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CARBON DIOXIDE, HYDROGRAPHIC, AND CHEMICAL DATA OBTAINED DURING THE R/Vs *ROGER REVELLE* AND *THOMAS THOMPSON* REPEAT HYDROGRAPHY CRUISES IN THE PACIFIC OCEAN: CLIVAR CO_2 SECTIONS P16S_2005 (6 JANUARY–19 FEBRUARY, 2005) AND P16N_2006 (13 FEBRUARY–30 MARCH, 2006)

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ABBREVIATIONS AND ACRONYMS

AMC	accelerator mass spectrometry
AOML	Atlantic Oceanographic and Meteorological Laboratory
CDIAC	Carbon Dioxide Information Analysis Center
CCHDO	CLIVAR and Carbon Hydrographic Data Office
CFC	chlorofluorocarbon
CLIVAR	Climate Variability (Program)
CO_2	carbon dioxide
CRM	certified reference material
CTD	conductivity, temperature, and depth
DOC	dissolved organic carbon
ECD	electron capture detector
emf	electromotive force (of an electrochemical cell)
EXPOCODE	expedition code
GC	gas chromatograph
HCFC	hydrochlorofluorocarbon
HDPE	high density polyethylene
IAPSO	International Association for the Physical Sciences of the Ocean
LCW	liquid-core waveguide
mCP	m-Cresol purple
MICA	multi-parameter inorganic carbon analyzer
NDP	numeric data package
NOAA	National Oceanic and Atmospheric Administration
NOSAMS	National Ocean Sciences Accelerator Mass Spectrometry Facility
NSF	National Science Foundation
ODF	Oceanographic Data Facility
ODV	Ocean Data View
PMEL	Pacific Marine Environmental Laboratory
RSMAS	Rosenstiel School of Marine and Atmospheric Science
R/V	research vessel
SIO	Scripps Institution of Oceanography
SOMMA	single-operator multi-parameter metabolic analyzer
SST	sea surface temperature
SSW	standard seawater
STS	Shipboard Technical Support
TALK	total alkalinity
TCO_2	total carbon dioxide or dissolved inorganic carbon
TN	total nitrogen (analyzer)
UCSB	University of California Santa Barbara
UH	University of Hawaii
UM	University of Miami
USF	University of South Florida
UW	University of Washington
WHP	WOCE Hydrographic Program
WOCE	World Ocean Circulation Experiment

ABSTRACT

Feely R. A., C. L. Sabine, F. J. Millero, C. Langdon, A. G. Dickson , R. A. Fine, J. L. Bullister, D.A. Hansell, C. A. Carlson, A. P. McNichol, R. M. Key, R. H. Byrne, and R. Wanninkhof. 2008. *Carbon Dioxide, Hydrographic, and Chemical Data Obtained During the R/Vs Roger Revelle and Thomas G. Thompson Repeat Hydrography Cruises in the Pacific Ocean: CLIVAR CO_2 Sections P16S_2005 (6 January–19 February 2005) and P16N_2006 (13 February–30 March, 2006)*. Ed. A. Kozyr. ORNL/CDIAC-155, NDP-090. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee, 54 pp. doi:10.3334/CDIAC/00002.

This report presents methods, and analytical and quality control procedures for salinity, oxygen, nutrients, total carbon dioxide (TCO_2), total alkalinity (TALK), pH, discrete CO_2 partial pressure (pCO_2), dissolved organic carbon (DOC), chlorofluorocarbons (CFCs), radiocarbon, $\delta^{13}C$, and underway carbon measurements performed during the P16S_2005 *(*6 January–19 February 2005*)* and P16N_2006 (13 February–30 March, 2006) cruises in the Pacific Ocean. The research vessel (R/V) *Roger Revelle* departed Papeete, Tahiti, on January 6, 2005 for the Repeat Section P16S, nominally along 150°W, ending in Wellington, New Zealand, on February 19. During this cruise, samples were taken from 36 depths at 111 CTD stations between 16°S and 71°S. The Repeat Section P16N, nominally along 152°W, consisted of two legs. Leg 1 started on February 13, 2006 in Papeete, Tahiti, and finished on March 3, in Honolulu, Hawaii. The R/V *Thomas G. Thompson* departed Honolulu for Leg 2 on March 10, 2006 and arrived in Kodiak, Alaska, on March 30. During the P16N cruises, samples were taken from 34 or 36 depths at 84 stations between 17°S and 56.28°N. The research conducted on these cruises was part of a series of repeat hydrography sections jointly funded by the National Oceanic and Atmospheric Administration (NOAA) and the National Science Foundation (NSF) as part of the Climate Variability Program (CLIVAR)/CO_2 Repeat Hydrography Program.

The P16S and P16N data sets are available free of charge as a numeric data package (NDP) from the Carbon Dioxide Information Analysis Center (CDIAC). The NDP consists of the oceanographic data files and this printed documentation, which describes the procedures and methods used to obtain the data.

Keywords: carbon dioxide, total CO_2, total alkalinity, carbon cycle, radiocarbon, coulometry, DOC, potentiometry, hydrographic measurements, CLIVAR, Pacific Ocean

1. BACKGROUND INFORMATION

The WOCE designated P16 line was sampled as part of the Climate Variability / Carbon Dioxide ($CLIVAR/CO_2$) Repeat Hydrography Program, sponsored by the National Oceanic and Atmospheric Administration (NOAA) and National Science Foundation (NSF). The goal of the Repeat Hydrogaphy Program is to measure decadal changes in circulation, heat and fresh water budgets, and carbon inventory in the ocean. The cruises repeat a subset of the WOCE Hydrographic Program (WHP) and Joint Global Ocean Flux Study (JGOFS) lines occupied in each major ocean basin in the 1990s. These measurements are of importance both for international research programs, such as CLIVAR or IMBER, and for operational activities such as the Global Ocean Observation System and the Global Climate Observing System. As outlined in the program documentation, one component of a global observing system for the physical climate/CO_2 system should include periodic observations of hydrographic variables, CO_2 system parameters, and other tracers. The large-scale observation component of the Ocean Carbon and Climate Change Program needs systematic observations of the invasion of anthropogenic carbon in the ocean superimposed on a variable natural background. The six topical areas addressed by the $CLIVAR/CO_2$ Repeat Hydrography program are:

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

The P16 line, which lies nominally along 150–152° W, between 72° S and 55° N (Fig. 1) was a reoccupation of a several meridional P16 cruises sampled during WOCE: P16N (NOAA CGC-91 cruise onboard R/V *Discoverer* in 1991, Feely et al. 1991); P16C (R/V *T. Washington* TUNES-3 cruise in 1991; NDP-060 at http://cdiac.ornl.gov/oceans/ndp_060/ndp060.html); P16S (R/V *T. Washington* TUNES-2 cruise in 1991, see NDP-054 at http://cdiac.ornl.gov/oceans/ndp_054/ndp054.html); and P16A (R/V *Knorr* Juno 9 cruise in 1992, see NDP-65 at http://cdiac.ornl.gov/oceans/ndp_065/ndp065.html).

The R/V *Roger Revelle* conducted the first $CLIVAR/CO_2$ P16 cruise designated as P16S. The cruise departed from Papeete, Tahiti, on January 9, 2005 conducting hydrographic profiles at one-half degree spacing nominally along 150°W from 16° S to 71°S. Scientists completed 111 full-depth conductivity, temperature, and depth (CTD)/rosette/lowered acoustic Doppler current profiler (LADCP) casts, 4 shallow colored dissolved organic matter (CDOM) rosette casts, 21 bio-optical casts and 58 trace metals CTD/rosette casts. In addition twelve ARGOS floats were deployed. The cruise ended in Wellington, New Zealand, on February 19, 2005.

The R/V *Thomas G. Thompson* departed Papeete, Tahiti, on February 13, 2006, for the beginning of Leg 1 of Section P16N. The first station was at 17° S, 150° W. This station and the next station at 16° S, 150° W repeated the occupation of two stations sampled in 2005 as part of Section P16S. The ship then proceeded north conducting a full depth CTD/rosette/LADCP cast every 60 nm to 21° N, 152° W. Station spacing was decreased to 30 miles between 2° S and 2° N. Thirty-four 12-L Niskin type bottles were used to collect water samples from throughout the water column at each station. Each Niskin bottle was sub-sampled on deck for a variety of analyses. Twenty projects were represented on Leg 1 of the cruise. A 1000 m trace metal cast was conducted at every other station, except between 2° S and 1° N where a profile was collected at every station for a total of 23 trace metal casts. The trace metal casts were conducted at approximately the same locations as the primary profiles and were either before or after the full-depth casts depending on time of day. One optical profile was collected each day on stations that

occurred between 10:00 and 14:00 local time. Near surface seawater (temperature, salinity, partial pressure of carbon dioxide [pCO_2], acoustic Doppler current profiler [ADCP]) and atmospheric measurements (CO_2, CFCs, aerosols) were also made along the cruise track. The last of 43 stations was completed on Thursday, March 2, 2006. The cruise ended in Honolulu, Hawaii, on March 3, 2006.

The R/V *Thomas G. Thompson* departed Honolulu, Hawaii, on March 10, 2006, for the start of Leg 2 of Section P16N. The first station was occupied at 22° N, 152° W. The ship then proceeded north while a full-depth CTD/rosette/LADCP cast was conducted every 60 nautical miles to 55° N, 152° W, where a series of 8 closely-spaced stations were conducted close to the Alaskan coast. Thirty-six 12-L Niskin bottles were used to collect water samples from throughout the water column at each station. Each Niskin bottle was sub-sampled on deck for a variety of analyses. Twenty projects were represented on Leg 2 of the cruise. A 1000 m trace metal cast was conducted approximately every other station for a total of 17 trace metal casts. The trace metal casts were conducted at approximately the same locations as the primary profiles and were either before or after the full-depth casts depending on time of day. One optical profile was collected each day on stations that occurred between 10:00 and 14:00 local time. A total of 41 stations were occupied on Leg 2. In addition, net tows were conducted at night at about 10 stations either while steaming towards a station or upon departure. As part of the Argo program, floats were deployed at 8 locations usually upon departure from a station. Underway measurements of surface seawater properties (temperature, salinity, pCO_2, ADCP) and atmospheric concentrations of CO_2, CFCs, and aerosols were also made along the cruise track. The last station was completed on Wednesday, March 29, 2006. The expedition ended in Kodiak, Alaska, on March 30, 2006.

This report presents methods, and analytical and quality control procedures for salinity, oxygen, nutrients, total carbon dioxide (TCO_2), total alkalinity (TALK), pH, discrete CO_2 partial pressure (pCO_2), dissolved organic carbon (DOC), chlorofluorocarbons (CFCs), carbon isotopes, and underway carbon measurements performed on these cruises. For information about other measurements from the P16 cruises see the cruise reports at CLIVAR and Carbon Hydrographic Data Office (CCHDO) (http://whpo.ucsd.edu/groups?id=p16).

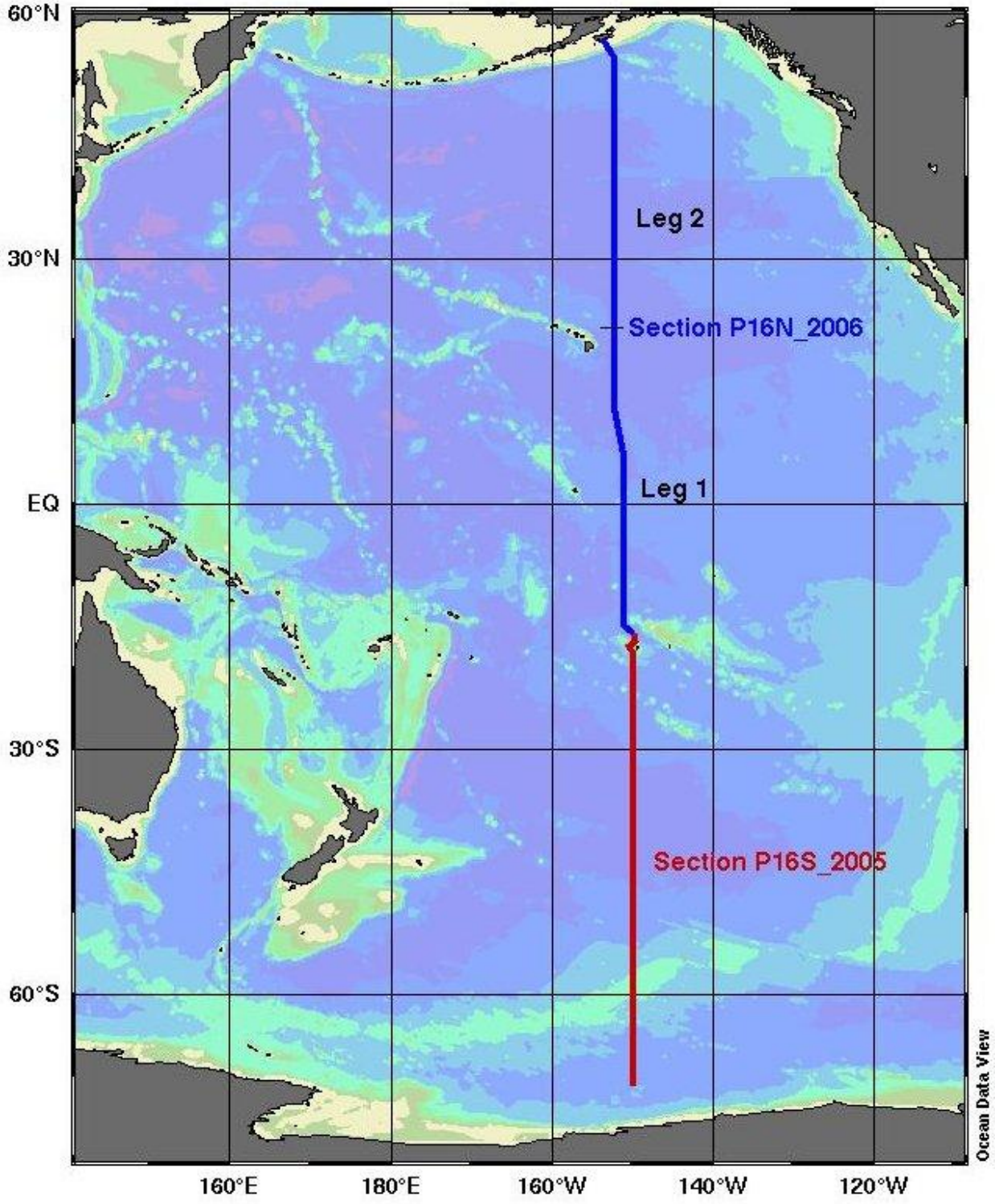

Fig. 1. Cruise tracks for the Pacific Ocean Sections P16S_2005 and P16N_2006.

2. DESCRIPTION OF THE EXPEDITIONS

2.1 R/V *Roger Revelle* P16S_2005 Cruise Information

Ship name	***Roger Revelle***
EXPOCODEs	33RR20050109
CLIVAR section	P16S_2005
Ports of call	Papeete, Tahiti–Wellington, New Zealand
Dates	January 06–February 19, 2005
Funding support	NOAA, NSF
Chief scientists/Co-Chief Scientist	Dr. Bernadette M. Sloyan/Woods Hole Oceanographic Institution (WHOI)
	Dr. James H. Swift/SIO

2.2 R/V *Thomas G. Thompson* P16N_2006 Cruise Information

Ship name	***Thomas G. Thompson***
EXPOCODEs	325020060213
CLIVAR section	P16N_2006, Leg 1 and 2
Ports of call	Leg 1: Papeete, Tahiti–Honolulu, Hawaii, USA
	Leg 2: Honolulu, Hawaii, USA–Kodiak, Alaska, USA
Dates	Leg 1: February 13–March 3, 2006
	Leg 2: March 10–March 30, 2006
Funding support	NOAA, NSF
Chief scientists/ Co-Chief Scientist	Leg 1: Christopher L. Sabine/NOAA-Pacific Marine Environmental Laboratory (PMEL) / Dr. Erica Key/ Rosenstiel School of Marine and Atmospheric Science (RSMAS)
	Leg 2: Dr. Richard A. Feely/NOAA-PMEL/ Sabine Mecking/University of Washington (UW)

2.3 Parameters Measured, Participating Institutions, and Responsible Investigators

Table 1. Parameters measured listed with responsible investigator and associated institution for Section P16S_2005

Parameter	Institution	Responsible Investigator
Conductivity, temperature, and depth (CTD) measurements	Scripps Institution of Oceanography (SIO)	J. Swift
Acoustic and lowered acoustic Doppler current profile	University of Hawaii (UH)	E. Firing
Salinity	SIO	J. Swift
Nutrients	SIO	J. Swift
Dissolved oxygen	SIO	J. Swift
Chlorofluorocarbons	Rosenstiel School of Marine and Atmospheric Science (RSMAS), University of Miami (UM)	R. Fine
Tritium, helium	Lamont Doherty Earth Observatory (LDEO)	P. Schlosser
Total carbon dioxide	Pacific Marine Environmental Laboratory (PMEL)	R. Feely/C. Sabine
Total alkalinity	SIO	A. Dickson
Dissolved organic carbon	University of California at Santa Barbara (UCSB)	C. Carlson
Trace elements	UH/Florida State University (FSU)	C. Measures/B. Landing
^{14}C, ^{13}C	Woods Hole Oceanographic Institution (WHOI)/Princeton University	A.McNichol/R. Key
Underway pCO_2	PMEL	C. Sabine

Table 2. Parameters measured listed with responsible investigator and associated institution for Section P16N_2006, Legs 1 and 2

Parameter	Institution	Responsible Investigator
CTD measurements	PMEL/Atlantic Oceanographic and Meteorological Laboratory (AOML)	G. Johnson/M. Baringer
Acoustic and lowered acoustic Doppler current profile	LDEO	J. Hummon/ A. Thurnherr
Salinity	PMEL/AOML	G. Johnson/M. Baringer
Oxygen	RSMAS, UM	C. Langdon
Nutrients	PMEL/AOML	C. Mordy/ J. Zhang
Meteorological Measurements	RSMAS, UM	P. J. Minnett
Chlorofluorocarbons	PMEL/University of Washington	J. Bullister/M. Warner
Tritium, helium	WHOI/LDEO	B. Jenkins/ P. Schlosser
Total carbon dioxide	PMEL	R. Feely/C. Sabine
Total alkalinity	RSMAS, UM	F. Millero
Discrete pCO_2	AOML	R. Wanninkhof
Underway TCO_2/pCO_2/pH	University of South Florida (USF)	R. Byrne
Dissolved organic carbon	RSMAS, UM	D. Hansell
Trace Elements	UH/FSU	C. Measures/B. Landing
^{14}C, ^{13}C	WHOI/University of Washington/Princeton University	A. McNichol/ P. Quay/R. Key

3. DESCRIPTION OF VARIABLES AND METHODS

3.1 Hydrographic Measurements

Samples for CFCs, helium isotopes (^{3}He, ^{4}He), oxygen (O_2), hydrochlorofluorocarbon (HCFCs), TCO_2, TALK, radiocarbon ($\Delta^{14}C$) and $\delta^{13}C$, tritium, DOC, salinity, and nutrients were drawn in this sequence from a conductivity, temperature, and depth (CTD) sampling package containing thirty-six 12-L Niskin bottles. A detailed description of methods for the CTD data, LADCP data, and bio-optical data are given in the cruise reports at http://whpo.ucsd.edu/data_access?ExpoCode=33RR200501 for Section P16S_2005 and http://whpo.ucsd.edu/data_access?ExpoCode=325020060213 for Section P16N_2006.

3.1.1 Section P16S_2005

Two Guildline Autosal Model 8400A salinometers (S/N 57-396 & S/N 48-266/backup), located in the aft hydro lab, were used for all **salinity** measurements. The salinometers were modified by the Oceanographic Data Facility (ODF) to contain an interface for computer-aided measurement. The water bath temperatures were set and maintained at a value near the laboratory air temperature. They were set to 21ºC for stations 1–18 and 25–34 analyses, then switched to 24ºC for stations 19–24 and 35–11. The salinity analyses were performed after samples had equilibrated to laboratory temperature, usually within 8–26 h after collection. The salinometers were standardized for each group of analyses (usually 1–3 casts, up to ~84 samples) using at least two fresh vials of standard seawater per group. Salinometer measurements were made by computer, with the software prompting the analyst to change samples and flush.

A total of 3,699 salinity measurements were made and approximately 220 vials of standard sea water (SSW) were used during the cruise. An additional 547 samples were taken by the Trace Metals group and analyzed by Shipboard Technical Support (STS)/ODF. Salinity samples were drawn into 200-mL Kimax high-alumina borosilicate bottles, which were rinsed three times with sample prior to filling. The bottles were sealed with custom-made plastic insert thimbles and Nalgene screw caps. This assembly provides very low container dissolution and sample evaporation. Prior to sample collection, inserts were inspected for proper fit and loose inserts replaced to ensure an airtight seal. The draw time and equilibration time were logged for all casts. Laboratory temperatures were logged at the beginning and end of each run. Salinity was calculated for each sample from the measured conductivity ratios. The difference (if any) between the initial vial of standard water and the next one run as an unknown was applied as a linear function of elapsed run time to the data. The corrected salinity data were then incorporated into the cruise database. The estimated accuracy of bottle salinities run at sea is usually better than +/-0.002 relative to the particular standard seawater batch used. The 95% confidence limit for residual differences between the bottle salinities and calibrated CTD salinity relative to SSW batch P-144 was ±0.0055 for all salinities, and ±0.0018 for salinities deeper than 1000 dB. Three adjustments other than bath temperature changes were made to the Autosal during the cruise. After station 20 salinity was run, it was discovered that the amplifier gain for proper balance between suppression ranges had not been adjusted. This was changed, and stations 1–20 salinities were recalculated. A minor adjustment was made to the Autosal before station 47, and maintenance was performed on the air pump before station 92 was run. The temperature in the salinometer laboratory varied from 17.8 to 24.0ºC during the cruise. The air temperature change during 80 of the 110 sample runs was less than ±0.4ºC, and 25 runs had a temperature difference of ±0.5ºC to ±0.9ºC. International Association for the Physical Sciences of the Ocean (IAPSO) standard seawater (SSW) Batch P-144 was used to standardize all salinity measurements.

Dissolved **oxygen** analyses were performed with an ODF-designed automated oxygen titrator using photometric end-point detection based on the absorption of 365 nm wavelength ultra-violet light. The titration of the samples and the data logging were controlled by computer. Thiosulfate was dispensed by a Dosimat 665 buret driver fitted with a 1.0 mL buret. ODF used a whole-bottle modified-Winkler

titration following the technique of Carpenter 1965, with modifications by Culberson et al. 1991, but with higher concentrations of potassium iodate standard (~0.012 mol/L) and thiosulfate solution (~55 gm/L). Pre-made liquid potassium iodate standards were run once a day approximately every 4 stations, unless changes were made to system or reagents. Reagent/distilled water blanks were determined every day or more often if a change in reagents required it to account for presence of oxidizing or reducing agents. The auto-titrator performed well.

A total of 3,892 oxygen measurements were made during this cruise. Samples were collected for dissolved oxygen analyses soon after the rosette was brought on board. Using a Tygon and silicone drawing tube, nominal 125 mL volume-calibrated iodine flasks were rinsed 3 times with minimal agitation, then filled and allowed to overflow for at least 3 flask volumes. The sample drawing temperatures were measured with a small platinum resistance thermometer embedded in the drawing tube. These temperatures were used to calculate μmol/kg concentrations and as a diagnostic check of bottle integrity. Reagents were added to fix the oxygen before the bottles were sealed. The flasks were shaken twice (10–12 inversions) to ensure thorough dispersion of the precipitate, once immediately after drawing, and then again after about 20 min. The samples were analyzed within 1–2 h of collection, and the data were incorporated into the cruise database.

Thiosulfate normalities were calculated from each standardization and corrected to 20ºC. The 20ºC normalities and the blanks were plotted versus time and were reviewed for possible problems. The sample drawing temperature thermometer during this leg was functional and calibrated at the beginning of the expedition. A noisy endpoint was occasionally acquired during the analyses, usually due to small water bath contaminations. These endpoints were checked and recalculated using STS/ODF-designed software. The blanks and thiosulfate normalities for each batch of thiosulfate were smoothed (linear fits) in four groups during the cruise and the oxygen values recalculated. Oxygen flask volumes were determined gravimetrically with degassed deionized water to determine flask volumes at the STS/ODF chemistry laboratory. This is done once before using flasks for the first time and periodically thereafter when a suspect volume is detected. The volumetric flasks used in preparing standards were volume-calibrated by the same method, as was the 10 mL Dosimat buret used to dispense standard iodate solution.

Nutrient analyses (phosphate, silicate, nitrate and nitrite) were performed on an ODF-modified 4-channel Technicon AutoAnalyzer II, generally within 1–2 h after sample collection. Occasionally samples were refrigerated up to 4 h at ~4ºC. All samples were brought to room temperature prior to analysis. The methods used are described by Gordon et al. 1992. The analog outputs from each of the four colorimeter channels were digitized and logged automatically by computer at 2-second intervals.

Silicate was analyzed using the technique of Armstrong et al.1967. An acidic solution of ammonium molybdate was added to a seawater sample to produce silicomolybdic acid, which was then reduced to silicomolybdous acid (a blue compound) following the addition of stannous chloride. Tartaric acid was also added to impede PO_4 color development. The sample was passed through a 15-mm flow cell and the absorbance was measured at 660nm.

A modification of the Armstrong et al. 1967 procedure was used for the analysis of nitrate and nitrite. For the nitrate analysis, the seawater sample was passed through a cadmium reduction column where nitrate was quantitatively reduced to nitrite. Sulfanilamide was introduced to the sample stream followed by N-(1-naphthyl) ethylenediamine dihydrochloride, which coupled to form a red azo dye. The stream was then passed through a 15-mm flow cell and the absorbance measured at 540 nm. The same technique was employed for nitrite analysis, except the cadmium column was bypassed, and a 50 mm flow cell was used for measurement.

Phosphate was analyzed using a modification of the Bernhardt and Wilhelms 1967 technique. An acidic solution of ammonium molybdate was added to the sample to produce phosphomolybdic acid, then reduced to phosphomolybdous acid (a blue compound) following the addition of dihydrazine sulfate. The reaction product was heated to ~55ºC to enhance color development, then passed through a 50 mm flow cell where the absorbance was measured at 820 nm.

A total of 3806 nutrient samples were analyzed during the cruise. An additional 547 samples were taken by the Trace Metals group and analyzed by STS/ODF. Nutrient samples were drawn into 45 mL screw-capped Nalgene "Oak Ridge" centrifuge tubes. The tubes were cleaned with 10% HCl and rinsed with sample 2–3 times before being filled. Standardizations were performed at the beginning and end of each group of analyses (typically one cast, up to 36 samples) with an intermediate concentration mixed nutrient standard prepared prior to each run from a secondary standard in a low-nutrient seawater matrix. The secondary standards were prepared aboard ship by diluting primary standard solutions. Dry standards were pre-weighed at the laboratory at ODF, and transported to the vessel for dilution to the primary standard. Sets of seven different standard concentrations were analyzed periodically to determine any deviation from linearity as a function of absorbance for each nutrient analysis. A correction for non-linearity was applied to the final nutrient concentrations when necessary. A correction for the difference in refractive indices of pure distilled water and seawater was periodically determined and applied where necessary. In addition, a "deep seawater" high nutrient concentration check sample was run with each station as an additional check on data quality. The pump tubing was changed 3 times. After each group of samples was analyzed, the raw data file was processed to produce another file of response factors, baseline values, and absorbencies. Computer-produced absorbance readings were checked for accuracy against values taken from a strip chart recording. The data were then added to the cruise database. Nutrients, reported in micromoles per kilogram, were converted from micromoles per liter by dividing by sample density calculated at 1 atm pressure (0 db), in situ salinity, and a per-analysis-measured laboratory temperature.

Primary standards for silicate (Na_2SiF_6) and nitrite ($NaNO_2$) were obtained from Johnson Matthey Chemical Co.; the supplier reported purities of >98% and 97%, respectively. Primary standards for nitrate (KNO_3) and phosphate (KH_2PO_4) were obtained from Fisher Chemical Co.; the supplier reported purities of 99.999% for each. The efficiency of the cadmium column used for nitrate was monitored throughout the cruise and ranged from 99–100%. No major problems were encountered with the measurements. The temperature of the laboratory used for the analyses ranged from 21.6ºC to 25.8ºC, but was relatively constant during any one station (±1.5ºC).

3.1.2 Section P16N_2006

A single Guildline Autosal Model 8400A salinometer (S/N 48-266), located in the forward analytical lab, was used for all **salinity** measurements during Legs 1 and 2 of Repeat Section P16N_2006. The salinometer was modified by SIO/ODF to contain an interface for computer-aided measurement. The water bath temperature was set and maintained at a value near the laboratory air temperature (24°C). The salinity analyses were performed after samples had equilibrated to laboratory temperature, usually within 6–8 h after collection. The salinometers were standardized for each group of analyses (usually 1–2 casts, up to ~40 samples) using at least two fresh vials of standard seawater per group. Salinometer measurements were made by computer, with the software prompting the analyst to change samples and flush.

A total of 1,692 salinity measurements were made and ~100 vials of SSW were used during Leg 1 of the cruise and 3,250 salinity measurements were made and ~200 vials of SSW were used during the Leg 2. Salinity samples were drawn into 200 mL Kimax high-alumina borosilicate bottles, which were rinsed three times with sample prior to filling. The bottles were sealed with custom-made plastic insert thimbles and Nalgene screw caps. The temperature in the salinometer laboratory varied from 21 to 24°C,

during the cruise. The air temperature change during any particular run varied from −1.2 to +2.2°C. The laboratory air temperature (21°C) was significantly lower than the bath temperature (24°C) for the first 7 casts of Leg 1. The estimated accuracy of bottle salinities run at sea was better than ±0.002 on both legs relative to the particular standard seawater batch used. The 95% confidence limit for residual differences between the bottle salinities and calibrated CTD salinity relative to SSW batch P-145 was ±0.010 for all salinities, and ±0.0035 for salinities collected in low gradients.

Dissolved **oxygen** analyses during Leg 1 were performed with an Friederich (MBARI)-designed automated oxygen titrator. During Leg 2 of the cruise dissolved oxygen analyses were performed with a Monterey Bay Aquarium Research Institute (MBARI)-designed automated oxygen titrator with photometric end-point detection based on the absorption of 365nm wavelength ultra-violet light. The titration of the samples and the data logging were controlled by computer. Thiosulfate was dispensed by a Dosimat 665 buret driver fitted with a 1.0 mL buret. A whole-bottle modified Winkler titration following the technique of Carpenter 1965 with modifications by Culberson et al. 1991 was used. Pre-made liquid potassium iodate standards were run every other day approximately every 4 stations, unless changes were made to the system or reagents. Reagent/distilled water blanks were determined every other day or more often if a change in reagents required accounting for the presence of oxidizing or reducing agents.

A total of 1,442 oxygen measurements were made during Leg 1 and 1,536 measurements were made during Leg 2 of the cruise. Samples were collected for dissolved oxygen analyses soon after the rosette was brought on board. Using a Tygon and silicone drawing tube, nominal 125 mL volume-calibrated iodine flasks were rinsed 3 times with minimal agitation, then filled and allowed to overflow for at least 3 flask volumes. The sample drawing temperatures were measured with a small glass bead thermistor thermometer embedded in the drawing tube. These temperatures were used to calculate μmol/kg concentrations, and as a diagnostic check of Niskin bottle integrity. Reagents were added to fix the oxygen before the samples were stoppered. The flasks were shaken twice (10–12 inversions) to ensure thorough dispersion of the precipitate, once immediately after drawing, and then again after about 20 min. The samples were analyzed within 1–4 h of collection, and the data were incorporated into the cruise database. Thiosulfate normalities were calculated from each standardization and corrected to 20°C. Oxygen flask volumes were determined gravimetrically with degassed deionized water at AOML.

In addition to the photometric end-point technique, samples from several stations during Leg 2 were analyzed using an amperometric detection method (Culberson and Huang, 1987) for comparison. This was done to test the amperometric detection method for future standard use. The difference between the two techniques was on average <1 μmol/kg.

Nutrient samples were collected from the Niskin bottles in acid-washed 25 mL linear olyethylene bottles after three complete seawater rinses and analyzed within 1 h of sample collection. Measurements were made in a temperature-controlled laboratory (20±2°C). Concentrations of nitrite, nitrate, phosphate, and silicate were determined using an Alpkem Flow Solution Auto-Analyzer aboard the ship. During the Section P16N_2006 cruise ~3000 samples were analyzed along with their standards and baseline samples.

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

Phosphate in the samples was determined by reacting with molybdenum (VI) and antimony (III) in an acidic medium to form an antimonyphosphomolybdate complex at room temperature. This complex

was subsequently reduced with ascorbic acid to form a blue complex, and the absorbance was measured at 710 nm.

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

Stock standard solutions were prepared by dissolving high purity standard materials (KNO_3, $NaNO_2$, KH_2PO_4 and Na_2SiF_6) in deionized water. Working standards were freshly made at each station by diluting the stock solutions in low nutrient seawater. The low nutrient seawater used for the preparation of working standards, determination of blank, and wash between samples was filtered seawater obtained from the surface of the Gulf Stream. Standardizations were performed prior to each sample run with working standard solutions. Two or three replicate samples were collected from the Niskin bottle sampled at deepest depth at each cast. The relative standard deviation from the results of these replicate samples was used to estimate the overall precision obtained by the sampling and analytical procedures. The precisions of these samples were 0.04 μmol/kg for nitrate, 0.01 μmol/kg for phosphate, and 0.1 μmol/kg for silicate.

3.2 Total CO_2 Measurements

3.2.1 Section P16S_2005

The TCO_2 analytical equipment was set up in a seagoing container modified for use as a shipboard laboratory. The analysis was done by coulometry with two analytical systems (PMEL-1 and PMEL-2) operated simultaneously on the P16S_2005 cruise by Dr. Christopher Sabine (PMEL) and Ms. Justine Afghan (SIO). Each system consisted of a coulometer (UIC, Inc.) coupled with a Single Operator Multiparameter Metabolic Analyzer (SOMMA) inlet system developed by Ken Johnson (Johnson et al. 1985, 1987, 1993; Johnson 1992) of Brookhaven National Laboratory (BNL). In the coulometric analysis of TCO_2, all carbonate species are converted to CO_2 (gas) by addition of excess hydrogen to the seawater sample, and the evolved CO_2 gas is carried into the titration cell of the coulometer, where it reacts quantitatively with a proprietary reagent based on ethanolamine to generate hydrogen ions. These are subsequently titrated with coulometrically generated OH^-. CO_2 is thus measured by integrating the total charge required to achieve this.

The coulometers were each calibrated by injecting aliquots of pure CO_2 (99.995% purity) by means of an 8-port valve outfitted with two sample loops (Wilke et al. 1993). The instruments were calibrated at the beginning of each station with a set of the gas loop injections. Subsequent calibrations were run either in the middle or end of the cast if replicate samples collected from the same Niskin, which were analyzed at different stages of analysis, differed by more than 2 μmol/kg.

Secondary standards were run throughout the cruise on each analytical system; these standards are Certified Reference Materials (CRMs) consisting of poisoned, filtered, and UV-irradiated seawater supplied by Dr. A. Dickson, SIO, and their accuracy is determined onshore manometrically. On this cruise, the overall accuracy and precision for the CRMs on both instruments was -1.7±0.8 μmol/kg (n=63) and -2.4±0.7 μmol/kg (n=64) for PMEL-1 and PMEL-2 respectively. The final TCO_2 data reported to the database have been corrected to the Batch 67 CRM value.

Samples were drawn from the Niskin-type bottles into cleaned, precombusted 300- mL Pyrex bottles using silicone tubing. Bottles were rinsed three times and filled from the bottom, overflowing half a volume, and care was taken not to entrain any bubbles. The tube was pinched off and withdrawn, creating a 3-mL headspace, and 0.2 mL of 50% saturated $HgCl_2$ solution was added as a preservative. The

sample bottles were sealed with glass stoppers lightly covered with Apiezon-L grease and were stored at room temperature for a maximum of 24 h prior to analysis.

TCO_2 values were reported for 2,882 samples or approximately 75% of the tripped bottles on this cruise. Full profiles were completed at odd-numbered stations on whole degrees, with replicate samples taken from the surface, oxygen minimum, and bottom depths. On the even-numbered (half degree) stations, as many samples as possible were drawn based on the current sample throughput; replicates were collected from the surface and bottom bottles. Typical even-numbered stations had between 8 and 20 bottles sampled.

Duplicate samples were drawn from 256 bottles and interspersed throughout the station analysis for quality assurance of the coulometer cell solution integrity. The average of the absolute value of the difference between duplicates was 1 μmol/kg for both systems. No systematic differences between the replicates were observed.

3.2.2 Section P16N_2006

The TCO_2 measurements on Section P16N_2006 were done by the coulometry with the same two analytical systems (PMEL-1 and PMEL-2) as on Section P16S_2005, operated simultaneously on the cruise by Bob Castle (NOAA/AOML) and Alex Kozyr (ORNL/CDIAC) on Leg 1 and Dana Greeley and David Wisegarver (both of NOAA/PMEL) on Leg 2 (Sect. 3.2.1 describes the system and method). On this cruise, the overall accuracy for the CRMs on both instruments combined was 0.8 μmol/kg (n=66) for each leg. The final TCO_2 data reported to the database have been corrected to the Batch 73 CRM value.

The TCO_2 values were reported for 2,648 samples or approximately 80% of the tripped bottles on this cruise. Full profiles were completed at stations on whole degrees, with replicate samples taken from the surface, oxygen minimum, and bottom depths. Duplicate samples were drawn from 121 bottles on Leg 1 and 72 bottles on Leg 2 and interspersed throughout the station analysis for quality assurance of the coulometer cell solution integrity. The average of the absolute value of the difference between duplicates was 1 μmol/kg for both systems. No systematic differences between the replicates were observed.

3.3 Total Alkalinity Measurements

3.3.1 Section P16S_2005

Dr. Andrew Dickson's group (SIO) was responsible for the TALK measurements during Section P16S_2005. Samples for TALK were collected in glass bottles made from Schott Duran® glass. They were preserved by the addition of 0.02% by volume of a saturated mercury (II) chloride solution ($HgCl_2$) (DOE 1994 – SOP 01), and analyzed—typically within 24 h—on board ship.

TALK measurements were made using an open-cell, two-stage, potentiometric titration procedure similar to that used to certify reference materials for TALK (see Dickson et al. 2003), except that samples were not weighed into the titration vessel but instead were dispensed using a 120-mL glass syringe. A metal frame attached to the syringe barrel and plunger controlled the maximum extent the plunger could be withdrawn in the barrel. This ensured that a reproducible amount of seawater was dispensed. The analytical procedure was as follows (equipment is listed in Table 3):

1. An aliquot of seawater was dispensed into the titration vessel (a jacketed glass beaker with its temperature controlled to ±0.02 °C at about 20.0 °C), a stirrer bar was added, and the temperature probe and burette tip were inserted in the solution.

2. The solution was then acidified to a pH of about 3.6 with a single aliquot of the titration acid and stirred vigorously while CO_2-free air was bubbled through for about 6 min to remove CO_2.

3. The main titration was then started and the solution was titrated using 0.05 mL increments to a pH of about 3.0. Data from the pH range 3.5–3.0 were used in a non-linear least squares process that corrects for the reactions with sulfate and fluoride ions to estimate the TALK of the sample—see Dickson et al. (2003) for more details.

Table 3. List of equipment used for alkalinity titrations for P16S_2005 cruise

120-cm^3 glass syringe with custom frame to ensure reproducible dispensing
250-cm^3 capacity glass jacketed beaker
Thermostat bath (Fisher model 9110)
Magnetic stirrer and stir bar
Calibrated thermometer ± 0.01 °C for cell temperature (Guildline model 9540)
Digital voltmeter (Kethley model 199)
Custom high-impedance voltage-follower amplifier
Ross-Orion combination pH electrode (model 1802)
Calibrated thermometer ± 0.1 °C for acid temperature (YSI model 4600)
Metrohm Dosimat® model 665 burette with calibrated 5 mL exchangeable burette unit and anti-diffusion tip

The hydrochloric acid used for the titration was made up in bulk and then stored in 1 L Pyrex bottles with greased ground-glass stoppers. The acid strength was approximately 0.100 mol/kg. The acid was made up in a 0.6 mol/kg sodium chloride background so as to approximate the ionic strength of seawater. Selected bottles of the acid were then analyzed coulometrically (Dickson et al. 2003) to assign a concentration to the batch.

The at-sea repeatability of the method was estimated by analyzing duplicate samples, collected on each cast. These results were used to estimate a standard deviation using the standard expression (DOE 1994, SOP 23). The repeatability was 1.06 μmol/kg based on 89 pairs of analyses.

In addition, analyses were made of the alkalinity of CO_2 reference material. These analyses were carried out regularly throughout the cruise, typically a pair of analyses every 12 h. The results are shown in Fig. 2.

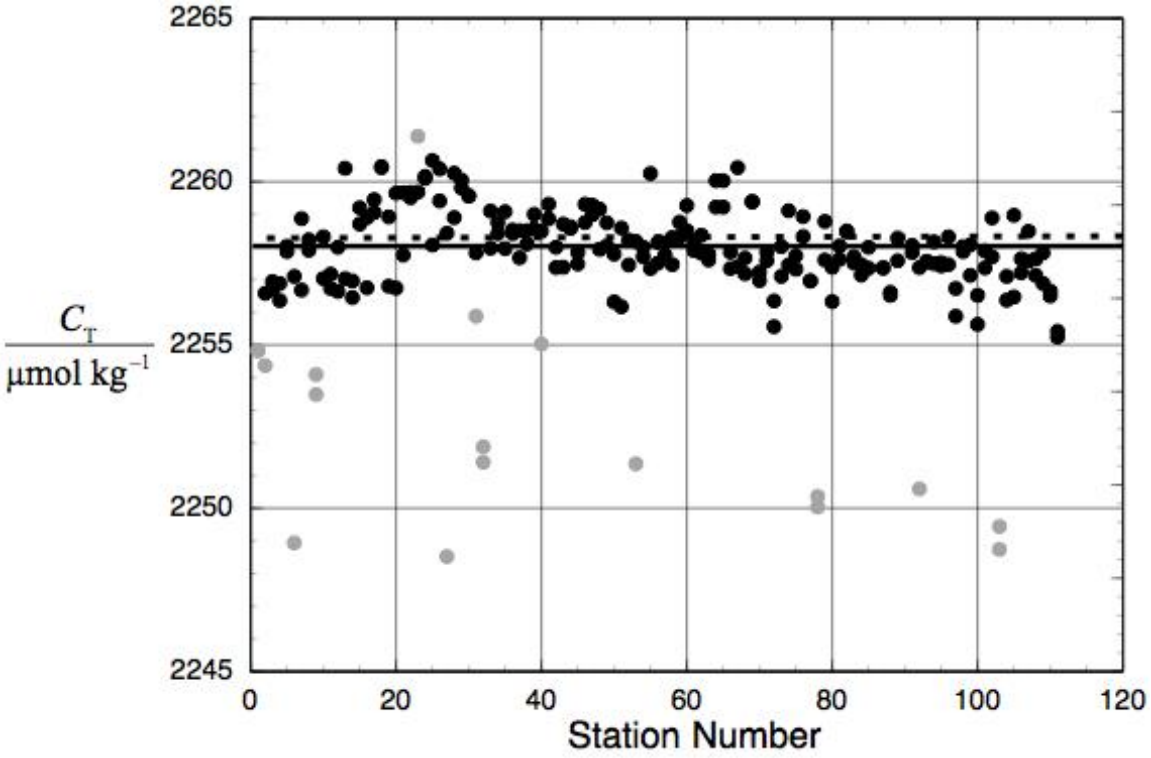

Fig. 2. Plot of the results of analyses of reference materials (Batch 67: certified value = 2258.27 µmol/kg plotted as dashed line). Values shown in gray are considered "outliers."

The measured average value for the CO_2 reference material was: 2258.02 ± 1.09 (200) µmol/kg, slightly lower than the certified value.

An examination of Fig. 2 suggests that there was no significant unambiguous change in the system calibration throughout the course. Therefore, the alkalinity data was adjusted by multiplying by a correction factor of 1.00011, derived by dividing the certified value by the average calculated CRM value: 2258.02 µmol/kg.

Finally, the adjusted alkalinity data results were multiplied by a factor of 1.0002 to correct for the dilution inherent in adding mercury (II) chloride to the sample to preserve it for analysis.

Once the at-sea alkalinity measurements had been adjusted in this fashion, they were normalized to a salinity of 35 and the resulting values plotted in Ocean Data View (ODV) to help identify any questionable data. As a result of this analysis, 15 points were identified as either questionable or bad, and flagged accordingly. (Outliers found in replicate data were thus identified at this stage.)

3.3.2 Section P16N_2006

Dr. Frank Millero's group (RSMAS/UM) was responsible for the TALK measurements during Section P16N_2006 Legs 1 and 2.The titration systems used consisted of a Metrohm 665 Dosimat titrator and a computer-controlled Orion 720A pH meter (Millero et al. 1993b). Both the acid titrant in a water jacketed burette and the seawater sample in a water jacketed cell were controlled to a constant temperature of 25 ± 0.1°C with a Neslab (RTE-17) constant temperature bath. The Plexiglas water jacketed cell used is shown in Fig. 3. The cells had fill-and-drain valves, which increased the reproducibility of the cell volume.

The TALK system consists of a manifold that allows the automated measurement of six samples in sequence. A set of pumps, valves, and relays are used to rinse, fill, and drain the TALK cell. The titration is controlled programmatically using National Instrument's Labwindows/CVI environment. The titration is made by adding HCl to seawater past the carbonic acid end point. A typical titration records the electromagnetic field (emf) reading after the readings become stable (± 0.05 mV) and adds enough acid to change the voltage to a pre-assigned increment (13 mV). A full titration (25 points) takes about 15 min. Using two automated systems, a 36-bottle station cast can be completed in 6 h.

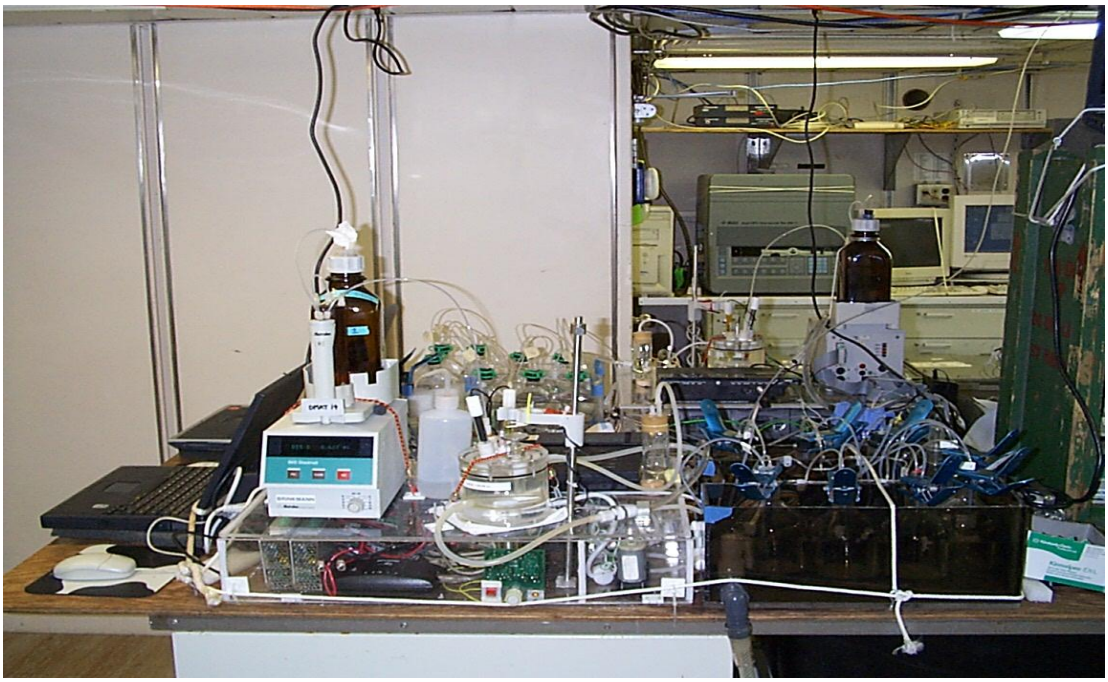

Fig. 3. Auto-titration system used during the Section P16N_2006 cruise.

The electrodes used to measure the emf of the sample during a titration consisted of a ROSS 8101 glass pH electrode and an Orion 90-02 double junction Ag/AgCl reference electrode. The filling solution used in the reference electrode was a 0.7 M NaCl solution to maintain a consistent junction potential between the solution and electrode.

The HCl used throughout the cruise was made, standardized, and stored in 500 mL glass bottles in the laboratory for use at sea. The 0.243402 ± 0.000022 M HCl solutions were made from 1 M Mallinckrodt standard solutions in 0.45 M NaCl to yield an ionic strength equivalent to that of average seawater (≈ 0.7 M). The acid was originally tested on seawater of a known TALK to determine the acid's reliability and later sent for final standardization using a coulometric technique (Taylor and Smith, 1959; Marinenko and Taylor, 1968) by Dickson's group.

The volumes of the cells used at sea were determined in the laboratory by making numerous measurements of seawater with a known TALK. Once the TALK values agree to ± 1.0 μmol/kg, the volume of the cell is determined to ± 0.01 mL from the value required to reproduce the TALK. Measurements on CRM samples were made to confirm the volume and reproduce the known TALK to ± 0.5 μmol/kg.

The volume of HCl delivered to the cell is traditionally assumed to have small uncertainties (Dickson 1981) and equated to the digital output of the titrator. Calibration of the burette of the Dosimat with Milli-Q water at 25°C indicates that the system delivers 3.000 mL (the value for a titration of seawater) to a precision of ± 0.0004 mL. This uncertainty results in an error of ± 0.4 μmol/kg in TALK and TCO_2. Since the titration systems are calibrated using standard solutions, the error in the accuracy of volume delivery will be partially canceled and included in the value of cell volumes assigned. The laboratory precision of the system was ± 1.0 μmol/kg.

The total alkalinity of seawater was evaluated from the proton balance at the alkalinity equivalence point, $pH_{equiv} = 4.5$, according to the exact definition of total alkalinity (Dickson 1981):

$$TALK = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}]$$

$$+ [SiO(OH)_3^-] - [H^+] - [HSO_4^-] - [HF] - [H_3PO_4] \quad (7)$$

At any point of the titration, the total alkalinity of seawater can be calculated from the equation

$$(V_0\, TA - VM)/(V_0 + V) = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-]$$

$$+ [HPO_4^{2-}] + 2[PO_4^{3-}] + [SiO(OH)_3^-] - [H^+] - [HSO_4^-] - [HF] - [H_3PO_4] \quad (8)$$

where V_0 is the volume of the cell, M is the molarity of the acid titrant, and V is the volume of acid added. In the calculation, all the volumes are converted to mass using the known densities of the solutions (Millero et al. 1993b).

A computer program has been developed in Labwindows/CVI to calculate the carbonate parameters (pH_{sw}, E*, TALK, TCO_2, and pK_1) in seawater solutions. The program is patterned after those developed by Dickson (1981), Johansson and Wedborg (1982), and DOE 1994. The fitting is performed using the STEPIT routine. The STEPIT software package minimizes the sum of squares of residuals by adjusting the parameters E*, TALK, TCO_2, and pK_1. The computer program is based on equation (8) and assumes that nutrients such as phosphate, silicate, and ammonia are negligible. This assumption is valid only for surface waters. Neglecting the concentration of nutrients in the seawater sample does not affect the accuracy of TALK, but does affect the carbonate alkalinity.

The pH and pK of the acids used in the program are on the seawater scale, $[H^+]_{sw} = [H^+] + [HSO_4^-] + [HF]$ (Dickson 1984). The Mehrbach et al (1973) dissociation constants used in the program were taken from Dickson and Millero (1987) for carbonic acid, from Dickson (1990a) for boric acid, from Dickson and Riley (1979) for HF, from Dickson (1990b) for HSO_4^-, and from Millero (1995) for water. The program requires as input the concentration of acid, volume of the cell, salinity, temperature, measured emf (E) and volume of HCl (V_{HCl}). To obtain a reliable TALK from a full titration, at least 25 data points should be collected (9 data points between pH 3.0 to 4.5). The precision of the fit is better than 0.4 μ mol/kg when pK_1 is allowed to vary and 1.5 μmol/kg when pK_1 is fixed. The titration program has been compared to the titration programs used by others (Johansson and Wedborg 1982, Bradshaw and Brewer 1988) and the values of TALK agree to within ± 1 μmol/kg.

The spectrophotometric pH and potentiometric TALK of CRM used during the cruise have been measured in the laboratory before the cruise to characterize the pH of the standard and make sure the titration systems were performing to the desired precision. During the cruise, titrations on CRM were

made to ensure that the two titration systems were giving consistent values. The values of pH and TALK for CRM #73 are summarized in Table 4. The precision of the potentiometric measurements of batch #73 were ± 3.0 µmol/kg for TALK and ± 0.006 for pH. For spectrophotometric measurements the average values agreed to ± 0.002 for CRM batch #73 and ± 0.003 for TRIS buffer solution. The deviations are within 2σ for most of the measurements. Small correction factors were made to the TALK to account for the offset with the CRM. To correct the TALK values, a ratio of the CRM value to the measured value, for each system, was taken and multiplied to each of the sample measurements. For pH, the average value was subtracted from the CRM value for each system, and this value was added to each of the sample measurements. These correction factors were made at the end of each station. The TALK values for System A appeared to drift over the course of the cruise; however, the correction factors made accounted for this drift as is evident in the duplicate results.

Table 4. Summary of certified reference material measurements

	TA µmol/kg	pH @ 25°C	Total runs
System A	2253.6 ± 4.1	7.826 ± 0.006	53
System B	2257.2 ± 2.0	7.826 ± 0.005	60
Combined	2255.5 ± 3.0	7.826 ± 0.006	113
Spectrophotometer			
CRM Batch 73		7.8417 ± 0.0020	9
TRIS		8.0525 ± 0.0033	32
Certified Values			
CRM Batch 73	2253.5	7.8417	

The precision of the instruments was tested by making duplicate or replicate measurements of samples throughout the cruise. These samples were taken from the same Niskin bottle, equilibrated for an equal amount of time, and then measured on each system for duplicates and the same system for replicates. A total of 62 duplicate samples were made on the titration systems yielding a precision of 0.3 ± 2.3 µmol/kg for TALK and -0.001 ± 0.008 for pH. These results validate the correction factors applied to each system as the deviations between the two systems are within the experimental error of the titrators (± 3.0 µmol/kg). A total of 59 and 74 replicate samples were run on Systems A and B, respectively, and 1051 replicate samples were made on the spectrometer. Results showed that the average replicate difference for TALK were 0.1 ± 1.2 µmol/kg for System A, 0.1 ± 1.0 µmol/kg for System B and, 0.0004 ± 0.0025 for spectrophotometric pH.

Table 5. Summary of duplicate measurements

	TALK µmol/kg	pH	Total runs
Duplicates	0.3 ± 2.3	-0.001 ± 0.008	62
Replicates			
System A	0.1 ± 1.2	0.001 ± 0.004	59
System B	0.1 ± 1.0	0.000 ± 0.003	74
Spectrophotometer		0.0004 ± 0.0025	1051
Combined	-0.1 ± 1.1	0.001 ± 0.003	133
Spectrophotometer - Titrator		0.015 ± 0.013	1414

3.4 pH Measurements

Discrete pH measurements were not collected on P16S. Two different groups (University of Miami and University of South Florida) measured pH using slightly different spectrophotometric techniques on P16N leg 1. Only the USF group measured pH on P16N leg 2. The pH measurements from both groups are reported on the total scale at 25°C.

Note: In the master data file **p16n_2006a_hy.csv** at CDIAC and CCHDO, the pH measurements from UM group reported for leg 1 (stations 1–43) and from USF for leg 2 (stations 44 –84). The separate file **p16n_2006a_all_ph.csv** with all pH measurements from both groups is posted at CDIAC at: http://cdiac.ornl.gov/ftp/oceans/CLIVAR/P16N_2006.data/

3.4.1 Section P16N_2006 UM pH Measurements

The pH measurements of seawater were made by Dr. Frank Millero's group from the University of Miami on the leg 1 of Section P16N_2006, using the spectrophotometric techniques of Clayton and Byrne (1993). The pH of the samples using m-Cresol Purple (mCP) is determined from

$$pH = pK_{ind} + \log [(R - 0.0069)/(2.222 - 0.133\ R)] \qquad (1)$$

where K_{ind} is the dissociation constant for the indicator and R (A578/A434) is the ratio of the absorbance of the acidic and basic forms of the indicator corrected for baseline absorbance at 730 nm. The pH of the samples is perturbed by the addition of the indicator. The magnitude of this perturbation is a function of the difference between the seawater acidity and indicator acidity; therefore, this correction was quantified for each batch of dye solution. To a sample of seawater (~5mL), a volume of 2 milli-molar mCP (0.008 mL) was added and the absorbance ratio was measured. From a second addition of mCP and absorbance ratio measurement, the change in pH per mL of added indicator (ΔpH) was calculated. From a series of such measurements over a range of seawater pH, the first addition of indicator used to calculate pH was described as a linear function of the pH measured with the subsequent addition of indicator (i.e., standard addition correction due to the indicator as a function of pH). In the course of routine seawater pH analyses, this correction was applied to every measured pH; i.e., the corrected pH is calculated as

$$pH = 1.0013(pH_i) - 0.0083 \qquad (2)$$

This equation was applied twice for double addition indicator runs and once for single addition indicator runs to yield pseudo replicate runs for every pH sample when a second addition of indicator was added.

Clayton and Byrne (1993) calibrated the mCP indicator using tris (hydroxymethyl) aminomethane (TRIS) buffers (Ramette et al. 1977) and the pH equations of Dickson (1993). They found that

$$pK_{ind} = 1245.69/T + 3.8275 + (2.11 \times 10^{-3})\ (35 - S) \qquad (3)$$

where T is temperature in degrees Kelvin and is valid from 293.15 to 303.15 K (20 to 30ºC) and S = 30 to 37. The values of pH calculated from equations (1) and (3) are on the total scale in units of mol/(kg-soln). The total proton scale (Hansson 1973) defines pH in terms of the sum of the concentrations of free hydrogen ion, $[H^+]$, and bisulfate, $[HSO_4^-]$

$$pH_T = -\log[H+]T = -\log\{[H^+] + [HSO_4^-]\} = -\log\{[H^+](1 + [SO_4^{2-}]/K_{HSO4})\} \qquad (4)$$

where the concentration of total sulfate, $[SO_4^{2-}] = 0.0282 \times S/35$ and K_{HSO4} is the dissociation constant for the bisulfate in seawater (Dickson 1990a).

Lee et al. (1996) have redetermined the value of pK_{ind} from 273.15 to 313.15 K (0 to 40 ºC) using a 0.04 m TRIS buffer (Ramette et al. 1977). The pH of the TRIS buffer was determined from the emf measurements made with the H_2, Pt/AgCl, Ag electrode system (Millero et al. 1993a). At 273.15 K (25ºC) the buffer had a pH of 8.076 and yielded spectrophotometric values of pH that were in excellent agreement (~ 0.0001) with those found using equations (1) and (3). These results from 273.15 to 313.15 K (0 to 40ºC) were fitted to the equation (S = 35)

$$pK_{ind} = 35.913 - 216.404/T - 10.9913 \log (T) \quad (5)$$

with the standard error of 0.001 in pK_{ind} where the constant is on the total scale in {mol/(kg-H_2O) }.

The values of pH calculated from equations (1) and (5) are on the total scale in units of {mol/(kg-H_2O)}. The conversion from the total scale (pH_T) {mol/(kg-H2O)} to the seawater scale (pH_{SWS}) in {mol/(kg-soln)} can be made using (Dickson and Riley 1979; Dickson and Millero 1987):

$$pH_{SWS} = pH_T - \log\{(1 + [SO_4^{2-}]/K_{HSO4} + [F^-]/K_{HF})/(1 + [SO_4^{-2}]/K_{HSO4})\} - \log (1 - 1.005 \times 10^{-3} S) \quad (6)$$

where the total concentration of fluoride, $[F^-] = 0.000067 \times 35/S$, and K_{HF} is the dissociation constant for hydrogen fluoride (Dickson and Riley 1979). The seawater pH scale (pH_{SWS}) was used in further calculations of the internal consistency (Millero et al. 1993b) of the four parameters since the carbonate constants used are on this scale (Dickson and Millero 1987).

The pH system is automated and makes measurements of discrete pH approximately every 12 min on a sample volume of 25 cm^3. A microprocessor-controlled syringe pump (Kloehn 50300) and sampling valve aspirates and injects the seawater sample into the 10 cm optical cell at a precisely controlled rate. The syringe rinses and primes the optical cell with 20 cm^3 of sample and the software permits 5 min for temperature stabilization. A refrigerated circulating temperature bath (Neslab RTE-17) regulates the temperature of the sample at 25 ± 0.01 ºC. An Agilent 8453 UV/VIS spectrophotometer measures the background absorbance of the sample. The automated syringe and sampling valves aspirates 4.90 cm^3 seawater and 0.008 cm^3 of indicator and injects the mixture into the cell. After the software permits 5 min for temperature stabilization, a Guildline 9540 digital platinum resistance thermometer measures the temperature and the spectrophotometer acquires the absorbance at 434, 578, and 730 nm. During Leg 2 of the cruise, the pH system was converted to an underway mode, in which a Seabird thermosalinograph was inserted on a flowing line from which the syringe pump could draw a sample every 10 min. The measurement process was the same as the procedure above, with the exception of the input salinity coming from the Seabird. The water jacket enclosing the 10 cm optical cell was thermostated with the same underway seawater to yield true in situ measurements totaling 1250 runs. Eight stations of discrete measurements were made at the temperature of the surface waters relative to when the measurement was made and were later normalized to 25°C

3.4.2 Section P16N_2006 USF pH Measurements

University of South Florida (USF) personnel measured seawater pH on the Section P16N legs 1 and 2 cruise using the procedures outlined in SOP 7 (DOE 1994) and in Clayton and Byrne (1993). The pH_T on the total scale is calculated using the following equation:

$$pH_T = 1245.69/T + 3.8275 - 0.00211(35 - S) + \log((R - 0.00691) / (2.222 - 0.1331R))$$

where T is the measurement temperature (T = 273.15 + t) and S is salinity. The overall precision of pH measurements from duplicate samples was better than 0.001.

On leg 1, twenty-eight of 43 stations were sampled. Discrete USF pH measurements were made on all water samples for which discrete TCO_2 measurements were made on leg 2.

USF personnel participating in P16N_2006 cruise are listed below.

Leg 1: Dr. Xuewu Liu
Dr. Renate Bernstein

Leg 2. Dr. Robert H. Byrne
Dr. Zhaohui Aleck Wang
Dr. Johan Schijf
Mr. Ryan Bell

Measurements of seawater pH were obtained using m-Cresol Purple (mCP) as an indicator. Seawater pH, on the total hydrogen ion concentration ($[H^+]_T$) scale, was calculated from the equation

 (1)

where e_1 = 0.00691; e_2=2.222; and e_3=0.1331. The temperature (T) and salinity (S) dependence of the mCP equilibrium constant ($_TK_I$) is given as:

 (2)

and pH_T is related to pH on the free hydrogen ion concentration scale (pH = -log[H^+]) as follows:

 (3)

where S_T is the total sulfate concentration and K_{HSO_4} is the HSO_4^- dissociation constant.

A stock solution of m-Cresol purple (mCP) (10 mM) was prepared with mCP sodium salt (Aldrich, catalogue number 211761) in MilliQ water. The R ratio (absorbance of the base form [I^{2-}] divided by the absorbance of the acid form (HI^-) of the stock solution was adjusted to 1.5 with an NaOH solution. The R ratio was checked periodically during the cruise and was shown to be stabilized at 1.44. The dye solution was stored in an aluminum-sandwiched plastic bag to exclude air exchange and light from the indicator.

pH samples were fed directly to 10 cm cylindrical glass cells via a 20 cm section of flexible silicone tubing. After the cell was flushed for 20 s, it was sealed with poly-tetrafluoroethene (PTFE) caps, ensuring that there was no trapped air. After the sealed cell was rinsed with tap water and dried with Kimwipes, samples were housed in a 36-position cell warmer at 25°C. After the cells had been thermostated for about 30 min, the pH measurements were initiated beginning with surface samples.

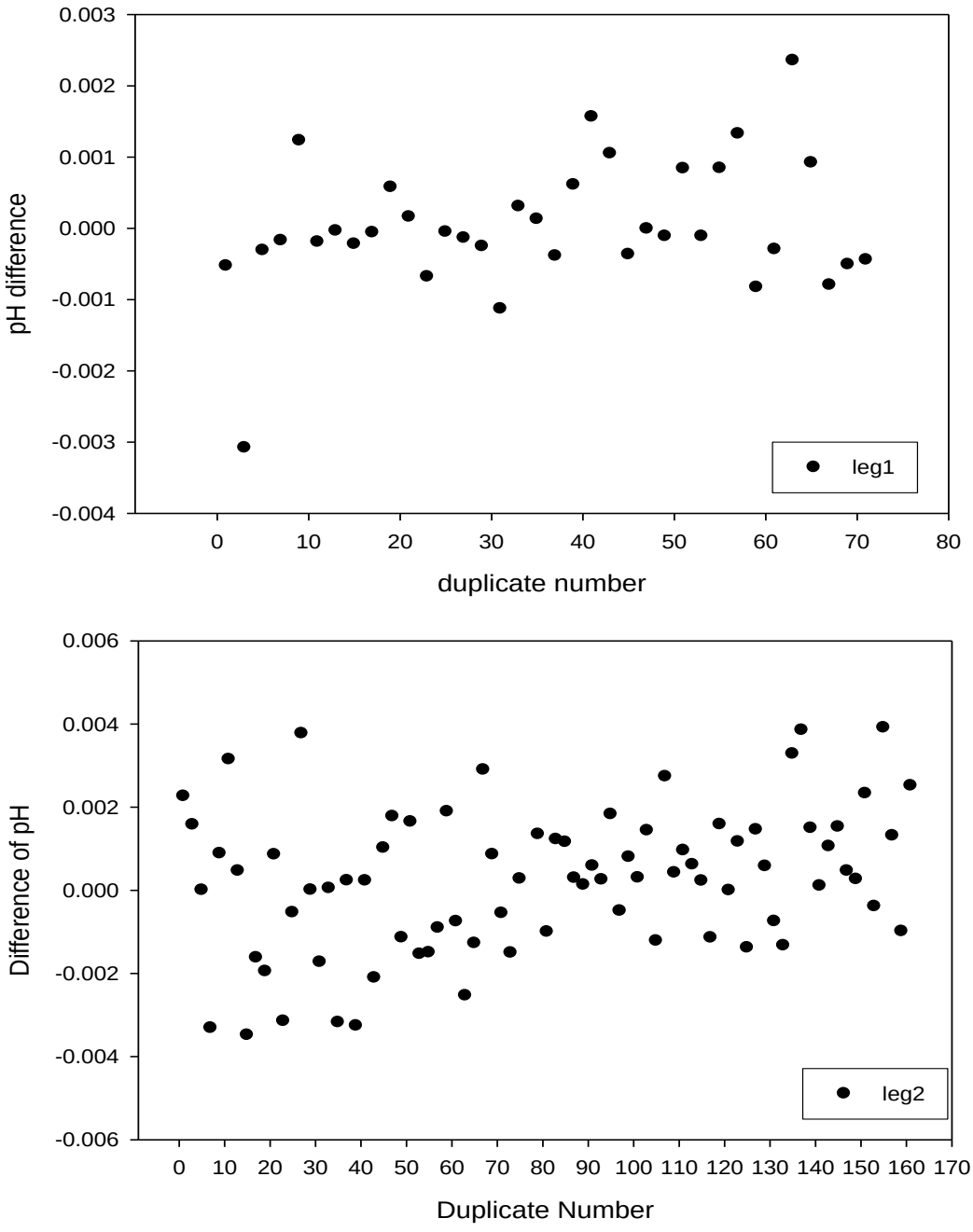

Fig. 4. The differences of duplicate measurements during the Section P16N_2006 cruise, Legs 1 and 2.

The exterior of the cell was carefully cleaned; the cell was then placed in the thermostated sample compartment of the spectrophotometer (Agilent 8453 UV-Vis Spectrophotometer). The baseline was recorded at three wavelengths (434, 578, and 700). One of the cell caps was then removed and indicator dye was added with a Gilmont pipette. The cap was replaced and the cell was briefly shaken to mix the

seawater and the dye. The cell was returned to the spectrophotometer and absorbances were recorded at three wavelengths.

The measurements were computer controlled with a macro code for sample information input, data acquisition, and storage. The program also implemented quality controls for baseline stability and measurement precision. The overall precisions of pH data were evaluated with duplicate samples during the cruise. The precisions of leg 1 pH data were 0.0006 (n=38) and the precision of leg 2 pH data were 0.0014 (n=82) (Fig. 4)

Table 6. Summary of indicator addition

Stations	Indicator volume
Station 1 to 44	10 μL
Station 45 to 54	15 μL
Station 55 to 84	20 μL

The indicator perturbation to seawater sample was evaluated empirically. A pair of additions of dye was made to each of a series seawater samples that had been adjusted to pH before 8.1 and 7.0. The stock indicator concentration was 10 mM. During the cruise, three different volumes of indicator were used.

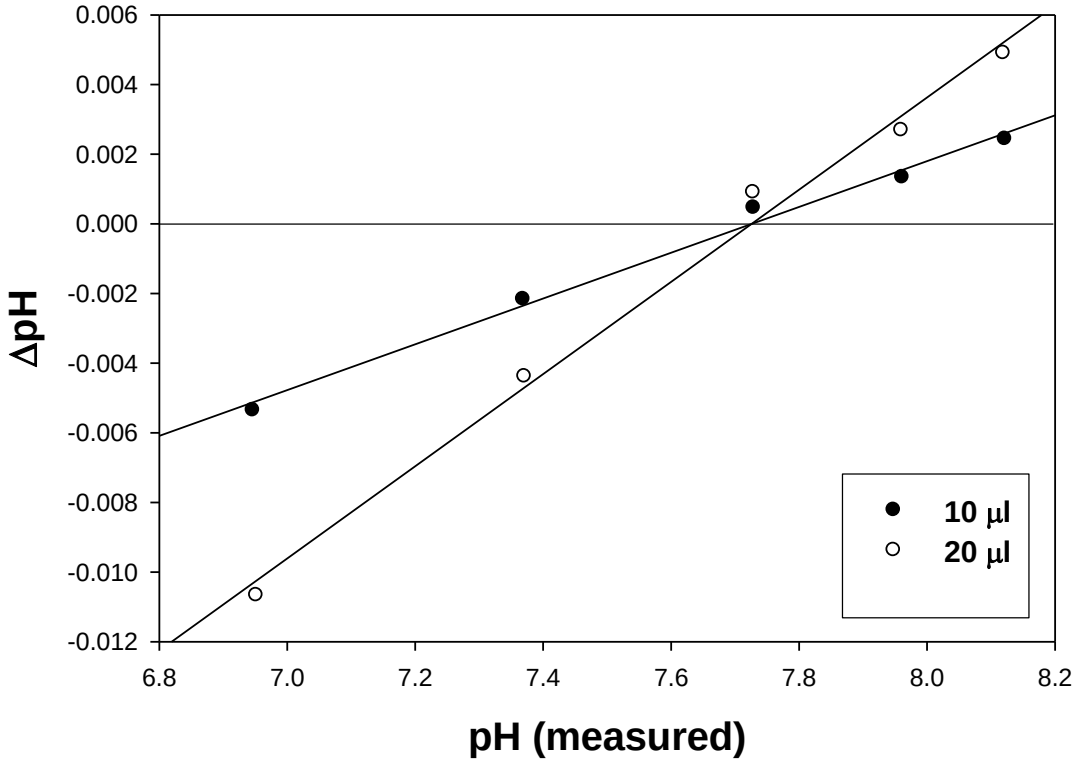

Fig. 5. The perturbation term vs. measured pH.

The perturbation term can be adequately expressed by following equations:

For 10 μL addition: $\Delta pH = 0.006574pH(measured) - 0.0508$, $r^2 = 0.992$ (4a)
For 20 μL addition: $\Delta pH = 0.01324pH(measured) - 0.1023$, $r^2 = 0.992$. (4b)

Thus, sample pH can be calculated using following equations:

For 10 μL addition: $pHcorr = 1.006574 \times pH(measured) - 0.0508$ (5a)
For 20 μL addition: $pHcorr = 1.01324 \times pH(measured) - 0.1023$ (5b)

The result suggested that perturbation term due to indicator addition is proportional to indicator volume added (Fig. 5). A few stations were measured with 15 μL indicator additions. The perturbation term was estimated based on average result of 10 and 20 μL addition.

For 15 μL addition: $pHcorr = 1.099 \times pH(measured) - 0.0766$ (6)

Sample temperature was controlled by circulating the water bath to 25°C. As soon as the sample was measured, its temperature was measured with a platinum temperature probe (traced to NIST standard). Most of the samples were measured at 25±0.1°C. The small temperature difference from 25°C will not add error to measurement due to the inherent properties of mCP and CO_2 chemistry. For example, if a sample is measured at 24.9 °C, but t = 25°C was assumed to produce a calculated pH = 8.0000, the pH calculated at 24.9°C would be 7.9985. Using CO_2 system thermodynamic relationships, when pH measurements at 24.9 °C are corrected to 25°C, the correction factor is 0.0014, resulting in a corrected value (in the example above) equal to 7.9999. When temperature differs by as much as 0.2°C, the error by assuming t = 25°C is less than 0.0002, which is well within the experimental error of the measurements. Thus no temperature corrections were made to the cruise dataset.

It has been demonstrated that due to the different impurities in indicator batches from different vendors, measured pH can be significantly different. We examined the effect of impurities as function of sample pH. Fig. 6 shows the pH discrepancies between Sigma-Aldrich mCP (indicator used during P16N_2006 cruise) and Kodak mCP (indicator used in 1991 cruise) over a range of pH. The pH offset between the two indicators decreases as sample pH decreases. In this case, it is seen that indicator impurities cause smaller pH measurement artifacts at lower pH. As a result, for ocean pH measurements, errors introduced from indicator impurities will be most significant for surface seawater samples. Figure 6 shows pH discrepancies from 7.2 to 8.2. The result shown in Fig. 6 can be fitted into the following equation:

$$pH(Sigma\text{-}Aldrich) - pH(Kodak) = 0.0010 + 0.0008 \times (pH(Sigma\text{-}Aldrich) - 7.2) + 0.0042*(pH(Sigma\text{-}Aldrich) - 7.2)^2. \quad (7)$$

Equation 7 provides an empirical approach to correct offsets in pH measurements attributable to different sources of indicator to make measurements directly comparable and consistent. Equation 7 was used to correct all of the data. Further corrections are possible subsequent to characterization of purified indicator dye.

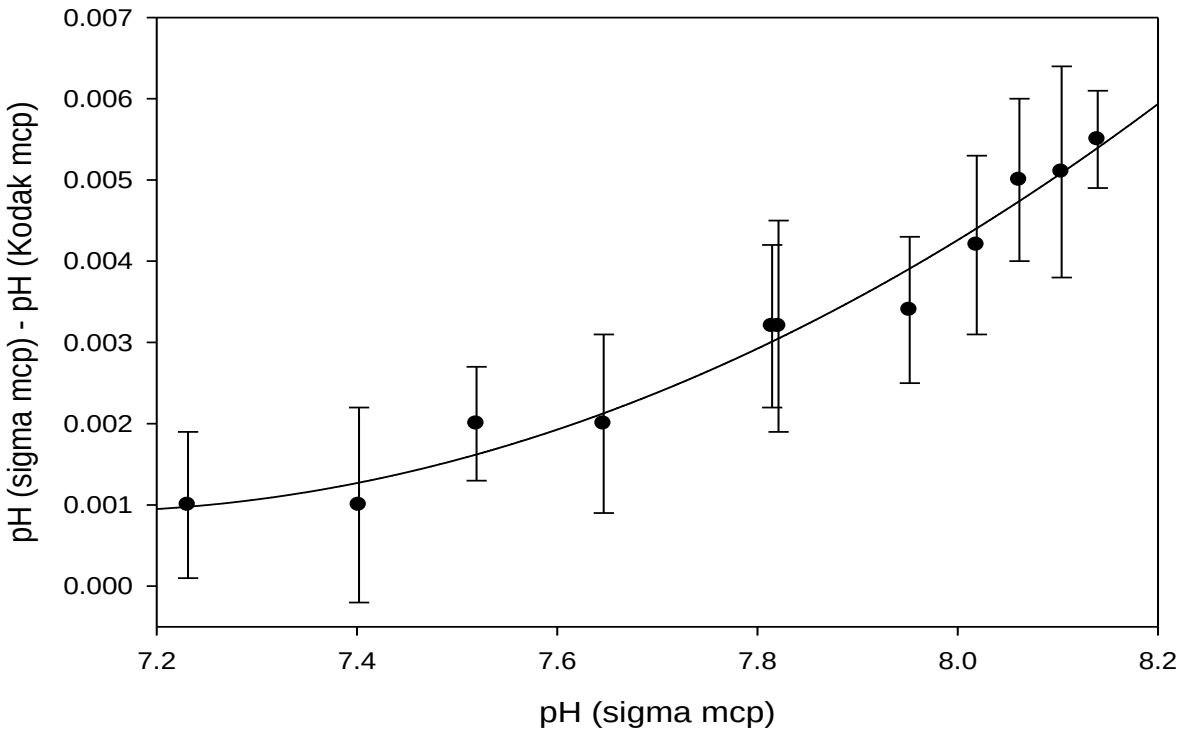

Fig. 6. Measured pH differences between Sigma-Aldrich and Kodak mCP as a function of sample pH.

3.5 Discrete pCO_2 Measurements

The discrete pCO_2 data were measured by Dr. Rik Wanninkhof's group from NOAA/AOML only on the P16N_2006 cruises. No discrete pCO_2 measurements were made on P16S_2005. The pCO_2 system is patterned after the instrument described in Chipman et al. (1993) and is discussed in detail in Wanninkhof and Thoning (1993) and Chen et al. (1995). The major difference between the two systems is that the Wanninkhof instrument uses a LI-COR (model 6262) non-dispersive infrared analyzer, while the Chipman instrument uses a gas chromatograph (GC) with a flame ionization detector.

Samples were drawn from Niskin bottles into 500-mL volumetric flasks using Tygon tubing with a silicone adapter that fit over the petcock to avoid contamination of DOM samples. Bottles were rinsed while inverted and filled from the bottom, overflowing half a volume taking care not to entrain any bubbles. About 5 mL of water was withdrawn to allow for expansion of the water as it warms and to provide space for the stopper, tubing, and frit of the analytical system. Saturated mercuric chloride solution ($HgCl_2$)(0.2 mL) was added as a preservative. The sample bottles were sealed with a screw cap containing a polyethylene liner. The samples were stored in coolers at room temperature usually for no more than 5 h. Generally, when samples were taken from the Niskin bottles, flasks were drawn on all the Niskins including four duplicates. Two of the duplicates were analyzed at different analysis temperatures. The duplicates run at different temperatures were normalized to 20ºC and compared. Normalization was performed using the constants and procedures as outlined in Peng et al. 1987 as incorporated in the GW BASIC data reduction program. Three types of duplicates were taken. The average difference:

$$[\text{ABS (sample1} - \text{sample2)} / \text{(sample1} + \text{sample2)} \times 100],$$

standard deviation and number for the three types are listed below:

Duplicates run at 20ºC:	av. dif. = 0.3 ± 0.23%	n = 33 (one value omitted)
Duplicates run at 12ºC:	av. dif. = 0.3 ± 0.18 %	n = 23 (one value omitted)
Duplicates run at 12ºC and 20ºC	av. dif = 0.7 ± 0.75 %	n = 59 (two values omitted)

The omitted values were due to a problem in analysis in one of the duplicates.

Using the constants as refit by Dickson and Millero and the salinity dependence of borate as proposed by Dickson gave an average difference of 1 %, that is, these constants yielded worse agreement in temperature normalization than using the constants listed in Peng et al. (1987).

Once the samples reached the analyses temperature, a 50-mL headspace was created by displacing the water using a compressed standard gas with a CO_2 mixing ratio close to the anticipated pCO_2 of the water. The headspace is circulated in a closed loop through the infrared analyzer that measures CO_2 and water vapor levels in the sample cell. The samples are equilibrated until the running mean of 20 consecutive 1-second readings from the analyzer differs by less than 0.1 ppm (parts per million by volume). This equilibration takes about 10 min. An expandable volume in the circulation loop near the flask consisting of a small, deflated balloon keeps the headspace of the flask at room pressure.

In order to maintain analytical accuracy, a set of 6 gas standards is run through the analyzer before and after every 10 seawater samples. The standards were obtained from Scott-Marin and referenced against primary standards purchased from C.D. Keeling in 1991, which are on the World Meteorological Organization (WMO)-78 scale. The cylinder serial numbers and mole fractions of CO_2 with balance artificial air are:

CA5998	205.1 ppm
CA5989	378.7 ppm
CA5988	593.6 ppm
CA5980	792.5 ppm
CA5984	1037.0 ppm
CA5940	1533.7 ppm

The calculation of pCO_2 in water from the headspace measurement involves several steps. The CO_2 concentrations in the headspace are determined via a second-degree polynomial fit using the nearest three standard concentrations. Corrections for the water vapor concentration, the barometric pressure, and the changes induced in the carbonate equilibrium by the headspace-water mass transfer are made. The corrected results are reported at the analytical temperature and at a reference temperature of 20°C.

No instrumental problems occurred during the cruise. The relatively time-consuming analyses and the presence of only one analyst limited the spatial coverage. Sampling and analyses focused on precision and accuracy rather than high throughput.

3.6 Carbon Isotope Measurements

Sections P16S_2005 and P16N_2006 were sampled for carbon isotopes. On average, full depth samples were collected every 5 degrees of latitude, and the upper water column was additionally sampled at the midpoint between full depth stations. Generally, 16 samples were collected for the upper water column stations and 32 samples for full depth stations. The sample collection and analysis procedures were identical to those used for WOCE and previous CLIVAR cruises. Briefly, ~500 mL samples were collected in Pyrex bottles fitted with high precision ground-glass stoppers. Before being used, the bottles were acid washed and annealed. The collected water samples were poisoned with 100µL of saturated $HgCL_2$, sealed, and returned to National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS) at WHOI where they were analyzed with the accelerator mass spectrometry radiocarbon

technique described in McNichol et al. (1994). The analytical procedure yields $\delta^{13}C$ values as part of the method. The routine estimated 1 sigma counting error for these samples was 23 ‰, but analysis of a very large number of replicate samples indicates the true radiocarbon error is between 3 and 4 ‰ (Elder et al. 1998). The mean reproducibility for duplicates collected on these two sections was 3.5 ‰ (24 pairs) for $DI^{14}C$ and 0.02 ‰ (21 pairs) for $DI^{13}C$.

After the analyses were completed, NOSAMS produced a final report for each set of samples (NOSAMS Data Report #08-001 and #08-003). The data were then transferred to Princeton for final QC and submission to the data centers (CDIAC and CCHDO).

Figure 7 shows the radiocarbon concentration results for these two cruises; dots represent sample locations. Topography is taken from the bottom depth measurement at each station. The North Pacific Deep Water minimum is located well south of the Alaskan slope. Waters with concentration greater than approximately 100‰ contain some bomb-produced radiocarbon contamination. At first glance, these data are quite similar to the WOCE occupation results for this section. The highest concentrations are found in near-surface waters in the subtropics. In these waters, the radiocarbon concentration generally mimics the density distribution. In deep water, the minimum concentration is found in North Pacific Deep Water with the extreme centered near 2500 m around 35°N. In the upper water column, the maximum concentrations are often at the surface as during WOCE, but more often now, maximum concentrations are found as deep as 250 m (not visible in figure).

While the overall distribution pattern measured on these two cruises is remarkably similar to that measured during WOCE, there are easily measured changes. Figure 8 shows the change in radiocarbon concentration in the upper 1500 m between WOCE and CLIVAR occupations along Section P16. Colors indicate the change in $\Delta^{14}C$ (‰). Only the zero (no change) contour line is shown as a heavy line. The light lines are contours of potential density along the section. In general, the change pattern follows the density distribution. The change at the far southern end of the section is not shown here, but implies a significant increase. This increase at the southern edge and the strong increase at the northern edge may be due to minor changes in the density structure rather than invasion of the bomb signal. Further investigation is needed in these areas. This figure was prepared by simply gridding the data from each occupation and then subtracting the WOCE results from the CLIVAR results. As in the concentration figure, the change distribution generally follows the density distribution. In the upper water column, the concentrations show a strong decrease while values in the thermocline generally show strong increases. The large increase adjacent to the Alaskan slope was unexpected and may be an artifact due to small changes in station locations and the density structure. Similar large increases at the southern end of the section are not shown in this figure since they could be an artifact of either the gridding or a small movement of the Circumpolar Current. The strong increases at both ends of this section will require much more careful analysis.

The overall distribution of ^{13}C is similar to that measured previously; the observed patterns differ from that of ^{14}C because ^{13}C is a tracer of biological as well as physical processes. Values in the southern hemisphere are enriched relative to those in the north due to the increased input of ^{13}C-depleted carbon from the oxidation of organic matter. Measurement of $DI^{13}C$ in the full water column of the northern section added detailed coverage to the deep waters, which were not measured during WOCE. The biggest changes over time are expected in the surface waters where there should be changes due to the equilibration of the surface ocean with the changing atmosphere. **At present we are unable to show these differences because of a systematic calibration issue affecting some of the $DI^{13}C$ data; future versions of this document will include a figure detailing the changes when the issue has been resolved.**

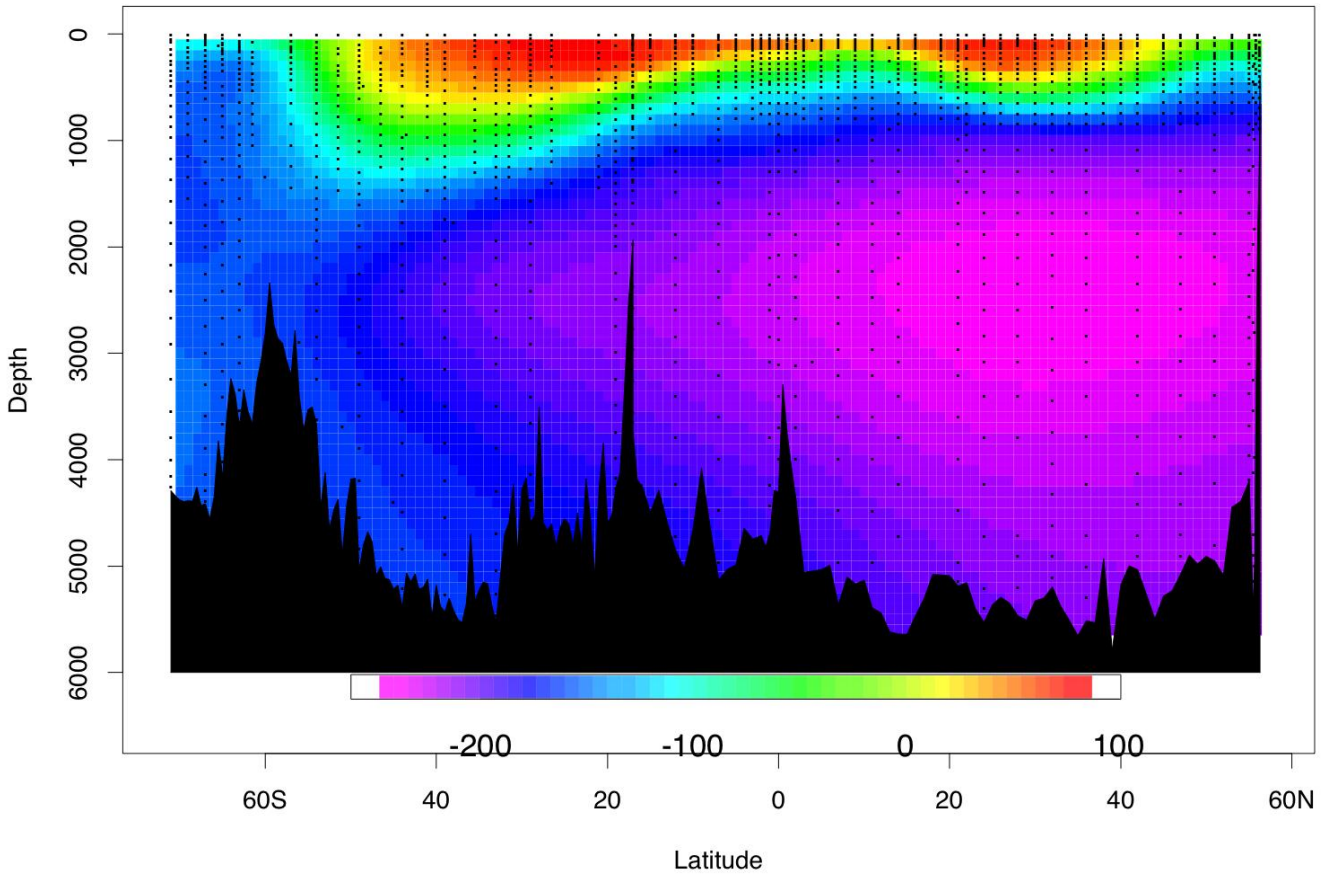

Fig. 7. $\Delta^{14}C$ (‰) distribution along Section P16.

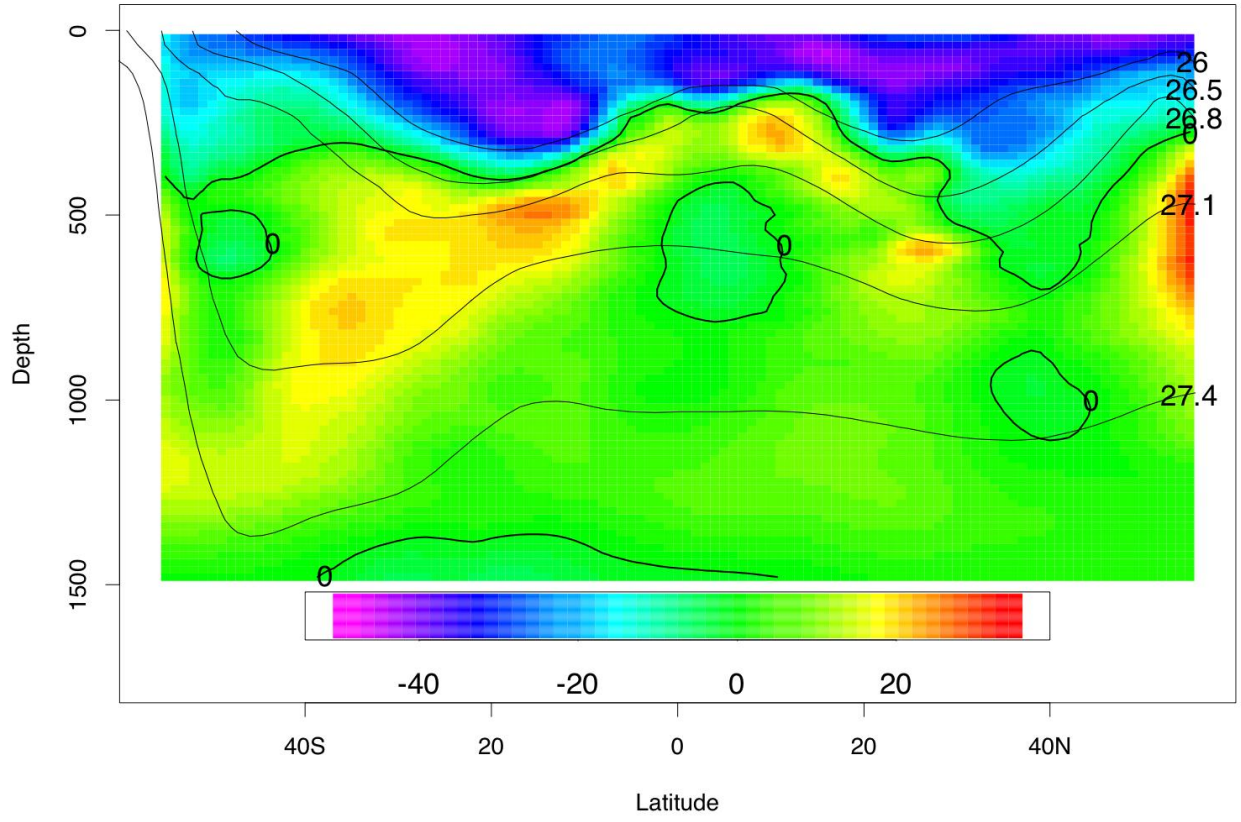

Fig. 8. Change in radiocarbon concentration in the upper 1500 m between WOCE and CLIVAR occupations along Section P16.

3.7 Dissolved Organic Carbon Measurements

3.7.1 Section P16S_2005

The DOC samples on Section P16S_2005 cruise were collected and analyzed by Dr. Craig Carlson's group from University of California, Santa Barbara (UCSB). All samples were collected directly from the Niskin bottles. Because particulate organic carbon concentrations in the surface waters can be elevated all samples collected from the upper 500 m were filtered. Water was filtered through a combusted GF/F housed in an acid-washed polycarbonate filter cartridge attached directly the Niskin bottle spigot. All samples were collected directly into an acid washed and Nanopure flushed high density polyethylene (HDPE) bottles (60 ml). Samples were immediately placed upright in a -20°C freezer and later were packed in dry ice and shipped to a shore laboratory. All samples were kept frozen at -20°C in an organic (volatile–free) environment for shore side analysis.

All DOC samples were analyzed via high temperature combustion using a Shimadzu TOC-V series TOC analyzer in a shore based laboratory at UCSB. The operating conditions of the Shimadzu TOC-V were slightly modified from the manufacturer's model system. The condensation coil was removed and the head space of an internal water trap was reduced to minimize the system's dead space. The combustion tube contained 0.5 cm Pt pillows placed on top of Pt alumina beads to improve peak shape and to reduce alteration of combustion matrix throughout the run. CO_2 free carrier gas was produced with

a Whatman gas generator (Carlson et al. 2004). Samples were drawn into 5 mL injection syringe and acidified with 2 M HCl (1.5%) and spared for 1.5 min with CO_2-free gas. Three to five replicate 100 µL of sample were injected into combustion tube heated to 680°C. The resulting gas stream was passed though several water, including an added magnesium perchlorate trap followed by a halide trap. The CO_2 in the carrier gas was analyzed with a non-dispersive infrared detector, and the resulting peak area was integrated with Shimadzu chromatographic software. Injections continued until at least three injections met the system-specified range of an SD of 0.1 area counts, CV ≤2%, or best 3 of 5 injections.

Extensive conditioning of the combustion tube with repeated injections of low-carbon water and deep seawater was essential to minimize the machine blanks. After conditioning, the system blank was assessed with ultra-violet-oxidized, low-carbon water. The system response was standardized with a four-point calibration curve of potassium hydrogen phthalate solution in low-carbon water. All samples were systematically referenced against low-carbon water, deep Sargasso Sea reference waters (2600 m) and Sargasso Sea surface water every 6 to 8 analyses (Hansell and Carlson 1998). The standard deviation of the deep and surface references analyzed throughout a run generally have a coefficient of variation ranging between 1–3% over the 3 to 7 independent analyses (number of references depends on size of the run) (see Hansell 2005). Daily reference waters were calibrated with DOC CRM provided by D. Hansell (RSMAS). The UCSB DOC laboratory exchanges references and samples with the Hansell DOC laboratory to ensure similar performance of DOC systems and comparability of data.

DOC calculation:

µMC = (average sample area – average machine blank area) / (slope of std curve)

3.7.2 Section P16N_2006

The DOC samples on Section P16N_2006 cruise were collected and analyzed by Dr. Dennis Hansell's group from RSMAS/UM. Water samples were collected from the rosette. Samples collected from the surface to 250 meters were filtered using precombusted (500ºC) GF/F inline filters as they were being collected from the Niskin bottle. At depths > 250 meters, the samples were collected without filtration. After collection, samples were frozen upright in 60 mL acid-cleaned HDPE bottles and remained cold until analysis. Prior to analysis, samples were returned to room temperature, then acidified to pH < 2 with concentrated hydrochloric acid. Analysis was performed on shore using a Shimadzu TOC-V_{CSH} TOC analyzer with the TNM-1 total nitrogen (TN) detector attached. Instrument conditions were as follows:

combustion temperature	680 °C
carrier gas	UHP oxygen
carrier flow rate	150 mL/min
ozone generation gas	zero air from Whatman TOC gas generator
ozone flow rate	500 mL/min
sample sparge time	2.0 min
minimum number of injections	3
maximum number of injections	5
number of washes	2
standard deviation maximum	0.1000
CV maximum	2.00%
injection volume	100 µL

The TOC system was calibrated using potassium hydrogen phthalate in Milli-Q water and the TN system was calibrated using potassium nitrate in Milli-Q water. System performance was verified daily

using consensus reference water distributed by Dr. Hansell's laboratory at RSMAS/UM. This reference water is deep Sargasso Seawater that has been acidified and sealed in 10 mL ampoules, the concentration of which (≈44 μM C) has been determined by the consensus of up to six expert and independent laboratories. After verifying proper operation of the TOC/TN instrument, samples were set up on an auto sampler for analysis. The run started with a QW (Q Water) blank and a reference seawater analysis. Then six samples were analyzed followed by another QW blank and reference seawater. This sequence was repeated until all samples for that run were analyzed. The run ended with a QW blank, reference water, and a non-acidified QW blank. This was done to verify that the hydrochloric acid used to acidify the samples was not contaminated. QW blanks and reference water samples were used to evaluate system performance during the analytical run. If a problem was detected with the blanks or reference waters, the samples were reanalyzed.

3.8 Chlorofluorocarbon Measurements

3.8.1 Section P16S_2005

During the Section P16S_2005, chlorofluorocarbons (CFC-11, CFC-12, and CFC-113) were measured on all 111 stations for a total of 3,078 samples, although the throughput rate of the analytical system necessitated selectively not sampling some Niskin bottles on most casts. The data set was minimally compromised by this procedure by selecting depths in mid-waters of relatively uniform hydrography. The results of this cruise are preliminary and may change by a small percentage after final scrutiny by the principal investigator.

All samples were collected from depth using 10-L Niskin bottles. Bottles had been cleaned prior to the cruise, and all o-rings, seals and taps were removed, washed in deacon solution and propan-2-ol, then baked out in a vacuum oven for 24 h. Of the original 36 bottles initially used, two were lost and replaced, and one was temporarily replaced, repaired and returned. None of the Niskin bottles used showed a CFC contamination during the cruise. All bottles in use remained inside the CTD hanger between casts. All spare bottles were stored on a spare rosette under a tarp, sitting on the main deck.

CFC sampling was conducted first at each station, according to WOCE protocol. This reduces contamination by air introduced at the top of the Niskin bottle as water was being removed. A water sample was collected directly from the Niskin bottle petcock using a 100 mL ground glass syringe which was fitted with a three-way stopcock that allowed flushing without removing the syringe from the petcock. Syringes were flushed several times and great care was taken to avoid contamination by air bubbles. Duplicate samples were randomly collected, nominally from every CTD cast. Duplicates were not taken when time was constrained due to a backlog of analyses. Air samples, pumped into the system using an Air Cadet pump, were run about every 2–4 days from a Dekoron air intake hose mounted high on the foremast. These samples were used to check CFC saturation levels in the surface water.

Halocarbon analyses were performed on a GC equipped with an electron capture detector (ECD). Samples were introduced into the GC-ECD via a purge and dual trap system. The samples were purged with nitrogen and the compounds of interest were trapped on a main Porapack N trap held at ~ −20°C with a Vortec Tube cooler. After the sample had been purged and trapped for several min at high flow, the gas stream was stripped of any water vapor via a magnesium perchlorate trap prior to transfer to the main trap. The main trap was isolated and heated by direct resistance to 140°C. The desorbed contents of the main trap were back-flushed and transferred with helium gas over a short period, to a small volume focus trap to improve chromatographic peak shape. The focus trap was also Porapak N and is held at ~ −20°C with a Vortec Tube cooler. The focus trap was flash heated by direct resistance to 155°C to release the compounds of interest onto the analytical pre-column. The analytical precolumn was held in-line with the main analytical column for the first 3 min of the chromatographic run. After 3 min, all of the compounds of interest were on the main column, and the pre-column was switched out of line and back-

flushed with a relatively high flow of nitrogen gas. This prevented later eluting compounds from building up on the analytical column, eventually eluting and causing the detector baseline signal to increase.

The syringes were stored in a flow-through seawater bath and analyzed within 8–12 h after collection. Bath temperature was recorded continuously for use in calculating the mass of water analyzed. Every ten measurements were followed by a purge blank and a standard, gas 2.68mL. Time permitting, the surface sample was held after measurement and was sent through the process to "restrip" it to determine the efficiency of the purging process.

For accuracy, the standard, S39, was cross-calibrated to the SIO-98 absolute calibration scale. A 19 point calibration curve was run every 4–9 days for all three halocarbons. Estimated accuracy is ± 2%. Precision for CFC-12, CFC-11 and CFC-113 is better than 1%.

Sample collection and measurement were largely very successful. The integration of the computer software with the GC-EDC system hardware made the procedure almost completely automated. A few problems were encountered initially. Some of the opto-isolator circuitry failed and required replacement. The bow air line filled with moisture transitioning from the warm humid outside air to the cold, dry air-conditioned Main Lab, flooding the magnesium perchlorate trap associated with the pump sample line; this was solved by installing an additional water trap in line just before the magnesium perchlorate trap. The rough seas played havoc with the particular brand of laptop computers integrated with the GC system, causing them to crash several times, which resulted in occasional sample losses. Two of the glass syringes appeared to be contaminated with CFC-11 and CFC-113, respectively, and were removed from service. How they were affected was not discovered, but since no other syringes were contaminated, the situation appeared isolated. To our knowledge, there were no other occurrences of contamination.

3.8.2 Section P16N_2006

Approximately 900 samples were drawn and analyzed for CFC during Section P16N_2006 Leg 1. In addition, 120 samples were analyzed for sulfur hexafluoride (SF_6). The precision of the CFC analysis, based on replicate pairs, is estimated to be the greater of 1% or 0.005 pmol/kg.

The CFC analysis was based on the work of Bullister and Weiss (1988). CFC samples were drawn from the Niskin bottles into glass syringes to prevent contamination from air. A 30 mL aliquot was injected into a glass-fritted reservoir, and clean nitrogen was bubbled through the water to remove the CFCs, which were dried over magnesium perchlorate and concentrated on a trap of Porapak N at −20°C. The trap was subsequently heated and the gases swept off of the trap with nitrogen and injected onto a precolumn of Porasil C (70°C). Once the gases of interest had passed through the precolumn, the remaining gases were vented while the CFCs passed to the 19 main analytical columns (carbograph 1AC, 70°C). The gases were detected by a Hewlett Packard ECD.

During Section P16N_2006 Leg 2, samples for the analysis of dissolved CFC-11, CFC-12, and CFC-113 were drawn from 960 of the 1300 water samples. Specially designed 12-L water sample bottles were used on the cruise to reduce CFC contamination. These bottles have the same outer diameter as standard 10-L Niskin bottles, but use a modified end-cap design to minimize the contact of the water sample with the end-cap O-rings after closing. The O-rings used in these water sample bottles were vacuum-baked prior to the first station. Stainless steel springs covered with a nylon powder coat were substituted for the internal elastic tubing provided with standard Niskin bottles. When taken, water samples for CFC analysis were the first samples drawn from the 12-L bottles. Care was taken to coordinate the sampling of CFCs with other samples to minimize the time between the initial opening of each bottle and the completion of sample drawing. In most cases, helium-3, dissolved oxygen, alkalinity

and pH samples were collected within several minutes of the initial opening of each bottle. To minimize contact with air, the CFC samples were drawn directly through the stopcocks of the 12-L bottles into 100 mL precision glass syringes equipped with 3-way plastic stopcocks. The syringes were immersed in a holding bath of freshwater until analyzed.

For air sampling, a ~100-m length of 3/8–in. outside diameter (OD) Dekaron tubing was run from the main laboratory to the bow of the ship. A flow of air was drawn through this line into the CFC van using an Air Cadet pump. The air was compressed in the pump, with the downstream pressure held at ~1.5 atm using a back-pressure regulator. A tee allowed a flow (100 mL/min) of the compressed air to be directed to the gas sample valves of the CFC and SF_6 analytical systems, while the bulk flow of the air (>7 L/min) was vented through the back pressure regulator. Air samples were generally analyzed when the ship was on station and the relative wind direction was within 60º of the bow of the ship to reduce the possibility of shipboard contamination. The pump was run for approximately 45 min prior to analysis to ensure that the air inlet lines and pump were thoroughly flushed. The average atmospheric concentrations determined during the cruise (from a set of 5 measurements analyzed approximately once per day, n=23) were 252.9 ± 4.4 parts per trillion (ppt) for CFC-11, 547.2 ± 5.0 ppt for CFC-12, and 76.3 ± 1.9 ppt for CFC-113.

Concentrations of CFC-11 and CFC-12, and CFC-113 in air samples, seawater, and gas standards were measured by shipboard ECD-GC using techniques modified from those described by Bullister and Weiss (1988). For seawater analyses, water was transferred from a glass syringe to a fixed volume chamber (~30 mL). The contents of the chamber were then injected into a glass sparging chamber. The dissolved gases in the seawater sample were extracted by passing a supply of CFC-free purge gas through the sparging chamber for 4 min at 70 mL/min. Water vapor was removed from the purge gas during passage through an 18 cm long, 3 in diameter glass tube packed with the desiccant magnesium perchlorate. The sample gases were concentrated on a cold-trap consisting of a 1/8-in OD stainless steel tube with a ~10 cm section packed tightly with Porapak N (60–80 mesh). A vortex cooler, using compressed air at 95 psi, was used to cool the trap, to approximately –20ºC. After 4 min of purging, the trap was isolated, and the trap was heated electrically to ~100ºC. The sample gases held in the trap were then injected onto a precolumn (~25 cm of 1/8-in OD stainless steel tubing packed with 80 to 100 mesh Porasil C, held at 70ºC) for the initial separation of CFC-12, CFC-11 and CFC-113 from other compounds. After the CFCs had passed from the pre-column into the main analytical column (~183 cm of 1/8-in OD stainless steel tubing packed with Carbograph 1AC, 80–100 mesh, held at 70ºC) of GC1 (a HP 5890 Series II gas chromatograph with ECD), the flow through the pre-column was reversed to backflush slower 23 eluting compounds. Both of the analytical systems were calibrated frequently using a standard gas of known CFC composition. Gas sample loops of known volume were thoroughly flushed with standard gas and injected into the system. The temperature and pressure was recorded so that the amount of gas injected could be calculated. The procedures used to transfer the standard gas to the trap, precolumn, main chromatographic column, and ECD were similar to those used for analyzing water samples. Two sizes of gas sample loops were used. Multiple injections of these loop volumes could be made to allow the system to be calibrated over a relatively wide range of concentrations. Air samples and system blanks (injections of loops of CFC-free gas) were injected and analyzed in a similar manner. The typical analysis time for seawater, air, standard, or blank samples was ~10.5 min.

Concentrations of the CFCs in air, seawater samples and gas standards are reported relative to the SIO98 calibration scale (Prinn et al. 2000). Concentrations in air and standard gas are reported in units of mole fraction CFC in dry gas, and are typically in the parts per trillion (ppt) range. Dissolved CFC concentrations are given in units of picomoles per kilogram seawater (pmol/kg). CFC concentrations in air and seawater samples were determined by fitting their chromatographic peak areas to multi-point calibration curves, generated by injecting multiple sample loops of gas from a working standard (UW cylinder 45191 for CFC-11: 386.94 ppt, CFC-12: 200.92 ppt, and CFC-113: 105.4 ppt) into the analytical

instrument. The response of the detector to the range of moles of CFC-12 and CFC-113 passing through the detector remained relatively constant during the cruise. A thorough baking of the column and trap after a power outage during trapping of a seawater sample introduced an unknown contaminant into the column changed the response of the detector to CFC-11. Full-range calibration curves were run at intervals of 10 days during the cruise. These were supplemented with occasional injections of multiple aliquots of the standard gas at more frequent intervals. Single injections of a fixed volume of standard gas at one atmosphere were run much more frequently (at intervals of ~90 min) to monitor short-term changes in detector sensitivity. The CFC-113 peak was often on a small bump on the baseline, resulting in a large dependence of the peak area on the choice of endpoints for integration. The height of the peak was instead used to provide better precision. The precisions of measurements of the standard gas in the fixed volume (n=395) were ± 0.44% for CFC-12, 0.56% for CFC-11, and 3.0% for CFC-113.

The efficiency of the purging process was evaluated periodically by re-stripping high concentration surface water samples and comparing the residual concentrations to initial values. These re-strip values were approximately <1% of the initial sample concentration for all 3 compounds. A fit of the re-strip efficiency as a function of temperature will be applied to the final data set. The determination of a blank due to sampling and analysis of CFC-free waters was hampered by a contamination peak that co-eluted with CFC-11 and varied greatly in size during this leg. The size of the peak decreased exponentially with time, but jumped to very high values (0.05 pmol/kg) after each of the four power outages encountered during Leg 2. Further investigation needs to be done to understand the origin of this contamination. CFC-113 and CFC-12 sampling blanks were less than 0.005 pmol/kg.

During the expedition, the precisions (1 standard deviation) of 0.45% or 0.004 pmol/kg (whichever is greater) for dissolved CFC-11, 0.36% or 0.003 pmol/kg for CFC-12 measurements, and 0.004 pmol/kg for CFC-113 was estimated based on the analysis of 38 duplicate samples. A very small number of water samples had anomalously high CFC concentrations relative to adjacent samples. These samples occurred sporadically during the cruise and were not clearly associated with other features in the water column (e.g. anomalous dissolved oxygen, salinity or temperature features). This suggests that these samples were probably contaminated with CFCs during the sampling or analysis processes. Measured concentrations for these anomalous samples are included in the data, but are given a quality flag value of either 3 (questionable measurement) or 4 (bad measurement). A quality flag of 5 was assigned to samples that were drawn from the rosette but never analyzed due to a variety of reasons (e.g., power outage during analysis).

3.9 Underway Surface pCO_2 Measurements on P16S_2005

The NOAA/PMEL group (Dr. Christopher Sabine, principal investigator) was responsible for underway surface pCO_2 measurements during the CLIVAR Repeat Hydrography Section P16S_2005. Dr. Sabine operated the system during the cruise.

The automated underway LICOR 6262 pCO_2 sensor with showerhead equilibrator was used during the cruise. The measurement method based on infrared absorption of dried gas and described in Feely et al. (1998) and Wanninkhof and Thoning (1993). Equilibrator volume was ~0.5 L with a headspace of ~ 0.8 L. During the cruise resolution/uncertainty was 0.3 µatm for equilibrator measurements, 0.2 µtam for atmospheric measurements.

Standard gases were supplied by NOAA's Climate Monitoring Diagnostics Laboratory in Boulder, Colorado, and were directly traceable to the WMO scale. Any value outside the range of the standards should be considered approximate, although the general trends should be indicative of the seawater chemistry.

Serial numbers and CO_2 concentrations for the cylinders used on this cruise:

LL55884	324.82
LL55879	351.07
LL55878	405.96
LL55877	483.45

The system ran a full cycle in approximately 112 min. The cycle started with 4 standard gases, then measured 10 atmospheric samples followed by 60 surface water samples. Each new gas was flushed through the LICOR analyzer for 4 min prior to a 10 second reading from the analyzer during which the sample cell was open to the atmosphere. Subsequent samples of the same gas are flushed through the LICOR Analyzer for 30 s prior to a stop-flow measurement.

All xCO_2 values are reported in parts per million by volume (ppmv) and fCO_2 values are reported in microatmospheres (μatm) assuming 100 % humidity at the equilibrator temperature.

The mixing ratios of ambient air and equilibrated headspace air were calculated by fitting a second-order polynomial through the hourly averaged response of the detector versus mixing ratios of the standards. Mixing ratios of dried equilibrated headspace and air are converted to fugacity of CO_2 in surface seawater and water saturated air to determine the fCO_2. For ambient air and equilibrator headspace the fCO_2a, or fCO_2eq is calculated assuming 100% water vapor content:

$$fCO_2a/eq = xCO_2a/eq(P - pH_2O)\exp(B11 + 2d12)P/RT$$

where fCO_2a/eq is the fugacity in ambient air or equilibrator, pH_2O is the water vapor pressure at the sea surface temperature, P is the atmospheric pressure (in atm), T is the sea surface temperature (SST) or equilibrator temperature (in K) and R is the ideal gas constant (82.057 $cm^3 \bullet atm \bullet deg^{-1} \bullet mol^{-1}$). The exponential term is the fugacity correction where B11 is the second virial coefficient of pure CO_2:

$$B11 = -1636.75 + 12.0408T - 0.032795T^2 + 3.16528E^{-5}\,T^3 \text{ and}$$
$$d12 = 57.7 - 0.118\,T$$

is the correction for an air-CO_2 mixture in units of $cm^3 \bullet mol^{-1}$ (Weiss 1974).

The calculation for the fugacity at SST involves a temperature correction term for the increase of fCO_2 due to heating of the water from passing through the pump and through 5 cm inside diameter (ID) PVC tubing within the ship. The water in the equilibrator is typically 0.2 °C warmer than sea surface temperature. The empirical temperature correction from equilibrator temperature to SST is outlined in Weiss et al. (1982):

$$\Delta\ln(fCO_2) = (T_{eq} - SST) \times (0.0317 - 2.7851E^{-4}\,T_{eq} - 1.839E^{-3}\ln(fCO_2eq))$$

where $\Delta\ln(fCO_2)$ is the difference between the natural logarithm of the fugacity at T_{eq} and SST, and T_{eq} is the equilibrator temperature in ºC.

3.10 Underway pH, fCO_2, and TCO_2 Measurements on P16N_2006

The USF group (Dr. Robert Byrne, principal investigator) was responsible for underway surface pH, fCO_2 and TCO_2 measurements during the CLIVAR Repeat Hydrography Section P16S_2005 using the automated Multi-Parameter Inorganic Carbon Analyzer (MICA) system. Drs. Xuewu Sherwood Liu and

Renate Bernstein operated the system during Leg 1 and Drs. Robert Byrne, Zhaohui 'Aleck' Wang, and Johan Schijf and Mr. Ryan Bell operated the system during Leg 2 of the cruise.

Technical details and performance evaluation of the MICA system can be found in Wang et al. (2007). The system consists of three seawater channels (surface seawater fCO_2, TCO_2, and pH). All measurements (three channels) were made at constant temperature (25 ˚C) and were based on similar spectrophotometric principles. The system operates autonomously with a sampling frequency of ~7/hour. For each sample, all three parameters are measured and recorded simultaneously.

Spectrophotometric pH measurements were based on the method described in Clayton and Byrne (1993), but used thymol blue as the pH indicator (Zhang and Byrne 1996; Wang et al. 2007). Thymol blue was directly injected into a stream of underway seawater and absorbance was monitored spectrophotometrically. Sample pH is linked to the absorbance ratio (R), dissociation constant (K_I), and molar absorbance ratios (e_1, e_2, and e_3) of the indicator with the following equation:

$$pH_T = -\log_T K_I + \log\frac{R - e_1}{e_2 - Re_3} \quad (1)$$

where the subscript T denotes parameters expressed on the total hydrogen ion scale. The calibrated constants of thymol blue are given by Zhang and Byrne (1996) as:

$$-\log_T K_I = \frac{4.706S}{T} + 26.3300 - 7.17218\ \log T - 0.017316S \quad (2)$$

$$e_1 = -0.00132 + 1.6\times10^{-5}T, \quad (3)$$

$$e_2 = 7.2326 - 0.0299717T + 4.6\times10^{-5}T^2, \quad (4) \text{ and}$$

$$e_3 = 0.0223 + 0.0003917T \quad (5)$$

where T is absolute temperature in K, and S is salinity.

For **seawater fCO_2** measurements, Teflon AF 2400 (DuPont) is used as both a CO_2 permeable membrane and a liquid-core waveguide (LCW) (Wang et al. 2007). Phenol red is used as the indicator (Yao and Byrne 2001). During each CO_2 measurement, the indicator solution, composed of Na_2CO_3 with constant total alkalinity (TALK), is motionless inside the LCW. The seawater samples were directed to flow outside the LCW. After CO_2 molecules equilibrate by diffusion with the LCW's internal solution, the equilibrium pH was determined by measurements of absorbance ratios. fCO_2 was then derived from the equilibrium pH with the following equation:

$$fCO_2 = \frac{TA}{2K_0K_1'K_2'[H^+]^{-2} + K_0K_1'[H^+]^{-1}} = \frac{a}{L} + b \quad (6)$$

where K_0 is the Henry's Law constant, K'_1 and K'_2 are carbonic acid dissociation constants, and $L = 2K_0K_1'K_2'[H^+]^{-2} + K_0K_1'[H^+]^{-1}$. Parameters "a" and "b" are derived through a calibration procedure using CO_2 gases at known concentrations. The pH of the indicator solution is determined spectrophotometrically, and the L term in Eq. 6 is then calculated. Since the TALK of the internal solution is constant, sample fCO_2 has a linear dependence on 1/L with a slope of "a" and an intercept of

"b." The calibration constants, "a" and "b," account for all uncertainties in Eq. 6 including the absolute value of TALK.

Spectrophotometric measurements of **TCO_2** using Teflon 2400 AF LCWs have been described by Byrne et al. (2002). Water samples are acidified before measurements (pH ≈ 2.7), whereupon the total CO^*_2 concentration equals the TCO_2 concentration. After the internal Na_2CO_3 -indicator (bromcresol purple) solution attains CO_2 equilibrium with the acidified water samples across the LCW CO_2-permeable walls, the TCO_2 of the outer solution can be written as:

$$\log DIC = \log\left(\frac{(K_0)_{ex}}{(K_0)_i}\right) + B - \log\left(\frac{R - e_1}{1 - Re_3 / e_2}\right), \quad (7) \text{ and}$$

$$\log\left(\frac{(K_0)_{ex}}{(K_0)_i}\right) = \left(\frac{50.20(\mu_{ex} - \mu_i)}{2.303}\right)\left(0.023517 - 0.023655\left(\frac{T}{100}\right) + 0.0047036\left(\frac{T}{100}\right)^2\right) \quad (8)$$

where B is an experimentally derived constant determined via calibration of the TCO_2 channel against CRM. The subscript "ex" refers to the acidified outer solution, "i" indicates the internal solution, and μ is ionic strength.

For each of the three indicators used, three wavelengths are chosen for measurement of absorbance. Two wavelengths assess the absorbance peaks of acid and base forms of the indicator, while a third wavelength serves as a reference wavelength. Absorbance varies at the acid and base wavelengths in response to pH changes, but not at the reference wavelength. Absorbance measurements at acid and base indicator maxima are used for determination of all CO_2 system parameters. The wavelengths chosen for the three channels are listed in Table 7.

Table 7. Wavelengths used for spectrophotometric determination of inorganic carbon species.

Channel	Indicator	Acid Wavelength	Base Wavelength	Reference Wavelength
Seawater fCO_2	*Phenol red*	434 nm	558 nm	700 nm
TCO_2	Bromcresol purple	432 nm	589 nm	700 nm
pH	Thymol blue	435 nm	596 nm	730 nm

The indicator solution for CO_2 measurements consists of a solution of 2 μM phenol red, 225 μmol/kg total alkalinity (Na_2CO_3), and 0.2 μM sodium lauryl sulfate. For TCO_2 measurements, the indicator solution is made of 2 μM bromcresol purple in 1000 μmol/kg total alkalinity (Na_2CO_3) and 0.2 μM sodium lauryl sulfate. The reference solutions of the CO_2 and TCO_2 measurements are similar solutions that contain no indicator. For pH measurements, the thymol blue stock solution is made in Milli-Q water with a concentration of 1.5 mM. The R ratio of thymol blue solution is adjusted (R~0.77) to minimize the magnitude of indicator-induced pH perturbations. All indicator and reference solutions are stored in gas-impermeable laminated bags. 3N HCl in Milli-Q water is stored in a 250 mL glass bottle and used to acidify TCO_2 samples.

Three Ocean Optic 2000 spectrophotometers were used to determine indicator absorbance for each of the three measurement channels. The light assemblies, spectrophotometers, and optical cells are connected with optic fibers. The light assembly of each channel consists of a high-temperature tungsten

lamp with blue and short-pass filters to achieve an improved balance of spectral intensity between 430 and 700 nm.

The optical cells of the CO_2 and TCO_2 channels are custom-machined from PolyEtherEtherKetone (PEEK) rods. The PEEK optical cell has a 27 mm OD and a 2 mm ID with a length of 15 cm. A Teflon AF 2400 LCW is located inside this optical cell. The sample inlet and outlet, and two optical fibers that connect the optical cell with the light source and spectrophotometer, are inserted into the ends of the LCW with two custom-made PEEK connectors. The ends of the LCW are sealed with two O-rings that are housed inside the connectors. The PEEK connectors allow both reagent and light to pass through the LCW. The pH optical cell is machined from a PEEK rod, but does not require special connectors since no LCW is used.

Indicator and reference solutions are pumped through separate lines into their respective channels by digital peristaltic pumps. Surface seawater is obtained continuously with a shipboard pumping system. It first flows through a SBE 49 CTD that records salinity and temperature, and is then pumped through three seawater channels (fCO_2, TCO_2, and pH). Before entering the TCO_2 channel, seawater samples are acidified with ~3 N HCl using a digital peristaltic pump. The mixing ratio is approximately ~700 (seawater to HCl). An in-line coil is used to facilitate mixing. For pH measurement, thymol blue is mixed with seawater sample at a mixing ratio of ~700 (seawater to thymol blue), whereupon the final thymol blue concentration in the mixed sample is ~ 2 µM. This low indicator concentration results in very small indicator-induced pH perturbations (< 0.001 pH units). An in-line mixing coil is also used in this case.

All channels are thermostated in a Lauda E100 water bath that is set to 25 ± 0.1°C. All samples, reference and indicator solutions are temperature pre-equilibrated to 25˚C in the water bath using PEEK and glass coils. All measurements, as well as calibrations, are taken at this temperature.

All components of the system are connected to a custom-made electronic motherboard that is controlled by a PC. The interface program cycles to operate the MICA autonomously. The time required for each measurement cycle depends on the equilibration time (7 min for the seawater fCO_2 and TCO_2 channels) and flushing time selected for the indicator/reference solution and samples (~2 min). The equilibration time required for pH measurements is very short. The following sequence was used during a measurement cycle:

1. Flush pH reference (seawater samples without indicator solution).

2. Flush reference for seawater fCO_2 and TCO_2.

3. Read and store reference readings.

4. Flush indicator solutions for seawater fCO_2 and TCO_2; mix thymol blue with seawater samples (pH measurements); acidify TCO_2 samples.

5. Seawater fCO_2 and TCO_2 equilibration (7 min).

6. Read and store measurements.

7. Repeat steps 4–6 five times.

8. End of one measurement cycle and repeat from the beginning.

Prior to the cruise, the CO_2 channel was calibrated against five standard CO_2 gases ranging from 280 to 550 ppm (xCO_2). TCO_2 was also calibrated before the cruise using a CRM. Thymol blue has been calibrated previously for seawater pH measurements (Zhang and Byrne, 1996). During the cruise, CO_2 gas standards and CRM were used periodically to evaluate calibration consistency for CO_2 and TCO_2 measurements. Re-calibration was performed if necessary.

The calibration for the CO_2 channel is related to xCO_2 readings of the standard CO_2 gas tanks, even though it is fCO_2 that drives equilibrium across the LCW membrane. Based on DOE (1994), xCO_2, pCO_2 and fCO_2 can be calculated from each other at various measurement conditions (temperature, salinity, and pressure). The MICA seawater fCO_2 measurements reflect fCO_2 at 25°C with 100% water vapor content. The fCO_2 at 25˚C was corrected to in-situ temperature to compare with PMEL LICOR underway pCO_2 measurements. The temperature correction used in this case is given by Millero (2007):

$$d(\ln fCO_2)/dT(deg^{-1}) = 0.044 - (8\times10^{-5})S \quad (9)$$

No correction was required for the MICA TCO_2 measurements since TCO_2 is expressed in µmol/kg. The MICA pH measurements gave pH values on the total scale at 25˚C.

The auxiliary salinity, temperature, and pressure data used for these corrections and calculations were obtained from underway measurements using shipboard instruments.

Quality control analysis was performed in three steps. First, suspect data were removed, as necessary, following reported cruise log malfunctions (e.g., possible sample contamination and observed malfunction of the thermostat) and spectrophotometric anomalies (e.g., sudden decrease of baseline light signal indicating entrapment of air bubbles). Secondly, data points with deviations > 3 standard deviations ($p < 0.01$) from the running average of the data were removed. Finally, two of the three measured carbonate parameters (fCO2, TCO2, pH) were used to calculate the third parameter, which was compared with direct MICA measurements of the parameter. Suspect data were eliminated based on this internal consistency check.

4. HOW TO OBTAIN THE DATA AND DOCUMENTATION

This database (NDP-090) is available free of charge from CDIAC. The complete documentation and data can be obtained from the CDIAC oceanographic web site (http://cdiac.ornl.gov/oceans/doc.html), through CDIAC's online ordering system (http://cdiac.ornl.gov/pns/how_order.html) or by contacting CDIAC.

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

ftp cdiac.ornl.gov or >ftp 160.91.18.18
Login: "anonymous" or "ftp"
Password: your e-mail address
ftp> cd pub/ndp090/
ftp> dir
ftp> mget (files)
ftp> quit

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

Contact information:

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

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