CLIVAR/Carbon A13.5

NOAAS Ronald H. Brown
8 March 2010 - 18 April 2010
Cape Town, South Africa - Takoradi, Ghana

Chief Scientist:
Dr. John L. Bullister
National Oceanic and Atmospheric Administration, PMEL

Co-Chief Scientist:
Dr. Robert M. Key
Princeton University

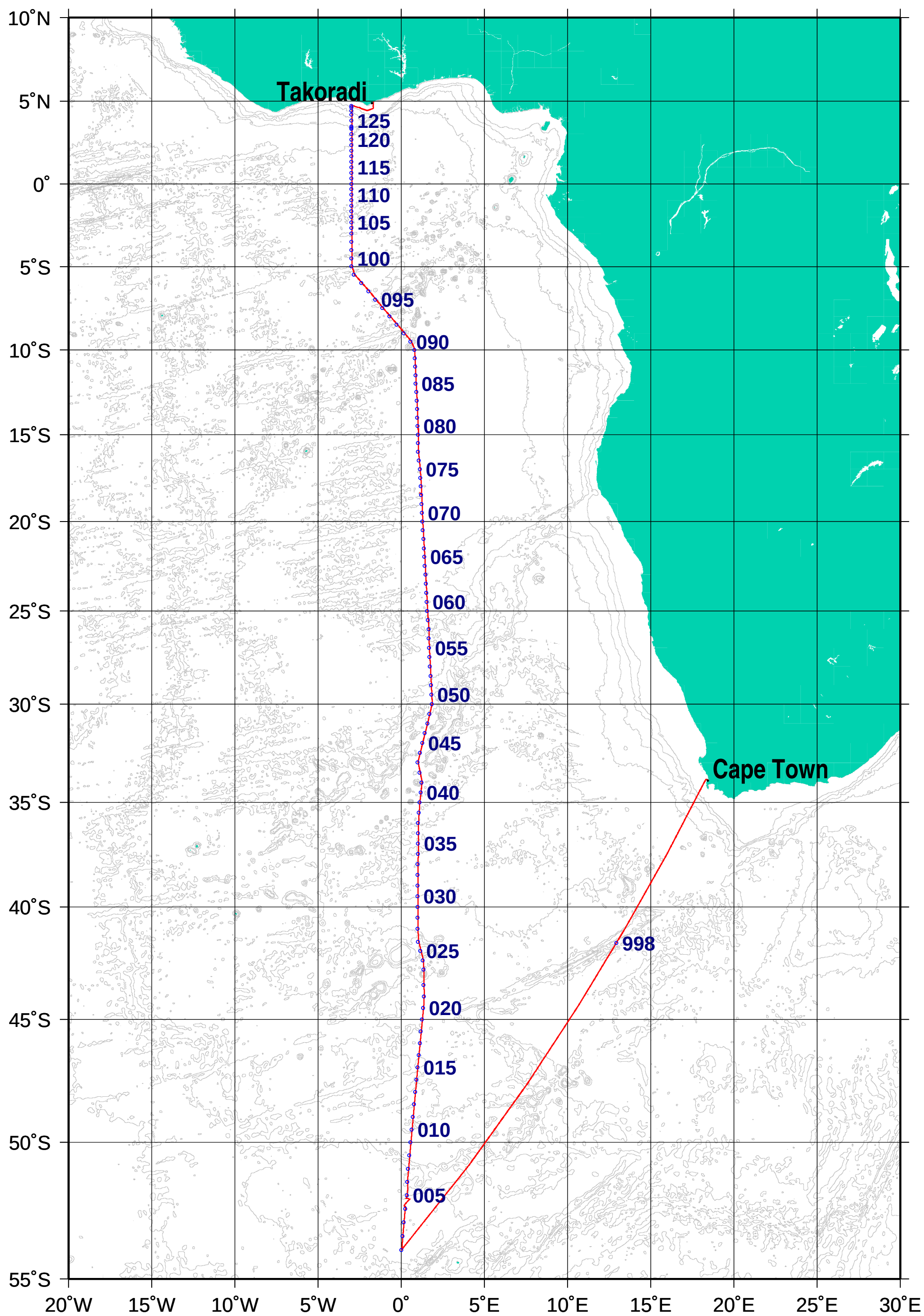
Preliminary Cruise Report
2 June 2010

CTD Data Submitted by:

Kristene E. McTaggart
Pacific Marine Environmental Laboratory (PMEL)
National Oceanic and Atmospheric Administration (NOAA)
Seattle, WA

Preliminary Bottle Data Submitted by:

Mary Carol Johnson
Shipboard Technical Support/Oceanographic Data Facility
Scripps Institution of Oceanography/UC San Diego
La Jolla, CA



CLIVAR/Carbon A13.5 Cruise Track

Introduction

A sea-going science team gathered from multiple oceanographic institutions and nations participated on the CLIVAR/Carbon A13.5 cruise. Several other science programs were supported with no dedicated cruise participant. The science team and their responsibilities are listed below.

CLIVAR/Carbon A13.5 Participating Institutions

Abbreviation	Institution
AOML	Atlantic Oceanographic and Meteorological Laboratory - NOAA
CDIAC	Carbon Dioxide Information Analysis Center
CPO	Climate Program Office - NOAA
ETH	Swiss Federal Institute of Technology
LDEO	Lamont-Doherty Earth Observatory/Columbia University
MLML	Moss Landing Marine Laboratory
NOAA	National Oceanic and Atmospheric Administration
Penn State	Pennsylvania State University
PMEL	Pacific Marine Environmental Laboratory - NOAA
Princeton	Princeton University
RSMAS	Rosenstiel School of Marine and Atmospheric Science/University of Miami
SIO	Scripps Institution of Oceanography/University of California at San Diego
TAMU	Texas A&M University
U Colorado	University of Colorado
U Ghana	University of Ghana
U Hawaii	University of Hawaii at Manoa
WHOI	Woods Hole Oceanographic Institution
WS_SA	South African Weather Service, Durban

Principal Programs of CLIVAR/Carbon A13.5

Analysis	Institution	Principal Investigator	email
CTDO	NOAA/PMEL NOAA/AOML	Gregory Johnson Molly Baringer	Gregory.C.Johnson@noaa.gov Molly.Baringer@noaa.gov
ADCP/Lowered ADCP	U Hawaii	Jules Hummon	hummon@hawaii.edu
Salinity	NOAA/AOML	Molly Baringer	Molly.Baringer@noaa.gov
Total CO_2(DIC)	NOAA/PMEL NOAA/AOML	Richard Feely Rik Wanninkhof	Richard.A.Feely@noaa.gov Rik.Wanninkhof@noaa.gov
UW & Discrete pCO_2	NOAA/AOML	Rik Wanninkhof	Rik.Wanninkhof@noaa.gov
Nutrients	NOAA/AOML NOAA/PMEL	Jia-Zhong Zhang Calvin Mordy	Jia-Zhong.Zhang@noaa.gov Calvin.W.Mordy@noaa.gov
Dissolved O_2	NOAA/AOML RSMAS	Molly Baringer Chris Langdon	Molly.Baringer@noaa.gov clangdon@rsmas.miami.edu
Total Alkalinity/pH	SIO	Andrew Dickson	adickson@ucsd.edu
Chlorofluorocarbons(CFCs)/SF_6	NOAA/PMEL	John Bullister	John.L.Bullister@noaa.gov
^3He/Tritium	LDEO WHOI	Peter Schlosser William Jenkins	peters@ldeo.columbia.edu wjenkins@whoi.edu
DOC/TDN	RSMAS	Dennis Hansell	dhansell@rsmas.miami.edu
$^{14}C/\,^{13}C$	Princeton WHOI	Robert Key Ann McNichol	key@princeton.edu amcnichol@whoi.edu
Transmissometry	TAMU	Wilf Gardner	wgardner@ocean.tamu.edu
Data Management	SIO SIO	James Swift Kristin Sanborn	jswift@ucsd.edu ksanborn@ucsd.edu
Observer Lead PI	NOAA/CPO	Steve Piotrowicz	Steve.Piotrowicz@noaa.gov
Argo Float deployments & XBT drops	NOAA/PMEL	Gregory C. Johnson	Gregory.C.Johnson@noaa.gov
Drifter Deployment	NOAA/AOML	Shaun Dolk	Shaun.Dolk@noaa.gov
Underway surface ocean, meteorological and bathymetry data	NOAA	Ship personnel	

Scientific Personnel CLIVAR/Carbon A13.5

Duties	Name	Affiliation	email
Chief Scientist	John Bullister	PMEL	John.L.Bullister@noaa.gov
Co-Chief Scientist	Robert Key	Princeton	key@princeton.edu
Observer	Benjamin Osei Botwe	U Ghana	boseibotwe@yahoo.co.uk
Data Management (ashore)	Mary Carol Johnson	SIO	mcj@ucsd.edu
CTD	Kristy McTaggart	PMEL	Kristene.E.Mctaggart@noaa.gov
CTD/ET/Salinity	Kyle Seaton	AOML	Kyle.Seaton@noaa.gov
CTD Helper	Maria Herrmann	Penn State	mxh367@psu.edu
CTD Helper	Katherine Morrice	MLML	kmorrice@mlml.calstate.edu
Chief Scientist Helper	Ivy Frenger	ETH	ivy.frenger@env.ethz.ch
Chief Survey Tech.	Jonathan Shannahoff	NOAA	
ADCP/LADCP	Francois Ascani	U Hawaii	fascani@hawaii.edu
Salinity	James Farrington	AOML	James.W.Farrington@noaa.gov
Dissolved O_2	George Berberian	AOML	George.Berberian@noaa.gov
Dissolved O_2	Chris Langdon	RSMAS	clangdon@rsmas.miami.edu
Nutrients	Calvin Mordy	PMEL	Calvin.W.Mordy@noaa.gov
Nutrients	Charles Fischer	AOML	Charles.Fischer@noaa.gov
Total CO_2(DIC)	Cynthia Peacock	PMEL	cynthia.peacock@noaa.gov
Total CO_2(DIC)	Alex Kozyr	CDIAC	ako@cdiac.ornl.gov
pCO_2 UW & Discrete	Kevin Sullivan	AOML	Kevin.Sullivan@noaa.gov
pCO_2 Discrete	Geun-Ha Park	AOML	Geun-Ha.Park@noaa.gov
CFCs/SF_6	David Wisegarver	PMEL	David.Wisegarver@noaa.gov
CFCs/SF_6	Patrick Boylan	U Colorado	Patrick.Boylan@Colorado.EDU
Total Alkalinity	Laura Fantozzi	SIO	lfantozzi@ucsd.edu
Total Alkalinity	Yui Takeshita	SIO	ytakeshita@ucsd.edu
pH	Adam Radich	SIO	jradich@ucsd.edu
pH	Emily Bockmon	SIO	ebockmon@ucsd.edu
^3He/Tritium	Anthony Dachille	LDEO	dachille@ldeo.columbia.edu
DOC/TDN	Darcy Metzler	RSMAS	dmetzler@rsmas.miami.edu

A13.5 Navigation and Bathymetry Data Acquisition

Navigation data were acquired at 1-second intervals from the ship's P-Code GPS receiver by a Linux system beginning 8 March 2010.

An attempt was made to log various underway data, including Bathymetric data from the ship's 3.5kHz ODEC Bathy 2000 echosounder, beginning 11 March 2010 at 0930 UTC. However, the stored data file is a fairly useless jumble of numbers; the data feed apparently changed when the winch was turned off, and later records appear as if several programs were writing to the file at once. The echosounder was typically turned off during casts, where cast pinger-return data was recorded instead of bottom depth. It was usually turned back on between casts.

Seabeam centerbeam depths were displayed continuously, and data were manually recorded at cast start/bottom/end on CTD Cast Logs.

Both the Seabeam and Bathy 2000 transducers were located on the hull of the ship, at approximately 5.8m depth. Ship's Seabeam data recorded during CTD casts were already corrected for transducer depth, but used 1500m/sec sound velocity to determine depth.

The manually recorded Seabeam depths were Carter-table corrected via software using actual latitude and longitude before reporting in data files.

Etopo2 bathymetry data were merged with navigation time-series data after each cast and used for bottle-depth sections shown elsewhere in this report.

CO_2/CLIVAR Repeat Hydrography Program 2010 Reoccupation of
WOCE Section A13.5
NOAA ship RONALD H. BROWN
Cape Town, South Africa – Takoradi, Ghana
March 8 – April 18, 2010

Chief Scientist: John Bullister
Co-Chief Scientist: Robert Key
Data Manager: Mary Johnson (from shore)
CTD Watchstander: Maria Hermann, Katie Morrice
Quality Control/Processing: Kristy McTaggart
Sample Salinity Analyst: Kyle Seaton, James Farrington
Sample Oxygen Analyst: Chris Langdon, George Berberian
Survey Technician: Jonathan Shannahoff
Ship's Electronics Technician: Jeff Hill

Summary

The hydrographic work during this cruise was a reoccupation of a meridional section nominally along 3W-1E (WOCE Section A13.5, occupied in 1987). Operations included CTD/O_2/LADCP/rosette casts. Underway data collected included upper-ocean currents from the shipboard ADCP, surface oceanographic and meteorological parameters from the ship's underway systems, and bathymetric data. Ancillary operations included surface drifter deployments and Argo SOLO float deployments.

After a 1-day delay, NOAA Ship Ronald H. Brown departed Cape Town, South Africa on 8 March 2010 at 1400 UTC. CLIVAR/Carbon A13.5 ended in Takoradi, Ghana on 18 April 2010.

A total of 130 stations were occupied during A13.5. 133 CTD/O_2/LADCP/rosette casts (including 1 test cast and 3 reoccupations at stations 72, 79, and 82) were collected. Eight Argo floats and 18 surface drifters were deployed. CTD/O_2 data, LADCP data, and water samples (up to 24) were collected on most rosette casts, in most cases to within 10 meters of the bottom.

Salinity, dissolved oxygen, and nutrient samples were analyzed for up to 24 water samples from each cast of the principal CTD/O_2/LADCP/rosette program. Water samples were also measured for CFCs, pCO_2, Total CO_2 (DIC), Total Alkalinity, and pH. Additional samples were collected for ^{3}He, Tritium, ^{13}C/ ^{14}C, and DOC/TDN.

CTD Underwater Packages

CTD/O_2 profiles were collected using one underwater package for the entire cruise. Sea-Bird instrumentation was mounted in a 24-position aluminum frame with 24 11-liter Niskin bottles. Instruments and sensors mounted in the 24-position frame included:

Instrument/Sensor	Serial No.	Calib. Date	Comment
SBE 9*plus* CTD + Paroscientific Digiquartz Pressure sensor	315	27-Jul-2007	stations 998, 1-72/1
	209	9-Jul-2007	stations 72/3-12
Primary pump circuit:			
SBE 3*plus* temperature	03P-4569	9-Sep-2009	primary T
SBE 4C conductivity	04C-3068	9-Sep-2009	primary C
SBE 43 oxygen	43-0312		stations 998, 1-7
	43-0313		stations 77-129
SBE 5 pump	"1a"		stations 998, 1-7
	"1b"		stations 78-129
Secondary pump circuit:			
SBE 3*plus* temperature	03P-4335	4-Sep-2009	secondary T
SBE 4C conductivity	04C-3157	9-Sep-2009	secondary C
SBE 5 pump	"2"		stations 998, 1-129
SBE 32 carousel	407		24-position
SBE 35RT Temperature (internally recording)	0064	20-Jun-2009	stations 998, 1-72/1, 102-12
RDI Workhorse 300 kHz LADCP	12734 (down-looker) unknown (up-looker)		
Simrad 807 altimeter	98110		
Wetlabs CStar transmissometer	CST-507DR		
Benthos pinger			
Markey DESH-5 Winches:			
Aft / 0.375" cable	single conductor	stations 998, 1-48, 72/3-7	
Forward / 0.322" cable	three conductors	stations 49-72/1, 79/3-12	

CTD Data Acquisition

The CTD data acquisition system consisted of an SBE-11*plus* (V1) deck unit s/n 367 and a networked Dell Optiplex 755 PC workstation running Windows XP Professional. SBE SeaSave v.7.18c software was used for data acquisition and to close bottles on the rosette. Real-time digital data were backed up onto Survey and PMEL networked PCs. No real-time data were lost.

CTD deployments were initiated by the console watch after the ship had stopped on station. The watch maintained a CTD Cast log containing a description of each deployment, a record of every attempt to close a bottle, and any pertinent comments.

Once the deck watch had deployed the rosette, the winch operator would lower it to a minimum of 10 meters. The CTD sensor pumps were configured with a 60 second startup delay, and were usually on by this time. The console operator checked the CTD data for proper sensor operation, waited an additional 60 seconds for sensors to stabilize, instructed the winch operator to bring the package to the surface, pause for 10 seconds, and descend to a target depth. The profiling rate was nominally 30 m/min to 50 m, 45 m/min to 200 m, and 60 m/min deeper than 200 m. These rates varied depending on sea cable tension and the sea state.

The console watch monitored the progress of the deployment and quality of the CTD data through interactive graphics and operational displays. Additionally, the watch created a sample log for the deployment that would be later used to record the correspondence between rosette bottles and analytical samples taken. The altimeter channel, CTD pressure, wire-out, pinger, and bathymetric depth were all monitored to determine the distance of the package from the bottom, usually allowing a safe approach to within 10 meters.

Bottles were closed on the up cast by operating an on-screen control, and were tripped 30 seconds after stopping at the trip location to allow the rosette wake to dissipate and the bottles to flush. The winch operator was instructed to proceed to the next bottle stop 10-20 seconds after closing bottles to ensure that stable CTD data were associated with the trip.

After the last near-surface bottle was closed, the console operator directed the deck watch to bring the rosette on deck. Once on deck, the console operator terminated the data acquisition, turned off the deck unit and assisted with rosette sampling.

Normally the CTD sensors were rinsed after each station using syringes fitted with Tygon tubing and filled with a fresh solution of dilute Triton-X in de-ionized water at the end of each cast. The syringes were generally left on the CTD between casts, with the temperature and conductivity sensors immersed in the rinsing solution, to guard against airborne contaminants.

Acquisition Problems

The CTD was initially connected to the aft winch, with a new termination on the 0.375-inch single-conductor EM cable. **Test cast 998** produced three modulo errors. Secondary temperature sensor s/n 4335 was low of the primary by about 7^{o}C throughout the profile. The correct calibration coefficients were entered into the configuration file post-cast. Secondary conductivity sensor s/n 3157 dropped out (to 0 kHz) around 3500 dbar on the downcast but came back around 3300 dbar on the upcast to within 0.002 mS/cm of the primary. The secondary conductivity cable was replaced after the cast. Also, the load cell was removed from the lifting bail because it looked like the connector and cable could interfere with or even damage the carousel latches.

Modulo errors persisted every cast while on the **aft winch** (stations 998,1-48), numbering from 1 to 140, increasing with wind speed and sea state. Processed data had to be edited for spikes and gaps in any one of the PTCO data channels. In spite of troubleshooting efforts, these modulo errors were not resolved.

Eventually the package was switched to the **forward winch** 0.322-inch three-conductor cable for stations 49-72. Modulo errors were few at first but increased to as many as 185 with choppier seas and level wind problems. A broken strand in the outer armor of the winch cable was removed during station 67 and the ends were taped. All subsequent casts using the forward winch cable were stopped at 4268 m wire out to inspect the area and re-tape it if necessary. During station 72 cast 1, communication was lost to the carousel. The modem board in CTD s/n 315 was suspect, so it was replaced with CTD s/n 209. Unfortunately, this didn't remedy the problem as expected and the package was moved to a new termination on the aft winch.

Modulo error counts were high on the **aft winch** (stations 72 cast 3 through 79 cast 1). Processed data had to be edited for spikes and gaps in any one of the PTCO data channels. Gaps and crossovers in the winch cable were discovered >5600m wire out as the source of noise and imbalance within the drum.

Blown sea cable fuses in the deck unit owing to a faulty sea cable pigtail necessitated moving the package to a new termination on the **forward winch**. This termination did not include the armor in the negative (ground) conductor. Profiles were successfully collected on this termination from station 79 cast 3 to the end of the cruise with only a few modulo errors occurring occasionally.

The **transmissometer** worked intermittently between stations 1-16 in spite of troubleshooting efforts. The cable was suspect and the instrument was removed from the underwater package for stations 17-18. Since this had no effect on the modulo errors at that time, and since the instrument and cable tested OK in the lab, it was put back on the frame for station 19 and worked well thereafter for the most part. Problem casts included stations 2, 5, 7, 10, 14, 16, 29, 31, 65-69, and 70.

Oxygen voltage presented "pulses" in profiles from 2300 dbar to depth beginning at station 73 (CTD s/n 209). The pulses occurred approximately every 200 dbar, were low by about 0.5 umol/kg, and lasted for 20-30 dbar. Oxygen sensor s/n 312 was replaced by s/n 313 after station 76. The primary pump was replaced after station 77. The oxygen cable was moved from V0 to V2 after station 78. On V2, the pulses were more frequent but less pronounced, and were usually within 2500-4000 dbar. The oxygen cable was replaced after station 95.

The secondary plumbing **air-bleed** was clogged at station 32, affecting secondary conductivity data from 0-50 dbar. After this cast, sensor differences were monitored closely at the beginning of each cast and the package was soaked at 50 dbar if necessary. The air-bleed was successfully cleared by station 36.

CTD Data Processing

The reduction of profile data began with a standard suite of processing modules using Sea-Bird Data Processing Version 7.19 software in the following order:

DATCNV converts raw data into engineering units and creates a .ROS bottle file. Both down and up casts were processed for scan, elapsed time(s), pressure, t0, t1, c0, c1, oxygen voltage, and oxygen. Optical sensor data were converted to voltages and also carried through the processing stream. MARKSCAN was used to skip over scans acquired on deck and while priming the system under water.

ALIGNCTD aligns temperature, conductivity, and oxygen measurements in time relative to pressure to ensure that derived parameters are made using measurements from the same parcel of water. Primary conductivity was automatically advanced in the V1 deck unit by 0.073 seconds. Primary conductivity sensor s/n 3068 was aligned by -0.026 seconds in ALIGNCTD for a net advance of 0.047 seconds. Secondary conductivity sensor s/n 3157 was advanced by 0.053 seconds in ALIGNCTD. It was not necessary to align temperature or oxygen.

BOTTLESUM averages burst data over an 8-second interval (+/- 4 seconds of the confirm bit) and derives both primary and secondary salinity, primary potential temperature ($\square$), and primary potential density anomaly ($\square_{\square}$). Oxygen (in $\square$mol/kg) were derived in DATCNV and averaged in BOTTLESUM, as recommended recently by Sea-Bird.

WILDEDIT makes two passes through the data in 100 scan bins. The first pass flags points greater than 2 standard deviations; the second pass removes points greater than 20 standard deviations from the mean with the flagged points excluded. Data were kept within 100 standard deviations of the mean (i.e. all data).

FILTER applies a low pass filter to pressure with a time constant of 0.15 seconds. In order to produce zero phase (no time shift) the filter is first run forward through the file and then run backwards through the file.

CELLTM uses a recursive filter to remove conductivity cell thermal mass effects from measured conductivity. In areas with steep temperature gradients the thermal mass correction is on the order of 0.005 PSS-78. In other areas the correction is negligible. Nominal values of 0.03 and 7.0 s were used for the thermal anomaly amplitude ($\square$) and the thermal anomaly time constant ($\square^{-1}$), respectively, as suggested by Sea-Bird.

LOOPEDIT removes scans associated with pressure slowdowns and reversals. If the CTD velocity is less than 0.25 m s^{-1} or the pressure is not greater than the previous maximum scan, the scan is omitted.

DERIVE uses 1-dbar averaged pressure, temperature, and conductivity to compute primary and secondary salinity, as well as more accurate oxygen.

BINAVG averages the data into 1-dbar bins. Each bin is centered on an integer pressure value, e.g. the 1-dbar bin averages scans where pressure is between 0.5 dbar and 1.5 dbar. There is no surface bin. The number of points averaged in each bin is included in the data file.

STRIP removes oxygen that was derived in DATCNV.

TRANS converts the binary data file to ASCII format.

Package slowdowns and reversals owing to ship roll can move mixed water in tow to in front of the CTD sensors and create artificial density inversions and other artifacts. In addition to Seasoft module LOOPEDIT, MATLAB program deloop.m computes values of density locally referenced between every 1 dbar of pressure to compute the square of the buoyancy frequency, N^2, and linearly interpolates temperature, conductivity, and oxygen voltage over those records where N^2 is less than or equal to $-1 \times 10^{-5}\ s^{-2}$. Seventeen profiles failed the criteria in the top 3-9 dbars. These data were retained by program deloop_post.m and were flagged as questionable in the final WOCE formatted files.

Program calctd.m reads the delooped data files and applies preliminary calibrations to temperature, conductivity, and oxygen; and computes calibrated salinity.

Pressure Calibration

Pressure calibrations for the CTD instrument used during this cruise were pre-cruise. No additional adjustments were applied. On deck pressure readings prior to each cast were examined and remained within 1 dbar of calibration. Differences between first and last submerged pressures for each cast were also examined and the residual pressure offsets were less than 1 dbar.

Temperature Calibration

A viscous heating correction of -0.0006 °C was applied at sea as recommended by Sea-Bird. Post-cruise, a linearly interpolated temperature sensor drift correction using pre and post-cruise calibration data for the midpoint of the cruise will be determined for each sensor. Viscous and drift corrections are applied to profile data using program calctd.m, and to burst data using calclo.m.

Data from the SBE 35 reference temperature sensor will be evaluated post-cruise and likely used to correct SBE 3 temperature sensor data.

Conductivity Calibration

Seasoft module BOTTLESUM creates a sample file for each cast. These files were appended using program sbecal.f. Program addsal.f matched sample salinities to CTD salinities by station/sample number.

For both conductivity sensors, stations were separated into three calibration groupings. Program calcop1.m (a constant conductivity offset, a linear pressure-dependent correction to conductivity, and a 1st order polynomial conductivity slope as a function of station number) produced the best fit to sample data for the primary conductivity sensor (s/n 3068) using the following station groups:

stations	1-40	41-57	58-129
number of points used	845	360	1432
total number of points	917	393	1689
% of points used in fit	92.15%	91.60%	84.78%
fit standard deviation	0.0009827	0.0012650	0.0012660
fit bias	-0.00074245453	-0.0022543675	-0.0048820669
fit co pressure fudge	-3.4860787e-07	-1.9902530e-07	-6.7475419e-08
min fit slope	1.0000314	1.0001195	1.0001716
max fit slope	1.0000817	1.0001577	1.0001851

Conductivity calibrations were applied to profile data using program calctd.m and to burst data using calclo.m. CTD-bottle conductivity differences plotted against station number (Figure 1) and pressure (Figure 2) allow a visual assessment of the success of the fits.

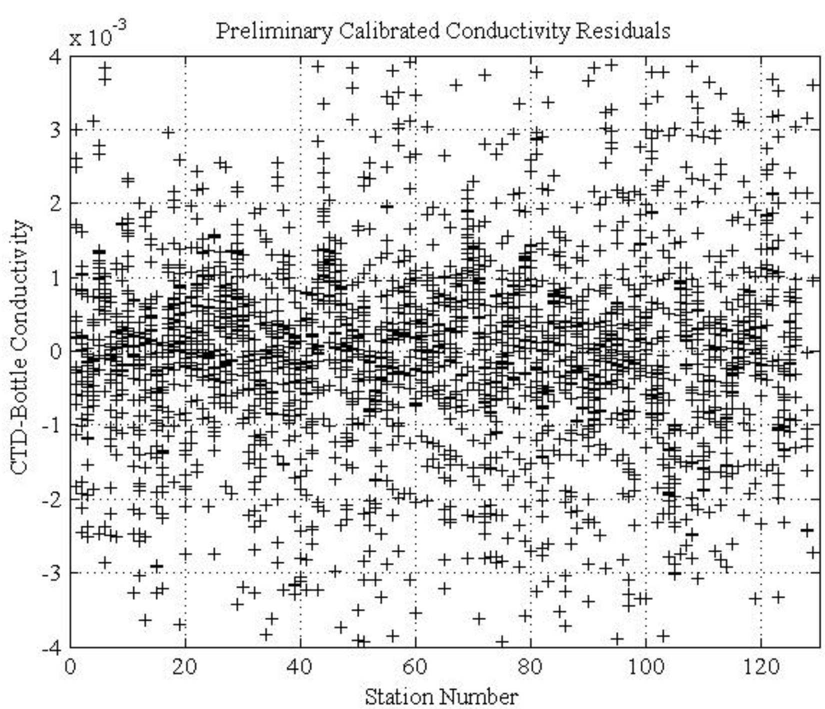


Figure 1 Primary sensor CTD-bottle conductivity residuals vs station number

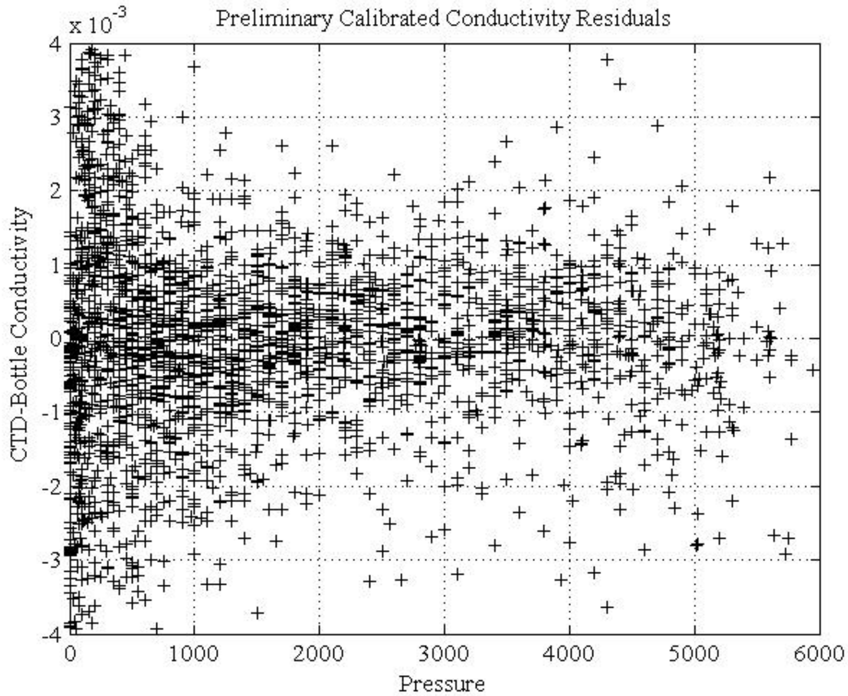


Figure 2 Primary sensor CTD-bottle conductivity residuals vs pressure

Oxygen Calibration

A hybrid of the Owens-Millard (1985) and Murphy-Larson (revised 2010) oxygen sensor modeling equations was used to calibrate the SBE-43 oxygen sensor data from this cruise. The equation has the form:

Ox=Soc*(V+Voff+Tau*exp(D1*P+D2*T)*dVdt)*Os*exp(Tcor*T)*exp(Pcor*P/(273.15+T))

Where:

Ox is the CTD oxygen (in µmol/kg)
V is the measured oxygen voltage (in volts)
dVdt is the temporal gradient of the oxygen voltage (in volts/s estimated by running linear fits made over 5 seconds)
P is the CTD pressure (in dbar)
T is the CTD temperature (in °C)
Os is the oxygen saturation computed from the CTD data following Garcia & Gordon (1992).

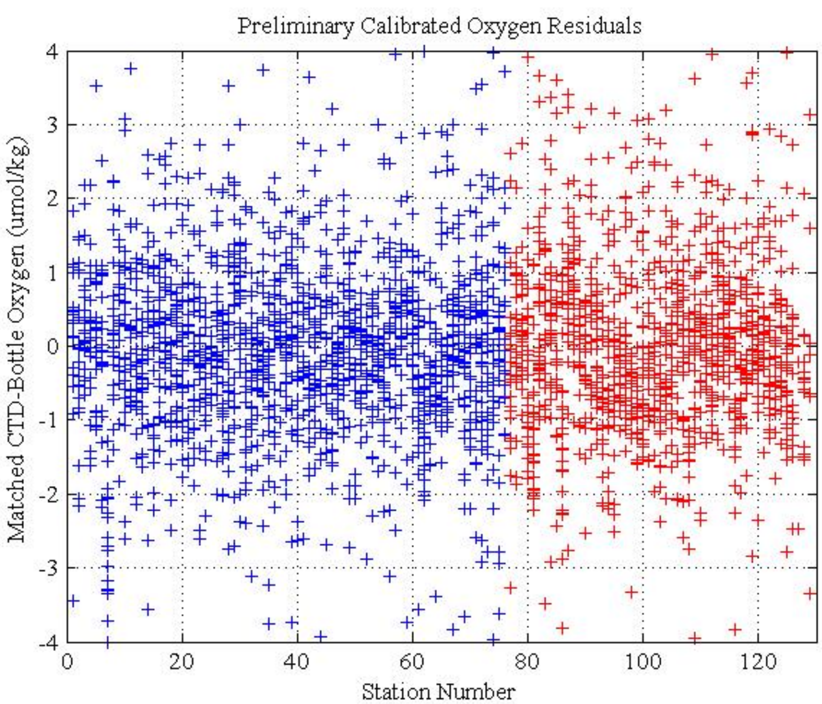
Oxygen sensor hysteresis was improved by matching upcast bottle oxygen data to downcast CTD data by potential density anomalies referenced to the closest 1000-dbar interval using program match_sgn.m. We used the values provided by SBE for each sensor for the constants D1 (1.9263e-4) and D2 (-4.6480e-2) to model the pressure and temperature dependence of the response time for the sensor. For each group of stations fit we determined values of Soc (sometimes station dependent), Voff, Tau, Tcor, and Pcor by minimizing the residuals between the bottle oxygen and CTD oxygen. Program addoxy.f matched bottle sample oxygen values to CTD oxygen values by station/sample number. Program run_oxygen_cal_ml.m was used to determine calibration coefficients for nine station groupings. These groupings were determined by visual inspection:

312 Stns	Soc Range	Voff	Tau	Tcor	Pcor	Points	Used	StdDev	
1- 13	0.4672-0.4672	-0.4523	7.4163	0.0009	0.0390	299	83.6%	0.7771	00
14- 28	0.4688-0.4688	-0.4422	6.3112	0.0002	0.0385	347	92.2%	0.7987	00
29- 37	0.4772-0.4806	-0.4518	5.5664	0.0001	0.0388	214	91.6%	0.8147	10
38- 51	0.4826-0.4826	-0.4583	7.2746	0.0001	0.0392	335	91.3%	0.6983	00
52- 70	0.4901-0.4961	-0.4765	7.8596	-0.0004	0.0394	446	87.9%	0.6977	10
71- 76	0.4886-0.4910	-0.4546	6.9079	-0.0003	0.0386	154	90.3%	1.0436	10

313 Stns	Soc Range	Voff	Tau	Tcor	Pcor	Points	Used	StdDev	
77	0.4473-0.4473	-0.4397	2.2679	0.0015	0.0406	24	95.8%	1.3709	00
78	0.4670-0.4670	-0.4588	10.099	0.0012	0.0403	23	95.7%	0.7904	00
79- 85	0.4794-0.4794	-0.4635	6.5813	0.0008	0.0394	178	86.5%	0.7211	00
86-129	0.4809-0.4829	-0.4672	7.5176	0.0007	0.0397	1023	90.0%	0.8508	10

Oxygen calibration coefficients were applied to profile data using program calctd.m, and to burst data using calclo.m.

Primary sensor CTD - bottle oxygen differences plotted against station number (Figure 3) and pressure (Figure 4) allow a visual assessment of the success of the fits.



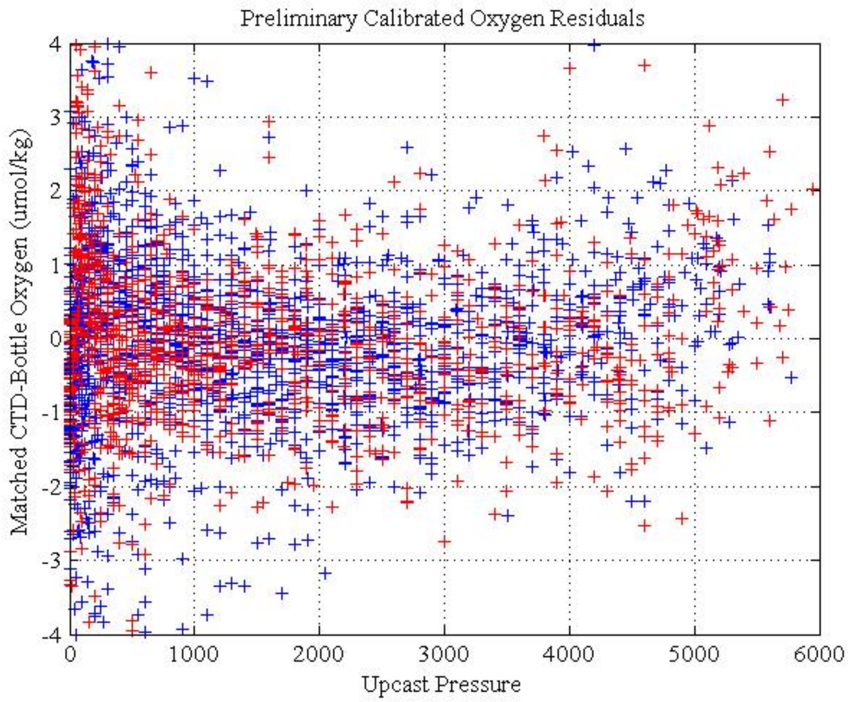


Figure 4 Primary sensor CTD-bottle oxygen residuals vs pressure

Final Processing

About 50% of the profiles had to be despiked owing to electrical termination problems. Programs interpolated over the larger range of salinity and oxygen in need of despiking. The programs are called clean_raw.m, a13_select_interp_ranges.m, and a13_apply_interp_sal_ox.m. Interpolated records are indicated with WOCE quality flags of 6.

A13.5 (2010) LADCP cruise report

A University of Hawaii (UH) system was used to collect Lowered Acoustic Doppler Current Profiler (LADCP) data. Preliminary processing was completed during the cruise using a Lamont-Doherty Earth Observatory (LDEO) LADCP software.

LADCP System Setup

One 24-bottle CTD rosette was used during the whole cruise. On deck, the rosette laid on a platform that can be tracked in and out the hangar. This system was necessary for LADCP operations as the LADCP cables are purposely short (to limit noise) and could not have reached the rosette outside the hangar.

The rosette has two WH300-kHz LADCP, one up-looker and one down-looker, and an oil-filled 58V rechargeable lead-acid battery pack. The installation on deck consisted of a Lenovo S10e for data acquisition and processing, as well as a TDK-Lambda battery charger/power supply. The LADCP heads and battery pack were mounted inside the 36-bottle rosette frame and connected using a custom designed, potted star cable assembly. One head (master) was placed looking downward underneath the bottles at approximately the same height as the CTD instruments, the other head looking upwards (slave) above the bottle trigger mechanism. The battery pack and LADCP were mounted on opposite sides of the rosette frame center to avoid unequal balancing.

Power supply and data transfer was handled independently from any CTD connections. While on deck the instrument communication was set up by means of a network of RS-232 and USB cables, using LDEO LADCP software for instrument control, data transmission and processing (using version IX_6beta) in Matlab [Thur08].

The set up of the two LADCP heads follows the master-slave set-up: one instrument (master) dictates when the second instrument (slave) starts and stops to ping. For deployment, the slave was first prepared and started to ping only once the master did. For retrieving the data, the master was first stopped to ping which immediately stopped the slave. The command files of the master and slave are shown below:

up-looker (slave) instrument	**down-looker (master) instrument**
CR1	CR1
WM15	WM15
TC2	TC2
TB 00:00:02.00	TB 00:00:02.00
TE 00:00:00.80	TE 00:00:00.80
TP 00:00.00	TP 00:00.00
WP 1	WP 1
WN20	WN20
WS0800	WS0800

WF0800	WF0800
WV330	WV330
EZ0011101	EZ0011101
EX00100	EX00100
CF11101	CF11101
SM2	SM1
SA001	SA001
ST0	SW05000

In the command file, SM1 and SM2 tell which instrument is the master and slave, respectively. The slave was set-up to ping 500 ms *after* the master in order to avoid interference: this is indicated by SW05000 in the master file.

At the beginning of the cruise, it was necessary to assure that the LADCP and CTD acquisition computer clocks be both in sync with the ship clock to assure that the absolute time recorded by the CTD and LADCP be the same.

LADCP Operation and Data Processing

On arrival at each station the LADCP heads were switched on for data acquisition by using the LADCP software. Then communications and power cabling were disconnected and all connections were sealed with dummy plugs. After each cast the data cable and the power supply were rinsed, reconnected, the data acquisition terminated, the battery charged, and the data downloaded by using the LADCP software. It took about 20 minutes to download the data from each data and during this time, the new battery was fully charged.

Immediately after each cast, a preliminary processing was executed, combining CTD, GPS, and shipboard ADCP data with the data from the LADCPs to produce both a shear and an inverse solution for the absolute velocities. The preliminary processing produced velocity profiles, rosette frame angular movements, and velocity ascii and Matlab files. Plots and data files were put on a website that can seen by all local computers.

Problems

No major problem was encountered. On station 12, the communication fails between the computer and the down-looker instrument so the cast was done only with the up-looker with no master-slave set up. Communication was re-established afterward.

For stations 72, LADCP data were taken for CTD cast #1 (from surface down to bottom then up to 1600 m) and #2 (1600 m up to the surface). CTD cast #1 and #2 were part of the same physical cast and CTD data acquired from the CTD group from both casts were merged to form one complete cast, renamed cast #1 for LADCP processing. It is believed that the official CTD data will be similarly merged and renamed. No LADCP data were taken for CTD cast #3 --which will be renamed cast #2 in the final version of the CTD data.

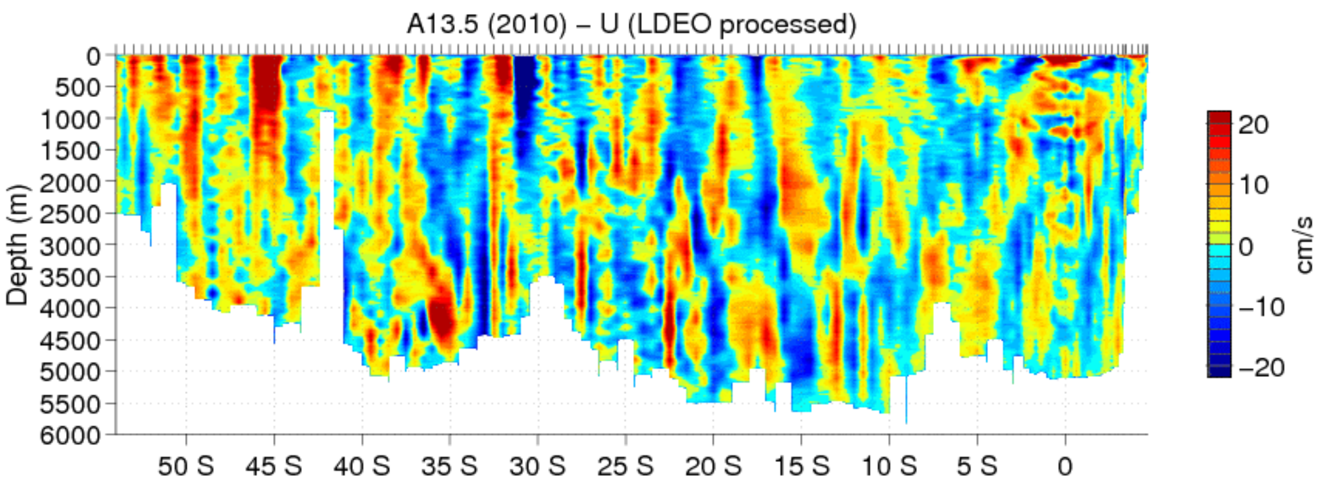
A similar procedure was followed for station 79 except that LADCP data were acquired for CTD cast #3. The official cast will be the first one.

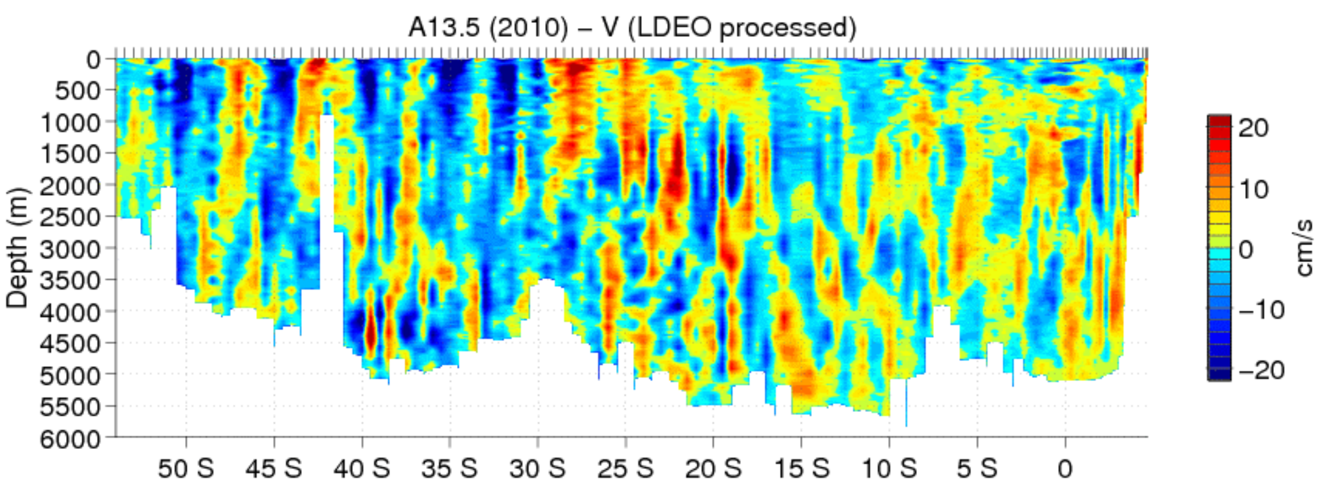
For station 82, there were two CTD casts, one full, one down to 1600 m only. LADCP data were acquired in both cases and the official cast will be the first one.

Between 102 and 103, we removed the up-looker ADCP to replace the rubbers that were sliding down with the ADCP. The ADCP was then put back. The rubbers used and the method to fix them on the ADCP frames were not preventing the ADCP from sliding down about 0.5-1 mm a day. The down-looker ADCP was secured by a line at the beginning of the cruise and stopped sliding down immediately. This was not the case for the up-looker and explains why we had to add a layer of rubber and re-position the instrument between station 102 and 103.

Preliminary results

The latitude-depth section up to station 106 of zonal (U) and meridional (V) velocity is shown below.





Several notables features were observed:

- a profile with a remarkable oscillating structure in the vertical (vertical wavelength of about 400-500 m) and with V being approximately 90 deg. out of phase near 48S,

- a strong surface eastward jet near 45S,

- a strong eastward bottom current near, unexpected given the relatively flat topography in the surrounding area near 36 S,

- a surface eddy associated with anomalies in salinity, oxygen, pH, etc likely to be a ring of warm water that shed from the Agulhas current to the southeast near 32S,

- the complex structure of equatorial currents within 3 deg. from the equator; in particular, the set of Equatorial Deep Jets on the equator (currents alternating with depth between 500 and 1500 m with a vertical wavelength of about 400 m) was well developed, unlike previous observations.

References

* Thurnherr, A. M., How To Process LADCP Data With the LDEO Software (last updated for version IX.5) July 9, 2008.

A13.5 Hydrographic Measurements Program

The distribution of bottle samples is illustrated in Figures 1-2 below.

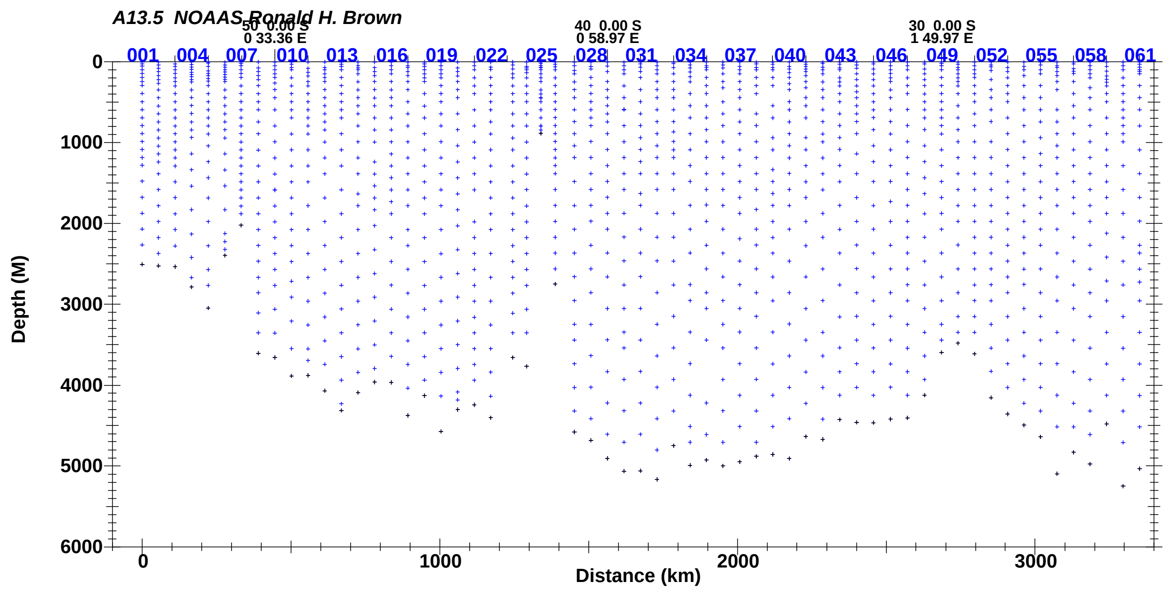


Figure 1 A13.5 Sample distribution, stations 1-61.

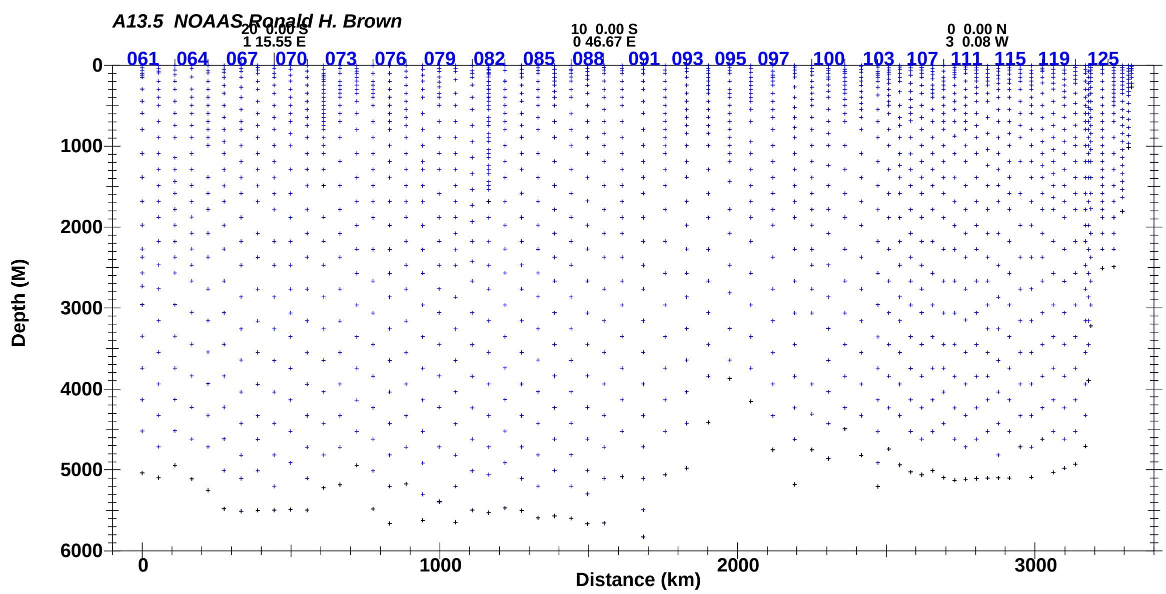


Figure 2 A13.5 Sample distribution, stations 61-129.

Bottle Sampling and Data Processing

Water Sampling

The NOAA Ship Ronald H. Brown has two Markey DESH-5 winches. The Aft winch was used for stations 998, 1-48 and 72/3-79/1. The Forward winch was used for stations 49-72/1 and 79/3-129. All but 5 rosette casts were lowered to within 3-20 meters of the bottom, using both the pinger and/or altimeter to determine distance.

Four sampling plans were used in rotation to choose standard sampling depths on each station throughout CLIVAR/Carbon A13.5.

Each bottle on the rosette had a unique serial number. This bottle identification was maintained independently of the bottle position on the rosette, which was used for sample identification. Three bottles (at trip positions 17, 22 and 23) were replaced on this cruise, and various parts of bottles were occasionally changed or repaired. Bottle 17 was changed out after station 8 due to repeated problems with leaking; bottle 23 apparently closed in air at the start of station 82/1 and later imploded, irreparably damaging bottle 22 in the process.

Rosette maintenance was performed on a regular basis. O-rings were changed and lanyards repaired as necessary. Bottle maintenance was performed each day to insure proper closure and sealing. Valves were inspected for leaks and repaired or replaced as needed.

The 36-place SBE32 carousel occasionally had problems releasing lanyards, causing mis-tripped bottles on multiple casts. Repair attempts and bottle height/lanyard adjustments were made as the cruise continued.

Bottle Sampling

At the end of each rosette deployment water samples were drawn from the bottles in the following order:

- Chlorofluorocarbons (CFCs)
- ^{3}He
- O_2
- pH
- pCO_2
- Dissolved Inorganic Carbon (DIC)
- Total Alkalinity (TAlk)
- ^{13}C and ^{14}C
- Dissolved Organic Carbon (DOC) / Total Dissolved Nitrogen (TDN)
- Tritium
- Nutrients
- Salinity

The correspondence between individual sample containers and the rosette bottle position (1-24) from which the sample was drawn was recorded on the sample log for the cast. This log also included any comments or anomalous conditions noted about the rosette and bottles. One member of the sampling team was designated the *sample cop*, whose sole responsibility was to maintain this log and insure that sampling progressed in the proper drawing order.

Normal sampling practice included opening the drain valve and then the air vent on the bottle, indicating an air leak if water escaped. This observation together with other diagnostic comments (e.g., "lanyard caught in lid", "valve left open") that might later prove useful in determining sample integrity were routinely noted on the sample log. Drawing oxygen samples also involved taking the sample draw temperature from the bottle. The temperature was noted on the sample log and was sometimes useful in determining leaking or mis-tripped bottles.

Once individual samples had been drawn and properly prepared, they were distributed for analysis. On-board analyses were performed on computer-assisted (PC) analytical equipment networked to the data processing computer for centralized data management.

Bottle Data Processing

Shipboard CTDO data were re-processed automatically at the end of each deployment using SIO/ODF CTD processing software v.5.1.5-4. The raw CTDO data and bottle trips acquired by SBE SeaSave on the Windows 2000 workstation were copied onto the Linux database and web server system. Pre-cruise calibration data were applied to CTD Pressure, Temperature and Conductivity sensor data, then the data were processed to a 0.5-second time series. A 2-decibar down-cast pressure series was created from the time series; CTDO data from downcasts were matched along isopycnals to upcast trips and extracted, then fit to bottle O_2 data at trips. The pressure series data were used by the web service for interactive plots, sections and on-board CTDO data distribution; the 0.5 second time series data were also available for distribution through the web service.

SIO/ODF CTDO data at bottle trips were extracted and added to the bottle database to use for CTD Pressure, Temperature and Salinity data in the preliminary bottle files. Downcast CTDO data, matched to upcast bottle trips along isopycnals, were used for preliminary bottle file CTDO data. When final CTDO data are submitted, the NOAA/PMEL final PTSO data will replace the preliminary SIO/ODF CTD data in the bottle files.

Water samples collected and properties analyzed shipboard were managed centrally in a relational database (PostgreSQL-8.1.18-2_el5_4.1) run on a Linux system. A web service (OpenACS-5.3.2-3 and AOLServer-4.5.1-1) front-end provided ship-wide access to CTD and water sample data. Web-based facilities included on-demand arbitrary property-property plots and vertical sections as well as data uploads and downloads.

ODF

The Sample Log information (and any diagnostic comments) were entered into the database once sampling was completed. Quality flags associated with sampled properties were set to indicate that the property had been sampled, and sample container identifications were noted where applicable (e.g., oxygen flask number).

Analytical results were provided on a regular basis by the various analytical groups and incorporated into the database. These results included a quality code associated with each measured value and followed the coding scheme developed for the World Ocean Circulation Experiment (WOCE) Hydrographic Programme (WHP) [Joyc94].

Various consistency checks and detailed examination of the data continued throughout the cruise.

Bottle Data Quality Code Summary and Comments

This section contains WOCE quality codes [Joyc94] used during this cruise, and remarks regarding bottle data.

Table 1 A13.5 Water Sample Quality Code Summary

Property	1	2	3	4	5	6	7	8	9	Total
Bottle	0	3035	8	49	0	0	0	0	42	3134
CFC-11	0	2524	16	35	40	0	0	0	21	2636
CFC-12	0	2518	21	36	40	0	0	0	21	2636
CCl_4	0	2193	12	34	376	0	0	0	21	2636
SF_6	0	2475	35	65	40	0	0	0	21	2636
^3He	488	0	0	0	0	0	0	0	0	488
O_2	0	2768	9	58	3	233	0	0	0	3071
pH	0	2536	21	21	6	462	0	0	31	3077
pCO_2	0	2592	4	12	3	182	0	0	14	2807
DIC	0	2675	17	15	14	321	0	0	23	3065
Total Alkalinity	0	2663	33	24	17	309	0	0	18	3064
$^{13}C/^{14}C$	681	0	0	0	0	0	0	0	0	681
DOC	1565	0	0	0	0	0	0	0	0	1565
TDN	1565	0	0	0	0	0	0	0	0	1565
Tritium	422	0	0	0	0	0	0	0	0	422
Nitrate	0	3002	1	45	0	0	0	0	22	3070
Nitrite	0	3026	1	21	0	0	0	0	22	3070
Phosphate	0	3020	6	21	1	0	0	0	22	3070
Silicic Acid	0	3001	25	22	0	0	0	0	22	3070
Salinity	0	3012	13	29	5	0	0	0	0	3059

Quality evaluation of data included comparison of SBE35RT temperature, bottle salinity and bottle oxygen data with CTDO data using plots of differences; and review of various property plots and vertical sections of the station profiles and adjoining stations. Comments from the Sample Logs and the results of investigations into bottle problems and anomalous sample values are included in this report. Sample number in this table is the cast number times 100 plus the bottle position number.

Table 2 A13.5 Bottle Quality Codes and Comments

Station /Cast	Sample Number	Property	Quality Code	Comment
1/1	ALL		-	boom did not retract, CTD/rosette in the air for some minutes, then put back in water until boom fixed, which took approximately half an hour.
1/1	101	Bottle	2	ran out of water for salt
1/1	103	Bottle	3	leaking at vent (no samples drawn except for nutrients/salt)
1/1	105	O2	4	outlier (high) compared to CTDO
1/1	109	Bottle	2	ran out of water for salt/nutrients/tritium
1/1	111	Bottle	3	leaking at vent (no samples drawn except for nutrients/salt)
1/1	113	O2	4	bottle o2 value high compared to CTDO, flask 13 calibration is suspect; flask removed from service after station 17. Code o2 bad.
1/1	117	Bottle	3	leaking at vent (no samples drawn except for nutrients/salt)
1/1	121	Bottle	2	ran out of water for salt/nutrients
1/1	121	Refc.Temp.	3	SBE35RT slightly low vs CTDT, unstable reading.
1/1	123	Bottle	2	ran out of water for salt
2/1	103	Bottle	3	leaking (possibly empty because of leaking); only salinity drawn.

Station /Cast	Sample Number	Property	Quality Code	Comment
2/1	113	O2	4	bottle o2 value high compared to CTDO, flask 13 calibration is suspect; flask removed from service after station 17. Code o2 bad.
2/1	120	Bottle	4	o2 draw temperature, o2, nuts, pH, dic, alkalinity are all similar to values for bottle 21, mis-trip.
2/1	120	CCl4	4	bottle mis-trip.
2/1	120	CFC-11	4	bottle mis-trip.
2/1	120	CFC-12	4	bottle mis-trip.
2/1	120	DIC	4	outlier, similar to values for bottle 21. mis-trip.
2/1	120	Nitrite	4	outlier, similar to values for bottle 21. mis-trip.
2/1	120	Nitrate	4	outlier, similar to values for bottle 21. mis-trip.
2/1	120	O2	4	outlier, similar to values for bottle 21. mis-trip.
2/1	120	pCO2	4	outlier, similar to values for bottle 21. mis-trip.
2/1	120	pH	4	outlier, similar to values for bottle 21. mis-trip.
2/1	120	Phosphate	4	outlier, similar to values for bottle 21. mis-trip.
2/1	120	Salinity	4	outlier, similar to values for bottle 21. mis-trip.
2/1	120	SF6	4	bottle mis-trip.
2/1	120	Silicate	4	outlier, similar to values for bottle 21. mis-trip.
2/1	120	TAlk	4	outlier, similar to values for bottle 21. mis-trip.
2/1	123	Bottle	3	leaking (no samples drawn except for nutrients)
3/1	ALL		-	bottle 124 not used
3/1	110	Bottle	2	all nutrients, talk, dic slightly low vs P; salinity, pH, sf6 slightly hi; small salinity/CTDS max at bottle 10, probably all values ok.
3/1	110	Nitrate	2	rmk: no3 a bit low vs P/T, mark 3. mcj: see bottle comment, no3 probably ok.
3/1	112	O2	4	bottle o2 value high compared to CTDO, flask 52 calibration is suspect; flask removed from service after station 17. Code o2 bad.
3/1	120	Bottle	2	possibly leaking (all samples drawn); all parameters look ok, bottle ok.
3/1	121	Refc.Temp.	3	SBE35RT high vs CTDT, unstable reading.
4/1	113	O2	4	bottle o2 value high compared to CTDO, flask 13 calibration is suspect; flask removed from service after station 17. Code o2 bad.
5/1	106	Bottle	9	not tripped (lanyard hang-up prevented both bottles from closing)
5/1	107	Bottle	9	not tripped (lanyard hang-up prevented both bottles from closing)
5/1	112	O2	4	bottle o2 value high compared to CTDO, flask 52 calibration is suspect; flask removed from service after station 17. Code o2 bad.
5/1	117	Bottle	2	leaking from vent (all samples drawn); all parameters look ok, bottle ok.
6/1	112	O2	4	bottle o2 value high compared to CTDO, flask 52 calibration is suspect; flask removed from service after station 17. Code o2 bad.
6/1	112	Phosphate	3	hi vs no3,ph,dic
6/1	115	Bottle	9	not tripped
6/1	116	Phosphate	3	hi vs no3,ph,dic
6/1	117	Bottle	2	leaking (all samples drawn); all parameters look ok, bottle ok.
7/1	105	Bottle	2	cap moved by lanyard (not in proper position), but bottle not leaking; no water for salt (did not run out of water as thought because vent had been closed again)
7/1	105	Phosphate	3	a bit lo vs P and T
7/1	112	O2	2	rmk: hi vs P and pH; ok compared to CTDO, code 3. mcj: looks ok vs all other parameters, code 2.
7/1	113	O2	4	bottle o2 value high compared to CTDO, flask 13 calibration is suspect; flask removed from service after station 17. Code o2 bad.
7/1	117	Bottle	3	leaking (no samples drawn except for salt; CFCs/Helium/Tritium sampled from 118 instead)
7/1	119	Bottle	2	ran out of water for salt
7/1	121	O2	4	very hi vs P; outlier (high) compared to CTDO data

Station /Cast	Sample Number	Property	Quality Code	Comment
7/1	121	Refc.Temp.	3	SBE35RT high vs CTDT, unstable reading.
8/1	104	Silicate	3	lo vs P, code 3
8/1	111	Bottle	2	bottle at small salinity/CTDS maximum; o2, talk, pH, salinity, sf6 slightly hi; nutrients, dic, cfc11/12 low; probably all values ok.
8/1	111	Phosphate	2	rmk: po4 a bit low vs P, CTDO; mark 3. mcj: correlates with small salinity maximum, no3/sio3 also a bit low. value ok.
8/1	112	O2	4	bottle o2 value high compared to CTDO, flask 52 calibration is suspect; flask removed from service after station 17. Code o2 bad; rmk: o2 very high
8/1	117	Bottle	3	leaking (no samples drawn); bottle replaced after this cast due to repeated leaking.
9/1	102	Bottle	4	draw temperature high (O2), bottle possibly tripped at the surface; mcj: nutrients, oxygen low; salinity high - suspect mis-trip at shallower pressure. Code bottle as mis-trip.
9/1	102	CCl4	4	cfcs low, mis-trip.
9/1	102	CFC-11	4	cfcs low, mis-trip.
9/1	102	CFC-12	4	cfcs low, mis-trip.
9/1	102	DIC	4	dic low, mis-trip.
9/1	102	Nitrite	4	nutrients low, mis-trip.
9/1	102	Nitrate	4	nutrients low, mis-trip.
9/1	102	O2	4	o2 low, mis-trip.
9/1	102	pCO2	4	pco2 low, mis-trip.
9/1	102	pH	4	pH low, mis-trip.
9/1	102	Phosphate	4	nutrients low, mis-trip.
9/1	102	Salinity	4	salinity high, mis-trip.
9/1	102	SF6	4	bottle mis-trip.
9/1	102	Silicate	4	nutrients low, mis-trip.
9/1	102	TAlk	4	alk low, mis-trip.
9/1	104	TAlk	3	alk low vs P; other parameters ok. code alkalinity bad.
9/1	106	Bottle	4	oxygen, nutrients, dic, alkalinity slightly low; salinity, pH slightly high, probable mis-trip near/at bottle 7 pressure.
9/1	106	CCl4	3	slightly low, mis-trip.
9/1	106	CFC-11	3	slightly low, mis-trip.
9/1	106	CFC-12	3	slightly low, mis-trip.
9/1	106	DIC	3	slightly low, mis-trip.
9/1	106	Nitrite	3	bottle mis-trip.
9/1	106	Nitrate	3	slightly low, mis-trip.
9/1	106	O2	3	slightly low, mis-trip.
9/1	106	pCO2	3	bottle mis-trip.
9/1	106	pH	3	slightly hi, mis-trip.
9/1	106	Phosphate	3	slightly low, mis-trip.
9/1	106	Salinity	3	slightly hi, mis-trip.
9/1	106	SF6	3	bottle mis-trip.
9/1	106	Silicate	3	slightly low, mis-trip.
9/1	106	TAlk	3	slightly low, mis-trip.
9/1	112	Bottle	4	Draw temperature high (O2), bottle possibly tripped at the surface
9/1	112	O2	4	bottle o2 value high compared to CTDO, flask 52 calibration is suspect; flask removed from service after station 17. Code o2 bad.
9/1	117	Bottle	9	not tripped this cast (lanyard of the neighboring bottle got hung up and prevented closing)
10/1	113	O2	4	bottle o2 value high compared to CTDO, flask 13 calibration is suspect; flask removed from service after station 17. Code o2 bad.

Station /Cast	Sample Number	Property	Quality Code	Comment
11/1	102	O2	4	flier; outlier (low) compared to CTDO
11/1	104	Bottle	9	Not tripped
11/1	106	Bottle	4	nutrients, oxygen slightly low; salinity high - mis-trip at/near bottle 8 pressure.
11/1	106	CCl4	4	cfcs low, probable mis-trip.
11/1	106	CFC-11	4	cfcs low, probable mis-trip.
11/1	106	CFC-12	4	cfcs low, probable mis-trip.
11/1	106	DIC	4	dic low; mis-trip.
11/1	106	Nitrite	4	nutrients slightly low; mis-trip.
11/1	106	Nitrate	4	nutrients slightly low; mis-trip.
11/1	106	O2	4	oxygen slightly low compared to CTDO; mis-trip.
11/1	106	pCO2	4	pco2 low; mis-trip.
11/1	106	pH	4	ph high; mis-trip.
11/1	106	Phosphate	4	nutrients slightly low; mis-trip.
11/1	106	Salinity	4	salinity high compared to CTDS; mis-trip.
11/1	106	SF6	4	probable mis-trip.
11/1	106	Silicate	4	nutrients slightly low; mis-trip.
11/1	106	TAlk	4	talk low; mis-trip.
11/1	112	O2	4	bottle o2 value high compared to CTDO, flask 52 calibration is suspect; flask removed from service after station 17. Code o2 bad.
12/1	102	Bottle	2	ran out of water for nutrients/salt
12/1	113	O2	4	bottle o2 value high compared to CTDO, flask 13 calibration is suspect; flask removed from service after station 17. Code o2 bad.
13/1	113	O2	4	bottle o2 value high compared to CTDO, flask 13 calibration is suspect; flask removed from service after station 17. Code o2 bad.
13/1	119	Salinity	5	salt marked as sampled on sample log, but not reported.
13/1	120	pH	3	lo vs P, CTDS; code 3
14/1	104	Bottle	9	not tripped
14/1	106	Bottle	4	bad bottle based on multiple parameter values; code as mis-trip
14/1	106	DIC	4	outlier (low); mis-trip.
14/1	106	Nitrite	4	bottle mis-trip.
14/1	106	Nitrate	4	outlier (low); mis-trip.
14/1	106	O2	4	slightly low compared to CTDO; mis-trip.
14/1	106	pH	4	outlier (high); mis-trip.
14/1	106	Phosphate	4	outlier (low); mis-trip.
14/1	106	Salinity	4	outlier (high) compared to CTDS; mis-trip.
14/1	106	Silicate	4	outlier (low); mis-trip.
14/1	106	TAlk	4	outlier (low); mis-trip.
14/1	113	O2	4	bottle o2 value high compared to CTDO, flask 13 calibration is suspect; flask removed from service after station 17. Code o2 bad.
15/1	112	O2	4	bottle o2 value high compared to CTDO, flask 52 calibration is suspect; flask removed from service after station 17. Code o2 bad.
16/1	102	Bottle	9	not tripped
16/1	104	Bottle	9	not tripped
16/1	113	O2	4	bottle o2 value high compared to CTDO, flask 13 calibration is suspect; flask removed from service after station 17. Code o2 bad.
17/1	102	Bottle	4	lifted up by 3cm after previous cast to hopefully make it trip more reliably; draw temperature too high; mis-tripped (possibly tripped at surface)
17/1	102	CCl4	4	cfcs low, mis-tripped.
17/1	102	CFC-11	4	cfcs low, mis-tripped.
17/1	102	CFC-12	4	cfcs low, mis-tripped.
17/1	102	DIC	4	very low; mis-tripped.

Station /Cast	Sample Number	Property	Quality Code	Comment
17/1	102	Nitrite	4	very high; mis-tripped.
17/1	102	Nitrate	4	very low; mis-tripped.
17/1	102	O2	4	outlier (very high) compared to CTDO; mis-tripped.
17/1	102	pH	4	very high; mis-tripped.
17/1	102	Phosphate	4	very low; mis-tripped.
17/1	102	Salinity	4	outlier (very low) compared to CTDS; mis-tripped.
17/1	102	SF6	4	cfcs low, mis-tripped.
17/1	102	Silicate	4	very low; mis-tripped.
17/1	102	TAlk	4	very low; mis-tripped.
17/1	104	Bottle	2	lifted up by 3cm after the last cast to hopefully make it trip more reliably (repeated non-tripping before)
17/1	114	Bottle	2	ran out of water for salt
19/1	117	Bottle	4	o2 temp bit off, all parameters indicate mis-trip.
19/1	117	CFC-11	4	cfcs low, mis-trip.
19/1	117	CFC-12	4	cfcs low, mis-trip.
19/1	117	DIC	4	very hi vs P, mis-trip.
19/1	117	Nitrite	4	no2 low, mis-trip.
19/1	117	Nitrate	4	no3 high, mis-trip.
19/1	117	O2	4	very lo vs P,T; outlier (low) compared to CTDO, mis-trip.
19/1	117	pCO2	4	pCO2 high, mis-trip.
19/1	117	pH	4	very very lo vs P, mis-trip.
19/1	117	Phosphate	4	po4 high, mis-trip.
19/1	117	Salinity	4	outlier (high) compared to CTDS, mis-trip.
19/1	117	SF6	4	cfcs low, mis-trip.
19/1	117	Silicate	4	very hi vs P,S, mis-trip.
19/1	117	TAlk	4	very hi vs P,S, mis-trip.
20/1	106	Bottle	4	o2 temp a bit off and other parameters indicate mis-trip.
20/1	106	DIC	4	bottle mis-trip.
20/1	106	Nitrite	4	bottle mis-trip.
20/1	106	Nitrate	4	bottle mis-trip.
20/1	106	O2	4	outlier (low) compared to CTDO; mis-trip.
20/1	106	pCO2	4	bottle mis-trip.
20/1	106	pH	4	bottle mis-trip.
20/1	106	Phosphate	4	bottle mis-trip.
20/1	106	Salinity	4	outlier (low) compared to CTDS; mis-trip.
20/1	106	Silicate	4	bottle mis-trip.
20/1	106	TAlk	4	bottle mis-trip.
21/1	107	Bottle	2	rmk: probable mis-trip based on all parameters. mcj: see o2 comment, probably a real feature, code all parameters ok.
21/1	107	CCl4	2	outlier, probable mis-trip.
21/1	107	CFC-11	2	outlier, probable mis-trip.
21/1	107	CFC-12	2	outlier, probable mis-trip.
21/1	107	DIC	2	dic slightly high, see o2 comment.
21/1	107	Nitrite	2	nutrients slightly high, see o2 comment.
21/1	107	Nitrate	2	nutrients slightly high, see o2 comment.
21/1	107	O2	2	o2 seems low vs pressure, but correlates well with CTDO feature seen down and upcasts.
21/1	107	pCO2	2	pCO2 slightly high, see o2 comment.
21/1	107	pH	2	pH slightly low, see o2 comment.
21/1	107	Phosphate	2	nutrients slightly high, see o2 comment.
21/1	107	Salinity	2	salinity agrees well with CTDS.

Station /Cast	Sample Number	Property	Quality Code	Comment
21/1	107	SF6	2	outlier, probable mis-trip.
21/1	107	Silicate	2	nutrients slightly high, see o2 comment.
21/1	107	TAlk	2	talk ok, see o2 comment.
24/1	101	Salinity	5	salt marked as sampled on sample log, but not reported.
24/1	102	Bottle	9	not tripped (got stuck on a knot in the lanyard, CFCs took duplicate from 103 instead)
24/1	103	Salinity	5	salt marked as sampled on sample log, but not reported.
24/1	104	Bottle	9	not tripped (lanyard didn't come off hook)
24/1	109	Silicate	4	total flier
24/1	110	Bottle	9	not tripped (lanyard/hook got stuck on green part attached to frame that holds up transmissometer, CFCs took sample from 111 instead)
25/1	ALL		-	bottles 123-124 not used: very shallow cast.
25/1	102	Bottle	2	bottles 1/2 same trip depth, o2 drawn from bottle 1 only.
25/1	105	Bottle	2	bottles 4/5 same trip depth, o2 drawn from bottle 4 only.
25/1	109	O2	3	rmk: o2 low vs P, sio3; probable mis-trip or leak. mcj: bottles 9/10 tripped at same pressure, nuts, salt and ph from both bottles match: not a mis-trip.
25/1	110	Bottle	2	bottles 9/10 same trip depth, o2 drawn from bottle 9 only.
25/1	110	pH	2	rmk: pH low vs CTDS, flag 3. mcj: correlates with CTDO feature; bottles 9/10 salinity, nutrients, pH all agree (tripped at same pressure). value probably ok.
25/1	111	O2	4	rmk: o2 low vs P, sio3, probable mis-trip or leak. mcj: bottle data seem to align ok, not a mis-trip.
25/1	118	Bottle	2	bottles 17/18 same trip depth, o2 drawn from bottle 17 only.
25/1	122	Bottle	2	bottles 21/22 same trip depth, o2 drawn from bottle 21 only.
27/1	114	TAlk	3	alk low vs CTDS, P; other parameters ok. code alkalinity bad.
28/1	105	TAlk	3	alk low vs P; other parameters ok. code alkalinity bad.
28/1	121	O2	4	outlier (high) compared to CTDO as well as in an o2 section plot
31/1	107	O2	4	value extremely low vs other properties & compared to neighbors; outlier (low) compared to CTDO
31/1	110	O2	4	value very very low vs P,T,DIC, etc.; outlier (low) compared to CTDO
31/1	118	TAlk	3	value very hi vs S,T,no3,pH
31/1	123	Bottle	2	ran out of water for salt
33/1	104	Bottle	4	draw temperature too high, apparently tripped shallower; no samples drawn by pH/pCO2/DIC/Alk/C14/DOC
33/1	104	CCl4	4	cfcs slightly high, mis-trip.
33/1	104	CFC-11	4	cfcs slightly high, mis-trip.
33/1	104	CFC-12	4	cfcs slightly high, mis-trip.
33/1	104	Nitrite	4	nutrients low, mis-trip.
33/1	104	Nitrate	4	nutrients low, mis-trip.
33/1	104	O2	4	outlier (high) compared to CTDO. mis-trip.
33/1	104	Phosphate	4	nutrients low, mis-trip.
33/1	104	Salinity	4	outlier (high) compared to CTDS. mis-trip.
33/1	104	SF6	4	cfcs slightly high, mis-trip.
33/1	104	Silicate	4	nutrients low, mis-trip.
33/1	119	Bottle	9	lanyard did not release, no samples drawn
35/1	116	Bottle	2	upper hose clamp broke
36/1	104	Bottle	9	not tripped (hook came unlocked but did not release lanyard)
37/1	102	Bottle	2	upper hose clamp broke
37/1	106	Bottle	2	bubbles (helium)
37/1	112	Bottle	2	ran out of water for salt
37/1	114	Bottle	2	ran out of water for salt; bubbles (helium)
37/1	116	Bottle	2	ran out of water for salt

Station /Cast	Sample Number	Property	Quality Code	Comment
37/1	118	O2	2	ph accidentally sampled before o2
40/1	119	Bottle	2	o2, pH, CCl4 slightly low; cfcs, dic, pco2 slightly high vs P, theta; ok, correlates with CTDO feature on down/upcasts and neighboring casts; bottle ok.
40/1	119	Salinity	4	outlier (high) compared to CTDS; too big to correspond with feature seen in other parameters, possibly sampled from bottle 21 by mistake.
40/1	119	TAlk	2	TAlk low compared to neighboring casts vs P, theta; seems more out of line than other parameters in this CTDO feature. Re-check.
40/1	123	Refc.Temp.	3	SBE35RT high vs CTDT, unstable reading.
41/1	104	Bottle	9	lanyard did not release, no samples
41/1	109	Bottle	2	no water left for salt
41/1	118	O2	3	lo vs P,T,no3
42/1	122	Refc.Temp.	3	SBE35RT low vs CTDT, unstable reading.
43/1	117	O2	4	totally unrealistic; outlier (low) compared to CTDO as well as in an o2 section plot
44/1	106	Bottle	2	no water left for salt
44/1	120	Bottle	2	upper hose clamp broke on deck
45/1	102	Bottle	4	draw temperature could be ok or a bit hi. Bottle values indicate tripped about 300dbar shallower, near niskin 3.
45/1	102	CCl4	4	cfcs low, mis-trip.
45/1	102	CFC-11	4	cfcs low, mis-trip.
45/1	102	CFC-12	4	cfcs low, mis-trip.
45/1	102	DIC	4	dic low, mis-trip.
45/1	102	Nitrite	4	bottle mis-trip.
45/1	102	Nitrate	4	nutrients low, mis-trip.
45/1	102	O2	4	hi vs P,T; outlier (high) compared to CTDO, mis-trip.
45/1	102	pCO2	4	pco2 low, mis-trip.
45/1	102	pH	4	pH slightly hi, mis-trip.
45/1	102	Phosphate	4	nutrients low, mis-trip.
45/1	102	Salinity	4	hi vs P,T; outlier (high) compared to CTDS, mis-trip.
45/1	102	SF6	4	cfcs low, mis-trip.
45/1	102	Silicate	4	nutrients low, mis-trip.
45/1	102	TAlk	4	bottle mis-trip.
45/1	117	Bottle	2	lower hose clamp broken.
47/1	123	Refc.Temp.	3	SBE35RT slightly high vs CTDT, unstable reading.
48/1	105	Bottle	2	upper hose clamp broke
49/1	114	Bottle	2	ran out of water for salt
49/1	116	Bottle	2	ran out of water for salt
49/1	117	CFC-11	2	rmk: cfcs low vs P, T and/or CTDS. mcj: correlates with sharp o2/CTDO minimum, values ok.
49/1	117	CFC-12	2	rmk: cfcs low vs P, T and/or CTDS. mcj: correlates with sharp o2/CTDO minimum, values ok.
49/1	117	SF6	2	rmk: cfcs low vs P, T and/or CTDS. mcj: correlates with sharp o2/CTDO minimum, values ok.
49/1	121	Bottle	2	ran out of water for salt
50/1	102	Salinity	3	outlier (high) compared to CTDS
50/1	117	Bottle	4	draw temperature relatively high for 116 or relatively low for 117; bottle 117 identified as the mis-trip when compared to CTD data.
50/1	117	DIC	4	dic slightly high, mis-trip.
50/1	117	Nitrite	4	no2 slightly high, mis-trip.
50/1	117	Nitrate	4	no3 slightly low, mis-trip.

Station /Cast	Sample Number	Property	Quality Code	Comment
50/1	117	O2	4	outlier (high) compared to CTDO as well as o2 section plot; draw temp low but o2 much further off than other parameters; suspect o2 problem in addition to mis-trip.
50/1	117	pCO2	4	pco2 slightly low, mis-trip.
50/1	117	pH	4	pH slightly high, mis-trip.
50/1	117	Phosphate	4	po4 slightly low, mis-trip.
50/1	117	Salinity	4	outlier (high) compared to CTDS, mis-trip.
50/1	117	Silicate	4	sio3 slightly high, mis-trip.
50/1	117	TAlk	4	bottle mis-trip.
51/1	123	Refc.Temp.	3	SBE35RT low vs CTDT, unstable reading.
52/1	102	Bottle	9	not tripped, latch ok, but lanyard not released
53/1	116	pH	4	very very hi vs no3 and others, flier
54/1	103	TAlk	3	very lo vs P,S
54/1	106	Bottle	9	not tripped
54/1	107	Bottle	2	spigot replaced before cast
54/1	116	Bottle	2	spigot replaced before cast
54/1	118	Bottle	2	spigot replaced before cast
54/1	123	Refc.Temp.	3	SBE35RT low vs CTDT, unstable reading.
54/1	124	Bottle	2	spigot replaced before cast; O-ring replaced after cast before samples were drawn
55/1	102	pH	4	unreasonable value
55/1	110	Bottle	9	lower niskin cap hung up on trans. frame
56/1	102	Bottle	4	draw temperature too high, mis-tripped near surface. cfc, pco2, dic, alk, nutrients not drawn.
56/1	102	O2	4	outlier (high) compared to CTDO, mis-trip.
56/1	102	pH	4	outlier (high), mis-trip.
56/1	102	Salinity	4	outlier (high) compared to CTDS, mis-trip.
56/1	113	TAlk	3	very hi vs P,S,pH, etc.
57/1	106	Bottle	2	bubbles (helium)
58/1	106	Bottle	4	draw temperature a bit high, all parameters indicate bottle mis-tripped near niskin 13 trip pressure.
58/1	106	CCl4	4	cfcs high, mis-trip.
58/1	106	CFC-11	4	cfcs high, mis-trip.
58/1	106	CFC-12	4	cfcs high, mis-trip.
58/1	106	DIC	4	dic high, mis-trip.
58/1	106	Nitrite	4	bottle mis-trip.
58/1	106	Nitrate	4	no3 high, mis-trip.
58/1	106	O2	4	outlier (low) compared to CTDO, mis-trip.
58/1	106	pCO2	4	pco2 high, mis-trip.
58/1	106	pH	4	pH low, mis-trip.
58/1	106	Phosphate	4	po4 high, mis-trip.
58/1	106	Salinity	4	outlier (low) compared to CTDS, mis-trip.
58/1	106	SF6	4	cfcs high, mis-trip.
58/1	106	Silicate	4	sio3 low, mis-trip.
59/1	111	SF6	4	extremely hi vs P, other gases
59/1	119	O2	4	o2 high, probably bubbles in o2 titrant: apparently started running out earlier than bottles 22-23.
59/1	120	O2	4	o2 high, probably bubbles in o2 titrant: apparently started running out earlier than bottles 22-23.
59/1	121	O2	4	o2 high, probably bubbles in o2 titrant: apparently started running out earlier than bottles 22-23.

Station /Cast	Sample Number	Property	Quality Code	Comment
59/1	122	O2	5	o2 100+ umol/kg high, burette ran low on titrant.
59/1	123	O2	5	o2 100+ umol/kg high, burette ran low on titrant.
60/1	106	Bottle	9	not tripped (although lanyard released)
60/1	113	SF6	3	sf6 low vs P (f11/f12 rise slightly with other parameters at this bottle); flag 3.
61/1	101	Bottle	2	rosette was lowered again after this bottle was closed (from 2100db back to 2773db) because of bad wraps of wire on drum
61/1	102	Bottle	2	all inner row bottles moved higher to improve angle of lanyards to carousel pins. Rosette was lowered again after this bottle was closed (from 2100db back to 2773db) because of bad wraps of wire on drum
61/1	103	Bottle	2	rosette was lowered again after this bottle was closed (from 2100db back to 2773db) because of bad wraps of wire on drum
61/1	104	Bottle	2	all inner row bottles moved higher to improve angle of lanyards to carousel pins. Rosette was lowered again after this bottle was closed (from 2100db back to 2773db) because of bad wraps of wire on drum
61/1	105	Bottle	2	rosette was lowered again after this bottle was closed (from 2100db back to 2773db) because of bad wraps of wire on drum
61/1	106	Bottle	2	all inner row bottles moved higher to improve angle of lanyards to carousel pins. Rosette was lowered again after this bottle was closed (from 2100db back to 2773db) because of bad wraps of wire on drum
61/1	107	Bottle	2	rosette was lowered again after this bottle was closed (from 2100db back to 2773db) because of bad wraps of wire on drum
61/1	108	Bottle	2	all inner row bottles moved higher to improve angle of lanyards to carousel pins. Rosette was lowered again after this bottle was closed (from 2100db back to 2773db) because of bad wraps of wire on drum
61/1	110	Bottle	2	all inner row bottles moved higher to improve angle of lanyards to carousel pins
61/1	111	SF6	3	sf6 hi vs P,T (other cfcs show no change at this bottle); flag 3.
61/1	112	Bottle	2	all inner row bottles moved higher to improve angle of lanyards to carousel pins
61/1	113	Bottle	2	all inner row bottles moved higher to improve angle of lanyards to carousel pins
61/1	114	Bottle	2	draw temperature too high, possibly delayed trip; mcj: all parameters look ok, o2 and salinity agree well with CTD. Code bottle ok.
61/1	115	Bottle	2	all inner row bottles moved higher to improve angle of lanyards to carousel pins
61/1	116	Bottle	2	difficult to push the spigot
61/1	117	Bottle	2	all inner row bottles moved higher to improve angle of lanyards to carousel pins
61/1	118	Bottle	2	difficult to push the spigot
61/1	119	Bottle	2	all inner row bottles moved higher to improve angle of lanyards to carousel pins
61/1	121	Bottle	2	all inner row bottles moved higher to improve angle of lanyards to carousel pins
61/1	123	Bottle	2	all inner row bottles moved higher to improve angle of lanyards to carousel pins
62/1	116	O2	4	outlier (low) compared to CTDO
62/1	119	Bottle	2	spigot replaced before cast
62/1	121	Phosphate	3	very low vs pressure and neighbors
63/1	106	Salinity	4	outlier (high) compared to CTDS
63/1	118	O2	3	hi in all prop-prop plots
63/1	119	pCO2	2	rmk: hi in several prop-prop plots, code 3. mcj: min/max in other parameters, possibly ok. coded 2.
64/1	109	DIC	3	hi in prop-prop plots
65/1	104	Bottle	4	hi compared to CTDO, also vi hi vs neighbors and pressure
65/1	104	CCl4	4	bottle mis-trip.
65/1	104	CFC-11	4	bottle mis-trip.
65/1	104	CFC-12	4	bottle mis-trip.
65/1	104	DIC	4	outlier (low), mis-trip.
65/1	104	Nitrite	4	bottle mis-trip.

Station /Cast	Sample Number	Property	Quality Code	Comment
65/1	104	Nitrate	4	bottle mis-trip.
65/1	104	O2	4	outlier (high) compared to CTDO, neighbors and pressure; mis-trip.
65/1	104	pCO2	4	slightly hi, mis-trip.
65/1	104	pH	4	slightly low, mis-trip.
65/1	104	Phosphate	4	bottle mis-trip.
65/1	104	Salinity	4	outlier (low) compared to CTDS, mis-trip.
65/1	104	SF6	4	bottle mis-trip.
65/1	104	Silicate	4	outlier (low), mis-trip.
65/1	104	TAlk	4	outlier (low), mis-trip.
65/1	112	Bottle	2	bubbles (helium)
65/1	122	ctds	2	CTDS1 offsets 185db upcast to surface; use CTDS2 for bottles 122-124. CTDS acceptable now.
65/1	122	CTDS1	4	not in agreement with CTDS2 and bottle salinity + abrupt shift at ˜195db
65/1	122	CTDS2	2	CTDS1 offsets 185db upcast to surface; use CTDS2 for bottles 122-124. CTDS acceptable now.
65/1	123	ctds	2	CTDS1 offsets 185db upcast to surface; use CTDS2 for bottles 122-124. CTDS acceptable now.
65/1	123	CTDS1	4	not in agreement with CTDS2 and bottle salinity + abrupt shift at ˜195db
65/1	123	CTDS2	2	CTDS1 offsets 185db upcast to surface; use CTDS2 for bottles 122-124. CTDS acceptable now.
65/1	124	ctds	2	CTDS1 offsets 185db upcast to surface; use CTDS2 for bottles 122-124. CTDS acceptable now.
65/1	124	CTDS1	4	not in agreement with CTDS2 and bottle salinity + abrupt shift at ˜195db
65/1	124	CTDS2	2	CTDS1 offsets 185db upcast to surface; use CTDS2 for bottles 122-124. CTDS acceptable now.
66/1	ALL		-	upcast took 3 hours (winch slowed down)
66/1	104	SF6	4	very very hi vs P, unreal
66/1	123	Refc.Temp.	3	SBE35RT low vs CTDT, unstable reading.
67/1	104	Bottle	2	rosette was lowered again after bottle 104 was closed (from 4335db back to 4430db) because of bad wraps of wire on drum
68/1	101	Salinity	3	outlier (high) compared to CTDS
68/1	112	TAlk	3	analysis low compared to other parameters and neighbors
68/1	122	Salinity	3	hi vs other parameters appears to be mis-sampled from bottle 23; outlier (high) compared to CTDS, agree that it appears to have been flipped with 123
68/1	123	Salinity	3	hi vs other parameters appears to be mis-sampled from bottle 22; outlier (low) compared to CTDS, agree that it appears to have been flipped with 122
70/1	113	Bottle	2	vent not closed during cast
70/1	114	Bottle	2	vent not closed during cast
70/1	115	Bottle	2	vent not closed during cast
70/1	116	Bottle	2	vent not closed during cast
70/1	117	Bottle	2	vent not closed during cast
70/1	118	Bottle	2	vent not closed during cast
70/1	119	Bottle	2	vent not closed during cast
70/1	120	Bottle	2	vent not closed during cast
70/1	121	Bottle	2	vent not closed during cast
70/1	122	Bottle	2	vent not closed during cast
70/1	123	Bottle	2	vent not closed during cast
70/1	123	TAlk	3	very very lo vs CTDS; other parameters ok. code alkalinity bad.
70/1	124	Bottle	2	vent not closed during cast

Station /Cast	Sample Number	Property	Quality Code	Comment
72/1	ALL		-	bottles 11-12 triggered at 1600db: no confirmation from carousel; cast restarted as number 2, still no trips. bottles 13-24 not tripped: cast was taken back on deck after failed confirmations. merged 2 parts of cast 1 together after cast.
72/1	101	TAlk	3	rmk: bottles 1-10 TAlk low vs P, and vs nearby casts. mcj: theta-TAlk plot of stations 71-73 shows 1,4,10 low; 3,9 also somewhat low. flag 1, 4, 10 questionable.
72/1	103	TAlk	2	rmk: bottles 1-10 TAlk low vs P, and vs nearby casts. mcj: theta-TAlk plot of stations 71-73 shows 1,4,10 low; 3,9 also somewhat low. flag 1, 4, 10 questionable.
72/1	104	TAlk	3	rmk: bottles 1-10 TAlk low vs P, and vs nearby casts. mcj: theta-TAlk plot of stations 71-73 shows 1,4,10 low; 3,9 also somewhat low. flag 1, 4, 10 questionable.
72/1	107	Salinity	3	outlier (high) compared to CTDS
72/1	109	TAlk	2	rmk: bottles 1-10 TAlk low vs P, and vs nearby casts. mcj: theta-TAlk plot of stations 71-73 shows 1,4,10 low; 3,9 also somewhat low. flag 1, 4, 10 questionable.
72/1	110	TAlk	3	rmk: bottles 1-10 TAlk low vs P, and vs nearby casts. mcj: theta-TAlk plot of stations 71-73 shows 1,4,10 low; 3,9 also somewhat low. flag 1, 4, 10 questionable.
72/3	300	Bottle	2	another cast numbered 3 to cover the upper profile; CTD replaced (now #209)
72/3	301	Bottle	2	after 306 tripped rosette was taken from 780db back to 1500db because of wire problems
72/3	302	Bottle	2	after 306 tripped rosette was taken from 780db back to 1500db because of wire problems
72/3	303	Bottle	2	after 306 tripped rosette was taken from 780db back to 1500db because of wire problems
72/3	304	Bottle	2	after 306 tripped rosette was taken from 780db back to 1500db because of wire problems
72/3	305	Bottle	2	after 306 tripped rosette was taken from 780db back to 1500db because of wire problems
72/3	306	Bottle	2	after 306 tripped rosette was taken from 780db back to 1500db because of wire problems
73/1	114	Bottle	2	ran out of water for salt
73/1	116	Bottle	2	ran out of water for salt
73/1	118	Bottle	2	ran out of water for tritium/nutrients/salt
73/1	119	Bottle	2	ran out of water for nutrients/salt; bubbles (tritium)
74/1	103	O2	4	outlier vs pressure and vs CTD value
76/1	102	O2	3	outlier (low) vs pressure/CTDO
77/1	106	SF6	3	very high vs T, P
78/1	102	SF6	3	very high vs T, P
78/1	111	Bottle	9	spigot broke when CFCs started to sample, replaced right away. No samples drawn.
79/1	ALL		-	enter key was apparently left depressed after bottle 1 was tripped; all bottles apparently triggered at the bottom approximately 1 second apart. Restarted upcast as cast 2, later merged with downcast as cast 1.
79/1	101	Bottle	4	o2 and salt values indicate all bottles but 3 and 4 tripped at bottom of cast.
79/1	101	Nitrite	9	samples collected but not analyzed due to tripping uncertainty.
79/1	101	Nitrate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	101	pCO2	9	samples collected but not analyzed due to tripping uncertainty.
79/1	101	pH	9	samples collected but not analyzed due to tripping uncertainty.
79/1	101	Phosphate	9	samples collected but not analyzed due to tripping uncertainty.

Station /Cast	Sample Number	Property	Quality Code	Comment
79/1	101	Silicate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	102	Bottle	4	o2 and salt values indicate all bottles but 3 and 4 tripped at bottom of cast.
79/1	102	Nitrite	9	samples collected but not analyzed due to tripping uncertainty.
79/1	102	Nitrate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	102	pH	9	samples collected but not analyzed due to tripping uncertainty.
79/1	102	Phosphate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	102	Silicate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	103	Bottle	4	o2 very low, salt very high vs CTD; niskin likely closed later than other bottles: mis-trip.
79/1	103	CCl4	9	samples collected but not analyzed due to tripping uncertainty.
79/1	103	CFC-11	9	samples collected but not analyzed due to tripping uncertainty.
79/1	103	CFC-12	9	samples collected but not analyzed due to tripping uncertainty.
79/1	103	Nitrite	9	samples collected but not analyzed due to tripping uncertainty.
79/1	103	Nitrate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	103	O2	4	o2 very low vs CTDO; niskin likely closed later than other bottles; mis-trip.
79/1	103	Phosphate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	103	Salinity	4	salt very high vs CTDS; niskin likely closed later than other bottles; mis-trip.
79/1	103	SF6	9	samples collected but not analyzed due to tripping uncertainty.
79/1	103	Silicate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	104	Bottle	9	bottle 4 did not close.
79/1	105	Bottle	4	o2 and salt values indicate all bottles but 3 and 4 tripped at bottom of cast.
79/1	105	CCl4	9	samples collected but not analyzed due to tripping uncertainty.
79/1	105	CFC-11	9	samples collected but not analyzed due to tripping uncertainty.
79/1	105	CFC-12	9	samples collected but not analyzed due to tripping uncertainty.
79/1	105	DIC	9	samples collected but not analyzed due to tripping uncertainty.
79/1	105	Nitrite	9	samples collected but not analyzed due to tripping uncertainty.
79/1	105	Nitrate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	105	pH	9	samples collected but not analyzed due to tripping uncertainty.
79/1	105	Phosphate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	105	SF6	9	samples collected but not analyzed due to tripping uncertainty.
79/1	105	Silicate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	106	Bottle	4	o2 and salt values indicate all bottles but 3 and 4 tripped at bottom of cast.
79/1	106	CCl4	9	samples collected but not analyzed due to tripping uncertainty.
79/1	106	CFC-11	9	samples collected but not analyzed due to tripping uncertainty.
79/1	106	CFC-12	9	samples collected but not analyzed due to tripping uncertainty.
79/1	106	DIC	9	samples collected but not analyzed due to tripping uncertainty.
79/1	106	Nitrite	9	samples collected but not analyzed due to tripping uncertainty.
79/1	106	Nitrate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	106	pH	9	samples collected but not analyzed due to tripping uncertainty.
79/1	106	Phosphate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	106	SF6	9	samples collected but not analyzed due to tripping uncertainty.
79/1	106	Silicate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	107	Bottle	4	o2 and salt values indicate all bottles but 3 and 4 tripped at bottom of cast.
79/1	107	CCl4	9	samples collected but not analyzed due to tripping uncertainty.
79/1	107	CFC-11	9	samples collected but not analyzed due to tripping uncertainty.
79/1	107	CFC-12	9	samples collected but not analyzed due to tripping uncertainty.
79/1	107	DIC	9	samples collected but not analyzed due to tripping uncertainty.
79/1	107	Nitrite	9	samples collected but not analyzed due to tripping uncertainty.
79/1	107	Nitrate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	107	pCO2	9	samples collected but not analyzed due to tripping uncertainty.
79/1	107	pH	9	samples collected but not analyzed due to tripping uncertainty.

Station /Cast	Sample Number	Property	Quality Code	Comment
79/1	107	Phosphate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	107	SF6	9	samples collected but not analyzed due to tripping uncertainty.
79/1	107	Silicate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	108	Bottle	4	o2 and salt values indicate all bottles but 3 and 4 tripped at bottom of cast.
79/1	108	CCl4	9	samples collected but not analyzed due to tripping uncertainty.
79/1	108	CFC-11	9	samples collected but not analyzed due to tripping uncertainty.
79/1	108	CFC-12	9	samples collected but not analyzed due to tripping uncertainty.
79/1	108	DIC	9	samples collected but not analyzed due to tripping uncertainty.
79/1	108	Nitrite	9	samples collected but not analyzed due to tripping uncertainty.
79/1	108	Nitrate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	108	pH	9	samples collected but not analyzed due to tripping uncertainty.
79/1	108	Phosphate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	108	SF6	9	samples collected but not analyzed due to tripping uncertainty.
79/1	108	Silicate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	108	TAlk	9	samples collected but not analyzed due to tripping uncertainty.
79/1	109	Bottle	4	o2 and salt values indicate all bottles but 3 and 4 tripped at bottom of cast.
79/1	109	CCl4	9	samples collected but not analyzed due to tripping uncertainty.
79/1	109	CFC-11	9	samples collected but not analyzed due to tripping uncertainty.
79/1	109	CFC-12	9	samples collected but not analyzed due to tripping uncertainty.
79/1	109	DIC	9	samples collected but not analyzed due to tripping uncertainty.
79/1	109	Nitrite	9	samples collected but not analyzed due to tripping uncertainty.
79/1	109	Nitrate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	109	pCO2	9	samples collected but not analyzed due to tripping uncertainty.
79/1	109	pH	9	samples collected but not analyzed due to tripping uncertainty.
79/1	109	Phosphate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	109	SF6	9	samples collected but not analyzed due to tripping uncertainty.
79/1	109	Silicate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	109	TAlk	9	samples collected but not analyzed due to tripping uncertainty.
79/1	110	Bottle	4	o2 and salt values indicate all bottles but 3 and 4 tripped at bottom of cast.
79/1	110	CCl4	9	samples collected but not analyzed due to tripping uncertainty.
79/1	110	CFC-11	9	samples collected but not analyzed due to tripping uncertainty.
79/1	110	CFC-12	9	samples collected but not analyzed due to tripping uncertainty.
79/1	110	DIC	9	samples collected but not analyzed due to tripping uncertainty.
79/1	110	Nitrite	9	samples collected but not analyzed due to tripping uncertainty.
79/1	110	Nitrate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	110	pH	9	samples collected but not analyzed due to tripping uncertainty.
79/1	110	Phosphate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	110	SF6	9	samples collected but not analyzed due to tripping uncertainty.
79/1	110	Silicate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	110	TAlk	9	samples collected but not analyzed due to tripping uncertainty.
79/1	111	Bottle	4	o2 and salt values indicate all bottles but 3 and 4 tripped at bottom of cast.
79/1	111	CCl4	9	samples collected but not analyzed due to tripping uncertainty.
79/1	111	CFC-11	9	samples collected but not analyzed due to tripping uncertainty.
79/1	111	CFC-12	9	samples collected but not analyzed due to tripping uncertainty.
79/1	111	DIC	9	samples collected but not analyzed due to tripping uncertainty.
79/1	111	Nitrite	9	samples collected but not analyzed due to tripping uncertainty.
79/1	111	Nitrate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	111	pH	9	samples collected but not analyzed due to tripping uncertainty.
79/1	111	Phosphate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	111	SF6	9	samples collected but not analyzed due to tripping uncertainty.
79/1	111	Silicate	9	samples collected but not analyzed due to tripping uncertainty.

Station /Cast	Sample Number	Property	Quality Code	Comment
79/1	111	TAlk	9	samples collected but not analyzed due to tripping uncertainty.
79/1	112	Bottle	4	o2 and salt values indicate all bottles but 3 and 4 tripped at bottom of cast.
79/1	112	CCl4	9	samples collected but not analyzed due to tripping uncertainty.
79/1	112	CFC-11	9	samples collected but not analyzed due to tripping uncertainty.
79/1	112	CFC-12	9	samples collected but not analyzed due to tripping uncertainty.
79/1	112	DIC	9	samples collected but not analyzed due to tripping uncertainty.
79/1	112	Nitrite	9	samples collected but not analyzed due to tripping uncertainty.
79/1	112	Nitrate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	112	pCO2	9	samples collected but not analyzed due to tripping uncertainty.
79/1	112	pH	9	samples collected but not analyzed due to tripping uncertainty.
79/1	112	Phosphate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	112	SF6	9	samples collected but not analyzed due to tripping uncertainty.
79/1	112	Silicate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	112	TAlk	9	samples collected but not analyzed due to tripping uncertainty.
79/1	113	Bottle	4	o2 and salt values indicate all bottles but 3 and 4 tripped at bottom of cast.
79/1	113	CCl4	9	samples collected but not analyzed due to tripping uncertainty.
79/1	113	CFC-11	9	samples collected but not analyzed due to tripping uncertainty.
79/1	113	CFC-12	9	samples collected but not analyzed due to tripping uncertainty.
79/1	113	DIC	9	samples collected but not analyzed due to tripping uncertainty.
79/1	113	Nitrite	9	samples collected but not analyzed due to tripping uncertainty.
79/1	113	Nitrate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	113	pCO2	9	samples collected but not analyzed due to tripping uncertainty.
79/1	113	pH	9	samples collected but not analyzed due to tripping uncertainty.
79/1	113	Phosphate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	113	SF6	9	samples collected but not analyzed due to tripping uncertainty.
79/1	113	Silicate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	113	TAlk	9	samples collected but not analyzed due to tripping uncertainty.
79/1	114	Bottle	4	o2 and salt values indicate all bottles but 3 and 4 tripped at bottom of cast.
79/1	114	CCl4	9	samples collected but not analyzed due to tripping uncertainty.
79/1	114	CFC-11	9	samples collected but not analyzed due to tripping uncertainty.
79/1	114	CFC-12	9	samples collected but not analyzed due to tripping uncertainty.
79/1	114	DIC	9	samples collected but not analyzed due to tripping uncertainty.
79/1	114	Nitrite	9	samples collected but not analyzed due to tripping uncertainty.
79/1	114	Nitrate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	114	pCO2	9	samples collected but not analyzed due to tripping uncertainty.
79/1	114	pH	9	samples collected but not analyzed due to tripping uncertainty.
79/1	114	Phosphate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	114	SF6	9	samples collected but not analyzed due to tripping uncertainty.
79/1	114	Silicate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	114	TAlk	9	samples collected but not analyzed due to tripping uncertainty.
79/1	115	Bottle	4	o2 and salt values indicate all bottles but 3 and 4 tripped at bottom of cast.
79/1	115	CCl4	9	samples collected but not analyzed due to tripping uncertainty.
79/1	115	CFC-11	9	samples collected but not analyzed due to tripping uncertainty.
79/1	115	CFC-12	9	samples collected but not analyzed due to tripping uncertainty.
79/1	115	DIC	9	samples collected but not analyzed due to tripping uncertainty.
79/1	115	Nitrite	9	samples collected but not analyzed due to tripping uncertainty.
79/1	115	Nitrate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	115	pH	9	samples collected but not analyzed due to tripping uncertainty.
79/1	115	Phosphate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	115	SF6	9	samples collected but not analyzed due to tripping uncertainty.
79/1	115	Silicate	9	samples collected but not analyzed due to tripping uncertainty.

Station /Cast	Sample Number	Property	Quality Code	Comment
79/1	115	TAlk	9	samples collected but not analyzed due to tripping uncertainty.
79/1	116	Bottle	4	o2 and salt values indicate all bottles but 3 and 4 tripped at bottom of cast.
79/1	116	CCl4	9	samples collected but not analyzed due to tripping uncertainty.
79/1	116	CFC-11	9	samples collected but not analyzed due to tripping uncertainty.
79/1	116	CFC-12	9	samples collected but not analyzed due to tripping uncertainty.
79/1	116	DIC	9	samples collected but not analyzed due to tripping uncertainty.
79/1	116	Nitrite	9	samples collected but not analyzed due to tripping uncertainty.
79/1	116	Nitrate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	116	pCO2	9	samples collected but not analyzed due to tripping uncertainty.
79/1	116	pH	9	samples collected but not analyzed due to tripping uncertainty.
79/1	116	Phosphate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	116	SF6	9	samples collected but not analyzed due to tripping uncertainty.
79/1	116	Silicate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	116	TAlk	9	samples collected but not analyzed due to tripping uncertainty.
79/1	117	Bottle	4	ran out of water for nutrients/salt; most likely tripped at the bottom like other bottles.
79/1	117	CCl4	9	samples collected but not analyzed due to tripping uncertainty.
79/1	117	CFC-11	9	samples collected but not analyzed due to tripping uncertainty.
79/1	117	CFC-12	9	samples collected but not analyzed due to tripping uncertainty.
79/1	117	DIC	9	samples collected but not analyzed due to tripping uncertainty.
79/1	117	pCO2	9	samples collected but not analyzed due to tripping uncertainty.
79/1	117	pH	9	samples collected but not analyzed due to tripping uncertainty.
79/1	117	SF6	9	samples collected but not analyzed due to tripping uncertainty.
79/1	117	TAlk	9	samples collected but not analyzed due to tripping uncertainty.
79/1	118	Bottle	4	o2 and salt values indicate all bottles but 3 and 4 tripped at bottom of cast.
79/1	118	CCl4	9	samples collected but not analyzed due to tripping uncertainty.
79/1	118	CFC-11	9	samples collected but not analyzed due to tripping uncertainty.
79/1	118	CFC-12	9	samples collected but not analyzed due to tripping uncertainty.
79/1	118	DIC	9	samples collected but not analyzed due to tripping uncertainty.
79/1	118	Nitrite	9	samples collected but not analyzed due to tripping uncertainty.
79/1	118	Nitrate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	118	pCO2	9	samples collected but not analyzed due to tripping uncertainty.
79/1	118	pH	9	samples collected but not analyzed due to tripping uncertainty.
79/1	118	Phosphate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	118	SF6	9	samples collected but not analyzed due to tripping uncertainty.
79/1	118	Silicate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	118	TAlk	9	samples collected but not analyzed due to tripping uncertainty.
79/1	119	Bottle	4	o2 and salt values indicate all bottles but 3 and 4 tripped at bottom of cast.
79/1	119	CCl4	9	samples collected but not analyzed due to tripping uncertainty.
79/1	119	CFC-11	9	samples collected but not analyzed due to tripping uncertainty.
79/1	119	CFC-12	9	samples collected but not analyzed due to tripping uncertainty.
79/1	119	DIC	9	samples collected but not analyzed due to tripping uncertainty.
79/1	119	Nitrite	9	samples collected but not analyzed due to tripping uncertainty.
79/1	119	Nitrate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	119	pCO2	9	samples collected but not analyzed due to tripping uncertainty.
79/1	119	pH	9	samples collected but not analyzed due to tripping uncertainty.
79/1	119	Phosphate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	119	SF6	9	samples collected but not analyzed due to tripping uncertainty.
79/1	119	Silicate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	119	TAlk	9	samples collected but not analyzed due to tripping uncertainty.
79/1	120	Bottle	4	o2 and salt values indicate all bottles but 3 and 4 tripped at bottom of cast.

Station /Cast	Sample Number	Property	Quality Code	Comment
79/1	120	CCl4	9	samples collected but not analyzed due to tripping uncertainty.
79/1	120	CFC-11	9	samples collected but not analyzed due to tripping uncertainty.
79/1	120	CFC-12	9	samples collected but not analyzed due to tripping uncertainty.
79/1	120	DIC	9	samples collected but not analyzed due to tripping uncertainty.
79/1	120	Nitrite	9	samples collected but not analyzed due to tripping uncertainty.
79/1	120	Nitrate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	120	pCO2	9	samples collected but not analyzed due to tripping uncertainty.
79/1	120	pH	9	samples collected but not analyzed due to tripping uncertainty.
79/1	120	Phosphate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	120	SF6	9	samples collected but not analyzed due to tripping uncertainty.
79/1	120	Silicate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	120	TAlk	9	samples collected but not analyzed due to tripping uncertainty.
79/1	121	Bottle	4	o2 and salt values indicate all bottles but 3 and 4 tripped at bottom of cast.
79/1	121	CCl4	9	samples collected but not analyzed due to tripping uncertainty.
79/1	121	CFC-11	9	samples collected but not analyzed due to tripping uncertainty.
79/1	121	CFC-12	9	samples collected but not analyzed due to tripping uncertainty.
79/1	121	DIC	9	samples collected but not analyzed due to tripping uncertainty.
79/1	121	Nitrite	9	samples collected but not analyzed due to tripping uncertainty.
79/1	121	Nitrate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	121	pH	9	samples collected but not analyzed due to tripping uncertainty.
79/1	121	Phosphate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	121	SF6	9	samples collected but not analyzed due to tripping uncertainty.
79/1	121	Silicate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	121	TAlk	9	samples collected but not analyzed due to tripping uncertainty.
79/1	122	Bottle	4	o2 and salt values indicate all bottles but 3 and 4 tripped at bottom of cast.
79/1	122	CCl4	9	samples collected but not analyzed due to tripping uncertainty.
79/1	122	CFC-11	9	samples collected but not analyzed due to tripping uncertainty.
79/1	122	CFC-12	9	samples collected but not analyzed due to tripping uncertainty.
79/1	122	DIC	9	samples collected but not analyzed due to tripping uncertainty.
79/1	122	Nitrite	9	samples collected but not analyzed due to tripping uncertainty.
79/1	122	Nitrate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	122	pH	9	samples collected but not analyzed due to tripping uncertainty.
79/1	122	Phosphate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	122	SF6	9	samples collected but not analyzed due to tripping uncertainty.
79/1	122	Silicate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	122	TAlk	9	samples collected but not analyzed due to tripping uncertainty.
79/1	123	Bottle	4	o2 and salt values indicate all bottles but 3 and 4 tripped at bottom of cast.
79/1	123	CCl4	9	samples collected but not analyzed due to tripping uncertainty.
79/1	123	CFC-11	9	samples collected but not analyzed due to tripping uncertainty.
79/1	123	CFC-12	9	samples collected but not analyzed due to tripping uncertainty.
79/1	123	DIC	9	samples collected but not analyzed due to tripping uncertainty.
79/1	123	Nitrite	9	samples collected but not analyzed due to tripping uncertainty.
79/1	123	Nitrate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	123	pCO2	9	samples collected but not analyzed due to tripping uncertainty.
79/1	123	pH	9	samples collected but not analyzed due to tripping uncertainty.
79/1	123	Phosphate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	123	SF6	9	samples collected but not analyzed due to tripping uncertainty.
79/1	123	Silicate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	123	TAlk	9	samples collected but not analyzed due to tripping uncertainty.
79/1	124	Bottle	4	o2 and salt values indicate all bottles but 3 and 4 tripped at bottom of cast.
79/1	124	CCl4	9	samples collected but not analyzed due to tripping uncertainty.

Station /Cast	Sample Number	Property	Quality Code	Comment
79/1	124	CFC-11	9	samples collected but not analyzed due to tripping uncertainty.
79/1	124	CFC-12	9	samples collected but not analyzed due to tripping uncertainty.
79/1	124	DIC	9	samples collected but not analyzed due to tripping uncertainty.
79/1	124	Nitrite	9	samples collected but not analyzed due to tripping uncertainty.
79/1	124	Nitrate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	124	pCO2	9	samples collected but not analyzed due to tripping uncertainty.
79/1	124	pH	9	samples collected but not analyzed due to tripping uncertainty.
79/1	124	Phosphate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	124	SF6	9	samples collected but not analyzed due to tripping uncertainty.
79/1	124	Silicate	9	samples collected but not analyzed due to tripping uncertainty.
79/1	124	TAlk	9	samples collected but not analyzed due to tripping uncertainty.
79/3	300	Bottle	2	return to station 79 and do a full cast numbered 3; bottle 4 did not close.
79/3	304	Bottle	9	bottle 4 did not close
80/1	104	Bottle	2	raised by another 2.54 cm after last cast
81/1	109	SF6	3	outlier relative to adjacent samples
81/1	111	SF6	3	outlier relative to adjacent samples
82/1	103	Bottle	9	bottle 3 did not close, reason unknown.
82/1	105	Bottle	2	cfcs, o2, pH, DIC show local minimum at this bottle; pCO2, salinity slight maximum; nuts slightly off; possible mis-trip, or ok?
82/1	105	O2	3	bottle o2 slightly low compared to CTDO, down or upcast.
82/1	105	Salinity	3	salinity slightly high compared to CTDS, down or upcast.
82/1	113	Bottle	9	bottles 13-24 did not close: piece of bottle 23 cap lodged under trip levers.
82/1	114	Bottle	9	bottles 13-24 did not close: piece of bottle 23 cap lodged under trip levers.
82/1	115	Bottle	9	bottles 13-24 did not close: piece of bottle 23 cap lodged under trip levers.
82/1	116	Bottle	9	bottles 13-24 did not close: piece of bottle 23 cap lodged under trip levers.
82/1	117	Bottle	9	bottles 13-24 did not close: piece of bottle 23 cap lodged under trip levers.
82/1	118	Bottle	9	bottles 13-24 did not close: piece of bottle 23 cap lodged under trip levers.
82/1	119	Bottle	9	bottles 13-24 did not close: piece of bottle 23 cap lodged under trip levers.
82/1	120	Bottle	9	bottles 13-24 did not close: piece of bottle 23 cap lodged under trip levers.
82/1	121	Bottle	9	bottles 13-24 did not close: piece of bottle 23 cap lodged under trip levers.
82/1	122	Bottle	9	bottle 122 destroyed by bottle 23 implosion
82/1	123	Bottle	9	apparently tripped in air on the way in, imploded at depth (inner spring compressed): destroyed bottle 22, parts of bottle 23 prevented the other bottles from tripping; bottles 22/23 replaced after cast.
82/1	124	Bottle	9	bottles 13-24 did not close: piece of bottle 23 cap lodged under trip levers.
82/2	200	Bottle	2	second cast to cover the upper profile of station 82
82/2	205	Bottle	4	draw temperature too high, bottle mis-tripped based on o2, salt, other parameters. pco2, talk, dic not sampled.
82/2	205	CCl4	4	cfcs high, mis-trip.
82/2	205	CFC-11	4	cfcs high, mis-trip.
82/2	205	CFC-12	4	cfcs high, mis-trip.
82/2	205	Nitrite	4	bottle mis-trip.
82/2	205	Nitrate	4	no3 high, mis-trip.
82/2	205	O2	4	outlier (low) compared to CTDO, mis-trip.
82/2	205	pH	4	pH very low, mis-trip.
82/2	205	Phosphate	4	po4 high, mis-trip.
82/2	205	Salinity	4	outlier (high) compared to CTDS
82/2	205	SF6	4	cfcs high, mis-trip.
82/2	205	Silicate	4	sio3 low, mis-trip.
82/2	216	Bottle	2	draw temperature high but salt/o2 ok compared to CTDS/CTDO.
83/1	102	Bottle	9	pin did not fully release bottle

Station /Cast	Sample Number	Property	Quality Code	Comment
83/1	114	CFC-12	3	outlier vs T, P
83/1	119	Bottle	9	pin did not fully release bottle
83/1	122	Bottle	2	tripped the same depth as 121
84/1	105	Bottle	4	draw temperature too high; parameters indicate bottle mis-tripped. pH, pco2, talk, dic not sampled.
84/1	105	CCl4	4	cfcs high, mis-trip.
84/1	105	CFC-11	4	cfcs high, mis-trip.
84/1	105	CFC-12	4	cfcs high, mis-trip.
84/1	105	Nitrite	4	bottle mis-trip.
84/1	105	Nitrate	4	no3 high, mis-trip.
84/1	105	O2	4	outlier (very low) compared to CTDO, mis-trip.
84/1	105	Phosphate	4	po4 high, mis-trip.
84/1	105	Salinity	4	outlier (very low) compared to CTDS, mis-trip.
84/1	105	SF6	4	cfcs high, mis-trip.
84/1	105	Silicate	4	sio3 low, mis-trip.
84/1	114	SF6	4	very very high relative to neighbors
85/1	103	O2	3	outlier (high) compared to CTDO
85/1	109	Salinity	4	hi compared to CTDS and to neighboring stations
88/1	110	Bottle	2	adjusted (height/direction) to make spigot better accessible
89/1	111	SF6	3	hi vs pressure and cfc12
89/1	113	O2	4	outlier (high) compared to CTDO; rmk: hi vs NO3, Si, PO4, sigma
90/1	113	SF6	3	hi vs pressure and cfc12
91/1	122	DIC	3	rmk: dic anomalous vs P, CTDO, pH by a fair bit, flag 3. mcj: aligns with CTDO feature, other properties also unusual. rmk: but dic is a bit too far off. flagged questionable.
93/1	101	Bottle	2	vent was not closed, o2 sample not drawn
94/1	108	Bottle	3	draw temperature high
96/1	ALL		-	altimeter cleaned and reseated cable connector on altimeter
97/1	121	Bottle	2	raised to the same height as the inner bottles
98/1	103	O2	3	slightly high (4300db)
98/1	118	SF6	3	lo vs adjacent stations and in comparison to other cfc and ccl4
99/1	105	TAlk	4	flier - TAlk very, very low.
100/1	116	CCl4	3	hi vs neighbors and in ratio to other cfcs and sf6
101/1	101	Nitrate	4	chemistry problem with nuts. All nitrate bad (low)
101/1	102	Nitrate	4	chemistry problem with nuts. All nitrate bad (low)
101/1	103	Nitrate	4	chemistry problem with nuts. All nitrate bad (low)
101/1	104	Nitrate	4	chemistry problem with nuts. All nitrate bad (low)
101/1	105	Nitrate	4	chemistry problem with nuts. All nitrate bad (low)
101/1	106	Nitrate	4	chemistry problem with nuts. All nitrate bad (low)
101/1	107	Nitrate	4	chemistry problem with nuts. All nitrate bad (low)
101/1	108	Nitrate	4	chemistry problem with nuts. All nitrate bad (low)
101/1	109	Nitrate	4	chemistry problem with nuts. All nitrate bad (low)
101/1	110	Nitrate	4	chemistry problem with nuts. All nitrate bad (low)
101/1	111	Nitrate	4	chemistry problem with nuts. All nitrate bad (low)
101/1	111	SF6	3	sf6 high vs P (f11/f12 drop slightly with other parameters at this bottle); flag 3.
101/1	112	Nitrate	4	chemistry problem with nuts. All nitrate bad (low)
101/1	113	Nitrate	4	chemistry problem with nuts. All nitrate bad (low)
101/1	114	Nitrate	4	chemistry problem with nuts. All nitrate bad (low)
101/1	115	Nitrate	4	chemistry problem with nuts. All nitrate bad (low)
101/1	116	Nitrate	4	chemistry problem with nuts. All nitrate bad (low)
101/1	117	Nitrate	4	chemistry problem with nuts. All nitrate bad (low)

Station /Cast	Sample Number	Property	Quality Code	Comment
101/1	118	Nitrate	4	chemistry problem with nuts. All nitrate bad (low)
101/1	119	Nitrate	4	chemistry problem with nuts. All nitrate bad (low)
101/1	120	Nitrate	4	chemistry problem with nuts. All nitrate bad (low)
101/1	121	Nitrate	4	chemistry problem with nuts. All nitrate bad (low)
101/1	122	Nitrate	4	chemistry problem with nuts. All nitrate bad (low)
101/1	123	Nitrate	4	chemistry problem with nuts. All nitrate bad (low)
101/1	124	Nitrate	4	chemistry problem with nuts. All nitrate bad (low)
103/1	105	Bottle	4	based on chem.evidence, bottle mis-tripped.
103/1	105	CCl4	4	bottle mis-trip.
103/1	105	CFC-11	4	bottle mis-trip.
103/1	105	CFC-12	4	bottle mis-trip.
103/1	105	DIC	4	outlier (low) vs pressure and others, mis-trip.
103/1	105	Nitrite	4	bottle mis-trip.
103/1	105	Nitrate	4	slightly low, mis-trip.
103/1	105	O2	4	outlier (low) compared to CTDO, mis-trip.
103/1	105	pCO2	4	slightly low, mis-trip.
103/1	105	pH	4	slightly low, mis-trip.
103/1	105	Phosphate	4	slightly low, mis-trip.
103/1	105	Salinity	4	outlier (high) compared to CTDS, mis-trip.
103/1	105	SF6	4	bottle mis-trip.
103/1	105	Silicate	4	outlier (low) vs pressure and others, mis-trip.
103/1	105	TAlk	4	outlier (low) vs pressure and others, mis-trip.
104/1	123	Refc.Temp.	3	SBE35RT high vs CTDT, unstable reading.
105/1	102	pH	3	hi compared to neighbors in pressure space
106/1	105	Bottle	4	draw temperature very high, mis-trip (surface trip); only cfc, helium, nuts, salinity sampled.
106/1	105	CCl4	4	outlier, mis-trip.
106/1	105	CFC-11	4	outlier, mis-trip.
106/1	105	CFC-12	4	outlier, mis-trip.
106/1	105	Nitrite	4	bottle mis-trip.
106/1	105	Nitrate	4	outlier vs p with neighbors, mis-trip.
106/1	105	Phosphate	4	outlier vs p with neighbors, mis-trip.
106/1	105	Salinity	4	outlier (high) compared to CTDS, mis-trip.
106/1	105	SF6	4	outlier, mis-trip.
106/1	105	Silicate	4	outlier vs p with neighbors, mis-trip.
106/1	119	Bottle	4	draw temperature high, o2 and salt high vs CTD, nuts low, cfcs hi; mis-trip.
106/1	119	CCl4	4	outlier, mis-trip.
106/1	119	CFC-11	4	outlier, mis-trip.
106/1	119	CFC-12	4	outlier, mis-trip.
106/1	119	DIC	4	outlier (low), mis-trip.
106/1	119	Nitrite	4	outlier (high), mis-trip.
106/1	119	Nitrate	4	outlier (low), mis-trip.
106/1	119	O2	4	outlier (high) compared to CTDO, mis-trip.
106/1	119	pCO2	4	outlier (low), mis-trip.
106/1	119	pH	4	outlier (high), mis-trip.
106/1	119	Phosphate	4	outlier (low), mis-trip.
106/1	119	Salinity	4	outlier (high) compared to CTDS, mis-trip.
106/1	119	SF6	4	outlier, mis-trip.
106/1	119	Silicate	4	outlier (low), mis-trip.
106/1	119	TAlk	4	outlier (high), mis-trip.
107/1	105	Bottle	2	raised before this cast

Station /Cast	Sample Number	Property	Quality Code	Comment
107/1	106	pH	3	hi vs pressure relative to neighboring samples and stations
107/1	111	Bottle	2	draw temperature high
107/1	114	Refc.Temp.	3	SBE35RT very high vs CTDT
107/1	121	Bottle	2	draw temperature very high. pH, pco2, dic, talk not sampled. o2, salinity agree well with CTD, other parameters also ok. code bottle ok.
108/1	102	Bottle	2	raised 1 inch before this cast
108/1	104	Bottle	9	not tripped (trigger released but lanyard not)
108/1	123	Refc.Temp.	3	SBE35RT high vs CTDT, unstable reading.
109/1	102	SF6	4	very very hi vs pressure and ccl4, unrealistic
110/1	104	Salinity	3	a bit high compared to CTDS, low vs pot T
111/1	104	Bottle	4	draw temperature high; cfcs, pH, pco2, dic, talk not sampled. o2, salinity, nutrients indicate mis-trip.
111/1	104	Nitrite	4	bottle mis-trip.
111/1	104	Nitrate	4	outlier (high), mis-trip.
111/1	104	O2	4	outlier (low) compared to CTDO, mis-trip.
111/1	104	Phosphate	4	outlier (high), mis-trip.
111/1	104	Salinity	4	outlier (low) compared to CTDS, mis-trip.
111/1	104	Silicate	4	outlier (low) vs pressure, bulls-eye on section plot; mis-trip.
112/1	103	CFC-12	4	very very hi and high in ratio
112/1	103	SF6	4	very very hi
112/1	105	TAlk	3	lo vs pressure and salt compared to adjacent and neighbors
112/1	106	CFC-12	4	very very hi and high in ratios
112/1	106	SF6	4	very very hi in profile
112/1	116	SF6	4	very very hi in profile
113/1	104	Bottle	4	all parameters indicate mis-trip.
113/1	104	DIC	4	outlier (low), mis-trip.
113/1	104	Nitrite	4	bottle mis-trip.
113/1	104	Nitrate	4	outlier (low), mis-trip.
113/1	104	O2	4	slightly low compared to CTDO; mis-trip.
113/1	104	pH	4	outlier (high), mis-trip.
113/1	104	Phosphate	4	outlier (low), mis-trip.
113/1	104	Salinity	4	outlier (high) compared to CTDS; mis-trip.
113/1	104	Silicate	4	very very low vs pressure, neighbors and section plot; mis-trip.
113/1	104	TAlk	4	outlier (low), mis-trip.
114/1	108	Salinity	4	lo vs CTD and pressure relative to other data
115/1	118	Bottle	2	no water left for salt sample.
115/1	118	CFC-11	4	unrealistic value (low)
116/1	ALL		-	no software confirmations at first three bottle stops, two trip attempts each; fired second try from deck unit for 2nd and 3rd levels from bottom, and ONLY from deck unit for next 18 bottles; bottles 21-24 did not close.
118/1	102	Salinity	3	low compared to CTDS
119/1	102	Salinity	3	high compared to CTDS
119/1	105	Phosphate	3	hi vs pressure and redfield off significantly. no3 ok
119/1	112	O2	4	very low (1350db)
120/1	101	Silicate	3	entire cast high by about 4% (deep water) or 2 umol/kg
120/1	102	Silicate	3	entire cast high by about 4% (deep water) or 2 umol/kg
120/1	103	Silicate	3	entire cast high by about 4% (deep water) or 2 umol/kg
120/1	104	Silicate	3	entire cast high by about 4% (deep water) or 2 umol/kg
120/1	105	Silicate	3	entire cast high by about 4% (deep water) or 2 umol/kg
120/1	106	Silicate	3	entire cast high by about 4% (deep water) or 2 umol/kg
120/1	107	Silicate	3	entire cast high by about 4% (deep water) or 2 umol/kg

Station /Cast	Sample Number	Property	Quality Code	Comment
120/1	108	Silicate	3	entire cast high by about 4% (deep water) or 2 umol/kg
120/1	109	Silicate	3	entire cast high by about 4% (deep water) or 2 umol/kg
120/1	110	Silicate	3	entire cast high by about 4% (deep water) or 2 umol/kg
120/1	111	Silicate	3	entire cast high by about 4% (deep water) or 2 umol/kg
120/1	112	Silicate	3	entire cast high by about 4% (deep water) or 2 umol/kg
120/1	113	Silicate	3	entire cast high by about 4% (deep water) or 2 umol/kg
120/1	114	Silicate	3	entire cast high by about 4% (deep water) or 2 umol/kg
120/1	115	Silicate	3	entire cast high by about 4% (deep water) or 2 umol/kg
120/1	116	Silicate	3	entire cast high by about 4% (deep water) or 2 umol/kg
120/1	117	Bottle	2	o-ring replaced before sampling
120/1	117	Silicate	3	entire cast high by about 4% (deep water) or 2 umol/kg
120/1	118	Bottle	2	rmk: bad bottle? anomalous in various property-property plots, including pressure. mcj: bottle is in a distinct feature/rise (down-/up-cast CTDO maximum from approx. 400-460dbar). o2 agrees with CTDO. Re-code sio3, cfcs from 3 to 2.
120/1	118	CCl4	2	CTDO shows a distinct feature/rise here, cfcs are probably ok.
120/1	118	CFC-11	2	CTDO shows a distinct feature/rise here, cfcs are probably ok.
120/1	118	CFC-12	2	CTDO shows a distinct feature/rise here, cfcs are probably ok.
120/1	118	O2	2	o2 agrees with down-/up-cast CTDO, bottle taken in middle of a distinct CTDO feature/rise.
120/1	118	pH	2	rmk: pH for 18 a bit hi vs CTDS, pH for 19 a bit low vs CTDS; looks as if samples collected backward, flag 3. mcj: bottle 18 aligns with CTDO feature, flag both ok.
120/1	118	SF6	2	CTDO shows a distinct feature/rise here, cfcs are probably ok.
120/1	118	Silicate	2	CTDO shows a distinct feature/rise here, sio3 is probably ok.
120/1	119	pH	2	rmk: pH for 18 a bit hi vs CTDS, pH for 19 a bit low vs CTDS; looks as if samples collected backward, flag 3. mcj: bottle 18 aligns with CTDO feature, flag both ok.
120/1	119	Silicate	3	entire cast high by about 4% (deep water) or 2 umol/kg
120/1	120	Silicate	3	entire cast high by about 4% (deep water) or 2 umol/kg
120/1	121	Silicate	3	entire cast high by about 4% (deep water) or 2 umol/kg
120/1	122	Silicate	3	entire cast high by about 4% (deep water) or 2 umol/kg
120/1	123	Silicate	3	entire cast high by about 4% (deep water) or 2 umol/kg
120/1	124	Silicate	3	entire cast high by about 4% (deep water) or 2 umol/kg
121/1	102	Bottle	4	draw temperature high; pco2, dic, talk, nuts not sampled.
121/1	102	CCl4	4	cfcs high, mis-trip.
121/1	102	CFC-11	4	cfcs high, mis-trip.
121/1	102	CFC-12	4	cfcs high, mis-trip.
121/1	102	O2	4	outlier (very low) compared to CTDO; mis-trip.
121/1	102	pH	4	outlier (very low), mis-trip.
121/1	102	Salinity	4	outlier (high) compared to CTDS; mis-trip.
121/1	102	SF6	4	cfcs high, mis-trip.
121/1	111	Bottle	2	dripping, possibly leaking; all parameters seem ok, bottle ok.
122/1	102	Bottle	2	raised by 1.5 inches prior to cast
122/1	104	Bottle	9	not tripped
123/1	104	Bottle	4	draw temperature high; only o2, cfcs sampled. o2 indicates bottle mis-tripped.
123/1	104	O2	4	outlier (low) compared to CTDO; mis-trip.
123/1	110	Bottle	2	draw temperature a little bit high
124/1	108	O2	4	outlier (low) compared to CTDO
124/1	109	O2	4	outlier (low) compared to CTDO
124/1	123	Salinity	3	salt hi vs CTDS; high gradient

Station /Cast	Sample Number	Property	Quality Code	Comment
125/1	102	Bottle	4	multiple parameters slightly off, similar to bottle 3 values. probable mis-trip.
125/1	102	CCl4	4	bottle mis-trip.
125/1	102	CFC-11	4	bottle mis-trip.
125/1	102	CFC-12	4	bottle mis-trip.
125/1	102	DIC	4	dic slightly low, similar to niskin 3 value; mis-trip.
125/1	102	Nitrite	4	bottle mis-trip.
125/1	102	Nitrate	4	nutrients slightly low, similar to niskin 3 value; mis-trip.
125/1	102	O2	4	o2 similar to niskin 3 value; mis-trip.
125/1	102	pH	4	similar to niskin 3 value; mis-trip.
125/1	102	Phosphate	4	nutrients slightly low, similar to niskin 3 value; mis-trip.
125/1	102	Salinity	4	salinity slightly high vs CTDS, similar to niskin 3 value; mis-trip.
125/1	102	SF6	4	bottle mis-trip.
125/1	102	Silicate	4	nutrients slightly low similar to niskin 3 value; mis-trip.
125/1	102	TAlk	4	alk low, lower than bottle 3; mis-trip.
126/1	102	Bottle	2	spigot fixed
126/1	104	Bottle	4	multiple outliers, most parameters similar to bottle 6 values instead of bottle 5 (tripped at same pressure); mis-trip.
126/1	104	Nitrite	4	bottle mis-trip.
126/1	104	Nitrate	4	outlier (high), mis-trip.
126/1	104	O2	4	outlier (low) compared to CTDO, mis-trip.
126/1	104	pH	4	outlier (low), mis-trip.
126/1	104	Phosphate	4	outlier (high), mis-trip.
126/1	104	Salinity	4	outlier (low) compared to CTDS, mis-trip.
126/1	104	Silicate	4	outlier (low), mis-trip.
126/1	104	TAlk	4	outlier (low), mis-trip.
126/1	114	O2	4	outlier (low) compared to CTDO
126/1	123	Salinity	3	salt hi vs CTDS; high gradient
126/1	123	TAlk	3	hi vs P, CTDS
127/1	118	Refc.Temp.	3	SBE35RT slightly low vs CTDT, unstable reading.
127/1	123	Salinity	4	salt very hi vs CTDS
129/1	117	Bottle	2	rmk: nutrient data apparently assigned to niskins backwards. mcj: data re-assigned to correct bottles by analyst, silicate now increases with depth; ok now.
129/1	118	Bottle	2	rmk: nutrient data apparently assigned to niskins backwards. mcj: data re-assigned to correct bottles by analyst, silicate now increases with depth; ok now.
129/1	119	Bottle	2	rmk: nutrient data apparently assigned to niskins backwards. mcj: data re-assigned to correct bottles by analyst, silicate now increases with depth; ok now.
129/1	119	Refc.Temp.	3	SBE35RT very low vs CTDT
129/1	120	Bottle	2	rmk: nutrient data apparently assigned to niskins backwards. mcj: data re-assigned to correct bottles by analyst, silicate now increases with depth; ok now.
129/1	121	Bottle	2	rmk: nutrient data apparently assigned to niskins backwards. mcj: data re-assigned to correct bottles by analyst, silicate now increases with depth; ok now.
129/1	122	Bottle	2	rmk: nutrient data apparently assigned to niskins backwards. mcj: data re-assigned to correct bottles by analyst, silicate now increases with depth; ok now.
129/1	123	Bottle	2	rmk: nutrient data apparently assigned to niskins backwards. mcj: data re-assigned to correct bottles by analyst, silicate now increases with depth; ok now.
129/1	123	Salinity	3	salt hi vs CTDS; high gradient
129/1	124	Bottle	2	rmk: nutrient data apparently assigned to niskins backwards. mcj: data re-assigned to correct bottles by analyst, silicate now increases with depth; ok now.

References

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CHLOROFLUOROCARBON (CFC) AND SULFUR HEXAFLUORIDE (SF_6) MEASUREMENTS ON CLIVAR A13.5

PI: John Bullister

Analysts: David Wisegarver
Patrick Boylan
Ivy Frenger

A PMEL analytical system (Bullister and Wisegarver, 2008) was used for CFC-11, CFC-12, carbon tetrachloride (CCl_4) and sulfur hexafluoride (SF_6) analyses on the CLIVAR A13.5 expedition. About 2800 seawater samples were analyzed for dissolved CFC-11, CFC-12, CCl_4 and SF_6 ('CFC/SF_6') concentrations. On several hundred of these samples, the analysis was modified to include the analysis of nitrous oxide (N_2O) in place of CCl_4. These N_2O analyses were done as part of an experimental study to try to develop more reliable methods for measuring this compound in seawater on future CLIVAR cruises. These N_2O measurements are not included in the report.

In general, the analytical system performed well on the cruise. Typical dissolved SF_6 concentrations in modern surface water are ~1 fmol kg^{-1} seawater (1 fmol= femtomole = 10^{-15} moles), approximately 1000 times lower than dissolved CFC-11 and CFC-12 concentrations. The limits of detection for SF_6 on CLIVAR A13.5 were approximately 0.02 fmol kg^{-1}. SF_6 measurements in seawater remain extremely challenging. Improvements in the analytical sensitivity to this compound at low concentrations are essential to make these measurements more routine on future CLIVAR cruises.

Water samples on CLIVAR A13.5 were collected in bottles designed with a modified end-cap to minimize the contact of the water sample with the end-cap O-rings after closing. 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 collected for dissolved CFC-11, CFC-12, CCl_4 and SF_6 analysis were the first samples drawn from the bottles. Care was taken to coordinate the sampling of CFC/SF_6 with other samples to minimize the time between the initial opening of each bottle and the completion of sample drawing. Samples easily impacted by gas exchange (dissolved oxygen, ^3He, DIC and pH) were collected within several minutes of the initial opening of each bottle. To minimize contact with air, the CFC/SF_6 samples were drawn directly through the stopcocks of the bottles into 250 ml precision glass syringes equipped with three-way plastic stopcocks. The syringes were immersed in a holding tank of clean surface seawater held at ~10^{O}C until ~20 minutes before being analyzed. At that time, the syringe was place in a bath of surface seawater heated to ~30^{o}C.

For atmospheric sampling, a ~75 m length of 3/8" OD Dekaron tubing was run from the CFC van located on the fantail to the bow of the ship. A flow of air was drawn through this line into the main laboratory 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 of ~100 ml min^{-1} of the compressed air to be directed to the gas sample valves of the CFC/SF_6 analytical systems, while the bulk flow of the air

($>$7 l min^{-1}) was vented through the back-pressure regulator. Air samples were analyzed only when the relative wind direction was within 60 degrees of the bow of the ship to reduce the possibility of shipboard contamination. Analysis of bow air was performed along the cruise track. At each location, at least five air measurements were made to increase the precision of the measurements.

Concentrations of CFC/SF_6 in air samples, seawater, and gas standards were measured by shipboard electron capture gas chromatography (EC-GC) using techniques modified from those described by Bullister and Weiss (1988) and Bullister and Wisegarver (2008) as outlined below. For seawater analyses, water was transferred from a glass syringe to a glass-sparging chamber (volume ~200 ml). The dissolved gases in the seawater sample were extracted by passing a supply of CFC/SF_6 free purge gas through the sparging chamber for a period of 6 minutes at ~150 ml min^{-1}. Water vapor was removed from the purge gas during passage through an 18 cm long, 3/8" diameter glass tube packed with the desiccant magnesium perchlorate. The sample gases were concentrated on a cold-trap consisting of a 1/16" OD stainless steel tube with a 2.5 cm section packed tightly with Porapak Q (60-80 mesh), a 22 cm section packed with Carboxen 1000, and a 2.5 cm section packed with molecular sieve MS5A. A Neslab Cryocool CC-100 was used to cool the trap to ~-70°C. After 6 minutes of purging, the trap was isolated, and it was heated electrically to ~160°C. The sample gases held in the trap were then injected onto a precolumn (~60 cm of 1/8" O.D. stainless steel tubing packed with 80-100 mesh Porasil B, held at 80°C) for the initial separation of CFC-12, CFC-11, SF_6 and CCl_4 from later eluting peaks.

After the SF_6 and CFC-12 had passed from the pre-column and into the second precolumn (5 cm of 1/8" O.D. stainless steel tubing packed with MS5A, 90°C) and into the analytical column #1 (240 cm of 1/8" OD stainless steel tubing packed with MS5A and held at 80°C), the outflow from the first precolumn was diverted to the second analytical column (150 cm 1/8" OD stainless steel tubing packed with Carbograph 1AC, 80-100 mesh, held at 90°C). After CFC-11 had passed through the first pre-column, the flow was diverted to a third analytical column (1.7 m , Carbograph 1AC, 90°C). The gases remaining after CCl_4 had passed through the first pre-column, were backflushed from the pre-column and vented. Column #1 and the first pre-column were held in a Shimadzu GC8 gas chromatograph with an electron capture detector (ECD) held at 340^{o}C. Column #2, column #3 and the second precolumn were in another Shimadzu GC8 gas chromatograph with ECD. The output from column #3 was plumbed to a Shimadzu Mini2 gas chromatograph with the ECD held at 250^{o}C. This was done, because the temperature control of the Mini2 was not adequate for this analysis. On the stations in which nitrous oxide was analyzed, the content of the second precolumn was directed to column #3. This prevented the analysis of carbon tetrachloride on those samples.

The analytical system was calibrated frequently using a standard gas of known CFC/SF_6 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. Four 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/SF_6 free gas) were injected and analyzed in a similar manner. The typical analysis time for seawater, air, standard or blank samples was ~11 minutes.

Concentrations of CFC-11, CFC-12 and CCl_4 in air, seawater samples, and gas standards are reported relative to the SIO98 calibration scale (Cunnold et al., 2000). Concentrations of SF_6 in air, seawater samples, and gas standards are reported relative to the SIO2005 calibration scale. Concentrations of CFC/SF_6 in air and standard gas are reported in units of mole fraction CFC/SF_6 in dry gas, and are typically in the parts per trillion (ppt) range. Dissolved CFC and CCl_4 concentrations are given in units of picomoles per kilogram seawater (pmol kg^{-1}) and SF_6 concentrations in fmol kg^{-1}. CFC/SF_6 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 (PMEL cylinder 72611) into the analytical instrument. The response of the detector to the range of moles of CFC/SF_6 passing through the detector remained relatively constant during the cruise. Full-range calibration curves were run at intervals of 4-5 days during the cruise. Single injections of a fixed volume of standard gas at one atmosphere were run much more frequently (at intervals of ~90 minutes) to monitor short-term changes in detector sensitivity.

The purging efficiency was estimated by re-purging a high-concentration water sample and measuring this residual signal. At a flow rate of 150 cc min^{-1} for 6 minutes, the purging efficiency for CFC-11, CFC-12 and SF_6 was about 99% or higher. N_2O had an efficiency of about 90% and carbon tetrachloride about 96%.

On this expedition, based on the analysis more than 200 pairs of duplicate samples, we estimate precisions (1 standard deviation) of about 1% or 0.002 pmol kg^{-1}.(whichever is greater) for both dissolved CFC-11 and CFC-12 measurements. The estimated precision for SF_6 was 2% or 0.02 fmol kg^{-1}, (whichever is greater) and 2% or 0.005 pmol kg^{-1} for carbon tetrachloride. The estimated precision of N_2O, based on 23 pairs of duplicate samples is less than 3%. Overall accuracy of the measurements (a function of the absolute accuracy of the calibration gases, volumetric calibrations of the sample gas loops and purge chamber, errors in fits to the calibration curves and other factors) is estimated to be about 2% or 0.004 pmol kg^{-1} for CFC-11 and CFC-12 and 4% or 0.04 fmol kg^{-1} for SF_6 and about 5% for N_2O and CCl_4.

A small number of water samples had anomalously high CFC/SF_6 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/SF_6 during the sampling or analysis processes.

Measured concentrations for these anomalous samples are included in the data file, but are given a quality flag value of either 3 (questionable measurement) or 4 (bad measurement). Less than 2% of samples were flagged as bad or questionable during this voyage. A quality flag of 5 was assigned to samples which were drawn from the rosette but never analyzed due to a variety of reasons (e.g., leaking stopcock, plunger jammed in syringe barrel, etc).

References

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Bullister, J.L., and D.P. Wisegarver (2008): The shipboard analysis of trace levels of sulfur hexafluoride, chlorofluorocarbon-11 and chlorofluorocarbon-12 in seawater. Deep-Sea Res. I, 55, 1063–1074. [PDF Version]

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Air Measurements

Lat	**Lon**	**SF6**	**f**	**F12**	**f**	**F11**	**f**	**F113**	**f**	**Ccl4**	**f**	**N2O**	**f**
deg	**deg**	**ppt**		**ppt**		**ppt**		**ppt**		**ppt**		**ppb**	
-54.0	0.0	6.80	2	531.9	2	247.6	2	75.3	2	82.7	2	-9	5
-45.0	1.2	6.77	2	532.4	2	238.4	2	-9.0	5	-9.0	5	-9	5
-41.6	1.9	6.67	2	531.7	2	250.2	2	74.9	2	111.5	4	-9	5
-38.5	1.0	6.69	2	532.7	2	242.9	2	-9.0	5	-9.0	5	-9	5
-36.0	1.0	6.64	2	530.4	2	241.8	2	78.2	2	104.8	4	-9	5
-26.0	1.6	6.78	2	532.4	2	241.6	2	77.5	2	95.9	4	-9	5
-18.5	1.2	6.75	2	529.6	2	241.8	2	77.3	2	88.9	2	-9	5
-7.5	-1.2	6.68	2	522.1	2	242.8	2	-9.0	5	-9.0	5	-9	5
-6.0	-2.4	6.96	2	529.6	2	250.9	2	78.3	2	85.1	2	-9	5
-2.3	-3.0	6.62	2	523.3	2	245.1	2	-9.0	5	-9.0	5	-9	5
4.7	-3.0	6.56	2	524.7	2	244.9	2	-9.0	5	-9.0	5	339	2

Table of replicated samples

sta	samp	F11	ff11	F12	ff12	F13	ff13	tet	ftet	sf6	fsf6
998	101	0.151	2	0.073	2	0.000	2	0.000	2		
998	101	0.153	2	0.071	2	0.000	2	0.000	2		
998	103	0.139	2	0.067	2	0.000	2	0.000	2		
998	103	0.087	3	0.027	4	0.000	2	0.000	2		
998	119	1.086	2	0.523	2	0.000	2	0.000	2		
998	119	1.085	2	0.523	2	0.000	2	0.000	2		
998	122	3.073	2	1.537	2	0.000	2	0.000	2		
998	122	1.329	2	1.296	2	0.000	2	0.000	2		
1	102	0.425	2	0.200	2	0.027	2	0.678	2	0.108	2
1	102	0.426	2	0.200	2	0.026	2	0.660	2	0.074	3
1	109	0.375	2	0.187	2	0.028	2	0.549	2	0.104	2
1	109	0.375	2	0.184	2	0.027	2	0.550	2	0.103	2
1	123	5.668	2	3.022	2	0.530	2	7.918	2	2.446	2
1	123	5.678	2	3.022	2	0.532	2	7.964	2	2.519	2
2	122	5.706	2	3.042	2	0.529	2	7.704	2	2.568	2
2	122	5.708	2	3.028	2	0.534	2	7.785	2	2.501	2
2	105	0.443	2	0.211	2	0.028	2	0.662	2	0.053	2
2	105	0.444	2	0.211	2	0.030	2	0.692	2	0.000	2
3	102	0.398	2	0.191	2	0.027	2	0.643	2	0.000	2
3	102	0.395	2	0.190	2	0.026	2	0.635	2	0.000	2
3	123	5.680	2	3.028	2	0.527	2	7.875	2	2.627	2
3	123	5.676	2	3.012	2	0.526	2	7.948	2	2.584	2
5	122	5.389	2	2.909	2	0.503	2	7.224	2	2.448	2
5	122	5.468	4	2.917	2	0.506	2	7.602	4	2.586	2
5	103	0.399	2	0.179	2	0.016	2	0.374	2	0.000	2
5	103			0.183	2	0.027	2	0.492	2		
6	104	0.290	2	0.135	2	0.019	2	0.392	2	0.000	2
6	104	0.312	2	0.148	2	0.020	2	0.435	2	0.000	2
6	120	5.569	2	2.928	2	0.514	2	7.522	2	2.297	2
6	120	5.236	2	2.818	2	0.487	2	7.690	2	2.248	2
8	103	0.368	2	0.172	2	0.021	2	0.648	2	0.047	2
8	103	0.369	2	0.172	2	0.023	2	0.650	2	0.000	2
8	122	4.948	2	2.588	2	0.439	2	6.557	2	2.000	2
8	122	4.916	2	2.587	2	0.437	2	6.665	2	1.969	2
9	122	5.131	2	2.767	2	0.477	2	7.201	2	2.312	2
9	122	5.145	2	2.762	2	0.476	2	7.222	2	2.373	2
10	101	0.439	2	0.202	2	0.030	2	0.727	2	0.000	2
10	101	0.447	2	0.208	2	0.032	2	0.747	2	0.124	2
10	124	4.531	2	2.477	2	0.416	2	6.759	2	2.102	2
10	124	4.508	2	2.482	2	0.413	2	6.474	2	2.005	2
11	103	0.389	2	0.181	2	0.025	2	0.668	2	0.056	2
11	103	0.387	2	0.182	2	0.025	2	0.663	2	0.000	2
11	122	4.986	2	2.696	2	0.458	2	6.976	2	2.177	2
11	122	4.982	2	2.706	2	0.458	2	6.933	2	2.188	2
12	103	0.331	2	0.156	2	0.020	2	0.600	2	0.062	3
12	103	0.332	2	0.154	2	0.019	2	0.591	2		
12	122	4.876	2	2.676	2	0.458	2	6.786	2	2.235	2
12	122	4.883	2	2.689	2	0.000	2	0.002	4	2.250	2
13	103	0.391	2	0.184	2	0.024	2	0.678	2	0.000	2
13	103	0.397	2	0.188	2	0.025	2	0.672	2	0.061	3
13	122	4.471	2	2.509	2	0.426	2	6.475	2	2.183	2
13	122	4.470	2	2.502	2	0.428	2	6.511	2	2.203	2
14	123	4.183	2	2.377	2	0.395	2	5.952	2	2.080	2
14	123	4.168	2	2.371	2	0.398	2	5.937	2	2.078	2

sta	samp	F11	ff11	F12	ff12	F13	ff13	tet	ftet	sf6	fsf6
15	119	3.698	2	1.941	2	0.306	2	4.841	2	1.196	2
15	119	3.709	2	1.947	2	0.307	2	4.795	2	1.168	2
16	103	0.253	2	0.119	2	0.015	2	0.458	2	0.038	2
16	103	0.255	2	0.122	2	0.017	2	0.463	2	0.075	3
16	122	4.392	2	2.495	2	0.413	2	5.917	2	2.211	2
16	122	4.390	2	2.492	2	0.413	2	5.731	2	2.188	2
17	122	4.109	2	2.344	2	0.383	2	5.443	2	2.016	2
17	122	4.107	2	2.349	2	0.384	2	5.436	2	2.000	2
18	103	0.248	2	0.120	2	0.017	2	0.418	2	0.035	2
18	103	0.247	2	0.119	2	0.016	2	0.414	2	0.041	2
19	122	3.514	2	2.049	2	0.000	2	0.000	2	1.847	2
19	122	3.530	2	2.085	2	0.000	2	0.000	2	1.763	2
19	103	0.180	2	0.089	2	0.000	2	0.000	2	0.062	2
19	103	0.180	2	0.089	2	0.000	2	0.000	2	0.000	2
20	103	0.188	2	0.088	2	0.012	2	0.430	2	0.030	2
20	103	0.197	2	0.094	2	0.013	2	0.424	2		
22	122	3.482	2	1.993	2	0.311	2	4.207	2	1.764	2
22	122	3.467	2	1.993	2	0.312	2	4.113	2	1.767	2
23	122	3.417	2	1.973	2	0.308	2	3.946	2	1.788	2
23	122	3.437	2	1.973	2	0.307	2	4.076	2	1.776	2
23	103	0.069	2	0.033	2	0.004	2	0.172	2	0.000	2
23	103	0.069	2	0.033	2	0.008	2	0.177	2	0.000	2
24	103	0.067	2	0.033	2	0.006	2	0.168	2	0.000	2
24	103	0.066	2	0.032	2	0.006	2	0.165	2	0.000	2
24	122	3.336	2	1.924	2	0.299	2	3.872	2	1.702	2
24	122	3.338	2	1.924	2	0.301	2	3.965	2	1.711	2
25	101	2.841	2	1.414	2	0.201	2	3.600	2	0.679	2
25	101	2.857	2	1.420	2	0.203	2	3.663	2	0.691	2
26	103	0.057	2	0.026	2	0.005	2	0.177	2	0.000	2
26	103	0.054	2	0.025	2	0.003	2	0.170	2	0.000	2
27	102	0.100	2	0.045	2	0.004	2	0.276	2	0.000	2
27	102	0.107	2	0.051	2	0.006	2	0.279	2	0.000	2
27	121	3.499	2	2.003	2	0.287	2	2.956	2	1.648	2
27	121	3.513	2	2.004	2	0.286	2	3.008	2	1.700	2
28	122	3.240	2	1.861	2	0.293	2	3.883	2	1.708	2
28	122	3.226	2	1.873	2	0.293	2	3.826	2	1.649	2
28	103	0.079	2	0.037	2	0.005	2	0.215	2	0.000	2
28	103	0.079	2	0.038	2	0.004	2	0.210	2	0.044	3
29	122	3.138	2	1.831	2	0.255	2	2.009	2	1.595	2
29	122	3.133	2	1.828	2	0.256	2	2.018	2	1.557	2
30	124	2.757	2	1.635	2	0.242	2	3.147	2	1.473	2
30	124	2.784	2	1.642	2	0.247	2	3.207	2	1.583	2
31	103	0.067	2	0.032	2	0.004	2	0.192	2	0.000	2
31	103	0.067	2	0.033	2	0.005	2	0.187	2	0.037	2
31	122	2.963	2	1.740	2	0.263	2	3.117	2	1.567	2
31	122	2.790	2	1.652	2	0.245	2	3.162	2	1.504	2
32	122	3.226	2	1.901	2	0.000	2	0.000	2	1.680	2
32	122	3.232	2	1.904	2	0.000	2	0.000	2	1.730	2
32	103	0.078	2	0.038	2	0.004	2	0.237	2	0.000	2
32	103	0.078	2	0.038	2	0.004	2	0.235	2	0.018	2
33	103	0.048	2	0.024	2	0.004	2	0.147	2	0.010	2
33	103	0.048	2	0.024	2	0.005	2	0.137	2	0.000	2
33	111	0.706	2	0.341	2	0.040	2	1.126	2	0.149	2
33	111	0.703	2	0.340	2	0.039	2	1.138	2	0.115	2
34	107	0.016	2	0.009	2	0.004	2	0.058	2	0.000	2
34	107	0.015	2	0.007	2	0.002	2	0.057	2	0.000	2

sta	samp	F11	ff11	F12	ff12	F13	ff13	tet	ftet	sf6	fsf6
35	122	2.812	2	1.692	2	0.244	2	2.460	2	1.470	2
35	122	2.806	2	1.648	2	0.240	2	2.477	2		
36	122	2.597	2	1.538	2	0.216	2	2.055	2	1.373	2
36	122	2.601	2	1.545	2	0.217	2	2.058	2	1.400	2
36	107	0.016	2	0.009	2	0.003	2	0.082	2	0.027	2
36	107	0.016	2	0.008	2	0.003	2	0.073	2	0.000	2
37	107	0.018	2	0.009	2	0.002	2	0.092	2	0.000	2
37	107	0.019	2	0.009	2	0.002	2	0.083	2	0.000	2
37	122	2.554	2	1.520	2	0.208	2	1.908	2	1.337	2
37	122	2.552	2	1.518	2	0.208	2	1.903	2	1.367	2
38	121	2.725	2	1.600	2	0.184	2	1.761	2	1.363	2
38	121	2.726	2	1.597	2	0.183	2	1.781	2	1.352	2
39	103	0.065	2	0.031	2	0.006	2	0.222	2	0.000	2
39	103	0.063	2	0.030	2	0.005	2	0.185	2	0.000	2
39	123	2.342	2	1.394	2	0.205	2	2.840	2	1.284	2
39	123	2.342	2	1.392	2	0.206	2	2.834	2	1.355	2
40	121	2.601	2	1.543	2	0.184	2	1.853	2	1.435	2
40	121	2.603	2	1.542	2	0.194	2	1.769	2	1.400	2
41	107	0.040	2	0.017	2	0.003	2	0.134	2	0.000	2
41	107	0.039	2	0.017	2	0.002	2	0.094	2	0.000	2
41	122	2.542	2	1.514	2	0.199	2	2.100	2	0.000	2
41	122	2.379	2	1.413	2	0.210	2	2.432	2	1.384	2
42	122	2.527	2	1.491	2	0.199	2	2.076	2	1.351	2
42	122	2.532	2	1.497	2	0.200	2	2.012	2	1.395	2
42	103	0.058	2	0.027	2	0.003	2	0.170	2	0.000	2
42	103	0.057	2	0.027	2	0.004	2	0.165	2	0.000	2
43	103	0.033	2	0.016	2	0.005	2	0.102	2	0.000	2
43	103	0.032	2	0.016	2	0.003	2	0.099	2	0.000	2
43	122	2.434	2	1.449	2	0.206	2	2.265	2	1.361	2
43	122	2.429	2	1.448	2	0.205	2	2.286	2	1.374	2
44	122	2.496	2	1.530	2	0.215	2	2.794	2	1.444	2
44	122	2.500	2	1.497	2	0.211	2	2.779	2		
45	103	0.016	2	0.010	2	0.005	2	0.078	2	0.037	2
45	103	0.015	2	0.010	2	0.003	2	0.083	2	0.000	2
45	122	2.371	2	1.421	2	0.179	2	2.114	2	1.267	2
45	122	2.355	2	1.416	2	0.179	2	2.128	2	1.278	2
46	120	2.543	2	1.520	2	0.181	2	1.725	2	1.358	2
46	120	2.543	2	1.518	2	0.181	2	1.676	2	1.317	2
46	104	0.011	2	0.005	2	0.003	2	0.043	2	0.000	2
46	104	0.004	2	0.004	2	0.002	2	0.027	2	0.000	2
47	103	0.014	2	0.009	2	0.002	2	0.062	2	0.000	2
47	103	0.014	2	0.010	2	0.001	2	0.067	2	0.040	2
47	122	2.528	2	1.507	2	0.206	2	2.370	2	1.360	2
47	122	2.525	2	1.510	2	0.206	2	2.352	2	1.327	2
48	120	2.733	2	1.647	2	0.000	2	0.000	2	1.296	2
48	120	2.727	2	1.646	2	0.000	2	0.000	2	1.340	2
49	122	2.027	2	1.244	2	0.182	2	2.925	2	1.185	2
49	122	2.023	2	1.238	2	0.182	2	2.768	2	1.160	2
49	107	0.023	2	0.012	2	0.004	2	0.096	2	0.000	2
49	107	0.024	2	0.012	2	0.004	2	0.098	2	0.018	2
50	124	2.010	2	1.234	2	0.183	2	2.858	2	1.183	2
50	124	2.019	2	1.245	2	0.186	2	2.840	2	1.242	2
51	122	2.570	2	1.546	2	0.208	2	1.886	2	1.385	2
51	122	2.583	2	1.548	2	0.207	2	1.802	2	1.397	2
52	122	2.530	2	1.508	2	0.217	2	2.424	2	1.382	2
52	122	2.538	2	1.520	2	0.217	2	2.464	2	1.494	2

sta	samp	F11	ff11	F12	ff12	F13	ff13	tet	ftet	sf6	fsf6
53	122	2.624	2	1.567	2	0.196	2	1.788	2	1.393	2
53	122	2.631	2	1.572	2	0.197	2	1.735	2	1.385	2
53	107	0.007	2	0.007	2	0.004	2	0.042	2	0.040	2
53	107	0.006	2	0.006	2	0.003	2	0.043	2	0.000	2
54	104	0.001	2	0.003	2	0.003	2	0.011	2	0.017	2
54	104	0.002	2	0.004	2	0.003	2	0.011	2	0.030	2
55	122	2.620	2	1.564	2	0.199	2	1.682	2	1.405	2
55	122	2.602	2	1.546	2	0.196	2	1.651	2	1.397	2
56	120	2.727	2	1.591	2	0.167	2	1.691	2	1.400	2
56	120	2.721	2	1.565	2	0.165	2	1.785	2	1.447	2
57	105	0.002	2	0.003	2	0.003	2	0.016	2	0.016	2
57	105	0.002	2	0.002	2	0.003	2	0.015	2	0.000	2
58	120	2.836	2	1.604	2	0.066	2	0.952	2	1.299	2
58	120	2.833	2	1.598	2	0.067	2	0.999	2	1.246	2
59	122	2.577	2	1.493	2	0.199	2	2.056	2	1.346	2
59	122	2.574	2	1.488	2	0.198	2	1.959	2	1.373	2
59	103	0.002	2	0.002	2	0.002	2	0.009	2	0.000	2
59	103	0.008	4	0.006	4	0.003	2	0.023	2	0.000	2
60	122	2.481	2	1.472	2	0.000	2	0.000	2	1.400	2
60	122	2.478	2	1.475	2	0.000	2	0.000	2	1.392	2
61	107	0.009	2	0.006	2	0.003	2	0.063	2	0.000	2
61	107	0.007	2	0.004	2	0.004	2	0.058	2	0.000	2
61	122	2.445	2	1.436	2	0.209	2	2.141	2	1.398	2
61	122	2.444	2	1.432	2	0.206	2	2.115	2	1.354	2
62	105	0.003	2	0.002	2	0.008	2	0.025	2	0.566	2
62	105					0.004	2	0.014	2	0.000	2
63	103	0.004	2	0.004	2	0.002	2	0.018	2	0.000	2
63	103										
63	122	2.568	2	1.496	2	0.191	2	1.435	2	1.398	2
63	122	2.567	2	1.495	2	0.190	2	1.456	2	1.338	2
64	118	0.990	2	0.499	2	0.041	2	0.861	2	0.176	2
64	118	0.994	2	0.498	2	0.042	2	0.887	2	0.170	2
65	121	2.906	2	1.641	2	0.071	2	0.999	2	1.213	2
65	121	2.906	2	1.644	2	0.072	2	0.981	2	1.225	2
65	104	0.001	2	0.001	2	0.002	2	0.014	2	0.000	2
65	104	0.003	2	0.002	2	0.002	2	0.016	2	0.000	2
66	122	2.550	2	1.491	2	0.192	2	1.539	2	1.362	2
66	122	2.555	2	1.490	2	0.192	2	1.544	2	1.313	2
67	103	0.003	2	0.003	2	0.000	2	0.000	2	0.000	2
67	103					0.000	2	0.000	2	0.000	2
67	122	2.415	2	1.446	2	0.000	2	0.000	2	1.257	2
67	122	2.416	2	1.442	2	0.000	2	0.000	2	1.329	2
68	122	2.326	2	1.383	2	0.199	2	2.038	2	1.300	2
68	122	2.325	2	1.384	2	0.197	2	1.931	2	1.264	2
69	106	0.002	2	0.002	2	0.003	2	0.011	2	0.000	2
69	106	0.002	2	0.001	2	0.003	2	0.010	2	0.000	2
69	121	2.706	2	1.560	2	0.090	2	0.847	2	1.221	2
69	121	2.694	2	1.550	2	0.090	2	0.894	2	1.250	2
70	122	2.364	2	1.396	2	0.188	2	1.921	2	1.275	2
70	122	2.377	2	1.399	2	0.186	2	1.796	2	1.268	2
71	108	0.003	2	0.002	2	0.003	2	0.013	2	0.000	2
71	108	0.003	2	0.003	2	0.002	2	0.031	2	0.000	2
71	122	2.576	2	1.481	2	0.103	2	0.705	2	1.224	2
71	122	2.590	2	1.478	2	0.103	2	0.748	2	1.087	2

sta	samp	F11	ff11	F12	ff12	F13	ff13	tet	ftet	sf6	fsf6
72	103	0.002	2	0.003	2	0.002	2	0.026	2	0.000	2
72	103	0.002	2	0.002	2	0.002	2	0.024	2	0.063	3
72	314	0.747	2	0.402	2	0.000	2	0.000	2	0.097	2
72	314	0.761	2	0.412	2	0.000	2	0.000	2	0.120	2
72	318	2.087	2	1.158	2	0.000	2	0.000	2	0.603	2
72	318	2.091	2	1.156	2	0.000	2	0.000	2	0.652	2
73	122	2.527	2	1.482	2	0.154	2	1.349	2	1.262	2
73	122	2.528	2	1.475	2	0.153	2	1.275	2	1.288	2
73	103	0.003	2	0.003	2	0.003	2	0.019	2	0.000	2
73	103	0.110	4	0.332	4	0.040	4	0.039	4	4.382	4
74	107	0.001	2	0.000	2	0.002	2	0.013	2	0.000	2
74	107	0.001	2	0.000	2	0.002	2	0.004	2	0.000	2
74	124	1.787	2	1.096	2	0.158	2	2.303	2	1.137	2
74	124	1.788	2	1.093	2	0.159	2	2.303	2	1.097	2
75	122	2.211	2	1.168	2	0.038	2	0.499	2	0.585	2
75	122	2.076	2	1.090	2	0.036	2	0.439	2	0.558	2
75	103	0.003	2	0.003	2	0.002	2	0.041	2	0.000	2
75	103	0.003	2	0.003	2	0.002	2	0.039	2	0.000	2
76	101	0.009	2	0.006	2	0.002	2	0.065	2	0.000	2
76	101	0.007	2	0.005	2	0.003	2	0.054	2	0.000	2
76	122	2.629	2	1.419	2	0.042	2	0.595	2	0.836	2
76	122	2.628	2	1.419	2	0.041	2	0.595	2	0.818	2
77	105	0.002	2	0.002	2	0.001	2	0.010	2	0.000	2
77	105	0.003	2	0.002	2	0.003	2	0.011	2	0.000	2
77	123	2.332	2	1.382	2	0.191	2	1.735	2	1.256	2
77	123	2.356	2	1.398	2	0.194	2	1.787	2	1.311	2
78	122	2.239	2	1.269	2	0.000	2	0.000	2	0.775	2
78	122	2.239	2	1.270	2	0.000	2	0.000	2	0.811	2
80	105	0.003	2	0.002	2	0.003	2	0.019	2	0.000	2
80	105	0.003	2	0.002	2	0.004	2	0.018	2	0.000	2
80	122	2.214	2	1.314	2	0.165	2	1.558	2	1.233	2
80	122	2.216	2	1.312	2	0.164	2	1.552	2	1.171	2
82	109	0.001	2	0.001	2	0.003	2	0.016	2	0.000	2
82	109	0.002	2	0.002	2	0.003	2	0.015	2	0.000	2
82	222	2.255	2	1.330	2	0.156	2	1.441	2	1.117	2
82	222	2.248	2	1.321	2	0.156	2	1.457	2	1.108	2
83	122	1.702	2	0.904	2	0.022	2	0.321	2	0.360	2
83	122	1.700	2	0.903	2	0.022	2	0.318	2	0.377	2
83	105	0.003	2	0.002	2	0.002	2	0.011	2	0.000	2
83	105	0.004	2	0.002	2	0.002	2	0.014	2	0.000	2
84	122	2.090	2	1.145	2	0.047	2	0.429	2	0.685	2
84	122	2.092	2	1.142	2	0.049	2	0.435	2	0.655	2
85	120	1.434	2	0.754	2	0.012	2	0.245	2	0.292	2
85	120	1.437	2	0.756	2	0.014	2	0.233	2	0.399	2
85	105	0.003	2	0.004	2	0.003	2	0.026	2	0.000	2
85	105	0.004	2	0.008	3	0.004	2	0.029	2	0.000	2
86	105	0.003	2	0.003	2	0.000	2	0.000	2	0.000	2
86	105	0.003	2	0.003	2	0.000	2	0.000	2	0.000	2
86	122	2.029	2	1.154	2	0.000	2	0.000	2	0.700	2
86	122	2.026	2	1.161	2	0.000	2	0.000	2	0.683	2
87	105	0.004	2	0.004	2	0.003	2	0.031	2	0.000	2
87	105	0.002	2	0.003	2	0.002	2	0.029	2	0.000	2
87	122	2.148	2	1.246	2	0.114	2	0.965	2	0.979	2
87	122	2.147	2	1.244	2	0.115	2	1.041	2	0.916	2
88	124	1.574	2	0.990	2	0.138	2	1.936	2	1.029	2
88	124	1.577	2	0.991	2	0.138	2	2.000	2	0.990	2

sta	samp	F11	ff11	F12	ff12	F13	ff13	tet	ftet	sf6	fsf6
90	105	0.005	2	0.003	2	0.002	2	0.024	2	0.000	2
90	105	0.002	2	0.002	2	0.002	2	0.020	2	0.000	2
90	122	2.059	2	1.162	2	0.067	2	0.484	2	0.738	2
90	122	2.061	2	1.163	2	0.068	2	0.479	2	0.708	2
91	105	0.005	2	0.005	2	0.002	2	0.044	2	0.000	2
91	105	0.005	2	0.004	2	0.002	2	0.044	2	0.000	2
91	120	1.115	2	0.587	2	0.011	2	0.233	2	0.168	2
91	120	1.118	2	0.588	2	0.012	2	0.245	2	0.173	2
92	121	1.767	2	0.936	2	0.021	2	0.363	2	0.377	2
92	121	1.772	2	0.942	2	0.021	2	0.385	2	0.377	2
93	105	0.002	2	0.002	2	0.000	2	0.000	2	0.000	2
93	105	0.002	2	0.002	2	0.000	2	0.000	2	0.000	2
93	120	1.696	2	0.919	2	0.000	2	0.000	2	0.414	2
93	120	1.699	2	0.917	2	0.000	2	0.000	2	0.416	2
94	120	2.052	2	1.111	2	0.023	2	0.321	2	0.547	2
94	120	2.047	2	1.109	2	0.023	2	0.326	2	0.551	2
97	105	0.002	2	0.002	2	0.003	2	0.036	2	0.000	2
97	105	0.004	2	0.004	2	0.003	2	0.041	2	0.087	4
98	124	1.541	2	0.964	2	0.139	2	1.890	2	0.991	2
98	124	1.533	2	0.962	2	0.137	2	1.871	2	0.983	2
98	118	0.682	2	0.354	2	0.011	2	0.268	2	0.087	2
98	118	0.682	2	0.354	2	0.012	2	0.278	2	0.000	2
99	120	1.922	2	1.018	2	0.020	2	0.364	2	0.479	2
99	120	1.919	2	1.024	2	0.020	2	0.367	2	0.506	2
100	117	1.002	2	0.521	2	0.013	2	0.259	2	0.150	2
100	117	1.005	2	0.522	2	0.012	2	0.253	2	0.134	2
101	116	1.031	2	0.546	2	0.000	2	0.000	2	0.179	2
101	116	1.030	2	0.552	2	0.000	2	0.000	2	0.216	2
101	122	2.243	2	1.276	2	0.000	2	0.000	2	0.895	2
101	122	2.245	2	1.273	2	0.000	2	0.000	2	0.854	2
102	120	2.179	2	1.194	2	0.018	2	0.280	2	0.652	2
102	120	2.173	2	1.188	2	0.019	2	0.268	2	0.663	2
103	103	0.047	2	0.025	2	0.007	2	0.223	2	0.000	2
103	103	0.048	2	0.025	2	0.007	2	0.226	2	0.000	2
103	123	1.671	2	1.019	2	0.121	2	1.507	2	0.953	2
103	123	1.679	2	1.024	2	0.122	2	1.584	2	0.988	2
105	122	2.225	2	1.280	2	0.000	2	0.000	2	0.859	2
105	122	2.218	2	1.276	2	0.000	2	0.000	2	0.806	2
105	118	0.976	2	0.517	2	0.000	2	0.000	2	0.150	2
105	118	0.975	2	0.518	2	0.000	2	0.000	2	0.136	2
108	120	2.207	2	1.214	2	0.026	2	0.437	2	0.695	2
108	120	2.223	2	1.226	2	0.026	2	0.445	2	0.671	2
110	122	2.168	2	1.244	2	0.070	2	0.588	2	0.874	2
110	122	2.169	2	1.237	2	0.071	2	0.600	2	0.833	2
111	111	0.207	2	0.103	2	0.011	2	0.578	2	0.000	2
111	111	0.206	2	0.104	2	0.013	2	0.540	2	0.000	2
112	105	0.021	2	0.014	2	0.000	2	0.000	2	0.000	2
112	105	0.021	2	0.013	2	0.000	2	0.000	2	0.000	2
113	120	2.193	2	1.202	2	0.026	2	0.419	2	0.677	2
113	120	2.191	2	1.201	2	0.026	2	0.430	2	0.650	2
114	118	1.457	2	0.757	2	0.018	2	0.393	2	0.278	2
114	118	1.450	2	0.752	2	0.018	2	0.405	2	0.225	2
115	103	0.028	2	0.015	2	0.004	2	0.114	2	0.000	2
115	103	0.029	2	0.017	2	0.005	2	0.158	2	0.000	2

sta	samp	F11	ff11	F12	ff12	F13	ff13	tet	ftet	sf6	fsf6
116	120	1.462	2	0.928	2	0.126	2	1.794	2	1.007	2
116	120	1.466	2	0.932	2	0.126	2	1.881	2	1.028	2
117	120	1.875	2	1.015	2	0.014	2	0.263	2	0.501	2
117	120	1.884	2	1.015	2	0.013	2	0.301	2	0.409	2
118	105	0.017	2	0.010	2	0.005	2	0.132	2	0.000	2
118	105	0.018	2	0.010	2	0.004	2	0.115	2	0.000	2
120	102	0.019	2	0.008	3	0.005	2	0.083	2	0.000	2
120	102	0.019	2			0.006	2	0.080	2	0.000	2
121	121	2.259	2	1.239	2	0.033	2	0.455	2	0.756	2
121	121	2.177	2	1.184	2	0.018	2	0.356	2	0.623	2
121	105	0.002	2	0.004	2	0.005	2	0.029	2	0.000	2
121	105	0.004	2	0.004	2	0.004	2	0.023	2	0.000	2
122	110	0.020	2	0.013	2	0.000	2	0.000	2	0.000	2
122	110	0.020	2	0.013	2	0.000	2	0.000	2	0.000	2
122	120	1.118	2	0.603	2	0.000	2	0.000	2	0.173	2
122	120	1.117	2	0.601	2	0.000	2	0.000	2	0.187	2
123	123	2.101	2	1.219	2	0.000	2	0.000	2	0.839	2
123	123	2.103	2	1.222	2	0.000	2	0.000	2	0.804	2
124	124	1.427	2	0.924	2	0.000	2	0.000	2	0.937	2
124	124	1.424	2	0.924	2	0.000	2	0.000	2	0.951	2
125	119	0.756	2	0.405	2	0.000	2	0.000	2	0.173	2
125	119	0.758	2	0.398	2	0.000	2	0.000	2	0.181	2
126	120	2.099	2	1.164	2	0.016	2	0.213	2	0.663	2
126	120	2.087	2	1.161	2	0.015	2	0.211	2	0.668	2
128	109	0.024	2	0.014	2	0.000	2	0.000	2	0.000	2
128	109	0.027	2	0.015	2	0.000	2	0.000	2	-0.010	2
128	119	1.565	2	0.860	2	0.000	2	0.000	2	0.341	2
128	119	1.168	2	0.636	2	0.000	2	0.000	2	0.189	2
129	117	1.224	2	0.660	2	0.000	2	0.000	2	0.167	2
129	117	1.226	2	0.664	2	0.000	2	0.000	2	0.154	2

Helium and Tritium

No documentation was submitted by the Helium/Tritium group. Contact information for this group can be found in the major programs and cruise participants tables.

Dissolved Oxygen Analysis

Equipment and Techniques

Dissolved oxygen analyses were performed with an automated oxygen titrator using amperometric end-point detection [Culb87]. The titration of the samples and the data logging and graphical display was performed on a PC running a LabView program written by Ulises Rivero of AOML. The titrations were performed in a climate-controlled lab at 18.5-22.5oC. Thiosulfate was dispensed by a 2 ml Gilmont syringe driven with a stepper motor controlled by the titrator. Tests in the lab were performed to confirm that the precision and accuracy of the volume dispensed were comparable or superior to the Dosimat 665. The whole-bottle titration technique of Carpenter [Carp65], with modifications by Culberson et al. [Culb91], was used. Four replicate 10 ml iodate standards were run every 3-4 days. The reagent blank determined as the difference between V1 and V2, the volumes of thiosulfate required to titrate 1-ml aliquots of the iodate standard, was determined five times during the cruise. This method was found during pre-cruise testing to produce a more reproducible blank value than the value determined as the intercept of a standard curve. The temperature-corrected molarity of the thiosulfate titrant was determined as given by Dickson [Dick94].

Sampling and Data Processing

Dissolved oxygen samples were drawn from Niskin bottles into calibrated 125-150 ml iodine titration flasks using silicon tubing to avoid contamination of DOC and CDOM samples. Bottles were rinsed three times and filled from the bottom, overflowing three volumes while taking care not to entrain any bubbles. The draw temperature was taken using a digital thermometer with a flexible thermistor probe that was inserted into the flask while the sample was being drawn during the overflow period. These temperatures were used to calculate umol/kg concentrations, and a diagnostic check of Niskin bottle integrity. 1 ml of MnCl sub 2 and 1 ml of NaOH/NaI were added immediately after drawing the sample was concluded using a Re-pipetor, the flasks were then stoppered and shaken well. DIW was added to the neck of each flask to create a water seal. 24 samples plus two duplicates were drawn from each station, depending on which rosette was used. The total number of samples collected from the rosette was xxx.

The flasks were stored in the lab in plastic totes at room temperature for 1.5 hours before analysis, and the data were incorporated into the cruise database shortly after analysis.

Thiosulfate normalities were calculated from each standardization and corrected to the laboratory temperature.

Volumetric Calibration

The dispenser used for the standard solution (SOCOREX Calibrex 520) and the burette were calibrated gravimetrically just before the cruise. Oxygen flask volumes were determined gravimetrically with degassed deionized water at AOML. The correction for buoyancy was applied. Flask volumes were corrected to the draw temperature.

Duplicate Samples

A total of xxx sets of duplicates were run. The average standard deviation of all sets was 0.18 umol/kg.

Problems

Three oxygen flasks were removed and replaced with different flasks during the cruise, after giving consistently high values. Duplicates were collected using each questionable flask and analyzed; if the values differed significantly, the flask was removed. The following flasks were tested and replaced:

Original Flask	Replacement Flask	Replaced After Station
13	83	16
42	82	16
52	92	16

References

Carp65.

Carpenter, J. H., "The Chesapeake Bay Institute technique for the Winkler dissolved oxygen method," Limnology and Oceanography, 10, pp. 141-143 (1965).

Culb87.

Culberson, C. H. and Huang, S., "Automated amperometric oxygen titration," Deep-Sea Res., 34, pp. 875-880. (1987).

Culb91.

Culberson, C. H., Knapp, G., Stalcup, M., Williams, R. T., and Zemlyak, F., "A comparison of methods for the determination of dissolved oxygen in seawater," Report WHPO 91-2, WOCE Hydrographic Programme Office (Aug. 1991).

Dick94.

Dickson, A. G., "Determination of dissolved oxygen in seawater by Winkler titration," WHP Operations and Methods (1994a).

PH_T (Adam Radich and Yuichiro Takeshita)

During this A13.5 CLIVAR cruise, approximately 3300 water samples were drawn and analyzed from rosette casts at 129 stations and 1 test station. Samples were analyzed using the method described in Dickson et al[1]. Analyses were made with an Agilent 8453 spectrophotometer equipped with a 10 cm jacketed flow cell using the sulfonephthalein indicator m-cresol purple (mCP). Results are reported on the total hydrogen ion scale. Sample introduction to the cell and dye addition were automated using a Kloehn V6 syringe pump.

All stations were sampled on the cruise, and the sampling scheme was to sample every bottle where an alkalinity or total carbon measurement was taken in order to generate a complete characterization of the carbon system. This resulted in full coverage of all tripped bottles. Samples were drawn from Niskin bottles on the rosette using silicone tubing into 300 mL Pyrex glass serum bottles. The serum bottles were rinsed three times, filled and allowed to overflow by one additional bottle volume. The bottles were poisoned with 0.02% saturated HgCl2 solution and capped with a rubber stopper without allowing any headspace. Analyses were completed within three hours of sampling. Prior to measurement, samples were brought to 20°C by partially submerging the serum bottles in a Neslab RTE7 temperature bath for 16 minutes.

Data precision was evaluated by analysis of duplicate samples (multiple samples from the same Niskin bottle on the rosette). The pooled standard deviation of the ~450 duplicate analyses is 0.0007 pH units.

Accuracy of spectrophotometric pH measurements is difficult to constrain with no agreed upon calibration procedure. For this cruise two approaches were made. First, since both total alkalinity and total carbon were measured on the same Niskin bottles as pH, an independent estimate of pH can be obtained from equilibrium equations. However, there are uncertainties involved in these calculations, and the pH can only be calculated accurately to 0.01 pH units. Second, pH analyses of 25 Certified Reference Materials (currently only certified for DIC and alkalinity) were performed. A review of the accuracy of the pH measurements is currently underway, and large changes (~0.01) in the final reported values are likely. Despite these uncertainties, confidence in the precision of the measurements remains high. Any changes will most likely be the addition of constant or an offset based on a function of pH.

No correction for HgCl2 addition has been made for the reported preliminary pH values. However, previous experiments suggest a very small correction for HgCl2 (~0.0003 pH unit increase) might be appropriate for all measured values.

REFERENCE:

Dickson, A.G., Sabine, C.L. and Christian, J.R. (Eds.), (2007): Guide to Best Practices for Ocean CO2 Measurements.

Discrete pCO_2

Samples were drawn from the Niskin bottles into 500 ml volumetric flasks for measurement of the partial pressure of the dissolved carbon dioxide (pCO_2). The samples were drawn using a Tygon© tube with a short length of silicone tubing to fit over the petcock to avoid contamination of CDOM samples. The flasks were rinsed while inverted and then filled from the bottom, overflowing half a volume while taking care not to entrain any bubbles. About 5 ml of water was withdrawn with a pipette to allow for expansion of the water as it warms and to provide space for the stopper, tubing, and frit of the analytical system. Mercuric chloride solution (0.244 ml at half-saturation) was added as a preservative. The sample flasks were sealed with a screw cap containing a polyethylene liner. The samples were stored in coolers at air-conditioned room temperature generally for no more than 4 hours.

All analyses were done at 20°C. A secondary bath was used to get the samples close to the analytical temperature prior to analysis. As soon as space was available in the secondary or primary bath, sample flasks were moved into the more controlled temperature bath. No flask was analyzed without spending at least 1.5 hours in these water baths.

The discrete pCO_2 system is patterned after the instrument described in Chipman et al. (1991) 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 and current instrument uses a LI-COR© model 6262 non-dispersive infrared analyzer, while the Chipman instrument utilizes a gas chromatograph with a flame ionization detector.

Once the samples reach the analytical temperature, a □50-ml headspace is created by displacing the water using a compressed standard gas with a CO2 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 concentrations. The samples are equilibrated until the running mean of 20 consecutive 1-second readings from the analyzer differ by less than 0.1 ppm (parts per million by volume). This equilibration takes about 10 minutes. An expandable volume in the circulation loop near the flask consisting of a small, deflated balloon keeps the headspace of the flask at ambient pressure.

In order to ensure analytical accuracy, a set of six gas standards is run through the analyzer before and after every eight seawater samples. cylinder serial numbers:

CA5998 [205.07 ppm]
CA5989 [378.71 ppm]
CA5988 [593.64 ppm]
CA5980 [792.51 ppm]
CA5984 [1036.95 ppm]
CA5940 [1533.7 ppm]

The standards were obtained from Scott-Marin and referenced against primary standards purchased from C.D. Keeling in 1991, which are on the WMO-78 scale.

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, the barometric pressure, and the changes induced in the carbonate equilibrium by the mass transfer of CO_2 in or out of the water sample are made. The corrected results are reported at a reference temperature of 20°C.

At the beginning of the cruise one of the gas circulation channels was performing at an acceptable, though not optimal flow rate. The equilibrations were requiring more time than in the other channel. Efforts were made over two days to improve the flow rate in the slow channel. The flows improved significantly after station 41. With continuous use of the pumps, excellent flows developed starting at station 50.

During the analyses of station 45, the temperature of the water bath began to drift. After some efforts to stabilize the temperature, the water bath was replaced. One pair of samples was lost, and the analyses of most of the samples from station 45 were delayed an additional 4 hours. Because of the delay, no samples were collected on station 46.

The relatively time-consuming analyses would not permit samples to be drawn from all Niskins at all stations. For the majority of the stations, twenty six flasks were drawn on the twenty four Niskins. Two pairs of duplicate flasks were drawn on most casts. Until the station spacing was shortened near the equator, a partial cast of sixteen or eighteen flasks was drawn about every fourth station. Across the equator and to the end of the cruise, full and partial cast were alternated. The number of flasks in the partial cast was adjusted to avoid a large backlog of samples.

Over 175 pairs of duplicate flasks from the same Niskin were drawn. The average percent difference between duplicates was 0.25% with a standard deviation of 0.29%. If the four pairs with differences exceeding 1% are not included, the average is 0.22% and the standard deviation is 0.21%.

References:

Chipman, D. W., T. Takahashi, D. Breger, and S.C. Sutherland (1991), Investigation of carbon dioxide in the South Atlantic and Northern Weddell areas (WOCE section A-12 and A-21) during the METEOR expedition 11/5 Jan.-March 1990, LDGO of Columbia University, Palisades.

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TOTAL DISSOLVED INORGANIC CARBON (DIC)

The DIC 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) used simultaneously on the cruise. Each system consisted of a coulometer (UIC, Inc.) coupled with a SOMMA (Single Operator Multiparameter Metabolic Analyzer) inlet system developed by Ken Johnson (Johnson et al., 1985, 1987, 1993; Johnson, 1992) of Brookhaven National Laboratory (BNL). In the coulometric analysis of DIC, 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 change required to achieve this.

The coulometers were each calibrated by injecting aliquots of pure CO_2 (99.995%) 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 two sets of the gas loop injections.

Secondary standards were run throughout the cruise (at least one per station) on each analytical system; these standards are Certified Reference Materials (CRMs), consisting of poisoned, filtered, and UV irradiated seawater supplied by Dr. A. Dickson of Scripps Institution of Oceanography (SIO), and their accuracy is determined shoreside manometrically. Preliminary DIC data reported to the database have been corrected to the batch 98 CRM value.

Samples were drawn from Niskin-type bottles into cleaned, precombusted 300-mL Pyrex bottles using Tygon and silicon tubing. Bottles were rinsed once 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 5-mL (2%) headspace, and 0.122 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 in a 20^{o}C water bath for a minimum of 20 minutes to bring them to temperature prior to analysis.

Over 3000 samples were analyzed for discrete DIC; full profiles were completed at almost every station, with replicate samples taken from the surface, oxygen minimum, and bottom Niskin-type bottles. Occasionally duplicates were not taken, due to high water use with other chemical analyses (determined by the chief scientist). The replicate samples were interspersed throughout the station analysis for quality assurance of the integrity of the coulometer cell solutions.

DIC measurements were performed by Cynthia Peacock (lead) from the University of Washington, Joint Institute for the Study of the Atmosphere and Ocean (JISAO), a contractor for the National Oceanic and Atmospheric Administration (NOAA), Pacific Marine Environmental Laboratory (PMEL); and Alex Kozyr, from the Carbon Dioxide Information Analysis Center (CDIAC) at Oak Ridge National Laboratory.

A total of over 400 pure (99.995%) CO2 gas calibrations were run on both SOMMA systems during this cruise. The precision and accuracy obtained from these calibrations can be described as follows:

1. The precision is displayed by the greater than 300 replicate samples drawn. The absolute average difference from the mean of these replicates is less than 0.75 µmol/kg. No significant systematic differences were noted.
2. The accuracy can be described by the greater than 120 Certified Reference Materials (batch 98) that were analyzed. The certified DIC value for these CRM's is 2013.85 µmol/kg. Our average value for these is 2011.69 µmol/kg with a standard deviation of 1.25 µmol/kg.

The overall accuracy and precision as described above, though excellent for the SOMMA systems, does not mean there will not be small corrections to the data made shore side after a more thorough examination and post cruise calibrations are performed. These final corrections may change the data by as much as 2-3 µmol/kg but in the majority the correction will be less than 1 µmol/kg. In addition, it is likely there will be a few changes made to the quality control flags.

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A13.5 Alkalinity

(Laura Fantozzi and Emily Bockmon, laboratory of Andrew G. Dickson, Marine Physical Laboratory, Scripps Institution of Oceanography)

Samples were taken from all Niskin bottles on every station. After thorough rinsing, samples were collected in 250 ml Pyrex serum bottles. Approximately 0.06 milliliters of a saturated mercuric chloride solution were added to each sample. A headspace of approximately 5mls was left for Stations 001-069. This was increased to ~20mls for Stations 070-129.

Starting at Station 008 samples were allowed to equilibrate (using a heater for the coldest) until near 20 degrees Celsius. Stations 001-007 were not allowed to properly equilibrate.

Samples of volume 99.9 mls were dispensed using a Metrohm 765 Dosimat with a 50 ml burette. The temperature of the samples at time of dispensing was taken using a YSI 4600 thermometer, to convert this volume to mass for analysis. For some number of samples, bubbles formed in the burette, most likely displacing volume. This was especially a problem on stations 050-070. By allowing the samples to degas, using a larger headspace and vigorous shaking, most bubbles were avoided after Station 070. One large bubble, displacing sample volume, causes an approximate error of 2 mmol/kg lower alkalinity.

Samples were analyzed using an open beaker titration procedure using two thermostated beakers; one sample being titrated while the second was being prepared and equilibrating to the system temperature of 20 degrees C. After an initial aliquot of approximately 2.5 mls of standardized hydrochloric acid (~0.1Molar HCl in ~0.6M NaCl solution), the sample was stirred for approximately 5 minutes to remove liberated carbon dioxide. The stir time has been minimized by bubbling carbon dioxide free air into the sample. After equilibration, 18 aliquots of 0.05 mls were added. The data within the pH range of 3.5 to 3.0 were processed using a non-linear least squares fit from which the alkalinity value of the sample was calculated (Dickson, et.al., 2007).

Dickson laboratory Certified Reference Materials (CRM) Batch B98 was used to determine the accuracy of the analysis.

Usually two duplicates, surface and deep were taken, but sometimes a third duplicate at the oxygen minimum was also analyzed. Occasionally when limited by sample water, only one, or no duplicates were taken. Throughout the cruise, approximately 250 duplicates were analyzed. The pooled standard deviation was approximately 1.4 μmol kg^{-1}.

The data should be considered preliminary since the correction for the difference between the CRMs stated and measured values has yet to be finalized and applied. Most likely this correction will be significant for part of the data, as a shift was seen in CRM values at several points throughout the cruise, most notably at Station 062. At this point it was necessary to change to the backup sample dispensing burette and it seems this shifted the CRM value down for a time.

Additionally, the correction for the mercuric chloride addition has yet to be applied. As part of the data evaluation, a determination was made for the possible contribution of the mercuric chloride to the alkalinity. The data indicate no contribution, either positive or negative, from the mercuric chloride.

REFERENCE:

Dickson, Andrew G., Chris Sabine and James R. Christian, editors, "Guide to Best Practices for Ocean CO2 Measurements", Pices Special Publication 3, IOCCP Report No. 8, October 2007, SOP 3b, "Determination of total alkalinity in sea water using an open-cell titration"

$^{13}C/^{14}C$ Sampling Program, Darcy Metzler

(R. Key & A. McNichol, PIs)

$^{13}C/^{14}C$ water samples were drawn routinely from the Rosette casts. The entire water column was sampled (24 samples) approximately every 5 degrees of latitude. In between most of the full profiles, the shallowest 16 bottles were sampled. Vertical profiles were collected at 34 of the 129 total stations.

Samples were collected in 500 ml glass stoppered bottles. First, the stopper was removed from the dry flask and placed aside. Using silicone tubing, the flasks were rinsed well with the water from the Niskin bottle. While keeping the tubing near the bottom of the flask, the flask was filled and allowed to overflow about half its volume. Once the sample was taken, a small amount (~30 ml) of water was removed to create a headspace and ~0.2 ml of a 50% saturated mercuric chloride solution was added. This was the same supply and amount of mercuric chloride solution as used with the DIC samples.

After all samples were collected from a station, the neck of each flask was carefully dried using Kimwipes. The stopper, previously lubricated with Apiezon grease, was inserted into the bottle. The stopper was examined to insure that the grease formed a smooth and continuous film between the flask and bottle. A rubber band was wrapped over the bottle to secure the stopper. The filled bottles were stored inside the ship's laboratory prior to being loaded into a container for shipment after the Brown returns to the U.S. The samples will be analyzed at the National Ocean Sciences AMS lab in Woods Hole, MA using published techniques developed for the WOCE program.

DOC/TDN Sampling

DOC/TDN samples were taken from every Niskin bottle at approximately every other station. 1594 samples were taken from 68 stations in total. Samples from up 250 m were filtered through GF/F filters using in-line filtration. Samples from deeper depths were not filtered. High density polyethylene 60 ml sample bottles were 10% HCl cleaned and Milli-Q water rinsed. Filters were combusted at 450^{o}C for overnight. Filter holders were 10% HCl cleaned and Milli-Q water rinsed. Samples were introduced into the sample bottles by a pre-cleaned silicone tubing. Bottles were rinsed by sample for 3 times before filling. 40-50 ml of water were taken for each sample. Samples were kept frozen in the ship's freezer room. Frozen samples will be shipped back by express shipping to RSMAS for DOC/TDN analysis.

Nutrient Measurements

Nutrient samples were collected from the Niskin bottles in acid-washed sample bottles after at least three seawater rinses. Sample analysis typically began within 1 hour of sample collection after the samples had warmed to room temperature while kept in the dark. Nutrients were analyzed with a continuous flow analyzer (CFA) using the standard and analysis protocols for the WOCE hydrographic program as set forth in the manual by L.I. Gordon, *et al.*

Analytical Methods

3049 samples were taken at discrete depths and analyzed for phosphate (PO_4^{-3}), nitrate (NO_3^-), nitrite (NO_2^-) and orthosilicic acid (H_4SiO_4). Nitrite was determined by diazotizing the sample with sulfanilamide and coupling with N-1 naphthyl ethylenediamine dihydrochloride to form an azo dye. The color produced is measured at 540 nm. Samples for nitrate analysis were passed through a cadmium column, which reduced nitrate to nitrite, and the resulting nitrite concentration (i.e. the sum of nitrate + nitrite which is signified as N+N) was then determined as described above. Nitrate concentrations were determined from the difference of N+N and nitrite. Phosphate was determined by reacting the sample with molybdic acid at a temperature of 55°C to form phosphomolybdic acid. This complex was subsequently reduced with hydrazine, and the absorbance of the resulting phosphomolybdous acid was measured at 820 nm. Silicic acid was analyzed by reacting the sample with molybdate in an acidic solution to form molybdosilicic acid. The molybdosilicic acid was then reduced with $SnCl_2$ to form molybdenum blue. The absorbance of the molybdenum blue was measured at 820 nm.

A typical analytical run consisted of distilled water blanks, standard blanks, working standards, a standard from the previous run, a deep sample from the previous run, samples, replicates, working standards, and standard and distilled water blanks. Replicates were usually run for the 4-7 deepest Niskin bottles from each cast, plus any samples with questionable peaks. The standard deviation of the deep replicates was used to estimate the overall precision of the method which was <1% full scale.

Table 1 Precision of Nutrient Measurements.

	Phosphate	Silicic Acid	Nitrate
Total number of replicates	849	887	891
Average standard deviation (µM)	0.006	0.1	0.1
Percent deviation*	0.36%	0.18%	0.36%

* for samples with PO4 concentrations >1 µM

Analytical precision and the measured nutrient content in deep water were similar to the Ajax cruise in 1983 as shown for Cape Basin (Figure 1). Significant offsets in oxygen, nitrate and phosphate were observed compared to the 1993 Discovery cruise.

Temperatures in the ship's main laboratory fluctuated with temperatures ranging from 18.7°C to 25.5°C; however, temperatures were generally stable during an individual analytical run. During the cruise, pump tubes were changed about 3 times per channel as needed.

Standardization

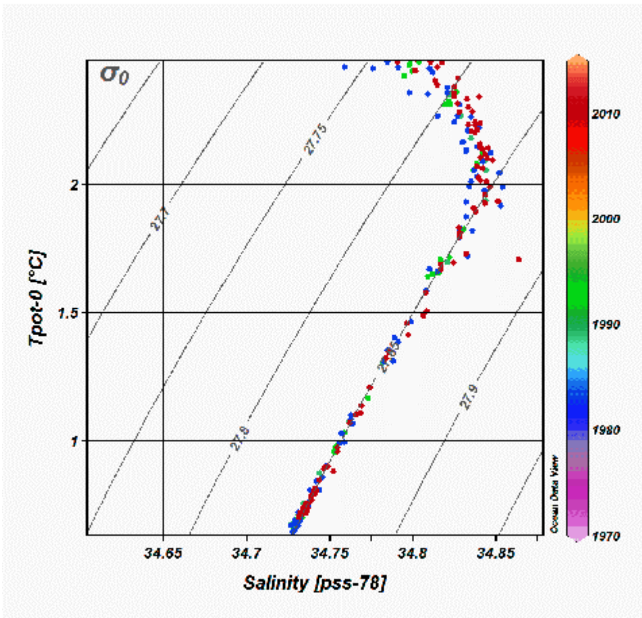
A mixed stock standard consisting of silicic acid, phosphate and nitrate was prepared by dissolving high purity standard materials (KNO_3, KH_2PO_4 and Na_2SiF_6) in deionized water using a two step dilution for phosphate and nitrate. This standard was stored at room temperature. A nitrite stock standard was prepared about every 10 days by dissolving $NaNO_2$ in distilled water, and this standard was stored in the refrigerator. Working standards were freshly made at each station by diluting the stock solutions in low nutrient seawater. Mixed standards were verified against commercial standards purchased from Ocean Scientific.

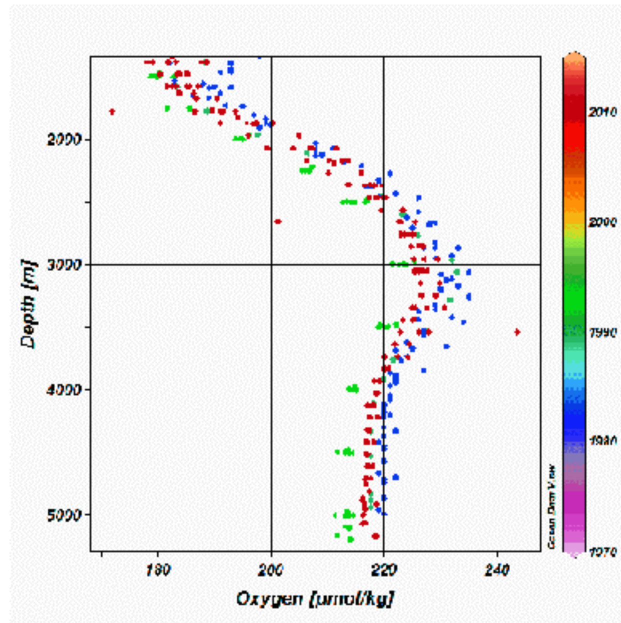
Problems

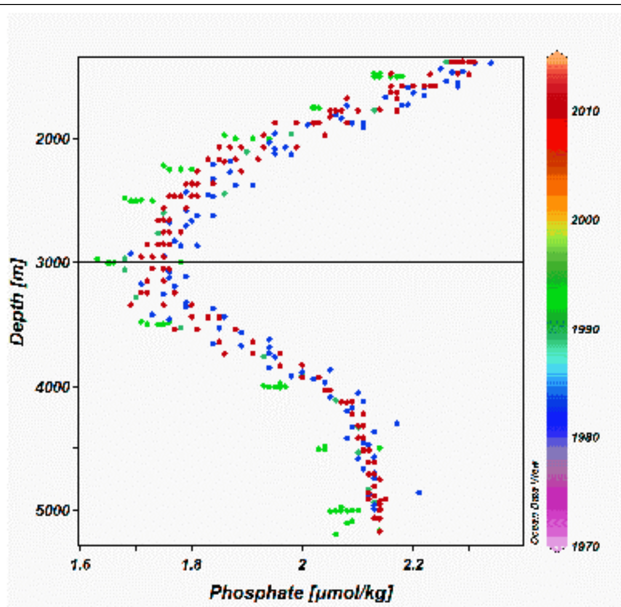
Due to problems with the Alpkem 301 sampler, a Westco CS9000 sampler using 20 ml plastic sample bottles on Stations 3 to 9. There was not enough volume in these sample bottles for sample reruns. During these stations, there was algal build-up that went unnoticed in the sample lines that was coincident with increased variability in the analysis. On Station 10, the Alpkem sampler was back in use, and all the sample lines were changed. Thereafter, sample lines were rinsed with 10% HCl between runs.

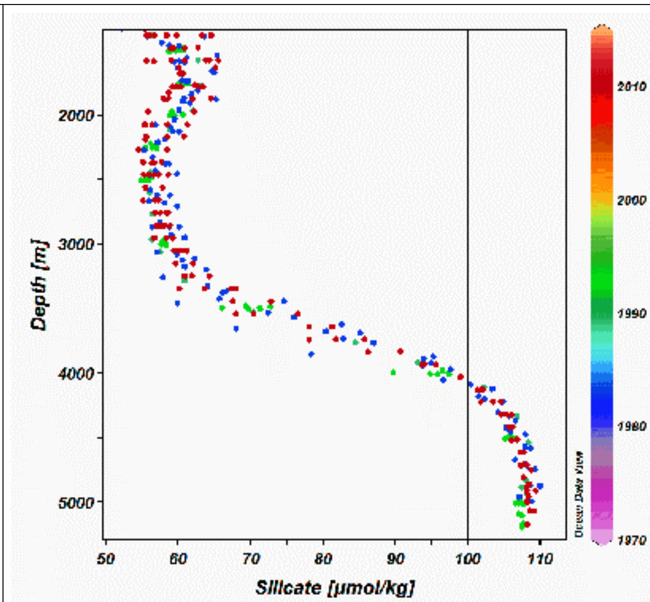
On Station 99, the nitrate peaks became very erratic. Several stations were analyzed before it could be determined that the ship's water was the source of the problem. Several batches of Imidazole were made from various sources of water on the ship, but Cd column had very low efficiencies. Instead of Imidazole, we used Low Nutrient Seawater as a buffer for Stations 101 to 104. The column efficiency was not completely stable during these runs, so we reran about half of each cast and found the precision to be ~1.5%. To stabilize the column, we added 1 ml CuSO4 to 1200ml LNSW and beginning at Station 105. For the remainder of the cruise, the column efficiency varied between ~80-100 percent (determined at the end of each run); however, the efficiency was stable for each individual run.

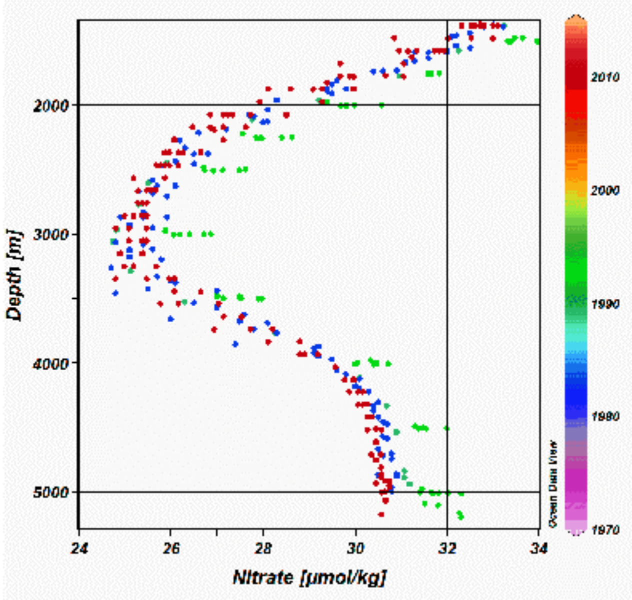
Figures 1-6 Depth profiles of oxygen, nitrate, silicic acid and phosphate in deep water of Cape Basin for this cruise (red), the 1993 meridional Discovery cruise (green), and the 1983 Ajax cruise (blue).


σ0
27.7
27.75
27.8
27.85
27.9
Tpot-0 [°C]
2
1.5
1
34.65
34.7
34.75
34.8
34.85
Salinity [pss-78]
2010
2000
1990
1980
1970
Ocean Data View

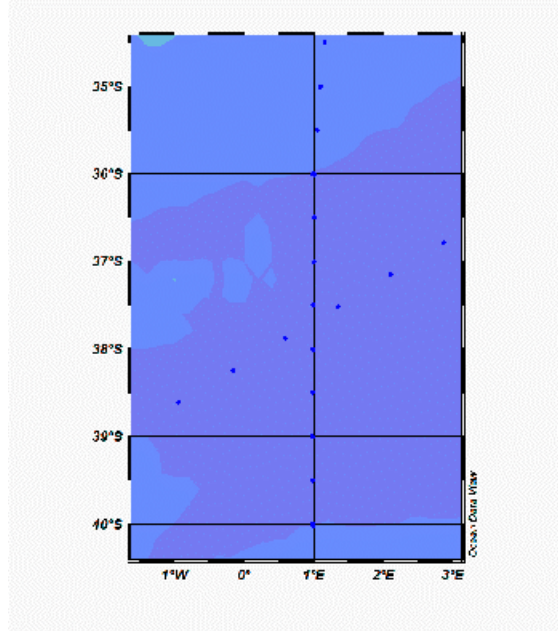

Depth [m]
2000
3000
4000
5000
180
200
220
240
Oxygen [µmol/kg]
2010
2000
1990
1980
1970
Ocean Data View


Depth [m]
2000
3000
4000
5000
1.6
1.8
2
2.2
Phosphate [µmol/kg]
2010
2000
1990
1980
1970
Ocean Data View


Depth [m]
2000
3000
4000
5000
50
60
70
80
90
100
110
Silicate [µmol/kg]
2010
2000
1990
1980
1970
Ocean Data View



Depth [m]
2000
3000
4000
5000
24
26
28
30
32
34
Nitrate [µmol/kg]
2010
2000
1990
1980
1970
Ocean Data View



35°S
36°S
37°S
38°S
39°S
40°S
1°W
0°
1°E
2°E
3°E
Ocean Data View

A13.5 Salinity Analysis

Equipment and Techniques

A single Guildline Autosal Model 8400B salinometer (S/N 61668), located in the aft Hydro lab, was used for all salinity measurements. The salinometer was connected to a computer interface for computer-aided measurement. The Autosal's water bath temperature was set to 24°C, which the Autosal is designed to automatically maintain. The laboratory's temperature was also set and maintained to just below 24°C, to help further stabilize reading values and improve accuracy. As an additional safeguard, the Autosal was powered through a UPS to prevent any power-related issues.

Salinity analyses were performed after samples had equilibrated to laboratory temperature, usually within 12 to 24 hours after collection. The salinometer was standardized for each group of samples analyzed (usually 1.5-2.5 casts and up to 65 samples) using two bottles of standard seawater: one at the beginning and end of each set of measurements. The salinometer's output was logged to a computer file by the interface software, which prompted the analyst to flush the instrument's cell and change samples when appropriate. For each sample, the salinometer cell was initially flushed at least 3 times before a set of conductivity ratio readings were taken.

Sampling and Data Processing

IAPSO Standard Seawater Batch P-147 was used to standardize all casts. Approximately 3000 salinity measurements were taken and approximately 140 vials of standard seawater (SSW) were used.

A duplicate sample was drawn for each cast in order to confirm sampling accuracy.

The salinity samples were deposited into 200 ml Kimax high-alumina borosilicate bottles, which were initially, rinsed a minimum of three times with sample water 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 insure an airtight seal. Laboratory temperature was also monitored electronically throughout the cruise.

PSS-78 salinity [UNES81] was calculated for each sample from the measured conductivity ratios. The offset between the initial standard seawater value and its reference value was applied to each sample. Then the difference (if any) between the initial and final vials of standard seawater was applied to each sample as a linear function of elapsed run time. The corrected salinity data were then incorporated into the cruise database. When duplicate measurements were deemed to have been collected and run properly they were averaged and submitted with a flag of '6'.

Salinity Accuracy Estimates

The latest IAPSO SSW comparison paper [Kawa06] and personal communication with the lead author [Kawa09] suggests the following batch-to-batch offsets are required:

Cruise	Date	Batch	K15	Salinity	batch-to-batch diffc. x1000 Mantyla's 1987 std.	 Kawano's 2006 refc.
A13.5	2010	P-147	0.99982	34.9929	-1.8	-0.5
Ajax-2	1984	P-92*	0.99988	34.9953	-1.5	-0.2
Ajax-1	1983	[P-90]	[2.00014]	[35.0028]	[-2.2]	

*for higher-latitude stations that overlap with A13.5 (2010)

The last column in the table is the recommended correction to each batch and related salinity data, based on using recent batches with better accuracy as the "standards". Kawano et al. IAPSO SSW comparisons start with batch P91, excluding most of Ajax-1 (batch P-90). Using batch differences for P-90 and P-92 in the original Mantyla paper [Mant87], one can infer that P-147 requires a correction about halfway between the two Ajax batches.

A cursory comparison of salinity data from several casts on A13.5 (2010) and Ajax-1/2 (1983-84) indicate A13.5 data is within WOCE accuracy specifications of 0.002.

References

Kawa06: Kawano, T., Aoyama, M., Joyce, T., Uchida, H., Takatsuki, Y., and Fukasawa, M., "The Latest Batch-to-batch Difference Table of Standard Seawater and Its Application to the WOCE Onetime Sections," Journal of Oceanography, 62, 6, pp. 777-792 (2006).

Kawa09: Kawano, T. (2009). Personal communication with M. C. Johnson.

Mant87:
Mantyla, A. W., "Standard Seawater Comparisons Updated," Journal of Physical Oceanography, 17.4, p. 547 (1987).

UNES81: UNESCO, "Background papers and supporting data on the Practical Salinity Scale, 1978," UNESCO Technical Papers in Marine Science, No. 37, p. 144 (1981).

Underway pCO2 System

An automated underway pCO_2 system from AOML has been situated in the hydro lab of the R/V Ronald H. Brown since it was commissioned in July 1997. The current system has been aboard since September, 2008, and is a model 8050 from General Oceanics, Inc (GO). Access to the data can be found at AOML's global carbon cycle web page (http://www.aoml.noaa.gov/ocd/gcc/rvbrown_introduction.php).

Early instrument designs are discussed in Wanninkhof and Thoning (1993) and in Feely et al. (l998). The current design as well as the data processing procedure is detailed in Pierrot et al. (2009).

Seawater continuously flows through a closed equilibration chamber at approximately 2 liters/minute. A spiral nozzle creates a conical spray that enhances the gas exchange with the enclosed gaseous headspace. During 'water' analyses this overlying headspace is pushed through an infrared analyzer and returned to the equilibrator. During air analyses, outside air is pulled from an inlet on the forward mast and pushed through the analyzer. The pressure and temperature inside the equilibrator are constantly being measured. With knowledge of the sea-surface temperature and salinity, along with all the parameters measured by the system, one can calculate the fugacity of CO_2 in the seawater and the atmosphere above it.

To ensure the accuracy of analyzer output, every 2.6 hours four standard gases are analyzed. (serial numbers CA06709 [284.75 ppm], CA02813 [363.24 ppm], CA07921 [423.57 ppm], and CA07931 [545.88 ppm]) They were purchased from NOAA/ESRL in Boulder, CO and are directly traceable to the WMO scale. After the standards, five air analyses and then fifty water analyses are done. With continuous operation, the current system provides over 920 water analyses per day. During this cruise, the operation was interrupted while the ship was maintaining station several times for testing and upgrades.

The first upgrade was done before the ship left Cape Town. A new equilibrator with a water jacket was installed. The new equilibrator has a seawater flow of approximately 1.5 liters/minute flowing through a concentric enclosure around the vertical walls. This thermal insulation improves the stability and accuracy of the temperature measured in the main equilibrator, especially with very cold waters.

Additional upgrades were associated with the firmware and software used to control the hardware. On 12 March, a new version of the software was installed and worked well. On 2 April, a new firmware and the necessary newer software were installed. Both software upgrades yielded a more stable and adaptable analytical system. On 9 April the GPS signal was switched from the dedicated deck box that comes with the GO system to the ship's GPS that is broadcast through the ship.

Other than these planned service events, the system ran continuously during the entire cruise. Preliminary examinations of the data confirm good analyses. Calculation of final values of fugacity will require some time given the volume of data.

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M-AERI Spectroradiometer Data

Contact Information:

Peter J. Minnett <pminnett@rsmas.miami.edu>

Miguel Angel Izaguirre <mizaguirre@rsmas.miami.edu>

For many years scanning radiometers on satellites have been providing global fields of sea-surface temperature (SST) and these have found many applications in oceanography, air-sea exchange studies, meteorology, including numerical weather forecasting, and climate change research. The utility of the satellite-derived SSTs is determined by their uncertainties and these are largely determined by the residual errors in the correction for the effects of the intervening atmosphere. The most reliable way to determine these uncertainties is to compare the satellite-derived values with those from an independent data source taken at the same time in the same place. Given the effects of variable near-surface temperature gradients, the best sources of validating data are ship-board radiometers, but for these to provide useful data they have to be very accurate (uncertainties $<0.1^{o}$K) with calibration traceable to National Institute of Standards and Technology reference standards. The Marine-Atmospheric Radiance Interferometer (M-AERI) is one of a few such radiometers, and the track of the NOAAS Ronald H Brown provides the opportunity to take validation measurements in a very under-sampled part of the ocean.

The M-AERI is a Fourier-Transform Infrared (FTIR) Spectroradiometer that operates in the range of infrared wavelengths from ~3 to ~18μm and measures spectra with a resolution of ~0.5 cm-1. It uses two infrared detectors to achieve this wide spectral range, and these are cooled to ~78^{o}K (close to the boiling point of liquid nitrogen) by a Stirling cycle cryo-cooler to reduce the noise equivalent temperature difference to levels well below 0.1^{o}K. The M-AERI includes two internal black-body cavities for accurate real-time calibration. A scan mirror, which is programmed to step through a pre-selected range of angles, directs the field of view from the interferometer to either of the black-body calibration targets or to the environment from nadir to zenith. The sea-surface measurement also includes a small component of reflected sky radiance, so the derivation of the skin SST from the M-AERI spectra requires compensation of the reflected sky radiances that are part of the sea-viewing measurement, and of the emission from the atmosphere between the instrument and the sea surface. The interferometer integrates measurements over a few tens of seconds, to obtain a satisfactory signal to noise ratio, and a typical cycle of measurements including two view angles to the atmosphere, one to the ocean, and calibration measurements, takes about ten minutes. The instrument is run continuously so that measurements are taken within minutes of the satellite overpasses.