

**CARBON DIOXIDE, HYDROGRAPHIC, AND CHEMICAL DATA OBTAINED
DURING THE NINE R/V *KNORR* CRUISES COMPRISING THE INDIAN OCEAN
CO₂ SURVEY (WOCE SECTIONS I8SI9S, I9N, I8NI5E, I3, I5WI4, I7N, I1, I10, and
I2;
DECEMBER 1, 1994–JANUARY 19, 1996)**

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ACRONYMS

| | |
|--------------------------|--|
| 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 |
| CO ₂ | carbon dioxide |
| CTD | conductivity, temperature, and depth sensor |
| CRM | certified reference material |
| d.f. | degree of freedom |
| DIW | deionized water |
| DOE | U.S. Department of Energy |
| EEZ | Exclusive Economic Zone |
| emf | electro-magnetic fields |
| EXPOCODE | expedition code |
| FSI | Falmouth Scientific Instruments |
| <i>f</i> CO ₂ | fugacity of CO ₂ |
| FTP | file transfer protocol |
| GO | General Oceanics |
| GMT | Greenwich mean time |
| GPS | global positioning system |
| Hcl | hydrochloric acid |
| IAPSO | International Association for the Physical Sciences of the Ocean |
| IMET | Improved METeorology |
| I/O | input-output |
| JGOFS | Joint Global Ocean Flux Study |
| kn | knots |
| LADCP | lowered ADCP |
| LDEO | Lamont-Doherty Earth Observatory |
| MATS | Miami University alkalinity titration systems |
| NBIS | Neil Brown Instrument system |
| NCSU | North Carolina State University |
| NDP | numeric data package |
| NOAA | National Oceanic and Atmospheric Administration |
| nm | nautical mile |
| NSF | National Science Foundation |
| ODF | Ocean Data Facility |
| ONR | Office of Naval Research |
| OSU | Oregon State University |
| PC | personal computer |
| PI | principal investigator |
| POC | particulate organic carbon |

| | |
|------------------|--|
| PMEL | Pacific Marine Environmental Laboratory |
| 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 |
| TAMU | Texas A&M University |
| 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. M., A. G. Dickson, G. Eischeid, C. Goyet, P. R. Guenther, R. M. Key, K. Lee, E. R. Lewis, F. J. Millero, D. Purkerson, C. L. Sabine, R. G. Schottle, D. W. R. Wallace, R. J. Wilke, and C. D. Winn. 2002. *Carbon Dioxide, Hydrographic and Chemical Data Obtained During the Nine R/V Knorr Cruises Comprising the Indian Ocean CO₂ Survey (WOCE Sections I8SI9S, I9N, I8NI5E, I3, I5WI4, I7N, I1, I10, and I2; December 1, 1994–January 22, 1996)*, Ed. A. Kozyr. ORNL/CDIAC-138, NDP-080. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee, 59 pp.

This document describes the procedures and methods used to measure total carbon dioxide (TCO₂) and total alkalinity (TALK) at hydrographic stations taken during the R/V *Knorr* Indian Ocean cruises (Sections I8SI9S, I9N, I8NI5E, I3, I5WI4, I7N, I1, I10, and I2) in 1994–1996. The measurements were conducted as part of the World Ocean Circulation Experiment (WOCE). The expedition began in Fremantle, Australia, on December 1, 1994, and ended in Mombasa, Kenya, on January 22, 1996. During the nine cruises, 12 WOCE sections were occupied.

Total carbon dioxide was extracted from water samples and measured using single-operator multiparameter metabolic analyzers (SOMMAs) coupled to coulometers. The overall precision and accuracy of the analyses was ± 1.20 Fmol/kg. The second carbonate system parameter, TALK, was determined by potentiometric titration. The precision of the measurements determined from 962 analyses of certified reference material was ± 4.2 Fmol/kg (REFERENCE). This work was supported by grants from the National Science Foundation, the U. S. Department of Energy, and the National Oceanographic and Atmospheric Administration.

The R/V *Knorr* Indian Ocean data set is available as a numeric data package (NDP) from the Carbon Dioxide Information Analysis Center (CDIAC). The NDP consists of 18 oceanographic data files, two FORTRAN 77 data retrieval routine files, a readme 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. Instructions for accessing the data are provided.

Keywords : carbon dioxide; TCO₂; total alkalinity; coulometry; gas chromatography; World Ocean Circulation Experiment; Indian Ocean; hydrographic measurements; carbon cycle.

PART 1:
OVERVIEW

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.

The carbon measurements, which were carried out on the U.S. WOCE Indian Ocean cruises, were supported as a core component of the Joint Global Ocean Flux Study (JGOFS). This coordinated effort received supported 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). Goals were to estimate the meridional transport of inorganic carbon in a manner analogous to the estimates of 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 in the oceans. The global data set includes approximately 23,000 stations. Wallace (2001) recently reviewed the goals, conduct, and initial findings of the survey.

This report discusses the CO_2 science team effort to sample the entire Indian Ocean for inorganic carbon (Fig. 1). The total CO_2 (TCO_2) and total alkalinity (TALK) were measured in the water column and the fugacity of CO_2 ($f\text{CO}_2$) in the surface waters [see Sabine and Key (1998) for a description of the $f\text{CO}_2$ methods and data]. The TCO_2 analytical systems were furnished and set up by Brookhaven National Laboratory under the supervision of D. W. R. Wallace and K. M. Johnson, and the alkalinity titrators were furnished and set up by the University of Miami under the supervision of F. J. Millero. During the survey, certified reference material (CRM) was used to ensure measurement accuracy. All shipboard measurements followed standard operating procedures (DOE 1994). This report focuses on TCO_2 and TALK measurements. Because the team shared equipment throughout all nine cruises and so much material, including quality assessments of the data, has already appeared in the refereed literature, it will be limited to a brief summary. Published documentation appears in appendices.

File Contains Data for PostScript Printers Only

Fig. 1. The cruise tracks during the R/V *Knorr* expeditions in the Indian Ocean along WOCE Sections I8SI9S, I9N, I8NI5E, I3, I5W14, I7N, I1, I10, and I2.

This figure was made using the Ocean Data View program (Schlitzer 2001).

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 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 the Woods Hole Oceanographic Institution in late 1991, the retrofit had taken 32 months. The P6 Section was the vessel’s first scientific cruise after the retrofit. 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*, while Table 2 provides individual cruise information, parameters measured, and responsible personnel with their institutional affiliations.

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

| | | | |
|--------------------------|--|---------------|------------|
| Ship name: | R/V <i>Knorr</i> | | |
| Call sign: | KCEJ | | |
| Basic dimensions: | | | |
| Gross registered tonnage | 2518 T | Displacement | 2958 l ton |
| 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 Indian Ocean CO₂ Survey Cruises Information

Ship name: R/V *Knorr*
 Cruise/Leg: WOCE Sections I8SI9S, I9N, I8NI5E, I3, I5WI4, I7N, I1, I10, and I2
 Ports of call: Fremantle Australia (start), and Mombasa, Kenya (end)
 Dates: December 1, 1994 – January 22, 1996
 TALK instrumentation: F. J. Millero, RSMAS
 TCO₂ instrumentation: D. W. R. Wallace and K. M. Johnson, Brookhaven National Laboratory (BNL)
 Reference material: A. D. Dickson, SIO
 Funding support: DOE, NSF
 Chief scientist: See Table 2

Table 2. Dates, ports of call, expedition codes (EXPOCODEs), and names of chief scientists during Indian Ocean CO₂ survey cruises

| Section | Start date | Finish date | From | To | EXPOCODE | Chief scientist (affiliated institution) ^a |
|----------|------------|-------------|------------|------------|---------------|---|
| I8SI9S | 12/01/94 | 01/19/95 | Fremantle | Fremantle | 316N145_5 | M. McCartney (WHOI) |
| I9N | 01/24/95 | 03/06/95 | Fremantle | Colombo | 316N145_6 | A. Gordon (LDEO) |
| I8NI5E | 03/10/95 | 04/16/95 | Colombo | Fremantle | 316N145__7 | L. Talley (SIO) |
| I3 | 04/20/95 | 06/07/95 | Fremantle | Port Louis | 316N145_8 | W. Nowlin (TAMU) |
| I5WI4 | 06/11/95 | 07/11/95 | Port Louis | Port Louis | 316N145_9 | J. Toole (WHOI) |
| I7N | 07/15/95 | 08/24/95 | Port Louis | Muscat | 316N145_10 | D. Olson (RSMAS) |
| I1 | 08/29/95 | 10/18/95 | Muscat | Singapore | 316N145_11,12 | J. Morrison (NCSU) |
| Dry Dock | 10/19/95 | 11/05/95 | Dampier | | | |
| I10 | 11/06/95 | 11/24/95 | Dampier | Singapore | 316N145_13 | N. Bray (SIO) |
| I2 | 11/28/95 | 01/22/96 | Singapore | Mombasa | 316N145_14,15 | G. Johnson (PMEL) |

^aParticipating institutions:

LDEO Lamont-Doherty Earth Observatory
 NCSU North Carolina State University
 PMEL Pacific Marine Environmental Laboratory
 RSMAS Rosenstiel School of Marine and Atmospheric Science
 SIO Scripps Institution of Oceanography
 WHOI Woods Hole Oceanographic Institution

The extent and nature of the complete measurement program and the responsible institutions for each cruise are summarized in Table 3.

Table 3. WOCE measurement programs and responsible institutions during Indian Ocean CO₂ survey cruises

| Program | Section/Cruise | | | | | | | | |
|----------------------------------|--------------------------------------|------|--------|-------|-------|-----|------|------|------|
| | I8SI9S | I9N | I8NI5E | I3 | I5WI4 | I7N | I1 | I10 | I2 |
| | Responsible institution ^a | | | | | | | | |
| CTD ^b /Rosette | WHOI | ODF | ODF | ODF | ODF | ODF | WHOI | ODF | WHOI |
| Bottle Oxygen | WHOI | ODF | ODF | ODF | ODF | ODF | WHOI | ODF | WHOI |
| Bottle Salts | WHOI | ODF | ODF | ODF | ODF | ODF | WHOI | ODF | WHOI |
| Nutrients | OSU | ODF | ODF | ODF | ODF | ODF | OSU | ODF | OSU |
| CFCs ^c | LDEO | UM | LDEO | SIO | UW | UM | UW | UM | PMEL |
| He ^d /Tr ^e | LDEO | WHOI | WHOI | WHOI | WHOI | UM | WHOI | WHOI | WHOI |
| Deep He/Tr | | | | LDEO | LDEO | | UM | WHOI | LDEO |
| ¹⁴ C ^f | UW | PU | PU | PU | PU | PU | PU | PU | PU |
| ADCP ^g | UH | UH | UH | OSU | UH | UH | SIO | SIO | UH |
| TCO ₂ , TALK | BNL | PU | UH | RSMAS | BNL | UH | SIO | SIO | UH |

^aParticipating institutions:

| | |
|-------|--|
| BNL | Brookhaven National Laboratory |
| LDEO | Lamont-Doherty Earth Observatory |
| NCSU | North Carolina State University |
| PMEL | Pacific Marine Environmental Laboratory |
| ODF | Ocean Data Facility (SIO) |
| OSU | Oregon State University |
| PU | Princeton University |
| RSMAS | Rosenstiel School of Marine and Atmospheric Science (UM) |
| SIO | Scripps Institution of Oceanography, University of California, San Diego |
| TAMU | Texas A&M University |
| UH | University of Hawaii |
| UM | University of Miami |
| UW | University of Washington |
| WHOI | Woods Hole Oceanographic Institute |

^bconductivity, temperature, and depth sensor

^cchlorofluorocarbons

^dhelium

^etritium

^fcarbon-14

^gacoustic Doppler current profiler

The principal investigators (PIs) and the senior technical staff for the WOCE measurements program are summarized in Table 4.

Table 4. Principal investigators and senior at-sea personnel responsible for WOCE measurement programs during Indian Ocean CO₂ survey cruises

| Program | Responsible personnel (Institution) |
|-------------------------|---|
| CTD/Rosette | James Swift (SIO/ODF), John Toole (WHOI), Frank Delahoyde (SIO/ODF), Carl Mattson (SIO/ODF), Marshall Swartz (WHOI), Laura Goepfert (WHOI) |
| Bottle oxygen | James Swift (SIO/ODF), John Toole (WHOI), George Knapp (WHOI), John Boaz (SIO/ODF) |
| Bottle salts | James Swift (SIO/ODF), John Toole (WHOI), George Knapp (WHOI) |
| Nutrients | Louis Gordon (OSU), James Swift (SIO/ODF), Marie-Claude Beaupre (ODF), Joe Jennings (OSU) |
| CFCs | John Bullister (PMEL), Rana Fine (RSMAS), William Smethie (LDEO), Mark Warner (UW), Ray Weiss (SIO), Kevin Sullivan (RSMAS), Frederick A. Van Woy (SIO) |
| He/Tr | William Jenkins (WHOI), Peter Schlosser (LDEO), Zafer Top (RSMAS), Peter Landry (WHOI) |
| ¹⁴ C | Robert Key (PU) |
| ADCP | Teri Chereskin (SIO), Peter Hacker (UH), Eric Firing (UH), Mike Kosro (OSU) |
| TCO ₂ , TALK | See Table 5 |

Table 5 contains a summary of the personnel responsible for the discrete carbonate system measurements.

Table 5. Personnel responsible for carbonate system parameter measurements, number of CTD stations, and number of TCO₂ and TALK analyses made during Indian Ocean CO₂ survey cruises

| Section | Institution | PI(s) | Group leader | Stations (No.) | TCO₂ (No.) | TALK (No.) |
|----------------|--------------------|--------------------------|---------------------|-----------------------|------------------------------|-------------------|
| I8SI9S | BNL | D. Wallace K. Johnson | K. Johnson | 147 | 2184 | 1910 |
| I9N | PU | R. Key C. Sabine | C. Sabine | 131 | 2511 | 2504 |
| I8NI5E | UH | C. Winn | C. Winn | 166 | 2419 | 2421 |
| I3 | RSMAS | F. Millero | D. Purkerson | 120 | 1734 | 1810 |
| I5WI4 | BNL | D. Wallace K. Johnson | R. Wilke | 136 | 1991 | 1831 |
| I7N | UH | C. Winn | R. Schottle | 156 | 2235 | 2577 |
| I1 | WHOI | C. Goyet | G. Eiseid | 158 | 2400 | 2387 |
| I10 | PU | R. Key C. Sabine | C. Sabine | 61 | 927 | 926 |
| I2 | UH | C. Winn | R. Schottle | 168 | 2562 | 2562 |
| Total | | | | 1244 | 18963 | 18928 |

A complete list of the CO₂ measurement team members and their home and sponsoring institutions appears in Appendix A.

2.3 Brief Cruise Summary

Unlike other CO₂ survey cruises where a single institution was responsible for all phases of the work, these cruises were a group effort in which the measurement groups used the same ship and instrumentation for a 14-month period. BNL supplied two single-operator multiparameter metabolic analyzers (SOMMA) systems [S/N 004(I) and 006(II)] that were certified at BNL. A complete back-up system (S/N 023) was supplied by WHOI. The alkalinity titrators were supplied by RSMAS. Preparation began with a 4-day workshop held in September 1994 at RSMAS under the direction of and in the laboratory of F. J. Millero. Cruise participants and group leaders from BNL, LDEO, SIO, RSMAS, PU, WHOI, and UH were instructed in the use of the alkalinity titrators by F. J. Millero and D. Campbell and in the use of the SOMMA-coulometer systems by K. M. Johnson and R. W. Wilke. The day after Thanksgiving the BNL and RSMAS TCO₂ groups left for Australia. Setup of the alkalinity and coulometric titration systems began on November 28, 1994. The I8SI9S cruise began on December 1, 1994.

The first of the nine cruises on the R/V *Knorr* was the longest continuous cruise during the survey. It occupied a series of CTD stations along two north-south tracks essentially proceeding from Australia to the ice edge (I8S) along 90° E and then back again to Australia (I9S) at approximately 110° E. Station spacing ranged from 5 to 40 nautical miles (nm). Testing and selection of the best of the available titration systems and components was completed during I8S. The alkalinity and especially the coulometric titration systems benefitted from this “shake-out” period. Components damaged during transit were identified and repaired or replaced. By the beginning of the I9S, operations were more or less routine. Except for one approximately 12-h period when high winds of ~60 knots (kn) made sampling impossible, work proceeded pretty much on schedule during the 50-day cruise. During the cruise the ability of a team of four marine mammal and bird observers onboard from PMEL, under the direction of C. Tynan, to remain in the cold weather and identify whales that were little more than blips on the horizon amazed all participants of the expedition. Both Christmas and New Year holidays were celebrated aboard the ship. The fine Christmas dinner was highlighted by the appearance of three humpback whales, who put on a spectacular display, jumping and passing under and about the ship. The ship docked in Fremantle, to the relief of the CO₂ team members, on January 19, 1995, after 147 stations were occupied. Measurement crews were exchanged, and the new team brought along some badly needed spare parts and components.

The ship departed Fremantle for I9N on January 24 with A. Gordon as Chief Scientist and a CO₂ measurement group from PU. This section was basically a northward continuation of I8S. The weather was perfect during all 43 days of the cruise. The participants celebrated the equator crossing on February 14. This cruise ended on March 5 in Colombo, Sri Lanka, with 131 stations logged. During the stopover, the carrier gas supply for the coulometric titrators was shifted from bottled high purity nitrogen to a calibration gas generator (Peak Scientific), which supplied CO₂-free carrier gas for the remaining of the cruises.

I8NI5E began in Colombo on March 10 with L. Talley as chief scientist and a CO₂ measurement group from UH on board. No problems were noted for the sampling program, and the weather remained excellent for most of this leg. The ship track proceeded southward from Sri Lanka along 88° E to 24° S, then angled southeastward to the junction of the Ninety-East Ridge and Broken Ridge. Next, the ship followed a 1987 section along approximately 32° S. This zonal section included the Central Indian Basin, and crossed the northward flow of deep water just west of Australia. Due to the good weather, some extra sampling was carried out, and by the time the ship docked in Fremantle on April 15, 166 stations had been occupied. On station 296, the rosette accidentally hit bottom at 3630 m, but the cast was successfully completed. A postcruise inspection

showed no apparent damage to the equipment. This cruise included sampling for particulate organic carbon (POC) in the surface waters near the equator. POC samples were also taken at 65 stations for $^{13}\text{C}/^{12}\text{C}$ analyses. Between April 15 and 23, measurement crews were exchanged and spare parts inventories were updated.

On April 23, the R/V *Knorr* departed Fremantle for section I3 with W. Nowlin as chief scientist and a CO_2 measurement group from RSMAS. The ship had to detour almost immediately back to Fremantle for a medical emergency. The injured analyst was able to rejoin the ship in Port Louis, Mauritius. In addition to the CTD work, this cruise included the deployment of current meters, drifters, and autonomous Lagrangian circulation explorer (ALACE) floats. The cruise track ran along 20° S from Australia to Mauritius to Madagascar, crossing the West Australian Basin, Ninety-East Ridge, Central Indian Basin, and Central Indian Ridge before veering southward to 22° S around Rodrigues Island. After this, it proceeded to the east coast of Mauritius, where a 2-day port stop was made in Port Louis. Returning to sea, the ship continued sampling westward along 20° S from the continental shelf to Madagascar. Weather was characterized by southeasterly winds of 10–20 kn, mostly sunny skies, occasional rain squalls, and 4–6 ft swells with slightly higher winds and seas in mid-May. The *Knorr* returned to Port Louis, Mauritius, on June 5 with 120 stations logged.

The next cruise, I4I5W, began on June 11 with J. Toole as chief scientist and a CO_2 measurement group from BNL on board. This leg focused on major circulation features of the southwest region of the Indian Ocean, including the region where the Agulhas Current originates and where dense waters filtering through fractures in the Southwest Indian Ridge form a northward deep boundary current east of Madagascar. The cruise track formed a closed box to aid in deducing the absolute circulation. A stop was made in Durban, South Africa, on June 21 to pick up a replacement drum of CTD wires. Attempts were also made to repair the ship's bow thruster, which had failed very early in the leg; although the repair was not successful, the lack of a bow thruster had no effect on the scientific work. The R/V *Knorr* departed Durban on June 22 and began I5W including reoccupation of stations where data had been taken in 1987. Bad weather was experienced on June 30 when wind gusts of 40–50 kn and high seas slowed winch operations. As the ship moved across the Madagascar Basin toward port, station spacing was decreased to 20 nm. When the ship arrived in port on July 11, 136 stations had been occupied—20 more than planned.

After four days in port, the R/V *Knorr* departed on I7N with D. Olson as chief scientist and a CO_2 measurement group from UH. The director of the U.S. WOCE office, Piers Chapman, was aboard and served as a salt analyst during the section. I7N was designed to define the water mass properties and transports across the Mascarene Basin and to measure water mass properties and baroclinic structure on a short section across the Amirante Passage, located between the Mascarene and Somali Basins. It included a cross-equatorial section and a reoccupation of stations previously sampled to confirm water mass flows. This work included sampling along 65° E in the central Arabian Basin. The concluding phase of the cruise was a deep line of stations up the center of the Gulf of Oman. The last station of this phase was in the Strait of Hormuz, and it identified inflows of Arabian (Persian) Gulf water into the Arabian Basin. The cruise terminated on August 24 in Muscat, Oman, with 156 stations occupied.

After a 5-day layover, the R/V *Knorr* departed Muscat on I1 with J. Morrison as chief scientist and a CO_2 measurement group from WHOI. I1 was the northernmost Indian Ocean section. It enclosed the Arabian Sea and Bay of Bengal, which are important sources of salt and fresh water, respectively. The *Knorr* proceeded from Muscat to the southern end of the Red Sea and then to the coast of Somali, where the zonal section started at a nominal latitude of 8° N. The section crossed the Arabian Sea, in part to study the carbon transport in and out of the Arabian Sea,

and ended on the continental shelf of India. After a brief port stop in Colombo, Sri Lanka, on September 28–30, the leg continued from the Sri Lankan shelf across the Bay of Bengal to the Myanmar continental shelf. CTD problems caused considerable difficulty for the scientific party and resulted in a somewhat noisy hydrographic data set compared to data obtained from the other sections. After the last station on the Myanmar shelf, the *Knorr* deadheaded to Singapore, arriving on October 16 with 158 stations logged. I1 was not only the northernmost section, it was clearly the most adventurous. ALACE float deployments had to be canceled in the territorial waters of India because the Indian observer on board refused to allow them, and then the threat of pirates caused the cancellation of a planned section across the Gulf of Aden. In the vicinity of Colombo, the ship had to be escorted by four Sri Lankan gunboats, and planned stops at stations over the Trincomalee Canyon could not be taken because of the threat of attack by the Tamil Tigers. Nevertheless, the *Knorr* was able to coordinate scientific activities and physical oceanographic measurements with the nearby R/V *Meteor* (F. Schott, chief scientist) in an area of German current meter moorings near Socotra. Sampling during I1 enabled comparison of bottle and TCO₂ data with earlier JGOFS results and *Meteor* Pegasus and *Knorr* lowered acoustic Doppler current profiler (LADCP) horizontal velocities. From Singapore, the *Knorr* proceeded to Dampier, Australia, where it was placed in dry dock from October 19 until November 5.

With the R/V *Knorr* back in the water, the I10 CO₂ measurement group from PU arrived. This group was required to do some additional work not normally part of the crew exchange routine. During the dry dock period, the CO₂ instrumentation had been depowered, and the measurement group had to repower and check the instrumentation. Some minor repairs were required for the coulometric titrators, including the replacement of one or two solenoid valves (the only valves replaced during the cruises). In addition, the sample pipettes and coolant lines were dismantled and cleaned of algal growth.

The R/V *Knorr* departed Dampier, Australia, on November 11 with N. Bray as chief scientist. WOCE Section I10 was set to run from Shark Bay, Western Australia, to the Indonesian Exclusive Economic Zone (EEZ) 120 nm south of Sunda Strait. However, constraints imposed by the Indonesian government caused the endpoint to be moved from the Sunda Strait to near central Java. The *Knorr* was not granted permission to enter the EEZ of Indonesia, and concluding stations had to be taken along the boundary of the EEZ. These restrictions prevented full resolution of the South Java current. Throughout the Indian Ocean survey, bottle casts were normally made to within 5–20 m of the bottom; however, on I10 four stations over the Java Trench this could not be done. Instead, the casts were made to the maximum CTD depth of 6000 m. The quality of the bottle data was considered to be excellent throughout with very few mis-trips. ALACE floats were also released during this cruise. A festive Thanksgiving was celebrated aboard the ship, and after the last station (1075), the *Knorr* steamed to Singapore, arriving on November 28, with 61 stations logged.

The R/V *Knorr* departed Singapore on December 2 for the last Indian Ocean WOCE section, I2, with G. Johnson as chief scientist and the UH CO₂ measurement group aboard. Again, clearance for work in the Indonesian EEZ was not available, and after a 3-day steam, work commenced with a reoccupation of the final station of the I10 Section (station 1075). The *Knorr* skirted the Indonesian EEZ and moved westward, crossing the Ninety-East Ridge and the Chagos-Laccadive Ridge. The ship continued at approximately 8° S until it made a brief port call in Diego Garcia from December 28–30. At this point, the chief scientist departed the ship and was replaced by Bruce Warren, accompanied by two Kenyan observers. The *Knorr* returned to the 8° S line, passing the crest of the Central Indian Ridge and then the Mascarene Plateau before it turned southwestward and crossed the Amirante Passage on the way to the northern tip of Madagascar. Rounding the tip, the ship headed northwest toward Africa, making a dogleg to avoid

the Tanzanian EEZ. After completing the final Indian Ocean Survey station 1244, it proceeded to Mombasa, arriving on January 22, 1996, with 168 stations logged.

For inorganic carbon, the principal analytical problems for the cruise centered on the breakage of glass components in the alkalinity titrators; resupply; accumulation of bubbles in the acid lines of the alkalinity titrators; damaged coulometric cathode electrodes; algal growth in the sample lines, baths, pipettes, and alkalinity cells; wide swings in laboratory temperature (19–33°C), and the failure of the TCO₂ glassware drying oven. Fortunately, glassware drying oven was repaired. Temperature swings (21–29°C) were also noted for the salinometer and nutrient laboratories. The most vexing problem for the inorganic carbon analysts was the failure of the refrigerated baths used by both the alkalinity and coulometric titration systems. The baths had to be constantly jury-rigged so that one bath did the work of two, repaired by ship's technicians when possible, or replaced when possible. The two groups used almost 12 different baths, and by the time the work ended, not one could be considered in reliable condition. Some were never repaired, while others were repaired and used for the North Atlantic survey in 1997.

3. DESCRIPTION OF VARIABLES AND METHODS

3.1 Hydrographic Measurements

During the survey, responsibility for hydrographic and bottle data was divided between ODF and WHOI. Each of these groups uses or may use different procedures. Hence, the hydrographic measurements are described in separate sections. Because the greater number of the cruises were made under the auspices of SIO/ODF, the bulk of the methods description is provided in Sect.

3.1.1. Information specific to WHOI is given in Sect. 3.1.2; in this section however, the discussion is limited to significant differences between the SIO/ODF and WHOI operations or methods.

Unless otherwise stated in Sect. 3.1.2, material presented in Sect. 3.1.1 applies to all cruises. Sect. 3.1.3 contains a brief description of the underway measurements common to all cruises.

3.1.1 SIO/ODF Methods and Instrumentation

Hydrographic measurements consisted of salinity, dissolved oxygen, and nutrient (nitrite, nitrate, phosphate, and silicate) samples collected from Niskin bottles filled during CTD/rosette casts, and temperature, pressure, salinity, and dissolved oxygen from the CTD. At 5- to 40-m intervals, depending on the topography, hydrographic casts were made to within 5–20 m of the bottom with a 36-bottle Rosette frame belonging to ODF. This unit consisted of a 36-bottle frame, thirty six 10-L bottles, and a 1016 General Oceanics (GO) 36-place pylon. The GO pylon was used in conjunction with an ODF-built deck unit and power supply. The underwater components comprising the CTD included an ODF-modified Neil Brown Instrument Systems (NBIS) Mark III CTD with conductivity, pressure, oxygen, and temperature sensors. The underwater package also consisted of a SeaTech transmissometer, an LADCP, a Sormedics dissolved oxygen sensor, a Falmouth Scientific Instruments (FSI) secondary PRT sensor, a Benthos altimeter, and a Benthos pinger. The CTD was mounted horizontally along the bottom of the frame, while the LADCP was vertically mounted inside the bottle rings. The system was suspended from and powered by a three-conductor 0.322-in. electromechanical cable. The Rosette was deployed from the starboard side using either the port side Markey CTD or the starboard side Almon Johnson winch. Standard CTD practices (i.e., soaking the conductivity and O₂ sensors in distilled water between casts and protecting the sensors against sunlight and wind by storing the rosette in the hanger between casts) were observed throughout the cruises. Regular CTD maintenance included the replacement of O-rings when needed, bottle inspections, and a regular cleaning of the transmissometer windows. At the beginning of each station the time, position, and bottom depth were logged. The CTD sensors were powered and control was transferred to the CTD acquisition and control system in the ship's laboratory. The CTD was lowered to within 10 m of the bottom if bottom returns were adequate. Continuous profiles of horizontal velocity from the sea surface to the bottom were made for most CTD/rosette casts using the LADCP.

The CTD's control and acquisition system displayed real-time data [pressure, depth, temperature, salinity (conductivity), oxygen, and density] on the video display of a SunSPARC LX computer. A video recorder was provided for real-time analog backup. The Sun computer system included a color display, a keyboard, a trackball, a 2.5-GB disk, 18 RS-232 ports, and an 8-mm cartridge tape. Two additional Sun systems were networked for display, backup, and processing. Two HP 1200 C color ink-jet printers provided hard copy. The ODF data acquisition software not only acquired the CTD data but also processed it so that the real-time data included preliminary

sensor corrections and calibration models for pressure, temperature, and conductivity. The sampling depths were selected using down-cast data. Bottles were tripped on the up-cast. Bottles on the rosette were identified with a serial number and the pylon tripping sequence, 1–36, where the first (deepest) bottle tripped was no. 1. For shallow-depth stations, fewer than 36 bottles were closed.

After the CTD was on deck, the acquisition system, the CTD, the pylon, and video recording were turned off and the sensor protective measures were completed before sampling began. If a full suite of samples was drawn, the sampling order was CFCs, ^3He , O_2 , TCO_2 , TALK, ^{14}C , ^3H , nutrients, and salinity. Only salinity, O_2 , and nutrients were measured at every station. A deck log was kept to document the sampling sequence and to note anomalies (e.g., status of bottle valves, leaks, etc.). One member of the sampling crew was designated the “sample cop,” and it was his or her responsibility to maintain this log and to ensure that the sampling order was followed. Oxygen sampling included measurement of the temperature, which proved useful for determining leaking or mis-tripped bottles. Following the cruises, WHP quality flags were assigned according to the WOCE Operations Manual (Joyce and Corry 1994) to each measured quantity.

The principal ODF CTD (no. 1) was calibrated for pressure and temperature at the ODF Calibration Facility (La Jolla, Calif.) in December 1994 prior to the five consecutive WOCE Indian Ocean sections beginning with I9N and ending with I7N. The CTD was also calibrated postcruise in September 1995 prior to the I10 cruise. Pre- and postcruise laboratory calibrations were used to generate tables of corrections, which were applied by the CTD data. At sea, bottle salinity and oxygen data were used to calibrate or check the CTD sensors. Additional details concerning calibration and the CTD data processing can be obtained from the chief scientists’ cruise reports at the WHPO web site: <http://whpo.uscd.edu/>.

Bottle **salinity** samples were collected in 200-mL Kimax high alumina borosilicate bottles, sealed with custom-made plastic insert thimbles and Nalgene screw caps. Salinity was determined after equilibration in a temperature-controlled laboratory, usually within 8–20 h of collection. Salinity was measured with two ODF-modified Guildline Autosal Model 8400A salinometers, normally at 21 or 24°C, depending on the prevailing temperature of the salinometer laboratory. The salinometers included interfaces for computer-aided measurements (e.g., acquiring the measurements, checking for consistency, logging results, and prompting the analyst). The salinometers were standardized with International Association for the Physical Sciences of the Ocean (IAPSO) Standard Seawater (SSW) Batches P-124, P-126, or P-128 using at least one fresh vial per cast (usually 36 samples). The accuracy of the determination was normally 0.002 relative to the SSW batch used. PSS-78 was then calculated for each sample (UNESCO 1981). On some stations (e.g., on Section I5E18N), bottle salinity exhibited small offsets (0.002–0.004) compared to the corresponding CTD results and bottle salinity from nearby stations, and corrections of this magnitude need to be applied to the bottle salinity. Errors of this magnitude have no practical effect on the calculated TCO_2 or TALK values. Hence, bottle salinity is sufficiently accurate to express inorganic carbon results in Fmol/kg .

Bottle **oxygen** was determined by rinsing 125-mL iodine flasks twice and then filling to overflowing (3x-bottle volume) with a draw tube. Sample temperature was measured immediately with a thermometer imbedded in the draw tube. The Winkler reagents were added; and the flask was stoppered, shaken, and then shaken again 20 min later to ensure that the dissolved O_2 was completely fixed. Oxygen was determined within 4 h of collection using a whole-bottle modified Winkler titration following the technique of Carpenter (1965) and incorporating the modifications of Culbertson et al. (1991) on an SIO/ODF-designed automated oxygen titrator. A Dosimat 665 burette driver fitted with a 1.0-mL burette was used to dispense thiosulfate solution (50 g/L).

Standards prepared from preweighed potassium iodate (0.012N) were run each time the automated titrator was used, and reagent blanks were determined by analyzing distilled water. The final oxygen results were converted to Fmol/kg using the in situ temperature. Bottle volumes were precalibrated at SIO. Laboratory temperature stability during the sections was considered poor, varying from 22 to 28°C over short time periods; and therefore, portable fans were used by ODF analysts to maintain temperature.

Phosphate, nitrate, nitrite, and silicate samples were collected in 45-mL high-density polypropylene, narrow-mouth, screw-capped centrifuge tubes which were cleaned with 10% hydrochloric acid (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 h of the cast, in a temperature-controlled laboratory. If the samples were stored for longer than 1 h prior to analysis, they were stored at 2–6°C (for no more than 4 h). The AutoAnalyzer incorporates the method of Armstrong, Stearns, and Strickland (1967) for silicate, this same method as modified for nitrate and nitrite, and the method of Bernhardt and Wilhelms (1967) for phosphate. The last method is described by Gordon and coworkers (Atlas et al. 1971; Hager et al. 1972; and 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 preweighed primary standards. Replicates were also drawn at each station for measurement of short-term precision. For reagent blanks, deionized water (DIW) from a Barnstead Nanopure deionizer fed from the ship’s potable water supply was analyzed. An aliquot of deep seawater was run with each set of samples as a substandard. The primary standard for silicate was Na_2SiF_6 ; and for nitrate, nitrite, and phosphate the standards were KNO_3 , NaNO_2 , and KH_2PO_4 , respectively. Chemical purity ranged from 99.97% (NaNO_2) to 99.999% (KNO_3).

Most hydrographic data sets met or exceeded the WHP requirements. Some exceptions for silicate were noted when differences between overlapping stations on I3 (Station 548) and I4I5W (Stations 705 and 574) approached 3%; these silicate data (Stations 702–707) were corrected by adding 3% to the original results. Instrument problems also caused difficulties for the nitrite and silicate analyses on many of the I2 cruise stations. Silicate problems were noted at some 30% of these stations, with errors typically being on the order of 2–4%. This required considerable post-cruise evaluation and workup before the desired between-station precision for deep water values of 1% was attained. However, users of the I2 silicate data are urged to use caution or to contact the analysts for assistance. Because of the difficulties with the nutrient analyses on the I2 cruise, the post-cruise I2 precision is given in Table 7 as a “worst case” for comparison with the WHP standards shown in Table 6. Short-term precision is the absolute mean difference between replicates analyzed within a sample run; the standard deviation of the differences is also shown. The authors know of no remaining CTD problems, that would affect the quality of the carbonate system data.

Table 6. Required WHP accuracy for deep water analyses

| Parameter | Required accuracy |
|-----------|---------------------------------|
| Salinity | 0.002 relative to SSW analysed |
| Oxygen | 1% (2 $\mu\text{mol/kg}$) |
| Nitrate | 1% (0.3–0.4 $\mu\text{mol/L}$) |

| | |
|-----------|-----------------------------------|
| Phosphate | 1% (0.02–0.03 $\mu\text{mol/L}$) |
| Silicate | 1% (1–5 $\mu\text{mol/L}$) |

Table 7. The short-term precision of the nutrient analyses for Indian Ocean Section 12

| Parameter | Difference ($\mu\text{mol/L}$) | \pm St. Dev. |
|--------------|----------------------------------|----------------|
| Nitrate | 0.123 | 0.093 |
| Phosphate | 0.015 | 0.009 |
| Silicic Acid | 0.440 | 0.260 |

3.1.2 WHOI Methods and Instrumentations

Unless otherwise stated procedures are as described in Sect. 3.1.1, above. For the hydrographic work on I8SI9S, I1, and I2, the R/V *Knorr* was outfitted with equipment belonging to both WHOI and SIO/ODF. For the I8SI9S section a NBIS CTD was used. For I1, four CTDs were available. The primary sensors were two new FSI CTDs belonging to WHOI with a Sensormedics oxygen sensors, a titanium pressure transducer, and a temperature monitor. The secondary sensors were two NBIS Mark-III CTDs (WHOI Nos. 9 and 12) also with a Sensormedics oxygen sensor, a titanium pressure transducer, and a temperature monitor. The MKIII CTDs experienced failures early during I1 (Stations 858 and 864), and the bulk of the hydrography was carried out using the FSI (Nos. 1338 and 1344) CTDs. Usually, the frame was set up with the two CTDs—one configured to send data up the wire and one configured to record data internally. Electrical modifications had to be made to the CTDs and the deck controllers before CTD data dropouts were eliminated and the confirmation of bottle closure from the pylon was restored.

For the CTDs, a FSI DT-1050 deck unit was initially used to demodulate the data, but this unit was replaced for most of the cruise with an EG&G MK-III deck unit. These units fed serial data to two personal computers (PCs) running EG&G CTD acquisition software, with one displaying graphical output and the other a running data listing. After each station, the CTD data were forwarded to another set of PCs running EG&G postprocessing and software modified by WHOI (Millard and Yang 1993) in which the data were centered into 2 dbar bins for data quality control, which included fitting to bottle salinity and oxygen results.

The CTDs were calibrated before and after the cruise for temperature and pressure at WHOI by M. Swartz and M. Plueddemann. Both calibrations were consistent, but the data set for I1 was considered to be only of fair quality because noise levels in the data set are somewhat larger than typical for other CTDs. For example, this data set has a salt noise level of 0.002 which is 2 times larger than the norm. Residuals between the bottle and profile data range from 0.001 to 0.004. For a detailed discussion of the CTD calibration and problems experienced at sea during I1, consult the chief scientist's cruise report on the WHPO web site.

For I2, WHOI CTD No. 9, a WHOI-modified NBIS MK-IIIb, was used. The CTD incorporated a Sensormedics oxygen sensor, titanium pressure transducer, and temperature sensor, which were calibrated in November 1995 immediately before the cruise. On most stations, one of the FSI CTDs was used in the memory mode and downloaded after station sampling to provide independent or backup CTD traces. An FSI Ocean Temperature Module was also attached to the MK-III and CTDs. The Mark-III CTD data were acquired using an NBIS Mark-III deck unit/display that provided demodulated data to two PCs, as described for the Section I1 cruise. A PC was also devoted to recovering the data from the FSI CTDs. Post-cruise calibration, including dunk tests of the CTDs, was completed in April and May of 1996 in the WHOI calibration laboratory. The procedure of Millard and Yang (1993) was used to correct the pressure temperature sensor calibration post-cruise to eliminate down/up pressure hysteresis. Multiple regression fits of the CTD data to the bottle data were used to calibrate the oxygen and conductivity sensors. See the chief scientist's report on the WHPO web site for further details.

Bottle **salinity** samples were collected in 200-mL glass bottles with removable polyethylene inserts and caps. Then they were removed to a temperature-controlled van at 23°C and analyzed on a Guildline Autosol Model 8400B salinometer (WHOI No. 11). The salinometer was standardized once a day using IAPSO SSW (128, dated July 18, 1995). The accuracy was ~0.002. A complete description of the WHOI measurement techniques is given by Knapp, Stalcup, and Stanley (1990).

Bottle **oxygen** was determined according to procedures given by Knapp, Stalcup, and Stanley (1990). WHOI used a modified Winkler technique similar to that described by Strickland and Parsons (1972). The oxygen reagents and bi-iodate standard were prepared at WHOI in August 1994. There was no evidence that the reagents or standard deteriorated during the 17 months they were aboard the Knorr. Standardization of the thiosulphate titrant was made daily. The accuracy of the method was 0.5%, or approximately 1.0 µmol/kg.

The nutrients were analyzed as described in Sect. 3.1.1 (see also Gordon et al. 1994).

3.1.3 Underway Measurements

Navigational data (heading, speed, time, date, and position) were acquired from the ship's Magnavox MX global positioning system (GPS) receiver via RS-232 and logged automatically at 1-min intervals on a SunSPARC station. Underway bathymetry was logged manually at 5-min intervals from the hull-mounted 12-kHz echo sounder and a Raytheon recorder corrected according to methods described by Carter (1980). These data were merged with the navigation data to provide a time-series of underway position, course, speed, and bathymetry data that were used for all station positions, depths, and vertical sections. The Improved METeorology (IMET) sensors logged meteorological data—which included air temperature, barometric pressure, relative humidity, sea surface temperature, and wind speed and direction—at 1-min intervals. Underway shipboard measurements were made throughout the work to document the horizontal velocity structure along the cruise tracks using a 150-kHz hull-mounted acoustic Doppler current profiler (ADCP) manufactured by RD Instruments. The ADCP was mounted at a depth of 5 m below the sea surface. Underway chemical measurements in water and air included salinity, pCO₂ (PU and SIO), pN₂O (SIO), and CH₄ (SIO). Two different systems were used for pCO₂; the PU group used a rotating disk equilibrator and infrared detector, while the Scripps group used a shower type equilibrator and gas chromatograph for the detection of CO₂. The pCO₂ measurements, including a comparison of the shower and disk equilibrator results, were described by Sabine and Key (1998).

A thermosalinograph (manufactured at FSI) was mounted on the bow approximately 3 m below the surface for underway salinity, which was calibrated against surface CTD and bottle salinity values after the cruise (Sabine and Key 1998). The CFC groups periodically analyzed air for CFCs using sampling lines from the bow and stern of the ship.

3.2 Total Carbon Dioxide Measurements

TCO₂ was determined on 18,963 samples using two automated single-operator multiparameter metabolic analyzers (SOMMA) with coulometric detection of the CO₂ 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 and a complete description of the sampling and analytical methods used for discrete TCO₂ on the Indian Ocean WOCE sections appear in Appendix B (Johnson et al. 1998). Further details concerning the coulometric titration can be found in Huffman (1977) and Johnson, King, and Sieburth (1985). The measurements for the Indian Ocean Survey were made on two systems provided by BNL (S/Ns 004 and 006) and a backup by WHOI (S/N 023).

TCO₂ samples were collected from approximately every other station [\sim 60 nm intervals, 50% of the stations (Fig. 2)] in 300-mL glass biological oxygen demand (BOD) bottles. They were immediately poisoned with 200 μ L of a 50% saturated solution of HgCl₂, thermally equilibrated at 20EC for at least 1 h, and analyzed within 24 h of collection (DOE Handbook of Methods 1994). Certified reference material (CRM) samples were routinely analyzed, usually at the beginning and end of the coulometer cell lifetime, according to DOE (1994). As an additional check of internal consistency, duplicate samples were usually collected on each cast at the surface and from the bottom waters. These duplicates were analyzed on the same system within the run of cast samples from which they originated, but the analyses were separated in time usually by \sim 3 h. Periodically, replicate samples were also drawn for shipboard analysis at sea using coulometry and for later analysis on shore at SIO by manometry. The latter samples, typically designated as the “Keeling samples,” consisted of two 500-mL replicate samples collected at two depths (four samples total per station). These were analyzed only if both replicates survived the storage and the return journey to SIO.

Seawater introduced from an automated “to-deliver” (TD) pipette into a stripping chamber was acidified, and the resultant CO₂ from continuous gas extraction was dried and coulometrically titrated on a model 5011 UIC coulometer. The coulometer was adjusted to give a maximum titration current of 50 mA, and it was run in the counts mode [the number of pulses or counts generated by the coulometer’s voltage-to-frequency converter (VFC)] during the time the titration was displayed and acquired by the computer. In the coulometer cell, the acid (hydroxyethylcarbamic acid) formed from the reaction of CO₂ 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 was related by Faraday’s constant to the number of moles of OH⁻ generated and thus to the moles of CO₂ that reacted with ethanolamine to form the acid. The age of each titration cell was logged from its birth (time that electrical current was applied to the cell) until its death (time when the current was turned off). The age was measured from birth (chronological age) and in mass of carbon (mgC) titrated since birth (carbon age). The systems were controlled with PCs equipped with RS232 serial ports for the coulometer and the barometer, a 24-line digital input/output (I/O) card for the solid state relays and valves, and an analog-to-digital (A/D) card for the temperature, conductivity, and pressure sensors.

These sensors monitored the temperature of the sample pipette, gas sample loops, and, in some cases, the coulometer cell. The controlling software was written in GWBASIC Version 3.20 (Microsoft Corp., Redmond, Wash.), and the instruments were driven from an options menu appearing on the PC monitor.

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**Fig. 2. Sampling depths at all hydrographic stations occupied during the R/V *Knorr*
Indian Ocean survey along WOCE Section I9N.**

The TD volume (V_{cal}) of the sample pipettes was determined gravimetrically prior to the cruise and periodically during the cruise by collecting aliquots of deionized water dispensed from the pipette into pre-weighed serum bottles which were sealed and re-weighed on shore. The apparent weight of water collected (W_{air}), corrected to the mass in vacuo (M_{vac}), was divided by the density of the calibration fluid at the calibration temperature to give V_{cal} . 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 ($1 \times 10^{-5}/EC$), and t is the temperature of the pipette at the time of a measurement. V_{cal} for the Indian Ocean CO2 survey cruises and a chronology of the pipette volume determinations appear in Appendix B.

The coulometers were electronically calibrated at BNL prior to the cruises and recalibrated periodically during the cruises (Sections I8SI9S and I5WI4) to check the factory calibration as described in Johnson et al. (1993) and DOE (1994). The results for the electronic intercepts (Int_{ec}) and slopes ($Slope_{ec}$) are given in Appendix B. For all titrations, the micromoles of carbon titrated (M) was

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

where 4824.45 (counts/ μmol) was the scaling factor obtained from the factory calibration, T_t was the length of the titration in minutes, *Blank* is the system blank in Fmol/min, and T_i the time of continuous current flow in minutes.

The SOMMA-coulometry systems were calibrated daily with pure CO₂ (calibration gas) by titrating the mass of CO₂ contained in two stainless steel gas sample loops of known volume and by analyzing CRM samples supplied by Dr. Andrew Dickson of the SIO. The ratio of the calculated (known) mass of CO₂ contained in the gas sample loops to the mass determined coulometrically was the CALFAC (~1.004). A complete history of the calibration results appears in Appendix B. For water and CRM samples, TCO₂ concentration in Fmol/kg was

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

where \bar{n} is the density of seawater in g/mL at the analytical t and S 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 cruises $d_{Hg} = 1.000666$).

System 006 was equipped with a conductance cell (Model SBE-4, Sea-Bird Electronics, Bellevue, Wash.) for the determination of salinity as described by Johnson et al. (1993). Whenever possible, SOMMA and CTD salinities were compared to identify mis-trips or other anomalies, but the bottle salinities (furnished by the chief scientist) have been used to calculate \bar{n} throughout.

Three CRM batches were used for the Indian Ocean Survey. The certified TCO₂ concentrations were determined by vacuum-extraction/manometry in the laboratory of C. D. Keeling at SIO and are given in Table 8.

Table 8. Certified salinity, TALK, and TCO₂ for CRM supplied for Indian Ocean CO₂ survey

| Batch | Salinity | TCO ₂ (μmol/kg) | TALK (μmol/kg) |
|-------|----------|-------------------------------|-------------------|
| 23 | 33.483 | 1993.10 | 2212.70 |
| 26 | 33.258 | 1978.34 | 2176.60 |
| 27 | 33.209 | 1988.10 | 2214.90 |

Optimal cell and platinum electrode configurations, according to criteria given in Appendix B, were selected on the first section (I8S) and were used on all subsequent cruises.

The quality control-quality assurance (QC-QA) of the coulometric TCO₂ determinations was assessed from analyses of 983 CRM samples during the nine Indian Ocean CO₂ survey cruises. For both coulometric titration systems (004 and 006) the average ΔTCO₂ (measurement minus CRM value) for the whole survey was +0.86 μmol/kg and the standard deviation was ±1.21 μmol/kg. A cruise-by-cruise breakdown of the accuracy and precision of the CRM analyses is given in Appendix B.

The small mean difference between the analyzed and certified TCO₂ and the very high precision (+1.21 μmol/kg) of the differences indicates that the two systems gave very accurate and virtually identical results over the entire survey (see also Fig. 6 in Appendix B).

The second phase of the QC-QA procedure was an assessment of sample precision, which is presented in Table 9. The sample precision was determined from duplicate samples analyzed on each system during sections I8SI9S at the beginning of the survey and I4I5W about half way through the survey. The pooled standard deviation (S_p^2), shown in Table 9, is the square root of the pooled variance according to Youden (1951) where K is the number of samples with one replicate analyzed on each system, n is the total number of replicates analyzed from K samples, and n - K is the degree of freedom (d.f.) for the calculation. Precision was calculated this way because TCO₂ was analyzed on two different systems, and an estimate of sample precision independent of the analytical system was required. Hence S_p^2 is the most conservative estimate of precision and includes all sources of random and systematic error (bias). Bias between systems would increase the imprecision of the measurements, but the excellent agreement between the S_p^2 values for natural seawater samples (Table 9) and the high precision of the CRM differences confirms the virtually uniform response, accuracy, and high precision of both systems during the survey. This finding confirms that the precision of the TCO₂ analyses during the Indian Ocean CO₂ survey was ±1.20 μmol/kg.

Table 9. Precision of discrete TCO₂ analyses during Indian Ocean CO₂ survey

| Section | S_p^2 (K, n, d.f) |
|---------|---------------------|
| I8SI9S | 1.26 (15, 30,15) |
| I4I5W | 0.91 (21, 42, 21) |

| | |
|-----|------|
| CRM | 1.21 |
|-----|------|

The next phase of the QC-QA procedure was the comparison of replicate samples analyzed at sea and in the shore-based laboratory. Samples from every cruise were analyzed at sea by continuous gas extraction/coulometry, and later, after storage, duplicate samples were analyzed on shore by vacuum extraction/manometry. The results of the analyses are summarized in Table 10.

Table 10. Mean Difference [$\Delta\text{TCO}_{2(\text{S}\pm\text{SIO})}$] and standard deviation of the differences [$\text{S.D.}_{(\text{S}\pm\text{SIO})}$] between at-sea TCO_2 by coulometry and on-shore TCO_2 by manometry on aliquots of the same sample from Indian Ocean CO_2 survey, and the mean replicate precision [$\text{S.D.}_{(\text{SIO})}$] of the manometric analyses

| Section | Pairs Analyzed (n) | $\Delta\text{TCO}_{2(\text{S}\pm\text{SIO})}$ ($\mu\text{mol/kg}$) | $\text{S.D.}_{(\text{S}\pm\text{SIO})}$ ($\mu\text{mol/kg}$) | $\text{S.D.}_{(\text{SIO})}^a$ ($\mu\text{mol/kg}$) |
|---------|--------------------|--|--|---|
| I8SI9S | 23 | ! 4.14 | 1.80 | 0.82 |
| I9N | 24 | ! 1.96 | 1.67 | 0.80 |
| I8NI5E | 17 | ! 4.80 | 2.87 | 1.31 |
| I3 | 29 | ! 3.29 | 1.26 | 0.82 |
| I4I5W | 16 | ! 2.95 | 1.40 | 1.30 |
| I7N | 13 | ! 5.37 | 1.92 | 1.40 |
| I1 | 26 | ! 5.59 | 1.38 | 1.05 |
| I10 | 8 | ! 4.94 | 1.52 | 1.28 |
| I2 | 10 | ! 4.42 | 1.50 | 0.83 |
| n | 166 | 9 | 9 | 9 |
| Mean | | ! 4.16 | 1.70 | 1.07 |
| S.D. | | 1.21 | 0.49 | 0.25 |

^aEach on-shore TCO_2 by manometry is always the mean of two analyses (see text).

In general, the reproducibility and the uniformity of the data as a whole, and specifically, the high precision of the manometric analyses shown in Table 10, indicate that the collection and return of the “Keeling samples” was successfully performed by each of the measurement groups. Poor sampling or storage techniques would probably have been manifested in a much higher imprecision for the on-shore replicate analyses and in the differences between the at-sea and on-shore analyses. However, the negative mean difference ($! 4.16 \pm 1.21$, $n = 9$) for the Indian Ocean sections was greater than the mean difference for WOCE sections in other oceans ($! 1.36 \pm 1.37$ $\mu\text{mol/kg}$, $n = 22$). The accuracy of the CRM analyses, the tendency for the coulometric analyses to give slightly lower results, and the reproducibility of the at-sea and on-shore differences are similar

everywhere, but the magnitude of the Indian Ocean difference is clearly the largest observed to date. Even if the consistent and slightly negative difference for the CRM is taken into account ($-0.86 \mu\text{mol/kg}$), the at-sea coulometric measurements are approximately $2 \mu\text{mol/kg}$ lower than the manometric method. A suite of samples from the 1997 North Atlantic sections remains to be analyzed. Until these analyses are completed and a thorough statistical evaluation of the entire CO_2 survey data set is made, the explanation of the at-sea and on-shore differences, including those found for the Indian Ocean, is not possible.

An additional step in the QA-QC was also undertaken. Inspection of Fig. 1 shows points where the cruise tracks cross or nearly cross. The agreement between TCO_2 measurements made at these crossover locations ($\pm 100 \text{ km}$) on different cruises was examined by assuming that the temporal and spatial variations in deep-ocean TCO_2 are small relative to the measurement accuracy and precision. Hence, deep ocean waters should have the same TCO_2 at different times in the absence of internal vertical motion, and because deep ocean motion probably occurs along constant density surfaces (isopycnals), the comparisons of TCO_2 measurements were made with reference to density and not depth. Appendixes B and D (Johnson et al. 1998 and Sabine et al. 1999) give a complete description of the statistical procedures used to make the crossover comparisons. Briefly, crossover points were selected for comparison of water samples collected below 2500 m. A smooth curve was fit through the TCO_2 data as a function of the density anomaly referenced to 3000 dbar ($\delta\sigma_t$) using Cleveland's LOESS smoother (Cleveland and Devlin 1988). A separate fit was performed for the data collected at each of the two intersecting crossover points, but the same tension parameter was used for all of the crossover points so that the smoothing function was consistently applied to all crossover locations. The difference between the two smoothed curves was evaluated at 50 evenly spaced points covering the density range where the two data sets overlapped. A mean and standard deviation for the 50 comparisons was calculated for each crossover point. For TCO_2 , differences never exceeded $3 \mu\text{mol/kg}$, and the overall mean and standard deviation of the differences was $-0.78 \pm 1.74 \mu\text{mol/kg}$. The latter differences were consistent with the overall precision of the CRM analyses ($\pm 1.2 \mu\text{mol/kg}$).

Tables 8–10 show an internally consistent TCO_2 data set for the Indian Ocean with excellent accuracy with respect to the CRM certified values, consistently good precision, no analytical bias between the coulometric titration systems, and crossover agreement to within the precision of the method. However, the agreement between the at-sea and on-shore analyses is not as good as for earlier WOCE sections from other oceans (i.e., the Pacific and the South Atlantic). Based on the accuracy of the CRM analyses and the high precision of the sample analyses, the TCO_2 data were not corrected in any way and were deemed to meet survey criteria for accuracy and precision.

3.3 Total Alkalinity Measurements

Total alkalinity was measured on 18,928 samples using two closed-cell automated potentiometric titration systems (hereafter designated as MATS) developed at the University of Miami. The MATS are described by Millero et al. (1993) and by Millero et al. (1998). The latter reprinted in Appendix C of this document, completely describes the Indian Ocean Survey TALK measurements and results. Briefly, the MATS consisted of three parts: a water-jacketed, fixed-volume (about 200 mL determined to $\pm 0.05 \text{ mL}$) closed Plexiglass sample cell, a Metrohm model 665 Dosimat titrator, and a pH meter (Orion, Model 720A), the last two controlled by a PC. The titration cell was similar to those used by Bradshaw and Brewer (1988), but had a greater volume to improve the precision of the measurements. The cell was equipped with flush-mounted fill and

drain valves to increase the reproducibility of the cell volume. The cell, titrant burette, and sample container were held at a temperature of $25 \pm 0.01^\circ\text{C}$ using a constant temperature bath (e.g., Neslab, Model RTE 221).

A Lab Windows C program was used to run the titrators, record the volume of titrant added, and record the measured electromotive force (emf) of the electrodes through RS232 serial interfaces. Two electrodes were used in each cell: a ROSS glass pH electrode (Orion, Model 810100) and a double-junction Ag/AgCl reference electrode (Orion, Model 900200). The specific electrodes used during the Indian Ocean survey were selected after careful screening for non-Nernstian behavior. Only those electrodes which gave TCO_2 results in good agreement with TCO_2 , as determined coulometrically, were used (Sect. 3.2).

Seawater samples were titrated by adding increments of HCl until the carbonic acid endpoint of the titration was exceeded. During a titration, the emf readings were monitored until they were stable (± 0.09 mV). Sufficient volume of acid was added to increase the emf by preassigned increment (~ 13 mV) in order to give an even distribution of data points over the course of a full titration, which consists of 25 data points. A single titration takes about 20 min. A FORTRAN computer program based on those developed by Dickson (1981) and by Johansson and Wedborg (1982) was used to calculate the carbonate parameters. The pH and pK of the acids used in the program are on the seawater scale, and the dissociation constants for carbonic acid were taken from Dickson and Millero (1987). For further details see Appendix C and DOE (1994).

The titrant (acid) used throughout the cruises was prepared prior to the cruise, standardized, and stored in 500-mL borosilicate glass bottles for use in the field. The 0.25-M HCl acid solution was prepared by dilution of 1-M HCl in 0.45-M NaCl to yield a solution with total ionic strength similar to that of seawater of salinity 35.0 ($I = 0.7$ M). The acid was standardized by coulometry (Taylor and Smith 1959; Marinenko and Taylor 1968), and was also checked by independent titration in A. Dickson's laboratory at SIO. The independent determinations agreed to ± 0.0001 M, which corresponds to an uncertainty in TALK of ~ 1 $\mu\text{mol/kg}$. The Dosimat titrator burettes were calibrated with Milli-Q water at 25°C to ± 0.0005 mL.

While CRM samples were available to the TCO_2 analysts from the beginning of the measurement program in 1990, the Indian Ocean cruises were the first to have a certified alkalinity standard as well. Hence, the accuracy of the method was checked in the laboratory by analyzing CRM samples from batches 23, 24, 26, 27, 29, and 30 and comparing the analyzed values with the certified TALK determined by A. Dickson at SIO (in the same manner as for TCO_2). These results are summarized in Table 11 (see also Appendix C). The mean difference between the MATS measurements in the laboratory and the certified TALK values was ± 0.8 $\mu\text{mol/kg}$ for CRM samples with a concentration range approximately one-half as large as the range of a typical seawater profile. The excellent agreement indicated that the CRM concept for alkalinity was valid and that the methodology for TALK was ready for the Indian Ocean survey. The results for the at-sea measurements of the CRM samples have been extracted from Table 2 of Appendix C, summarized, and are given in Table 12.

Table 11. Mean analytical difference (Δ TALK) between analyzed and certified TALK for CRM used during Indian Ocean CO₂ survey

| Batch | Salinity | Certified values | | MATS mean TALK ($\mu\text{mol/kg}$) | Δ TALK (MATS - CRM) ($\mu\text{mol/kg}$) |
|-------|----------|---|-----------------------------|---------------------------------------|---|
| | | TCO ₂ ($\mu\text{mol/kg}$) | TALK ($\mu\text{mol/kg}$) | | |
| 23 | 33.483 | 1993.10 | 2212.7 | 2213.7 | 1.0 |
| 24 | 33.264 | 1987.53 | 2215.5 | 2215.8 | 0.3 |
| 26 | 33.258 | 1978.34 | 2176.6 | 2175.1 | -1.5 |
| 27 | 33.209 | 1988.10 | 2214.9 | 2214.3 | -0.6 |
| 29 | 33.701 | 1902.33 | 2184.8 | 2182.3 | -2.5 |
| 30 | 33.420 | 1988.78 | 2201.9 | 2200.5 | -1.4 |
| Range | 0.492 | 90.77 | 38 | 40.7 | 3.5 |
| Mean | | | | | -0.8 |

The analytical differences are for the most part within the precision of the measurements (~ 2–5 $\mu\text{mol/kg}$) except for the I7N Section. The larger at-sea differences were attributed to operator error or procedures and to uncertainties in the volume of cells, especially after repairs due to leakage, breakage, or repositioning the electrodes after changing the inner filling solutions. Variations between different MATS systems used on a single cruise were corrected using the adjustments required to reproduce the values assigned for the CRM (see Table 11). The at-sea sample titrations were corrected using the results of the at-sea CRM analyses. For TALK, the calibration factor (CF) used to correct the at sea measurements was

$$CF = \text{TALK (meas., CRM)} - \text{CRM (certified value)},$$

and the corrected TALK (TALK_c) was

$$(\text{TALK}_c) = \text{TALK (meas., Spl)} \times [\text{CRM} / (\text{CRM} + \text{CF})],$$

where CRM was the certified TALK and Spl was the measured sample TALK.

The overall precision of TALK determinations during the Indian Ocean survey was $\pm 4.2 \mu\text{mol/kg}$. The precision of the potentiometric pH and TCO₂ measurements are given in Table 3 of Appendix C.

Table 12. Mean analytical difference (Δ TALK) between analyzed and certified TALK for each section during Indian Ocean CO₂ survey

| Batch | Section | Certified TALK ($\mu\text{mol/kg}$) | MATS mean TALK ($\mu\text{mol/kg}$) | S.D. (n) ($\mu\text{mol/kg}$) | Δ TALK (MATS - CRM) ($\mu\text{mol/kg}$) |
|-------|---------|---------------------------------------|---------------------------------------|---------------------------------|---|
| 23 | I8SI9S | 2212.7 | 2221.5 | 5.1 (49) | 8.8 |
| 23 | I9N | 2212.7 | 2216.2 | 3.3 (138) | 3.5 |
| 23 | I8NI5E | 2212.7 | 2211.6 | 4.9 (80) | ! 1.1 |
| 23 | I3 | 2212.7 | 2215.4 | 1.4 (65) | 2.7 |
| 26 | I3 | 2176.6 | 2178.0 | 1.2 (30) | 1.4 |
| 26 | I5WI4 | 2176.6 | 2182.6 | 3.8 (79) | 6.0 |
| 26 | I7N | 2176.6 | 2184.0 | 5.7 (59) | 7.4 |
| 27 | I7N | 2214.9 | 2221.5 | 3.1 (8) | 6.6 |
| 23 | I7N | 2212.7 | 2222.4 | 7.4 (10) | 9.7 |
| 27 | I1 | 2214.9 | 2219.4 | 3.9 (244) | 4.5 |
| 27 | I10 | 2214.9 | 2212.9 | 4.0 (62) | ! 2.0 |
| 27 | I2 | 2214.9 | 2219.4 | 4.5 (67) | 4.5 |
| n | | | | 891 | 12 |

TALK was also checked at the crossover locations of two cruises in the same way as TCO₂. The agreement between the corrected TALK measurements made at the crossover locations (± 100 km) on different cruises was examined by assuming that the temporal and spatial variations of the deep-ocean TALK were small relative to measurement accuracy and precision. Hence, deep ocean waters should have the same TALK at different times in the absence of internal vertical motion, and because deep ocean motion probably occurs along constant-density surfaces (isopycnals), the comparisons of TALK measurements were made with reference to density and not depth. Appendixes C and D give a description of the statistical procedures used to make the crossover comparisons. For water samples collected below 2500 m, a smooth curve was fit through the TALK data as a function of the density anomaly referenced to 3000 dbar (σ_t) using Cleveland's LOESS smoother (Cleveland and Devlin 1988). A separate fit was performed on the data collected at each of the two intersecting crossover points, with the same tension parameter being used for all of the crossovers so that the smoothing function was consistently applied. The difference between the two smoothed curves was evaluated at 50 evenly-spaced points covering the density range where the two data sets overlapped. Mean and standard deviations for the differences at the 50 points were calculated for each crossover point. For TALK, differences never exceeded 6 $\mu\text{mol/kg}$, and the overall mean and standard deviation of the differences was 2.1

$\pm 2.1 \mu\text{mol/kg}$. The latter were consistent with the overall precision of the CRM analyses ($\pm 4 \mu\text{mol/kg}$).

Table 13 is a final summation of the inorganic carbon analytical work completed during the Indian Ocean CO₂ survey from 1994 to 1996.

Table 13. Final count of carbonate system parameter (CSP) analyses during Indian Ocean CO₂ survey

| Parameters | No. of CSP determinations | | |
|------------------|---------------------------|-------|--------|
| | Discrete | CRM | Total |
| TCO ₂ | 18,963 | 983 | 19,946 |
| TALK | 18,928 | 949 | 19,877 |
| Total | 37,891 | 1,932 | 39,823 |

3.4 Carbon Data Synthesis and Analysis

In accordance with one of the stated goals of the program, an evaluation of the data set with respect to estimated anthropogenic CO₂ distributions in the Indian Ocean has been completed and published by Sabine et al. (1999) (see Appendix D). The document is appended to this report as Appendix D. Additional crossover comparisons of the survey data with data gathered in the 1980s and in 1993 by French scientists are included. Briefly, the sequestering of anthropogenic CO₂ has been estimated by comparing the Indian Ocean survey results with the Indian Ocean GEOSECS expedition data from 1977 to 1978. Although CRM samples were not available for evaluating the earlier data, statistical methods were used to fit these data and correct for calibration offsets so that they could be compared with the current survey data. The data analysis was complicated by regions of pronounced denitrification (Arabian basin) and other regional variations that had to be considered and quantified. In summary, the estimate of the anthropogenic inventory was relatively small in the Indian and Southern Oceans, with anthropogenic carbon uptake lower by a factor of 2 compared to that of the Atlantic Ocean. Importantly, discrepancies between model and data-based estimates were found especially for the Southern Ocean where carbon uptake appears to have been traditionally overestimated by the extant circulation models. (See Appendix D for further details.) The initial data synthesis work indicates that the survey data will provide an important baseline with respect to future studies and that the spatial distribution of anthropogenic carbon can be an important tool for understanding model-based carbon uptake estimates and the response of models to atmospheric increases in CO₂.

3.5 Radiocarbon Measurements

Full information on the radiocarbon measurement method, instrumentation, and results can be found in Appendix E of this document.

4. DATA CHECKS AND PROCESSING PERFORMED BY CDIAC

An important part of the numeric data packaging process at the Carbon Dioxide Information Analysis Center (CDIAC) involves the quality assurance (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 I8SI9S, I9N, I8NI5E, I3, I5WI4, I7N, I1, I10, and I2 in the Indian Ocean.

1. The final carbon-related data were provided to CDIAC by the ocean carbon measurement PIs listed in Table 5. The final hydrographic and chemical measurements and the station information files were provided by the WOCE Hydrographic Program Office (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 outliers using the Ocean Data View (ODV) software (Schlitzer 2001) Station Mode (Fig. 3).
3. The section plots for every parameter were generated using the ODV's Section Mode in order to map a general distribution of each property along all Indian Ocean sections (Fig. 4).
4. To identify "noisy" data and possible systematic, methodological errors, property-property plots for all parameters were generated (Fig. 5), carefully examined, and compared with plots from previous expeditions in the Indian Ocean.
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 < 1994 or > 1996; TIME < 0000 or > 2400; LATITUDE < ! 70.000 or > 60.000; LONGITUDE < 19.000 or > 119.000).
7. Station locations (latitudes and longitudes) and sampling times were examined for consistency with maps and cruise information supplied by PIs.
8. The designation for missing values, given as ! 9.0 in the original files, was changed to ! 999.9 for the consistency with other oceanographic data sets.

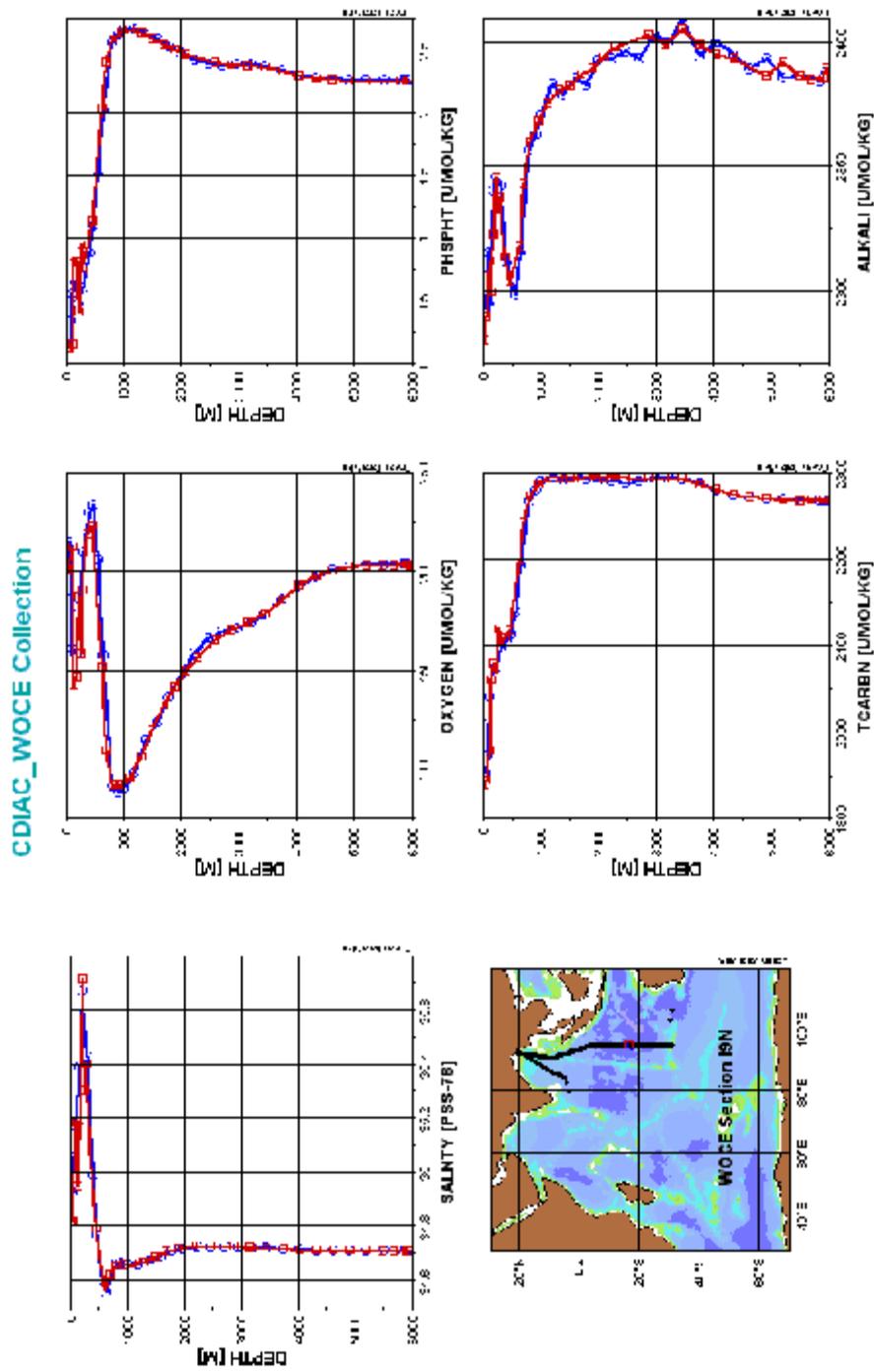


Fig. 3. Example of ODV station mode plot: Measurements vs depth for Stations 172–174 of Section I9N.

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Fig. 4. Distribution of the TCO₂ and TALK in seawater along WOCE Section I9N.

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Fig. 5. Property-property plots for all stations occupied during the R/V *Knorr* cruise along WOCE Section I9N.

5. HOW TO OBTAIN THE DATA AND DOCUMENTATION

This database (NDP-077) 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 cdiaac.ornl.gov or >ftp 160.91.18.18
Login: "anonymous" or "ftp"
Password: your e-mail address
ftp> cd pub/ndp080/
ftp> dir
ftp> mget (files)
ftp> quit
```

Contact information:

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Internet: <http://cdiac.ornl.gov/>

6. REFERENCES

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PART 2:

CONTENT AND FORMAT OF DATA FILES

7. FILE DESCRIPTIONS

This section describes the content and format of each of the nine files that constitute this NDP-080 (see Table 14). Because CDIAC distributes the data set in several ways (via the Web, CDIAC's online ordering system, or anonymous FTP), each of the 21 files is referenced by both an ASCII file name, which is given in lowercase, bold-faced type (e.g., **ndp080.txt**), and a file number. The remainder of this section describes (or lists, where appropriate) the contents of each file.

Table 14. Content, size, and format of data files

| File number, name, and description | Logical records | File size in bytes |
|---|--------------------|-----------------------|
| 1. ndp080.txt : A detailed description of the cruise network, the two FORTRAN 90 data-retrieval routines, and the eighteen oceanographic data files | 2,091 | 128,813 |
| 2. IOstainv.for : A FORTRAN 90 data-retrieval routine to read and print i*sta.dat (Files 4–12) | 44 | 1,411 |
| 3. IOdat.for : A FORTRAN 90 data-retrieval routine to read and print i*.dat (Files 13–21) | 58 | 2,407 |
| 4–12. i08si09ssta.dat | 156 | 12,573 |
| i09nsta.dat | 139 | 11,340 |
| i08ni05esta.dat | 175 | 14,260 |
| i03sta.dat | 140 | 11,390 |
| i05wi04sta.dat | 145 | 11,688 |
| i07nsta.dat | 159 | 12,949 |
| i01sta.dat | 167 | 13,650 |
| i10sta.dat | 70 | 5,684 |
| i02sta.dat : A listing of the station locations, sampling dates, and sounding bottom depths for each station of the WOCE Sections I8S19S, I9N, I8N15E, I3, I5W14, I7N, I1, I10, and I2 | 177 | 14,420 |
| 13–21. i08si09s.dat | 4,566 | 898,494 |
| i09n.dat | 4,537 | 892,942 |
| i08ni05e.dat | 5,477 | 1,078,087 |

| | | |
|--|---------------|------------------|
| i03.dat | 4,017 | 790,348 |
| i05wi04.dat | 4,028 | 792,411 |
| i07n.dat | 5,128 | 1,009,334 |
| i01.dat | 4,601 | 905,550 |
| i10.dat | 1,748 | 343,395 |
| i02.dat: | 5,567 | 1,095,817 |
| Hydrographic, carbon dioxide, and chemical data from all stations occupied on WOCE Sections I8SI9S, I9N, I8NI5E, I3, I5WI4, I7N, I1, I10, and I2 | | |
| Total | 43,190 | 8,046,963 |

7.1 ndp080.txt (File 1)

This file contains a detailed description of the data set, the two FORTRAN 90 data-retrieval routines, and the 18 oceanographic data files. It exists primarily for the benefit of individuals who acquire this database as machine-readable data files from CDIAC.

7.2 IOstainv.for (File 2)

This file contains a FORTRAN 90 data-retrieval routine to read and print **i*sta.dat** (Files 4–12). The following is a listing of this program. For additional information regarding variable definitions, variable lengths, variable types, units, and codes, please see the description for **i*sta.dat** in Sect. 7.4.

```

c*****
c* This is a Fortran 90 retrieval code to read and format the
c* station inventory during the R/V Knorr Cruises along the WOCE
c* Sections I8SI9S, I9N, I8NI5E, I3, I5WI4, I7N, I1, I10, and I2
c* in the Indian Ocean
c*****

c*Defines variables*

      INTEGER stat, cast, depth
      REAL latdcm, londcm
      CHARACTER expo*10, sect*4, date*10, time*4
      OPEN (unit=1, file='i*sta.dat')
      OPEN (unit=2, file='i*sta.data')
      write (2, 5)

c*Writes out column labels*

5      format (1X,'EXPCODE',8X,'SECT',2X,'STNBR',2X,'CAST',9X,
2      'DATE',2X,'TIME',2X,'LATITUDE',2X,'LONGITUDE',2X,'DEPTH',/)

```

```

c*Sets up a loop to read and format all the data in the file*

      read (1, 6)
6      format (/////////)

7      CONTINUE
      read (1, 10, end=999) expo, sect, stat, cast, date, time,
1 latdcm, londcm, depth

10     format (1X, A10, 6X, A4, 3X, I4, 5X, I1, 3X, A10, 2X, A4, 3X,
1 F7.3, 3X, F8.3, 3X, I4)

      write (2, 20) expo, sect, stat, cast, date, time,
1 latdcm, londcm, depth

20     format (1X, A10, 6X, A4, 3X, I4, 5X, I1, 3X, A10, 2X, A4, 3X,
1 F7.3, 3X, F8.3, 3X, I4)

      GOTO 7
999    close(unit=5)
      close(unit=2)
      stop
      end

```

7.3 i*.dat.for (File 3)

This file contains a FORTRAN 90 data-retrieval routine to read and print **i*.dat** (Files 13–21). The following is a listing of this program. For additional information regarding variable definitions, variable lengths, variable types, units, and codes, please see the description for **i*.dat** in Sect. 7.5.

```

c*****
c* FORTRAN 90 data retrieval routine to read and print the files
c* named "i*.dat" (Files 13-21)
c*****
      CHARACTER qual*15, bot*6
      INTEGER sta, cast, samp
      REAL pre, ctdtmp, ctdsal, ctdoxy, theta, sal, oxy, silca
      REAL nitrat, nitrit, phspht, cfc11, cfc12, tcarb, alkali
      REAL delc14, c14er, delc13
      OPEN (unit=1, file='i08si09s.dat')
      OPEN (unit=2, file='i08si09s.data')
      write (2, 5)

c*Writes out column labels*

5      format (2X, 'STNNBR', 2X, 'CASTNO', 2X, 'SAMPNO', 2X, 'BTLNBR', 2X,
1 'CTDPRS', 2X, 'CTDTMP', 2X, 'CTDSAL', 2X, 'CTDOXY', 3X, 'THETA', 4X,
2 'SALNTY', 2X, 'OXYGEN', 2X, 'SILCAT', 2X, 'NITRAT', 2X, 'NITRIT', 2X,
3 'PHSPHT', 3X, 'CFC-11', 3X, 'CFC-12', 2X, 'TCARBN', 2X, 'ALKALI', 2X,

```

```

4 'DELCL14',2X,'C14ERR',2X,'DELCL13',10X,'QUALT1',/,
5 36X,'DBAR',2X,'ITS-90',2X,'PSS-78',1X,'UMOL/KG',
6 2X,'ITS_90',4X,'PSS-78',1X,5('UMOL/KG',1X),1X,'PMOL/KG',2X,
7 'PMOL/KG',1X,2('UMOL/KG',1X),1X,3('/MILLE',2X),13X,'*',/,
8 25X,'*****',17X,2('*****',1X),10X,6('*****',1X),1X,
9 '*****',2X,4('*****',1X),8X,"*****",15X,'*')

c*Sets up a loop to read and format all the data in the file*

      read (1, 6)
6      format (//////////)

7      CONTINUE
      read (1, 10, end=999) sta, cast, samp, bot, pre, ctdtmp,
1      ctdsal, ctdoxy, theta, sal, oxy, silca, nitrat, nitrit,
2      phspht, cfc11, cfc12, tcarb, alkali, delc14, c14er, delc13,
3      qualt

10     format (4X, I4, 7X, I1, 6X, I2, 2X, A6, 1X, F7.1, 1X, F7.4,
1      1X, F7.4, 1X, F7.1, 1X, F7.4, 1X, F9.4, 1X, F7.1, 1X, F7.2,
2      1X, F7.2, 1X, F7.2, 1X, F7.2, 1X, F8.3, 1X, F8.3, 1X, F7.1,
3      1X, F7.1, 1X, F7.1, 1X, F7.1, 1X, F7.1, 1X, A15)

      write (2, 20) sta, cast, samp, bot, pre, ctdtmp,
1      ctdsal, ctdoxy, theta, sal, oxy, silca, nitrat, nitrit,
2      phspht, cfc11, cfc12, tcarb, alkali, delc14, c14er, delc13,
3      qualt

20     format (4X, I3, 7X, I1, 6X, I2, 2X, A6, 1X, F7.1, 1X, F7.4,
1      1X, F7.4, 1X, F7.1, 1X, F7.4, 1X, F9.4, 1X, F7.1, 1X, F7.2,
2      1X, F7.2, 1X, F7.2, 1X, F7.2, 1X, F8.3, 1X, F8.3, 1X, F7.1,
3      1X, F7.1, 1X, F7.1, 1X, F7.1, 1X, F7.1, 1X, A15)

      GOTO 7
999    close(unit=1)
      close(unit=2)
      stop
      end

```

7.4 i*sta.dat (Files 4–12)

These files, **i08si09ssta.dat**, **i09nsta.dat**, **i08ni05esta.dat**, **i03sta.dat**, **i05wi04sta.dat**, **i07nsta.dat**, **i01sta.dat**, **i10sta.dat**, and **i02sta.dat**, provide station inventory information for each station occupied during the R/V *Knorr* cruises along WOCE Sections I8SI9S, I9N, I8NI5E, I3, I5WI4, I7N, I1, I10, and I2. Each line in the files contains an expocode, section number, station number, cast number, sampling date (month/date/year), sampling time, latitude, longitude,

and sounding depth. The files are sorted by station number and can be read by using the following FORTRAN 90 code (contained in **IOstainv.for**, File 2):

```

      INTEGER  stat, cast, depth
      REAL    latdcm, londcm
      CHARACTER expo*10, sect*4, date*10, time*4

      read (1, 10, end=999) expo, sect, stat, cast, date, time,
1 latdcm, londcm, depth

10    format (1X, A10, 6X, A4, 3X, I4, 5X, I1, 3X, A10, 2X, A4, 3X,
1 F7.3, 3X, F8.3, 3X, I4)

```

Stated in tabular form, the contents include the following:

| Variable | Variable type | Variable width | Starting column | Ending column |
|---------------|---------------|----------------|-----------------|---------------|
| expo | Character | 10 | 2 | 11 |
| sect | Character | 4 | 18 | 21 |
| stat | Numeric | 4 | 25 | 28 |
| cast | Numeric | 1 | 34 | 34 |
| date | Character | 10 | 38 | 47 |
| time | Character | 4 | 50 | 53 |
| latdcm | Numeric | 7 | 57 | 63 |
| londcm | Numeric | 8 | 67 | 74 |
| depth | Numeric | 4 | 78 | 81 |

The variables are defined as follows:

| | |
|---------------|--|
| expo | expedition code of the cruise |
| sect | WOCE section number |
| stat | station number |
| cast | cast number |
| date | sampling date (month/day/year) |
| time | sampling time [Greenwich mean time (GMT)] |
| latdcm | latitude of the station (in decimal degrees; negative values indicate the Southern Hemisphere) |

loncem longitude of the station (in decimal degrees; negative values indicate the Western Hemisphere)

depth sounding depth of the station (in meters)

7.5 i*.dat (Files 13–21)

These files, **i08si09s.dat**, **i09n.dat**, **i08ni05e.dat**, **i03.dat**, **i05wi04.dat**, **i07n.dat**, **i01.dat**, **i10.dat**, and **i02.dat**, provide hydrographic, carbon dioxide, and chemical data for all stations occupied during the R/V *Knorr* cruises along WOCE Sections I8SI9S, I9N, I8NI5E, I3, I5WI4, I7N, I1, I10, and I2. Each line consists of station number, cast number, sample number, bottle number, CTD pressure, CTD temperature, CTD salinity, CTD oxygen, potential temperature, bottle salinity, bottle oxygen, silicate, nitrate, nitrite, phosphate, CFC-11, CFC-12, TCO₂, TALK, $\delta^{14}\text{C}$, ^{14}C error, $\delta^{13}\text{C}$, and data-quality flags. The files are sorted by station number and pressure and can be read by using the following FORTRAN 90 code (contained in **i*.dat.for**, File 3):

```

CHARACTER qualt*15, bot*6
INTEGER sta, cast, samp
REAL pre, ctdtmp, ctdsal, ctdoxy, theta, sal, oxy, silca
REAL nitrat, nitrit, phspht, cfc11, cfc12, tcarb, alkali
REAL delc14, c14er, delc13

read (1, 10, end=999) sta, cast, samp, bot, pre, ctdtmp,
1 ctdsal, ctdoxy, theta, sal, oxy, silca, nitrat, nitrit,
2 phspht, cfc11, cfc12, tcarb, alkali, delc14, c14er, delc13,
3 qualt

10 format (4X, I4, 7X, I1, 6X, I2, 2X, A6, 1X, F7.1, 1X, F7.4,
1 1X, F7.4, 1X, F7.1, 1X, F7.4, 1X, F9.4, 1X, F7.1, 1X, F7.2,
2 1X, F7.2, 1X, F7.2, 1X, F7.2, 1X, F8.3, 1X, F8.3, 1X, F7.1,
3 1X, F7.1, 1X, F7.1, 1X, F7.1, 1X, F7.1, 1X, A15)

```

Stated in tabular form, the contents include the following:

| Variable | Variable type | Variable width | Starting column | Ending column |
|-------------|---------------|----------------|-----------------|---------------|
| sta | Numeric | 4 | 5 | 8 |
| cast | Numeric | 1 | 16 | 16 |
| samp | Numeric | 2 | 23 | 24 |
| bot | Character | 6 | 27 | 32 |
| pre | Numeric | 7 | 34 | 40 |

| | | | | |
|---------------|-----------|----|-----|-----|
| ctdtmp | Numeric | 7 | 42 | 48 |
| ctdsal | Numeric | 7 | 50 | 56 |
| ctdoxy | Numeric | 7 | 58 | 64 |
| theta | Numeric | 7 | 66 | 72 |
| sal | Numeric | 9 | 74 | 82 |
| oxy | Numeric | 7 | 84 | 90 |
| silca | Numeric | 7 | 92 | 98 |
| nitrat | Numeric | 7 | 100 | 106 |
| nitrit | Numeric | 7 | 108 | 114 |
| phspht | Numeric | 7 | 116 | 122 |
| cfc11 | Numeric | 8 | 124 | 131 |
| cfc12 | Numeric | 8 | 133 | 140 |
| tcarb | Numeric | 7 | 142 | 148 |
| alkali | Numeric | 7 | 150 | 156 |
| delc14 | Numeric | 7 | 158 | 164 |
| c14er | Numeric | 7 | 166 | 172 |
| delc13 | Numeric | 7 | 174 | 180 |
| qualt | Character | 15 | 182 | 196 |

The variables are defined as follows:

| | |
|---------------------------|--|
| sta | station number |
| cast | cast number |
| samp | sample number |
| bot^a | bottle number |
| pre | CTD pressure (dbar) |
| ctdtmp | CTD temperature (°C) |
| ctdsal^a | CTD salinity [on the Practical Salinity Scale (PSS)] |
| ctdoxy^a | CTD oxygen (Fmol/kg) |
| theta | potential temperature (°C) |
| sal^a | bottle salinity (on the PSS) |
| oxy^a | oxygen concentration (Fmol/kg) |
| silca^a | silicate concentration (Fmol/kg) |

| | |
|-----------------------------------|---|
| <u>nitrat</u> ^a | nitrate concentration (Fmol/kg) |
| <u>nitrit</u> ^a | nitrite concentration (Fmol/kg) |
| <u>phspht</u> ^a | phosphate concentration (Fmol/kg) |
| <u>cfc11</u> ^a | chlorofluorocarbon 11 (pmol/kg) |
| <u>cfc12</u> ^a | chlorofluorocarbon 21(pmol/kg) |
| <u>tcarb</u> ^a | total carbon dioxide concentration (Fmol/kg) |
| <u>alkali</u> ^a | total alkalinity (Fmol/kg) |
| <u>delc14</u> ^a | radiocarbon delta ¹⁴ C (per mille) |
| <u>c14er</u> | error of delta ¹⁴ C (percent) |
| <u>delc13</u> ^a | is the radiocarbon delta ¹³ C (per mille); |
| <u>qualt</u> | 15-digit character variable that contains data-quality flag codes for parameters underlined with asterisks (*****) in the file header |

^aVariables 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
- 7 = manual chromatographic peak measurement
- 8 = irregular digital chromatographic peak integration
- 9 = sample not drawn for this measurement from this bottle

APPENDIX A:

**List of CO₂ measurement group members participating in the Indian Ocean CO₂ Survey
aboard the R/V *Knorr* in 1994–1996**

Appendix A

List of CO₂ measurement group members participating in the Indian Ocean CO₂ Survey aboard the R/V *Knorr* in 1994–1996

(CO₂ group leaders for each section are given in Table 4 in the text)

| Section | Name | Sponsoring institute | Affiliation (if known) |
|---------|---|-------------------------|----------------------------|
| I8SI9S | Haynes, Charlotte H Haynes, Elizabeth M Wysor, Brian S. | BNL BNL BNL | WDNR RU SHC |
| I9N | Dorety, Art Kozyr, Alex Suntharalingam, Parv | PU PU PU | PU ORNL/CDIAC PU |
| I8NI5E | Parks, Justine Popp, Brian Schottle, R. | UH UH UH | SIO UH UH |
| I3 | Aicher, Jennifer Edwards, Christopher Krenisky, Joann | RSMAS RSMAS RSMAS | RSMAS RSMAS RSMAS |
| I4I5W | Lewis, Ernie Pikanowski, Linda Zotz, Michelle | BNL BNL BNL | BNL SHML BNL |
| I7N | Adams, Angela Angeley, Kelly Phillips, Jennifer | UH UH UH | UH UHH |
| I1 | Amaoka, Toshitaka Okuda, Kozo Ording, Philip | WHOI WHOI WHOI | GSEESHU GSEESHU WHOI |
| I10 | Boehme, Sue Markham, Marion Mcdonald, Gerard | PU PU PU | RU PU PU |
| I2 | Admas, Angela Cipolla, Cathy Phillips, Jennifer | UH UH UH | UH GSOURI UHH |

Participating institutions:

| | |
|------------|--|
| BNL | Brookhaven National Laboratory |
| ORNL/CDIAC | Oak Ridge National Laboratory/Carbon Dioxide Information Analysis Center |
| GSEESHU | Graduate School of Environmental and Earth Science, Hokkaido University |
| GSOURI | Graduate School of Oceanography, University of Rhode Island |
| PU | Princeton University |
| RSMAS | Rosenstiel School of Marine and Atmospheric Science, University of Miami |
| RU | Rutgers University |
| SHC | South Hampton College |
| SHML | Sandy Hook Marine Laboratory |
| SIO | Scripps Institution of Oceanography |
| UH | University of Hawaii, Honolulu |
| UHH | University of Hawaii at Hilo |
| WDNR | Wisconsin Department of Natural Resources |
| WHOI | Woods Hole Oceanographic Institution |

APPENDIX B:

REPRINT OF PERTINENT LITERATURE

Johnson, K. M., A. G. Dickson, G. Eiseid, C. Goyet, P. R. Guenther, R. M. Key, F. J. Millero, D. Purkerson, C. L. Sabine, R. G. Schotle, D. W. R. Wallace, R. J. Wilke, and C. D. Winn. 1998. Coulometric total carbon dioxide analysis for marine studies: Assessment of the quality of total inorganic carbon measurements made during the U.S. Indian Ocean CO₂ Survey 1994–1996. *Marine Chemistry* 63:21–37.

APPENDIX C:

REPRINT OF PERTINENT LITERATURE

Millero, F. J., A. G. Dickson, G. Eiseid, C. Goyet, P. R. Guenther, K. M. Johnson, K. Lee, E. Lewis, D. Purkerson, C. L. Sabine, R. Key, R. G. Schottle, D. R. W. Wallace, and C. D. Winn. 1998. Total alkalinity measurements in the Indian Ocean during the WOCE hydrographic program CO₂ survey cruises 1994–1996. *Marine Chemistry* 63:9–20.

APPENDIX D:

REPRINT OF PERTINENT LITERATURE

Sabine, C. L., R. M. Key, K. M. Johnson, F. J. Millero, J. L. Sarmiento, D. R. W. Wallace, and C. D. Winn. 1999. Anthropogenic CO₂ inventory of the Indian Ocean. *Global Biogeochemical Cycles* 13:179–98.

APPENDIX E:

REPRINT OF PERTINENT LITERATURE

Key R. M., and P. D. Quay. 2002. U.S. WOCE Indian Ocean Survey: Final Report for Radiocarbon. Technical Report. Princeton University, Princeton, N.J.