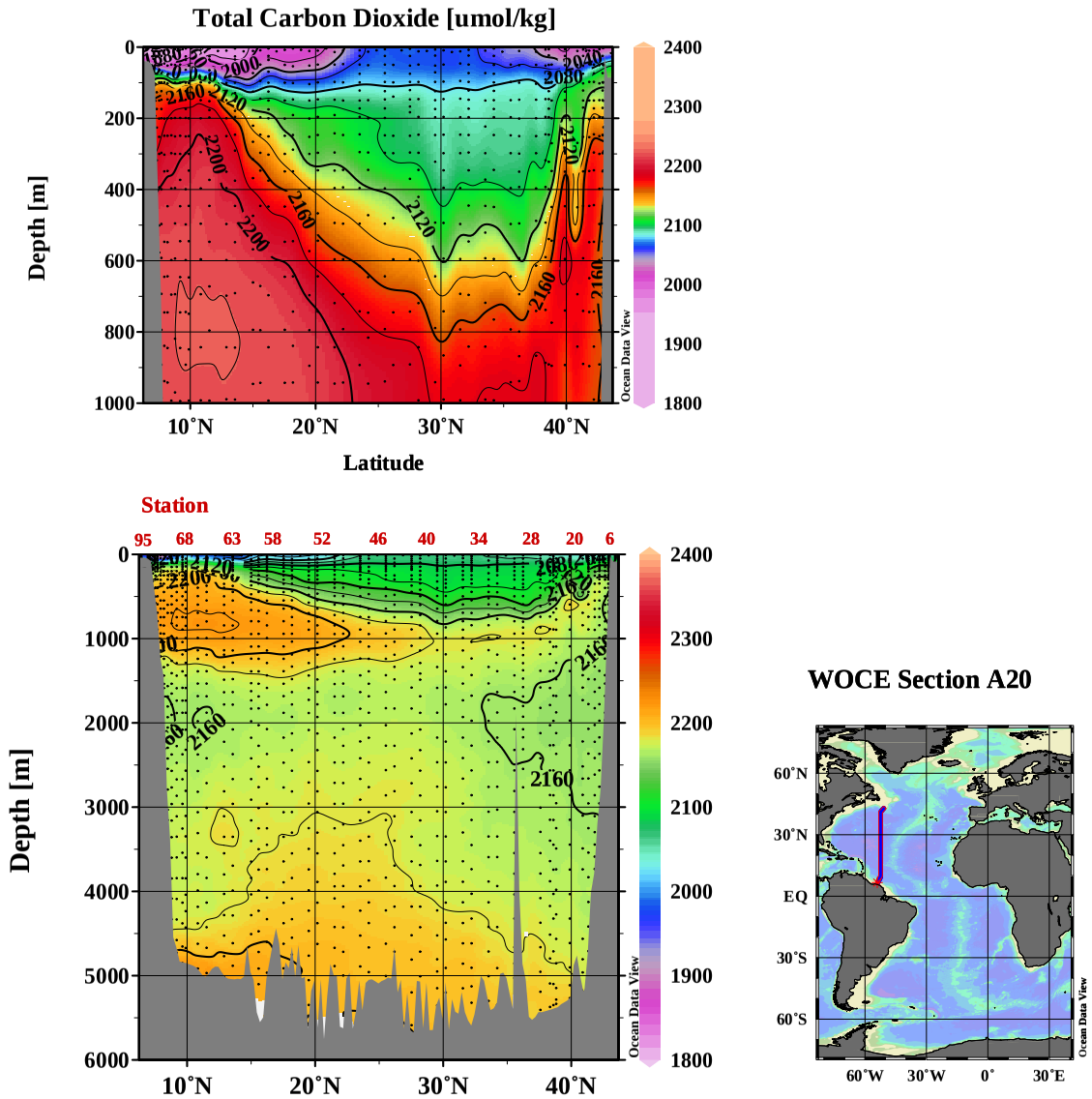

Fig. 6. Distribution of TCO_2 in seawater along WOCE Section A20.

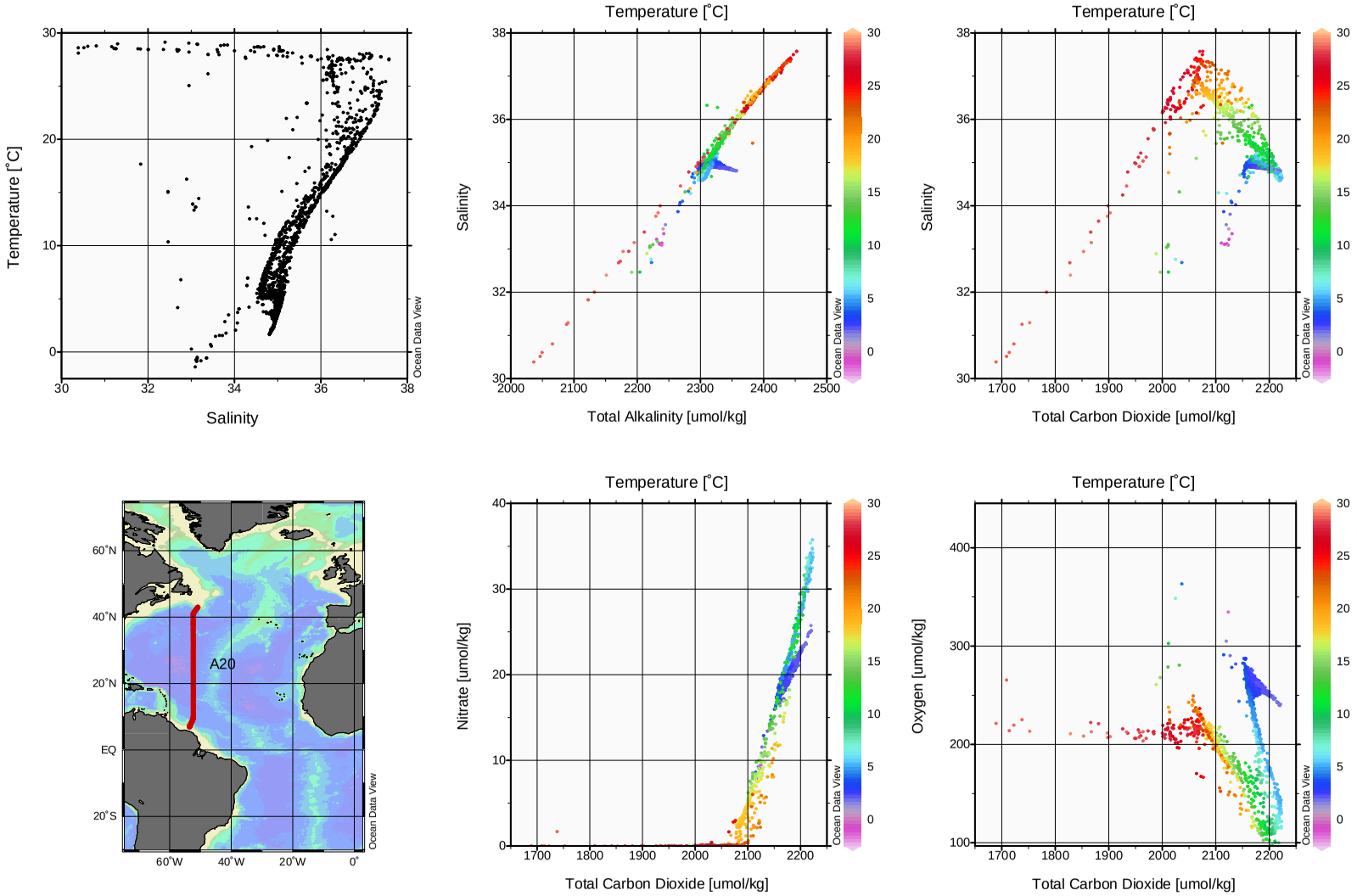

Fig. 7. Property-property plots for all stations occupied during the R/V *Knorr* cruise along WOCE Section A20.

5. HOW TO OBTAIN THE DATA AND DOCUMENTATION

This data base (NDP-082) 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 (see below).

The data are also available from CDIAC's anonymous file transfer protocol (FTP) area via the Internet. Please note that, to access these files, your computer must have FTP software loaded on it (this is built into most newer operating systems). Use the following commands to obtain the data base.

ftp cdiac.ornl.gov or >ftp 160.91.18.18
Login: "anonymous" or "ftp"
Password: your e-mail address
ftp> cd pub/ndp082/
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
U.S.A.

Telephone: (865) 574-3645

Telefax: (865) 574-2232

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

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7. DATA PACKAGE DESCRIPTIONS

7.1 File Content and Format Descriptions

This section describes the content and format of each of the data files that constitute NDP-082 (see Table 7).

Table 7. Content, size, and format of data files

File number, name, and description		File size in bytes
1–2.	**ndp082.txt**	106,779
	ndp082.pdf	5,101,440
A detailed description of the cruise network, and oceanographic data files in simple text and PDF formats		
3–6.	**a20sta.dat**	7,838
	a22sta.dat	6,926
	a24sta.dat	12,702
	ar24sta.dat	15,438
A listing of the station locations, sampling dates, and sounding bottom depths for each station of WOCE Sections A20, A22, A24, and AR24 in the original WOCE format		
7–10.	**a20.dat**	476,060
	a22.dat	403,860
	a24.dat	657,510
	ar24.dat	598,397
Hydrographic, carbon dioxide, and chemical data from all stations occupied on WOCE Sections A20, A22, A24, and AR24. The files are reported in the original WOCE format		
11–14.	**a20_hy1.csv**	857,377
	a22_hy1.csv	701,706
	a24_hy1.csv	1,050,215
	ar24_hy1.csv	932,634
Hydrographic, carbon dioxide, and chemical data from all stations occupied on WOCE Sections A20, A22, A24, and AR24. The files are provided as WOCE exchange format files [comma-separated value (CSV) files].		
15.	**NA_ODV_data.txt**	2,410,877
The Ocean Data View spread sheet data file. The file consists of data from all four sections of the North Atlantic survey		
Total size		13,339759

7.2 Descriptions of Variables

The station inventory file (*sta.dat) variables are defined as follows:

EXPOCODE	Character (A10)	expedition code of the cruise
SECT	Character (A4)	WOCE section number
STNBR	Numeric (I3)	station number
CAST	Numeric (I1)	cast number
DATE	Character (A10)	sampling date (month/day/year)
TIME	Character (A4)	sampling time [Greenwich mean time (GMT)]
LATITUDE	Numeric (F7.3)	latitude of the station (in decimal degrees; negative values indicate the Southern Hemisphere)
LONGITUDE	Numeric (F8.3)	longitude of the station (in decimal degrees; negative values indicate the Western Hemisphere)
DEPTH	Numeric (I4)	sounding depth of the station (in meters)

The data file (*.dat) variables are defined as follows:

STNBR	Numeric (I3)	station number
CASTNO	Numeric (I1)	cast number
SAMPNO	Numeric (I2)	sample number
BTLNBR[a]	Numeric (I2)	bottle number
CTDPRS	Numeric (F7.1)	CTD pressure (dbar)
CTDTMP	Numeric (F7.4)	CTD temperature (°C)
CTDSAL[a]	Numeric (F7.4)	CTD salinity
CTDOXY[a]	Numeric (F7.1)	CTD oxygen (μmol/kg)
THETA	Numeric (F7.4)	potential temperature (°C)
SALNTY[a]	Numeric (F9.4)	bottle salinity
OXYGEN[a]	Numeric (F7.1)	oxygen concentration (μmol/kg)

SILCAT[a]	Numeric (F7.2)	silicate concentration (μmol/kg)
NITRAT[a]	Numeric (F7.2)	nitrate concentration (μmol/kg)
NITRIT[a]	Numeric (F7.2)	nitrite concentration (μmol/kg)
PHSPHT[a]	Numeric (F7.2)	phosphate concentration (μmol/kg)
CFC-11[a]	Numeric (F8.3)	chlorofluorocarbon 11 (picamole/kg)
CFC-12[a]	Numeric (F8.3)	chlorofluorocarbon 12 (picamole/kg)
TCARBN[a]	Numeric (F7.1)	total carbon dioxide concentration (μmol/kg)
ALKALI[a]	Numeric (F7.1)	total alkalinity (μmol/kg)
PCO2[a]	Numeric (F7.1)	partial pressure of CO_2 (μatm)
PH[a]	Numeric (F8.3)	pH
QUALT1	Character (A15)	15-digit character variable that contains data-quality flag codes for parameters underlined with asterisks (*******) in the file header

[a]Variables that are underlined with asterisks in the data file's header indicate they have a data-quality flag. Data-quality flags are defined as follows:

1 = sample for this measurement was drawn from water bottle but analysis was not received
2 = acceptable measurement
3 = questionable measurement
4 = bad measurement
5 = not reported
6 = mean of replicate measurements
9 = sample not drawn for this measurement from this bottle