A. Preliminary Cruise Report: P02_2004 (2006.JUN.27)



WHP Cruise Summary Information

WOCE section designation	P02_2004			
Expedition designation (ExpoCode)	318M200406			
Chief Scientists	Leg 1: Chief Scientist Leg 1: Co-Chief Scientist	Paul Robbins • UCSD/SIO Andreas Thurnherr • LDEO		
	Leg 2: Chief Scientist	James H. Swift • UCSD/SIO		
	Leg 2: Co-Chief Scientist	Dong-Ha Min • Penn State		
Dates	Leg 1: 15 June 2004 25 July 2004 Leg 2: 28 July 2004 27 August 2004			
Ship	R/V Melville			
Ports of call	Leg 1: Yokohama, Japan — Honolulu, Hawaii Leg 2: Honolulu, Hawaii — San Diego, California			
Number of stations Leg 1	107 LADCP/CTD / Rosette sta	tions, 52 trace metals casts		
Leg 2	82 LADCP/CTD / Rosette sta	tions, 38 trace metals casts		
	Leg 1	Leg 2		
Station Coorrespin houndaries	32°44.94'N	32°38.62'N		
Station Geographic boundaries	133°6.73'E 165°7.36	'W 166°26.74'W 117°23.03'W		
	29°57.27'N	29°58.9'N		
Floats and drifters deployed	12 profiling CTD floats deployed			
Moorings deployed or recovered	0			

Contributing Authors							
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Click to go to text location or use Acrobat Reader navigation tools. Shaded headings were not applicable to this cruise or were not available when this report was assembled.

Cruise Summary Information		Hydrographic Measurements			
Description of scientific pro	gram		CTD Data		
	Leg 1	Leg 2	Pressure	Leg 1	Leg 2
Geographic boundaries of	the survey		Temperature	Leg 1	Leg 2
Cruise track figures	Leg 1	Leg 2	Conductivity/salinity	Leg 1	Leg 2
Description of stations	Leg 1	Leg 2	Dissolved oxygen	Leg 1	Leg 2
Description of parameters	sampled (b	ooth legs)	Bottle Data		
Bottle depth distributions	Leg 1	Leg 2	Salinity	Leg 1	Leg 2
Floats and drifters deploye	b		Oxygen	Leg 1	Leg 2
Moorings deployed or reco	vered		Nutrients	Leg 1	Leg 2
			CFCs		
Principal Investigators	Leg 1	Leg 2	Helium		
Cruise Participants			Tritium		
			Radiocarbon		
Problems and goals not ac	hieved		CO2 System	Leg 1	Leg 2
Other incidents of note			Other parameters		
Underway Data Informati	on		References		
Navigation	Leg 1	Leg 2	Bottle Data		
Bathymetry	Leg 1	Leg 2	CTD Data	Leg 1	Leg 2
LADCP	Leg 1	Leg 2	DIC	Leg 1	Leg 2
Meteorological observation	S		pCO2		
Atmospheric chemistry data	a				

Acknowledgments

Data Processing Notes

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Science Programs and Science Team Leaders

A.1. Cruise Summary

Cruise Track

Station location maps for both legs of P02_2004 can be seen on the previous page. (PDF only)

Sampling

The following water sample measurements were made:

CTDRAW	CTDPRS	CTDTMP	CTDSAL	CTDOXY	THETA	SALNTY	OXYGEN	SILCAT
NITRAT	NITRIT	PHSPHT	CFC-11	CFC-12	CFC113	TCARBN	ALKALI	DELC13
DELC14	ALUMN	IRON						

Summary

The immediate goal of the "P02" expedition was to carry out a trans-Pacific transect along 30°N, angling north to Japan and California at the ends. This was a repeat of the WOCE-era "P02" transect, carried out via four 1993-1994 cruises led by Japanese oceanographers. The principal program of measurements was reference quality CTDO casts with bottle sampling for salinity, oxygen, nutrients, a host of carbon parameters, CFCs, helium and tritium, and radiocarbon, plus a suite of underway measurements, as part of the NSF and NOAA supported US Global Ocean Carbon and Repeat Hydrography program. There were also CTD/rosette casts with separate equipment for an NSF-funded trace metals program, ARGO float deployments, and plankton tows for an SIO investigator.

A.2. Narrative – Leg 1

(P Robbins)

The *R/V Melville* departed Yokohama, Japan on 15 June 2004. A total of 107 LADCP/CTD/Rosette stations were occupied and 52 trace metals casts were made from 16 June – 22 July. Water samples (up to 36), LADCP and CTD data were collected, in many cases to within 10 meters of the bottom. Salinity, dissolved oxygen and nutrient samples were analyzed from every bottle sampled on the rosette.

Weather Delays

The peril of working in the western subtropics in summer and fall is the persistent threat of cyclones. Although cyclones in June are rare, we were subject to the effects of two. Typhoon Dianmu required us to cease operations on 19 June after station #13 and run east approximately 400 km to avoid its path. While waiting for the sea state from the typhoon to diminish, we decided to occupy the stations along the transect heading back west. Station numbering was chosen to preserve geographic sense rather then temporal. Hence we occupied stations 21,20,19.... back to station 14. Station 14 was occupied 3 days, 7 hours after Station 13. After station 14, we again steamed east and picked up the line at Station 22. The trace metal cast at station 20 was occupied during this eastward steam since the seas had been too rough for its deployment previously. The total time between the primary rosette cast and the trace metal cast at station 20 was 3 days. All together, approximately 44 hours was lost due to weather delays associated with typhoon Dianmu.

Starting around 29 June, the weather again began to deteriorate due a a second typhoon, Tingting, to the south. Station spacing was increased from 30 nm to 34 nm in an attempt to get further east and out of the path of the typhoon. The sea state continued to build and after station #40 it was decided that we would

again have to run east overnight. On 1 July we were able to occupy a station (#42) approximately 85 nm east of station #40. At this point the typhoon was approximately 420 nm distant to our southeast. Given the predicted track of the typhoon (NE) we could not remain in the area nor return west to pick up station #41. Thus, station #41 was not occupied and we continued westward with a 39 nm spacing in an attempt to provide greater distance between us and the expected track of the typhoon. This larger (39nm) station spacing was continued until station #58, when the combination of distance from the typhoon and resoluton of the winch issues (see below) allowed for a decrease in station separation to 34 nm.

Ship Malfunction

The ships equipment performed well during leg 1, however some time was lost to level-winding problems on the winch used for the primary CTD casts. Prior to this expedition, a new hydro-boom was installed on the starboard side of the ship, just aft of the starboard hanger. A similar configuration was in place on the R/V Knorr throughout the WOCE expeditions and deemed successful. The new hydro-boom required using a winch (DESH-5) which had not been used for many years. Prior to this cruise, the DESH-5 winch and hydro-boom had performed well on casts up to 2000 m deep.

Starting about station #12, with bottom depths in excess of 4500 m, problems related to malfunction of the level-wind were noted on upcasts. The chief engineer attempted several adjustments and replacement of some parts but was unable to correct the problem. Casts could proceed but required constant attention, and adjustment to the winch during upcasts. It was eventually determined that the problems with the winch were not due to any malfunction of the level-wind mechanism but due to unevenness of wraps deep on the drum. In an attempt to fix this, a deep cast, with only a dead weight, was made in the Izu Ogasawara Trench. 8856m of wire was unspoiled and carefully respelled. Eight hours of ship time was devoted to this effort. Unfortunately, this did not suffice to fix the problem which persisted, and worsened over the next several days. The decision was made to switch to the aft winch (DESH-6) and conduct the primary ctd casts from the starboard A-frame. This necessitated repositioning the trace metal rosette and winch to the stern A-frame. Owing to high sea state, relocating the primary rosette to the starboard A-frame could not be accomplished until after station #50. All together, time lost to level winding problems on DESH-5 totaled about 15 hours. All stations subsequent to station #49 used the DESH-6 winch and no significant delays occurred. Stations using the DESH-5 winch with particularly slow upcasts are listed below. In total, about 14 hours of station time was lost to winch malfunctions.

A.3. Narrative – Leg 2

(J Swift)

R/V Melville arrived at the University of Hawaii's Marine Facility at Sand Island in Honolulu on the morning of 25 July 2004 to provide a short break for the officers, crew, and continuing members of the science team, disembark some of the Leg 1 science team, board new science team members, and load tons of provisions and fuel. The ship departed on schedule on the afternoon of 28 July, heading for the area near 30°N and 165°W where the Leg 1 team had broken off the P02 trans-Pacific section they started in mid-June.

Training casts en route helped the new team members to learn the ropes. Scientific work on Leg 2 began with a 3-station overlap of the eastern end of Leg 1, continuing eastward along 30°N. The plan was to carry out CTD/rosette profiles at ca. 50 km intervals. During the first week at sea, however, it was necessary to divert R/V Melville to Kauai, Hawaii, to disembark a crew member, an operation which caused a loss of 75

hours, equivalent to approximately 15 of the planned stations. To make up the lost time the station interval was widened to ca. 60 km, and later to 65 km. Excellent between-station ship speeds, due to good fortune with weather and seas, plus attention to saving time during casts helped to make up some of the lost time. Later in the expedition it became possible to reduce the station spacing to 60 km and finally to 50 km. The eastern end of the section was completed according to the original cruise plan. In all, 81 stations were completed of the 93 stations planned for Leg 2 (87%).

There were two science activities during Leg 2 which did not take place on Leg 1: ARGO float deployments and plankton tows. The ARGO floats are fascinating devices, easy to start up and deploy, which when launched proceed to sink to a pre-set level (ca. 1000 meters), meanwhile profiling temperature and salinity while they sink, drift at depth for a set number of days, sink to 2000 meters, rise to the surface (again generating a vertical profile), squirt data to a satellite, then repeat the whole endeavor, over and over, for up to five years. The plankton tows will form the basis for Dr. John McGowan (SIO) to carry out a 1969-2004 comparison of ecosystem structure in the subtropical gyre versus the California Current. This set of data will be an important part of a larger study aimed at understanding how oceanic systems respond to global change. The shipboard party enjoyed something different/new to do.

One perplexing oddity was noted: It was discovered that different groups in the SIO Ship Operations and Marine Technical Support Division used independent leg numbers for the P02 cruise (and other recent R/V Melville cruises). This dual numbering will undoubtedly lead to data confusion in the future. For example, a person who wanted to examine the deck log versus the underway systems data would need the deck log for Leg 22 and the underway data from Leg 33. The situation was clearly unsatisfactory and was called to the attention of the operating institution. Hopefully in the near future SIO will institute reforms which will end this confusing practice.

The scientific work along Line P02 was mostly uneventful. There were only a few days during which the winds picked up; otherwise winds were mostly light. The ship was almost always able to make excellent speed between stations, accounting for making up a good share of the time lost on the unplanned 75 hour run to/from Kauai.

At station 127 there were intermittent, then nearly permanent upcast data dropouts on both of the temperature/conductivity pairs of sensors on the CTD. The cast was aborted and the CTD was removed to the lab. Investigation revealed that the CTD had at some point in the past taken on a small amount of water inside its pressure case, which finally caused enough corrosion that the CTD ceased to function normally. Scott Hiller soon switched out the CTD and the science team repeated the portion of the cast where the data had dropped out, all told losing about 4 hours.

A problem downloading LADCP data led to temporarily removing the LADCP for cast 163/02. The problem was solved and the LADCP replaced for the next station with little loss of time.

Temporal evolution of transient tracers such as CFCs in the interior of the ocean is one of the research interests of the Repeat Hydrography Program, as this helps to infer the major pathways and rate which anthropogenic carbon spreads in the ocean. Preliminary comparisons with WOCE stations occupied during the mid-1990s suggests that the CFC concentrations have increased in the upper 1000-2000 meters of the water column during the past decade. We also observed what was at first a minute but abrupt increase of CFC-12 blank level since the beginning of Leg 2. We tried changing the tripping sequence of the rosette

bottles, and checked the syringe sampling and analysis orders, sample storage, and computation steps. Although we determined that changed calibration curve fitting coefficients for very low CFC-12 concentrations probably explained the apparent blank increase, there remained consistent marginallyelevated CFC-12 concentrations (by ca. 0.005-0.010 pM) in the several hundred meters of water above the seafloor during Leg 2 strengthening in the east, finally disappearing as we came up the base of the continental slope off California. This bottom feature of CFC-12 cannot be fully explained by any contamination or bias in sampling and analysis, or potential link to newly ventilated bottom water from the south and provided an interesting mystery to contemplate.

We were fortunate to have on board students eager to learn and do everything, so we had them learn and do everything! It was truly a pleasure to observe them discovering what life at sea holds for them. Students ran the CTD console, helped launch and recover the rosette, helped draw water samples and act as sample cop, carried out nearly all of the radiocarbon sampling program, carried out nearly all of the plankton sampling program, ran salinity analyses, and carried out many other tasks. The three new SIO physical oceanography graduate students compared the P02 data with Atlantic Ocean profiles to view the Big Picture, and with North Pacific WOCE Hydrographic Program data to examine differences during the past decade, as well as relative noise levels in data from different cruises.

Minor diversions helped break the often monotonous routine. For example, the night watch crew noticed at one station large numbers of sea striders under the lights and collected samples for return to San Diego. They were present in such abundance that it was easy to catch them in a bucket. These are fascinating little creatures that live on top of the sea, exploiting surface tension.

During the 2004 edition of the Perseid meteor shower R/V Melville was on station with the bow dark and pointed east during the peak hours, making for pleasant viewing. (One bonus watching this from sea: no insects!) Meteor sightings averaged a bit more than a one per minute pace, though there were some periods with higher rates. Some were bright, with trails, and one was a very bright, short flash, equivalent to mid-distance lightning or an onboard flash photo.

Life was comfortable on board, thanks to good environmental controls, light seas, and good food. As an aside, the chief scientist is an oceanographer who has done mostly high latitude work. He enjoyed the novelty of finding conditions appropriate for taking relaxing breaks on deck, enjoying the sun and breeze, iced drink (non-alcoholic) in hand. He also found the stars at night were magnificent.

R/V Melville docked at the UCSD Scripps Institution of Oceanography's Nimitz Marine Facility at 1000 local time, Friday, 27 August 2004. This was nominally one day early, but because the analytic groups required one day of analyses after the final station, and because the final station was immediately outside the entrance to San Diego Bay, rather than stare wistfully at the shore for the final day, we brought the ship to the dock to complete the work.

A.4. Notes on the CTDO / Rosette / LADCP Program

(J. Swift)

The rosette water sampler frame which was used on this expeditions was the large ODF-constructed 36position frame, with a single ring outfitted on each side with staggered scallops for 18 10-liter Niskin type bottles, which are attached to the frame with hose clamps. This method of mounting provides outstanding bottle security plus, because lanyard guides are also attached with hose clamps, it can be easily adjusted to provide best performance. Cross members on the bottom of the frame provide mounting points for the various electronics and batteries, with approximately half of the bottom frame open so that the LADCP transducers will have unobstructed acoustic paths. The ODF-constructed ODF/Bullister design Niskin-type bottles provided outstanding performance throughout this cruise, with near-zero incidence of leaking bottles. Spigots tended to be very tight, because grease-like lubricants permitted on some cruises cannot be used on cruises for this program. Careful and repeated inspection and maintenance helped to keep the spigots in adjustment. The nylon-coated stainless steel springs must be inspected occasionally in order that any rust spots - detrimental to phosphate analyses for example - can be re-coated.

There was some concern before this program began in 2003 that the 10-liter bottles (which, like Niskin 10-liter bottles actually hold closer to 9 liters) would be too small. It is in fact entirely conceivable that in some situations the capacity would be insufficient. For example, on one cruise for this program there were two CFC groups running side by side. More obviously, if CFC, helium/tritium, carbon system, and radiocarbon programs were to sample from the same bottle, experience shows that there may well not be water left for a salinity sample, and the water is so severely drawn down that one must begin to suspect, for the final carbon-system samples, the possibility of contamination from the air drawn into the head space of the bottle. These problems were avoided during P02 mostly by control of overlapping sampling. This was made easy by the fact that the carbon programs tended to do their heavy sampling on alternate stations (and at some points during the cruise did almost no sampling on their 'light' stations). Radiocarbon sampling was always coordinated with the 'heavy' carbon stations. And in most cases helium/tritium sampling was scheduled for the 'light' stations. For that program, full overlap with CFC sampling was required, but with nearly-full CFC sampling available every station, that was not a problem.

The other decision regarding the rosette program was how to stagger the sampling in the vertical, over multiple stations, to provide the most information for the various parameters. Paul Robbins, chief scientist on Leg 1, created the scheme used for the entire section: three different vertical sampling schemes were used in strict rotation. Thus the every-second -station carbon parameters went, over six stations, through the same rotation the CTDO/S/O2/nutrient/CFC programs sampled. This scheme was judged by Paul to provide optimum information for objective mapping schemes. It is shown in the table below.

Helium/tritium and radiocarbon sampling, ARGO deployments, and net tows were done at the closest stations to the longitudes requested by the investigators in charge of the programs. Small (no more than one station) adjustments were sometimes made to align radiocarbon with full carbon stations, and to avoid helium/tritium sampling on radiocarbon stations.

scheme 1	scheme 2	scheme 3
5	5	5
50	35	40
100	70	85
150	120	135
200	170	185
250	220	235
300	270	285
350	320	335
400	370	385
450	420	435
500	470	485
600	540	570
700	640	670
800	740	770
900	840	870
1000	940	970
1100	1040	1070
1200	1140	1170
1300	1240	1270
1400	1340	1370
1500	1440	1470
1600	1540	1570
(1700)	(1640)	(1670)
1800	1740	1770
(1900)	(1840)	(1870)
2000	1940	1970
2250	2100	2170
2500	2350	2420
2750	2600	2670
3000	2850	2920
3400 / (3250)	3100	3250 / (3170)
3800 / (3500)	3500 / (3350)	3650 / (3420)
4200 / (3750)	3900 / (3600)	4050 / (3670)
4600 / (4000)	4300 / (3850)	4450 / (3920)
5000 / (4250)	4700 / (4100)	4850 / (4170)
5400 / (bottom)	5200 / (bottom)	5250 / (bottom)
bottom-200	5600	bottom-200
bottom	bottom	bottom

For the final 16 stations, in order to better determine isopleth slopes in the upper layers near the North American boundary, the sampling schemes were slightly altered:

bottle count	new Scheme 1	new Scheme 2	new Scheme 3
1	5	5	5
2	25	35	20
3	55	70	45
4	80	95	85
5	105	120	110
6	130	145	135
7	155	170	160
8	180	195	185
9	215	220	210
10	250	270	235
11	300	320	285
12	350	370	335
13	400	420	385
14	450	470	435
15	500	540	485
16	600	640	570
17	700	740	670
18	800	840	770
19	900	940	870
20	1000	1040	970
21	1100	1140	1070
22	1200	1240	1170
23	1300	1340	1270
24	1400	1440	1370
25	1500	1540	1470
26	1600	(1640)	1570
27	(1700)	1740	(1670)
28	1800	(1840)	1770
29	(1900)	1940	(1870)
30	2000	2100	1970
31	2250	2350	2170
32	2500	2600	2420
33	2750	2850	2670
34	3000	3100	2920
35	3400 / (3250)	3500 / (3350)	3250 / (3170)
36	3800 / (3500)	3900 / (3600)	3650 / (3420)
	4200 / (3750)	4300 / (3850)	4050 / (3670)
	4600 / (4000)	4700 / (4100)	4450 / (3920)

A.5. Winch and Deck Operations with the 36-Place Rosette

Deck operations on Leg 2 went well enough, but this may have been partly a result of the benign weather/sea conditions experienced. There were several deficiencies in the deck operations, including:

- The winch operator could not see the rosette on deck, making it more of a challenge to set the rosette down on the cart (done by hand signals).
- The A-frame was narrow and the rosette track at an angle to it. This combined to make for tighter than optimal quarters. Certainly it limited personnel access in the area. There was also no room for air tuggers, and the angles and placement of tag lines was not ideal.
- The A-frame was somewhat aft of amidships, hence the effects of pitch were more apparent than in an amidships location.

CTD/rosette operations during Leg 1 began in the amidships area, deployed from a boom, and served from the forward/starboard staging area. There were problems with the winch and wire, however, and so during Leg 1 operations were shifted to the starboard aft quarter A-frame and port/after staging bay, and a different CTD winch and cable. Although the other winch/wire problems were largely repaired in Honolulu, operations continued from the aft quarter during Leg 2. Reasons included the unknown condition of the drum and the mechanism on the amidships winch, slow operation of the amidship's boom, sampler's preference for the aft hangar, and provisions for net tows from the amidships location during Leg 2.

It should be noted that a cruise with repetitive operations and a full schedule is subject to the accumulative effect of small variables. For example, one of R/V Melville's 4 winch operators was more tentative than the others, taking 15-30 seconds per bottle longer to raise the rosette between depths than the other winch operators. If he ran 25% of the upcasts on both legs (likely), that would be equivalent to 189/4 = 47 casts. Being conservative and saying he lost 15 seconds per bottle, that would be 47 casts x 36 bottles x 15 seconds, or 42300 seconds, which is nearly 12 hours: more than one station per leg lost. For an example on the other sign of time impact, the bridge did not try to hit exact station positions, which could have eaten up considerable time. They quickly came 'close enough' onto station, and they made good progress coming up to speed leaving station. This was very much appreciated. Even 5 minutes saved per station would mean nearly 16 hours saved, or three stations.

A.6. Analytical Laboratory Temperature Control

The relationship of laboratory temperature control to data quality is well known in the analytic community. Although the requirements have been provided to those who oversee the design, construction, refitting, and maintenance of research vessels, it is rare to find a research vessel with at least one laboratory meeting the specifications. R/V Melville's analytic laboratory is close to the mark, certainly closer than is the case with the matching laboratory on the sister ship R/V Knorr. The outstanding precision of the nutrient, salinity, and (perhaps) dissolved oxygen data is likely in part due to the tight temperature control in the analytic laboratory, where these analyses took place. (Of course the care and skill of the analysts is the leading factor in this regard.)

A.7. ARGO Floats (Leg 2 only)

(G. Johnson, J. Swift)

ARGO floats were deployed along the expedition track at the stations nearest the longitude requested by the ARGO team at PMEL. The only exception was one float whose deployment location was changed to a position along the track from Kauai back to the P02 line when the ARGO PIs realized the emergency trip to Kauai provided an opportunity to place a float in an underrepresented area. The ARGO float start-up and deployment instructions were thorough and easy to follow. The deployments took approximately 5 minutes each, always when the ship left station except for the one deployed on the Kauai to P02 run. The floats themselves posed a minor storage problem because their boxes must be kept out of the sun (and always under 120°F), yet are bulky and must be kept horizontal at all times (making it difficult to take between decks inside a ship unless one of the deck hatches is longer than the ARGO box). These restrictions were worked around with success on this cruise. The ARGO group at PMEL was outstanding in terms of response to questions and providing information.

Methodology

Twelve profiling CTD floats (Webb Research Corp. Apex 260 floats equipped with SeaBird Electronic Inc. SBE-41 CTDs) were launched by members of the eastern leg of the Repeat Hydrography Program 2004 P02 section for the ARGO Program. These instruments were tested at NOAA/PMEL prior to shipment to Hawaii for loading on the R/V Melville. Approximate deployment positions and dates for the P02 cruise are given below.

Long (E)	Lat (N)	Mo / Da Year		Long (E)	Lat (N)	Mo / Da Year
194.88	30.00	08 / 01 2004		213.36	30.00	08 / 13 2004
198.23	30.00	08 / 03 2004		216.39	30.00	08 / 14 2004
200.88	27.00	08 / 06 2004		219.37	30.00	08 / 15 2004
200.97	30.00	08 / 07 2004	-	222.38	30.00	08 / 17 2004
203.77	30.00	08 / 08 2004	-	225.26	30.00	08 / 18 2004
209.58	30.00	08 / 11 2004		233.00	30.00	08 / 22 2004

These floats are programmed to telemeter data from the surface for six hours after start-up (and deployment) then sink to 1000-dbar and remain there drifting freely for 10 days. After this period they ascend to the surface, measuring 60 temperature/salinity/pressure triplets at increasingly smaller pressure intervals with decreasing pressure during the 3.5-hour ascent. They remain at the surface for under 12 hours to telemeter their data via Service Argos, and then descend to their 1000-dbar drift depth for another 10 days. Every 3rd cycle they descend to 2000 dbar 6 hours prior to ascending, and take 73 triplets during the 7-hour ascent.

Eleven out of the 12 floats are functioning well as of 8 September 2004 (the date of writing this report), with optimal life expectancies of 5 years. One of the floats functioned well during start-up and its deployment went, but it failed to telemeter data as expected after its first 10-day drift period. The cause of its premature failure is not apparent from the data available.

Data Quality

Pressure and temperature accuracies for the lives of the floats are expected to be 5 dbar and 0.005C. Salinity accuracy is thought to be usually (95% of the time) better than 0.02 (PSS-78). Historical T-S data (including eventually the P02 2004 repeat section data) are used to monitor salinity accuracy in a delayed mode, and salinity adjustments are made when required. Delayed-mode data are also eventually available from the GDACS.

NOAA/PMEL float activities are documented at

http://floats.pmel.noaa.gov/

Data from these and all other ARGO Program floats are available in near-real time at either of the ARGO Program Global Data Assembly Centers (GDACS):

http://www.usgodae.org/argo/argo.html http://www.ifremer.fr/coriolis/

A.8. Net Tows — Leg 2 only

(J. Swift)

Five plankton net tows were carried out by resident technician Cambria Colt and the students on board to meet a request for this work from John McGowan (SIO). The casts were carried out within the position limits provided by Dr. McGowan, and to his specifications regarding methodology. The samples were preserved as per Dr. McGowan's instructions, and returned to him by Cambria Colt. The net sampling provided a novel and interesting opportunity for the students. The tows took approximately 30 minutes each.

B. Underway Measurements

B.1. Acoustic Doppler Current Profilers

NOTE: A more extensive separate LADCP cruise report should be available from the same source as the main cruise report. Alternatively, a copy can be requested by e-mail from Andreas Thurnherr <a href="mailto: <a hre

B.1.2. LADCP System – Leg 1

(P. Robbins)

Two separate ADCP heads were used as LADCPs during the cruise: a 150kHzRDI broadband instrument (BB150) and a 300 kHz RDI Workhorse (WH300).The BB150 was installed looking downward on all stations. The WH300 was used as an uplooker on stations 1--30 (across the Kuroshio, Sikoku Basin, and the Izu Ogasawara Trench) and as a secondary downlooker during bottom-track tests during LADCP casts 82--87 (see below). On the remaining stations the WH300 was not installed on the rosette but kept as a spare.

Each instrument had its own battery --- the BB150 a new oil-filled rechargeable lead-acid battery, while the WH300 used non-rechargeable alkaline battery packs in a pressure housing. Only one set of alkaline batteries was used during the cruise. There was plenty of time for charging the oil-filled battery between stations. The battery was found to be easy to vent and performed flawlessly during the cruise. The fact that it does not require a pressure housing is a big advantage. While on deck, both ADCPs were connected to a Dell Latitude laptop(model PP01L) running Linux. It handled both communications and data processing. The WH300 was connected to the computer via a long (~20m)RS-232 cable, while the BB150 communicated via RS-422 and a 422/232 converter. Both instruments were hooked up to the same Key span USA-49W4-port RS-232-to-USB converter.

Communications with the instruments was carried out with software written by A. Thurnherr (bbabble and expectscripts), avoiding the need for a Windows PC. Data downloading was carried out in parallel from both instruments at full nominal speed(115kbps) without any problems. (The effective download speed of theBB150 is approximately 3 times lower than that of the WH300.)-

Instrument Setup

A command file for the BB150 was provided by Eric Firing and Jules Hummon. The WH300 parameters were set for consistency with the BB150. The only change that was made to the setup provided by the UH group was to increase the bin size from 8m to 10m (and adjust the number of bins accordingly) from station 8 onward, because of memory limitation on theWH300. The setup was not changed back on later casts when only theBB150 was used.

In order to distribute previous-ping interference (PPI) across two depth layers, the BB150 was set up for staggered pings(1.0/1.6s intervals). The WH300 was set up to ping once every 0.9s,except during the bottom-tracking tests (see below). Pinging was not synchronized between the instruments. Single-ping ensembles were used throughout and most of the data were collected in beam coordinates.(Earth coordinates were used for the uplooking WH300 on casts 7-10,while the processing software was being adapted to handle uplooker beam coordinates.) No bottom-tracking pings were used, except during the bottom-tracking test casts 82--87 (see below). The ambiguity velocity of the WH300 was increased from

2.5m/s to 3 and 4m/s during casts 7--20 in order to diagnose a large-velocity warning, which was later found to be caused by surface contamination. LADCP casts before 7 and after 20 used an ambiguity velocity of 2.5m/s.

Based on earlier experiences of A. Thurnherr during the KAOS and An slope cruises, the blanking distance of the WH300 was set to zero and the first bin was always discarded. On the other hand, the blanking distance of the BB150 was set to 16m, the same size as the transmit length. Note that this implies that the bin length is shorter than the transmit length -- it was found that during a cast the instrument resets the transmit length to the bin length. It is therefore not clear what effect, if any, the long transmit length has.

Data Processing

The data were processed on the Dell laptop using Martin Visbeck's inversion software version 8b. During the cruise, many modifications to the software were implemented -- these are described in the separate LADCP cruise report In particular, it was found that previous-ping interference from the BB150 had to be filtered and this is not possible with the original software. All LADCP profiles were processed in 20mbins.

During data processing the LADCP data were merged with shipboard ADCP data (see below) and with CTD data, the latter provided in a suitable format by the shipboard CTD group. Because of data-acquisition problems of the OS-75 SADCP system, no SADCP data were used for shipboard processing of LADCP casts 10 & 11. Because of large water depths, no bottom-track data are available for LADCP casts 29, 35 and 37.

Station/Cast Numbering

CTD station numbering was done geographically, rather than sequentially(in time). The advantage of this is that the station numbers increase monotonically from west to east along the section, while the disadvantage is that the stations were not occupied sequentially and that station number 41 is missing, because of a weather-related change in plans. LADCP cast numbers were done sequentially, on the other hand. The full CTD station/cast number was used as the LADCP station name -- note that it is the station name, rather than the LADCP cast number, that is used as the plot title in the plots produced by the Lamont software (found in the same directory as the processed data files). The following table gives the association between CTD stations and LADCP cast numbers:

CTD Station	LADCP Cast Number	Notes
999	000	test station
001-013	001-013	identical
014-021	021-014	reversed order
022-040	022-040	identical
042-108	041-107	offset by 1

In addition to the station number, every CTD file has a cast number of 01 or 02 associated with it, depending on whether a prior trace-metal cast was carried out at the same location. With the exception of the following CTD station numbers, all CTD data files have cast number 01:999, 6, 10, 12, 14, 16, 24, 26, 32, 38, 40, 46, 56, 62, 64, 68, 70, 74,80, 84, 86, 90, 96, 102, 106, 108. Thus, the CTD files for the test station are named 99902 and while those of the first real station are 00101. 56, 62, 64, 68, 70, 74,80, 84, 86, 90, 96, 102, 106, 108. Thus, the CTD files for the test station are named 99902 and while those of the first real station are 00101.

Bottom-Tracking Tests

If true bottom tracking (using dedicated BT pings) were to be used, less water-track data could be collected. Therefore, the BB150 was not configured for BT pings and bottom-tracked velocities were calculated by post-processing the water-track data. Geometric considerations imply that this method is associated with potential bias when there is significant horizontal package motion over ground (see Anslope II cruise report). In order to test whether such bias occurs in practice,both ADCPs were mounted as downlookers during LADCP casts 81-86(corresponding to CTD stations 82-87); the standard BB150 configuration was used, while the WH300 was configured to use true BT pings. Additionally, during CTD station 86, the Melville was steaming slowly (at 1-2 knots) during the entire downcast and during the first 200m of the upcast in order to force horizontal package motion over ground. While this may appear extreme, it should be noted that we drifted less during this test station than earlier on in the cruise when we were occupying stations in the Kuroshio in strong winds (e.g. on station 13). The BT tests were very useful, as they not only confirmed the presence of post-processed BT biases of order 5 cm/s both on stations with and without significant drift, but because they also indicate processing-software problems resulting in strong erroneous shears in the bottom-tracked velocity profiles on stations with strong drift. See separate LADCP cruise report for details.

Data Quality

The following comments apply to the processing that was carried out during the cruise. The data will be reprocessed with all the other CLIVAR data after all the CLIVAR cruises have been carried out. The quality of LADCP data is difficult to assess. The simplest test consists in checking the consistency between the shear- and inverse solutions and, perhaps, also between the downcast- and upcast-only inverse solutions. When the data-processing software detects large inconsistencies, it empirically increases the magnitude of the formal error estimates. In the case of the CLIVAR P02 data set, removal of previous-ping interference (PPI) led to a decrease in consistency in some of the profiles, in particular near the sea bed. Therefore, the results of two separate processing runs (both with and without data editing) are provided as part of the cruise data. It is recommended that any user of the LADCP data carry out a careful station-by-station visual quality check before interpretation of the data, especially where small-scale features are concerned.

On stations 1--30 independent data from two ADCP heads are available and those can be processed separately if desired. (During the steaming to Hawaii at the end of the cruise a novel data quality assessment was attempted. The data from each cast were processed twice, each time using half of the available ensembles. The resulting profiles were then checked for mutual consistency and for consistency with the formal error bars of the full solution. See LADCP cruise report for details). As indicated above, there is some uncertainty as to the quality of the bottom-tracking data, in particular for casts where the CTD package drifted more than a few 100 meters while in range of the sea bed. Any bottom-tracking errors are likely to contaminate the resulting LADCP profiles, in particular near the sea bed. The drift velocity of each cast is printed on top of the top panels of processing-figures 13.

In general, the data in the western part of the section are of higher quality than those farther east. This is most likely primarily due to the fact that the instrument range dropped toward the east, because of reduced number of scatterers in the water column. (The dual-head configuration used early on during the cast further improves the quality of the western data).

Files and Directories

The LADCP data should contain (at least) the following directories:

raw:	raw data, instrument-setup command files, communication log files
CTD:	CTD time series and profiles used for LADCP processing
SADCP:	shipboard ADCP data used for LADCP processing
processed:	processed data files and processing figures
processed_noedit:	2 nd processing run carried out without data editing

The contents of these directories should be everything that is needed in order to fully reprocess the LADCP data.

B.1.3. SADCP

Two separate shipboard ADCP systems were installed on the Melville during the cruise: an older 150kHz narrow band instrument and a new Ocean Surveyor 75 kHz instrument, both from RDI. After some initial confusion we got the ok from Eric Firing and Jules Hummon in Hawaii to run both instruments at the same time. The narrow-band SADCP was turned on just after midnight GMT on June 17. During the cruise, only the OS-75 data were processed but the data from both instruments were archived and handed over to the Hawaii group at the end of the leg in Honolulu. The OS-75 data were processed using a separate laptop and software provided by the Hawaii group.

Processing includes a calibration step; the information from an early calibration was emailed to Hawaii to make sure that the instrument was working properly. Later calibrations were consistent with the early one, and the calibration was subsequently applied to all SADCP data during processing. The agreement between on-station SADCP and LADCP data is excellent and the SADCP data were therefore used for LADCP processing (see above). Sometime near the middle of the cruise, Paul Robbins started using underway SADCP data and determined that there appeared to be a calibration error of 1--2 degrees, which resulted in false apparent cross-track velocities while the Melville was underway. Since a calibration error of such small magnitude is of no concern for the (on-station) LADCP processing (expected LADCP compass errors are perhaps 5--10 degrees) no attempt was made to correct the errors during the cruise.

Problems

On several occasions during the cruise, the data acquisition system of the OS-75 failed. The first time this happened, it went unnoticed for approximately 17 hours. The failure was later traced to a maintenance reboot of the network file server onto which the data had been logged. Unfortunately, the RDI data acquisition software reacts to such are boot by failing to write any more data, even though it manages to write error messages into a log file that resides in the same directory as the data files. Even worse, the errors are only written to the log file, while no message is displayed on screen. In order to avoid similar problems in the future, we began to monitor the log files. This was made more difficult because of very frequent (every 0.5--10s) NAV errors that had been suspected to be benign because they did not appear to degrade the SADCP data quality. (This was later confirmed by RDI customer support.)

The NAV errors were, however, the most likely cause of most of the later OS-75 data acquisition failures. According to RDI customer support, data acquisition can fail when the log file gets too big because the system does not have time to open, seek to the end, write, and close the file in rapid succession. Again, no on-screen error message is produced in this case. Eventually, we found a way to avoid NAV errors by not writing to a network drive any more, but only to the local hard disk. A serious disadvantage of this setup is that the SADCP data are not backed up at the source any more. As a workaround, the OS-75 data were backed upon to an external hard disk connected to the LADCP data logging computer once every 24 hours. In the long run, this is an unsatisfactory solution, however.

B.1.4. LADCP -- Leg 2

(Ethan Coon • Columbia University • 2103@columbia.edu)

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Overview of Operations

LADCP System

The LADCP system used on this cruise was nearly identical to the Leg 1 (VANC 32) cruise, and more detail can be found in that report, but a summary and all differences are provided here. During this cruise, a 150 kHz RDI broadband ADCP (BB150 hereafter) was mounted facing downwards on the main rosette on all LADCP casts. The ADCP was powered by a dedicated oil-filled rechargeable lead-acid battery. The battery was extremely reliable and took very little maintenance, simply requiring to be vented occasionally. Recharging after a typical cast took approximately an hour; this coincided nicely with the data download time. The BB150 was connected to a Dell Latitude laptop (model PP01L) running Linux by a long RS-422 cable while on deck. The connection to the ADCP required constant attention; as it was repeatedly being plugged and unplugged with each cast, moisture in the dry-plug connector caused downloading problems at times. The RS-422 connection was converted to RS-232 and finally to USB.

Andreas Thurnherr's "bbabble" and "expect" scripts from Leg 1 were used for all communications.

Set-up Parameters

The BB150 command file used was identical to that of the Leg 1 cruise, as provided by Eric Firing and Jules Hummon. This included a bin size of 10 m and staggered pings on 1.0/1.6 s intervals to minimize previous ping interference (PPI) effects. Single-ping ensembles and beam coordinates were used throughout; all processing was carried out on the laptop. No bottom-track pings were used.

Processing

All on-board processing was carried out on the laptop using Martin Visbeck's inversion software version 8b, including modifications to the control script and data editing make by A. Thurnherr during Leg 1. The modifications for the removal of side-lobe contamination and a time domain spike filter were used, though the PPI filter was disabled, as Leg 1 testing indicated the time spike filter often remedied PPI more robustly than the PPI filter. The only modification made to this software was fixing a minor bug to accommodate Matlab's way of dealing with imaginary numbers. Matlab stipulates that the imaginary component of their structure 'NaN' is zero. Therefore, when a velocity was explicitly assigned to be NaN, only the zonal component became NaN; the meridional velocity component became zero, introducing false data. Ship position, CTD data, post-processed bottom tracking, and two ship-mounted ADCP units provided constraints for the inversion software.

Data Structure and Quality

Directory Structure

LADCP data should contain most if not all of the following directories:

- raw: raw data including logfiles and command files
- CTD: CTD time series and profiles
- SADCP: shipboard ADCP data to constrain LADCP processing
- processed: processed ASCII velocity profile files and Postscript figures
- processed_test: re-processed data using the PPI filter for obvious PPI shear problems in a few stations

Methodology

As CTD stations were numbered geographically from west to east while LADCP data was collected sequentially, the file STATIONNUMBERS contains a reference list to correlate the data. This list consists of three columns of numbers: the LADCP number, CTD station number, and cast number at that CTD station. As the CTD stations were continued numbers from Leg 1, the CTD stations begin with #109, while the LADCP numbers begin with #1. A quick summary of the numbering convention and more information about skipped stations follow:

LADCP #	CTD #
1-18	109-126
19-20	127 cast 2,3
21-55	128-162
56-72	164-180
73-79	182-188
80-81	189 cast 1,2
82	190

At CTD station 127, the CTD failed partway through the upcast, so the cast was aborted. Once the problem was fixed, the rosette was deployed back down to 1100 m to finish the station (LADCP casts 19 and 20 respectively). See the CTD section of the cruise report for more on this.

After LADCP cast 54, the download of data from the ADCP aborted prematurely. As the problem was not fixed before cast 55, the LADCP was started again and a second deployment was started. After cast 55, the download failed again. Since the problem was still not fixed in time for CTD station 163, and the ADCP's onboard memory was full, there is no LADCP data for CTD station 163. Fortunately, the problem was diagnosed as a full hard disk. This simple yet perplexing problem should be alleviated in the future by adding a disk space check and more descriptive error message to the communication scripts.

Prior to CTD station 181, the ship lost power temporarily, causing Melville, the onboard UNIX server, to go down for several hours. At the time of deployment of 181, Melville was still down, which caused the script starting the LADCP to fail when it attempted to synchronize its clock to Melville's time. As the cast had been delayed an hour already, it was decided by the scientist on duty to continue the cast without the LADCP. Once the LADCP technician was notified of the problem, the expect script was changed to synchronize its clock to Harpo, the CTD console, which also synchronizes its time to Melville. Since the synchronization is necessary to match up CTD depth information with LADCP velocity profiles, synchronizing LADCP data to

the CTD console directly seems the better choice, and would have avoided this problem, as the cast could not start without the CTD.

Also as a result of the power failure, the shipboard ADCPs were taken offline for casts 73-77 as per the computer technician. This effects the number of constraints on the least squares problem, and as there was no up-looking instrument, drastically decreases the number of observations of the upper level velocities.

CTD station 189 was repeated due to sample bottle problems, so both casts were profiled.

Data Quality

In general, the quality of LADCP data is hard to judge, especially without extensive processing. However, several problems are readily apparent. The majority of the stations, especially those in the deeper segment of the leg to the west, exhibit a linear shear bias in the individual downcast and upcast inversions (see, for the most obvious cases, LADCP casts 1, 2, 7, 9, 16, and 26). This trend was seen in Leg 1 data, especially in stations near where Leg 2 began. It has been hypothesized that this is a result of few scatterers in the water. As the cruise continued into the shallower waters just west of San Diego, this bias has decreased significantly. In general, the quality of the data is better in the eastern section of the leg.

Also, several cases of PPI (LADCP casts 4 and 47) were not eliminated by time-domain spike filtering. However, both were removed using the PPI data editing during processing.

B.2. Underway pCO₂ – Legs 1 and 2

(D. Feely;, C. Sabine)

The underway surface pCO_2 system operated on an hourly cycle with the first quarter of each hour devoted to calibration with three CO_2 standards, each measured for 5 minutes (Feely et al., 1998). A second order polynomial calibration curve is calculated from the voltage values of the standards. The remaining time in each hour is used to measure equilibrator air (15 min), bow air (15 min), and equilibrator air once again (15 min). The analytical precision of the system is approximately 0.3-0.4 ppm for seawater and for air.

In addition, discrete samples were drawn and analyzed for both DIC and TAlk (Total Alkalinity) from the underway seawater system one to two times daily. These samples will be used in conjunction with the surface underway pCO_2 system, as a mechanism for the over-determination of the ocean carbon system (Lewis et al., 1998).

References:

- Feely, R.A., R. Wanninkhof, H.B. Milburn, C.E. Cosca, M. Stapp, and P.P. Murphy (1998): A new automated underway system for making high precision pCO₂ measurements aboard research ships. Anal. Chim. Acta, 377, 185–191.
- Lewis, E. and D. W. R. Wallace (1998) Program developed for CO₂ system calculations. Oak Ridge, Oak Ridge National Laboratory. http://cdiac.esd.ornl.gov/oceans/

C. Bottle Data - Leg 1

Bottle Sampling

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

- CFCs
- ³He
- O₂
- DIC/Total Alkalinity
- DOC/DON/DCNS/CDOM
- Tritium
- ¹⁴C
- Nutrients
- Salinity

The correspondence between individual sample containers and the rosette bottle 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. Oxygen, nutrient and salinity analyses were performed on computer-assisted (PC) analytical equipment networked to the data processing computer for centralized data management.

Bottle Data Processing

Water samples collected and properties analyzed shipboard were managed centrally in a relational database (PostgreSQL-7.4.2) run on one of the Linux workstations. A web service (OpenAcs-5.0.1 and AOLServer-4.0) front-end provided ship-wide access to CTD and water sample data through web pages. Web-based facilities included on-demand arbitrary property-property plots and vertical sections as well as data downloads.

The sample log (and any diagnostic comments) was 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 appropriate (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.

C.1. Salinity Analysis

Equipment and Techniques

Two Guildline Autosal Model 8400A salinometers (S/N 48-266 & 57-396) located in the forward analytical lab were used for all salinity measurements. The salinometers were modified by ODF to contain an interface for computer-aided measurement. The water bath temperatures were set and maintained at a value near the laboratory air temperature. They were set to 24° C for the entire leg.

The salinity analyses were performed after samples had equilibrated to laboratory temperature, usually within 10-20 hours after collection. The salinometers were standardized for each group of analyses (usually 1-3 casts, up to ~80 samples) using at least one fresh vial of standard seawater per group. Salinometer measurements were made by computer, the analyst being prompted by software to change samples and flush.

Sampling and Data Processing

Salinity samples were drawn into 200 ml Kimax high-alumina borosilicate bottles, which were rinsed three times with sample prior to filling. The bottles were sealed with custom-made plastic insert thimbles and Nalgene screw caps. This assembly provides very low container dissolution and sample evaporation. Prior to sample collection, inserts were inspected for proper fit and loose inserts replaced to insure an airtight seal. The draw time and equilibration time were logged for all casts. Laboratory temperatures were logged at the beginning and end of each run.

PSS-78 salinity [UNES81] was calculated for each sample from the measured conductivity ratios. The difference (if any) between the initial vial of standard water and the next one run as an unknown was applied as a linear function of elapsed run time to the data. The corrected salinity data were then incorporated into the cruise database. 4217 salinity measurements were made and approximately 200 vials of standard water were used. Temperature control was somewhat problematic and several runs were rendered unusable for calibration purposes because of a lack of temperature stability. Many samples were run without allowing adequate thermal equilibration time, resulting in systematically high and low runs. Standards were also sometimes run without adequate equilibration time, or without adequate flushing, systematically biasing entire runs. The estimated accuracy of bottle salinities run at sea is usually better than ± 0.002 PSU relative to the particular standard seawater batch used. The 95% confi dence limit for residual differences between the bottle salinities and calibrated CTD salinity relative to SSW batch P-144 was ± 0.0049 PSU for all salinities, and ± 0.0024 PSU for salinities deeper than 1000db.

Laboratory Temperature

The temperature in the salinometer laboratory varied from 21.9 to 25.1° C, during the cruise. The air temperature change during any single run of samples was less than $\pm 1.5^{\circ}$ C.

Standards

IAPSO Standard Seawater (SSW) Batch P-144 was used to standardize all salinity measurements.

C.2. Oxygen Analysis

Equipment and Techniques

Dissolved oxygen analyses were performed with an ODF-designed automated oxygen titrator using photometric end-point detection based on the absorption of 365nm wavelength ultra-violet light. The titration of the samples and the data logging were controlled by PC software. Thiosulfate was dispensed by a Dosimat 665 buret driver fitted with a 1.0 ml buret. ODF used a whole-bottle modifi ed-Winkler titration following the technique of Carpenter [Carp65] with modifi cations by Culberson *et al.* [Culb91], but with higher concentrations of potassium iodate standard (~0.012N) and thiosulfate solution (~65 gm/l). Pre-made liquid potassium iodate standards were run at the beginning of each session of analyses, which typically included from 1 to 3 stations. Reagent/distilled water blanks were determined every other day or more often if a change in reagents required it to account for presence of oxidizing or reducing agents. The auto-titrator generally performed well.

Sampling and Data Processing

Samples were collected for dissolved oxygen analyses soon after the rosette was brought on board. Using a Tygon and silicone drawing tube, nominal 125ml volume-calibrated iodine fasks were rinsed 3 times with minimal agitation, then fi lled and allowed to overfbw for at least 3 fask volumes. The sample drawing temperatures were measured with a small platinum resistance thermometer embedded in the drawing tube. These temperatures were used to calculate uM/kg concentrations, and as a diagnostic check of bottle integrity. Reagents were added to fi x the oxygen before stoppering. The fasks were shaken twice (10-12 inversions) to assure thorough dispersion of the precipitate, once immediately after drawing, and then again after about 20 minutes.

The samples were analyzed within 1-6 hours of collection, and the data incorporated into the cruise database.

Thiosulfate normalities were calculated from each standardization and corrected to 20° C. The 20° C normalities and the blanks were plotted versus time and were reviewed for possible problems.

As samples warmed up to room temperature they would occasionally degas which would cause a noisy endpoint due to gas bubbles in the light path. The sample drawing temperature thermometer was intermittently functional and uncalibrated from cast 17/1. 3609 oxygen measurements were made.

The blank volumes and thiosulfate normalities were smoothed (linear fits) at the end of the cruise and the oxygen values recalculated.

Volumetric Calibration

Oxygen fask volumes were determined gravimetrically with degassed deionized water to determine fask volumes at ODF's chemistry laboratory. This is done once before using fasks for the first time and periodically thereafter when a suspect bottle volume is detected. The volumetric fasks used in preparing standards were volume-calibrated by the same method, as was the 10 ml Dosimat buret used to dispense standard iodate solution.

Standards

Liquid potassium iodate standards were prepared and bottled in ODF's chemistry laboratory prior to the cruise. The normality of the liquid standard was determined at ODF by calculation from weight. A single standard batch was used during P2 2004 Leg 1. Potassium iodate was obtained from Acros Chemical Co. and was reported by the supplier to be >99.4% pure. All other reagents were "reagent grade" and were tested for levels of oxidizing and reducing impurities prior to use.

C.3. Nutrient Analysis

Equipment and Techniques

Nutrient analyses (phosphate, silicate, nitrate and nitrite) were performed on an ODF-modifi ed 4-channel Technicon AutoAnalyzer II, generally within one hour after sample collection. Occasionally samples were refrigerated up to 4 hours at ~4° C. All samples were brought to room temperature prior to analysis.

The methods used are described by Gordon *et al.* [Gord92]. The analog outputs from each of the four colorimeter channels were digitized and logged automatically by computer (PC) at 2-second intervals.

Silicate was analyzed using the technique of Armstrong *et al.* [Arms67]. An acidic solution of ammonium molybdate was added to a seawater sample to produce silicomolybdic acid which was then reduced to silicomolybdous acid (a blue compound) following the addition of stannous chloride. Tartaric acid was also added to impede PO_4 color development. The sample was passed through a 15mm fbwcell and the absorbance measured at 660nm.

A modification of the Armstrong *et al.* [Arms67] procedure was used for the analysis of nitrate and nitrite. For the nitrate analysis, the seawater sample was passed through a cadmium reduction column where nitrate was quantitatively reduced to nitrite. Sulfanilamide was introduced to the sample stream followed by N-(1-naphthyl)ethylenediamine dihydrochloride which coupled to form a red azo dye. The stream was then passed through a 15mm fbwcell and the absorbance measured at 540nm. The same technique was employed for nitrite analysis, except the cadmium column was bypassed, and a 50mm fbwcell was used for measurement.

Phosphate was analyzed using a modification of the Bernhardt and Wilhelms [Bern67] technique. An acidic solution of ammonium molybdate was added to the sample to produce phosphomolybdic acid, then reduced to phosphomolybdous acid (a blue compound) following the addition of dihydrazine sulfate. The reaction product was heated to ~55° C to enhance color development, then passed through a 50mm fbwcell and the absorbance measured at 820nm.

Sampling and Data Processing

Nutrient samples were drawn into 45 ml polypropylene, screw-capped "oak-ridge type" centrifuge tubes. The tubes were cleaned with 10% HCl and rinsed with sample 2-3 times before filling. Standardizations were performed at the beginning and end of each group of analyses (typically one cast, up to 36 samples) with an intermediate concentration mixed nutrient standard prepared prior to each run from a secondary standard in a low-nutrient seawater matrix. The secondary standards were prepared aboard ship by dilution from primary standard solutions. Dry standards were pre-weighed at the laboratory at ODF, and transported to the vessel for dilution to the primary standard. Sets of 6-7 different standard concentrations were analyzed periodically to determine any deviation from linearity as a function of concentrations when necessary.

After each group of samples was analyzed, the raw data file was processed to produce another file of response factors, baseline values, and absorbances. Computer-produced absorbance readings were checked for accuracy against values taken from a strip chart recording. The data were then added to the cruise database.

Nutrients, reported in micromoles per kilogram, were converted from micromoles per liter by dividing by sample density calculated at 1 atm pressure (0 db), *in situ* salinity, and a per-analysis measured laboratory temperature.

4217 nutrient samples were analyzed. The pump tubing was changed 4 times.

Standards

Primary standards for silicate (Na_2SiF_6) and nitrite ($NaNO_2$) were obtained from Johnson Matthey Chemical Co.; the supplier reported purities of >98% and 97%, respectively. Primary standards for nitrate (KNO_3) and phosphate (KH_2PO_4) were obtained from Fisher Chemical Co.; the supplier reported purities

of 99.999% and 99.999%, respectively. The efficiency of the cadmium column used for nitrate was monitored throughout the cruise and ranged from 99-100%.

No major problems were encountered with the measurements. The temperature of the laboratory used for the analyses ranged from 21.9° C to 25.1° C, but was relatively constant during any one station (±1.5° C).

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C.4. Carbon System

C.4.1. Alkalinity Analyses

During Leg 1, samples were collected and analyzed for alkalinity by personnel from the laboratory of Andrew G. Dickson, Scripps Institution of Oceanography. Samples were collected from all Niskins at the even numbered stations. Replicates were drawn and analyzed from Niskin bottle 1 (the deep bottle), Niskin 18 (an intermediate bottle), and Niskin 36 (the surface bottle). On the odd numbered stations, from 1 to 25 samples were collected along with replicates from the deep and surface bottles. Sampling on the odd numbered stations was done in conjunction with samples collected for the analysis of dissolved inorganic carbon (D.I.C.).

Samples of ~280 mls were collected in Pyrex bottles with 20 mm serum style closures. Bottles were rinsed three times before sample collection. 57 microliters of a saturated mercuric chloride solution were added to inhibit biological activity after collection. A 109 mls sample was delivered into a jacketed beaker using a calibrated glass syringe. The beaker was connected to a bath set to 22.5°C. ~0.1 molar HCl in ~0.6M NaCl was used to titrate the sample as follows: while the sample was being stirred gently, an initial aliquot of ~2.7 mls of acid was added to the sample. Immediately after this addition the sample was stirred vigorously while CO_2 free air was bubbled into the solution at 200 mls/min. After 4 minutes, the titration was completed by the addition of 20 increments of 0.05 mls of the acid using a Dosimat 665 titrator. During the course of the titration, the emf of the solution was monitored using a Ross-Orion combination pH electrode . At each titration point, the volume of solution added, the voltage and the temperature of the sample were recorded. The titration data were processed using a modified Gran plot.

The accuracy of the system was monitored using Batch 65 certified reference materials for D.I.C. and alkalinity supplied by the Dickson laboratory.

C.4.2. 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. The instruments were calibrated at the beginning, middle, and end of each station with a set of the gas loop injections.

Secondary standards were run throughout the cruise on each analytical system; these standards are Certified Reference Materials (CRMs) consisting of poisoned, filtered, and UV irradiated seawater supplied by Dr. A. Dickson of Scripps Institution of Oceanography (SIO), and their accuracy is determined shoreside manometrically. On this cruise, the overall accuracy and precision for the CRMs on both instruments combined was 0.7±1.4 µmol/kg respectively (n=154). Preliminary DIC data reported to the database have not yet been corrected to the Batch 65 CRM value, but a more careful quality assurance to be completed shoreside will have final data corrected to the secondary standard on a per instrument basis.

Samples were drawn from the Niskin-type bottles into cleaned, pre-combusted 500-mL Pyrex bottles using Tygon 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 headspace, and 0.2 ml of saturated HgCl₂ solution was added as a preservative. The sample bottles were sealed with glass stoppers lightly covered with Apiezon-L grease, and were stored at room temperature for a maximum of 24 hours prior to analysis.

Over 2700 samples were analyzed for DIC; full profiles were completed at even numbered stations, with replicate samples taken from the surface, oxygen minimum, and bottom Niskin-type bottles. On the odd numbered stations, samples were drawn throughout the upper 1200m; on three occasions were only surface replicates drawn due to equipment problems, resulting in a backlog of samples. All replicate samples were run at different times during the station analysis for quality assurance of the integrity of the coulometer cell solutions. No systematic differences

between the replicates were observed. In addition, samples were drawn from the underway seawater system, generally one to two times daily.

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C.5. Hyperbaric Styrofoam Compression Experiments (HBSCE)

Opting for quality rather than quantity, only two Hyperbaric Styrofoam Compression Experiments (HBSCEs) were carried out during the cruise. One experiment involved 2 Styrofoam cups (actually, squarish bath-tub shaped parts of a storage box) and the other a painted Styrofoam head. The Styrofoam head was lowered to 5300m and came back very well proportioned. The Styrofoam cups were lowered into the Izu Ogasawara Trench during an attempt to re-spool suspect winch wire by lowering a 500lbs dead weight. Because of justin-time considerations, the artistic decoration of the cups left to be desired and they were lowered in a ziplock bag attached to the weight. Immediately prior to deployment, a couple of holes were punched into the bag to prevent it from being positively buoyant because of trapped air. Both the chief engineer and the captain wanted to limit the wire out of the re-spooling cast to a total of 8800m, but the co-chief scientist would not have it and, after some negotiation, a minimum wire out of 8848m (the height of Mount Everest) was agreed upon. In the end, a maximum wire out of 8856m was achieved. Based on the relationship between wire out and pressure on a subsequent CTD station that was carried out a couple of hours later at the same location (10 dbar @7mwo; 6002 dbar @ 5906 mwo), and considering the calm conditions and lack of strong flow encountered on that station, the best estimate for the achieved depth is 8809m, which may be a new record. Pictures of the Styrofoam cup can be requested by email from <ant@ldeo.columbia.edu>with a subject of "2004 CLIVAR P02 HBSCE 0001."

C.6. Dissolved Organic Carbon and Nitrogen (DOC / DON) – Legs 1 and 2

(D. Hansell • Leg 1; C. Carlson • Leg 2)

The Hansell and Carlson groups collected samples for dissolved organic carbon and nitrogen (DOC / DON) analyses. The samples were collected by Stacy Brown of the University of Miami. These samples will be processed at shore based laboratories to ensure the highest quality data set. On the P02 cruise each PI will take responsibility for separate legs of the transect. Hansell will be responsible for analyses of samples collected on leg 1 of the cruise (Japan to Hawaii) and Carlson will be responsible for analyses of the second leg of samples (Hawaii to San Diego). Both laboratories perform intercalibration exercises for quality control. On the P02 cruise samples were collected from 24 - 36 depths for every other station. The depths and station from which these samples were collected coincided with samples and depths collected for DIC. Samples were collect at sea and stored frozen at -20° C and transported frozen to each shore based laboratory at the University of Miami or University of California, Santa Barbara.

Data will be available approximately 6 - 9 months from their arrival at the respective laboratories.

Instruments and Methods

Sample will be analyzed via the high temperature combustion technique using Shimadzu TOC-V systems with total nitrogen chemiluminescent detection. Samples will be sparged of inorganic carbon by acidification with HCI and sparging with CO_2 free gas for several minutes. A minimum of triplicate injections of 100 ul of sample will be injected onto a Pt alumina combustion catalyst heated to 680°C. The CO_2 signal will then detected with a non-dispersive infra red detector. Total nitrogen is converted to NOx and detected via chemiluminescent.

C.7. Chlorofluorocarbons (CFCs)

Analysts: Leg 1 – *Jim Happell* and *Fred Menzia* Leg 2 - *Eugene Gorman* and *Brice Loose*

The objective was to provide a high quality CFC data set, and make it available nearly immediately to the community as required by the Global Repeat program. The program is in support of CLIVAR and the Carbon Science Programs, and is a component of a global observing system for the physical climate/CO2 system. The data will contribute to documenting and understanding how ventilation and ocean carbon change over time. A number of indirect methods use CFC data to estimate the uptake of anthropogenic CO_2 by the oceans. These data will contribute to quantifying the inventory and flux of anthropogenic CO_2 in the oceans, and to understanding its variability.

Sample Collection

Samples were collected from 10 liter Niskin bottles attached to a 36 bottle rosette for CFC-11, CFC-12 and CFC-113 analysis. A water sample was collected directly from the Niskin bottle petcock using a 100 ml ground glass syringe which was fitted with a three-way stopcock. CFC sampling was conducted first at each station to avoid contamination from air introduced in the top of the Niskin bottle as water was being removed. Subsequent to collection, the syringes were stored in a flow-through seawater bath and analyzed within 6-8 hours after collection. Bath temperature was recorded continuously for use in calculating the mass of water analyzed.

Analysis

CFC analyses were performed on a gas chromatograph (GC) equipped with an electron capture detector (ECD). Samples are introduced into the GC-ECD via a purge and dual trap system. The samples are purged with nitrogen and the compounds of interest are trapped on a main Porapack N trap held at ~ -15°C with a Vortec Tube cooler. After the sample has been purged and trapped for several minutes at high flow, the gas stream is stripped of any water vapor via a magnesium perchlorate trap prior to transfer to the main trap. The main trap is isolated and heated by direct resistance to 140°C. The desorbed contents of the main trap are back-flushed and transferred, with helium gas, over a short period of time, to a small volume focus trap in order to improve chromatographic peak shape. The focus trap is also Porapak N and is held at ~ -15°C with a Vortec Tube cooler. The focus trap is flash heated by direct resistance to 155°C to release the compounds of interest onto the analytical pre-column. The analytical pre-column is held in-line with the main analytical column for the first 1.5 minutes of the chromatographic run. After 1.5 minutes, all of the compounds of interest are on the main column and the pre-column is switched out of line and back-flushed with a relatively high flow of nitrogen gas. This prevents later eluting compounds from building up on the analytical column, eventually eluting and causing the detector baseline signal to increase.

Depending on the depth-at-station, between 17 and 36 samples were collected at each of the 108 stations during Leg 1 and at each of the 81 stations during Leg 2. Two purge blanks and a gas standard were interspersed between ca. each 12 measurements. Time permitting, the surface sample was held after measurement and was sent through the purging process again in order to "restrip" it to determine the efficiency of the purging process. In all cases, the re-stripped sample contained no more concentration of targeted halocarbons than the purge blanks.

Air samples were collected every 1 - 2 days in order to determine the atmospheric concentrations of CFC's and as a check of system accuracy. Samples were collected from the bow of the boat while underway or when the bow was headed into the wind.

Calibration and Precision

The standard used was designated S39 and was cross-calibrated to the SIO-98 absolute calibration scale. A 15 point calibration curve was run every 5-7 days for all four halocarbons. Estimated accuracy is +/- 2%. Precision for CFC-12, CFC-11 and CFC-113 is less than 1%.

Post-processing

The GC-ECD was operated via a laptop computer and data acquisition software (LabView). Following chromatogram generation, the peaks of CFC-11, 12, and 113 were manually reintegrated to obtain more detailed beginning and end points for curve integration.

Final Comments

In large part, sample collection and measurement were successful. There were no major mechanical problems and the automatic data collection system permits analysis of one sample every 10 minutes. The magnesium perchlorate trap was replaced at least daily. There was considerable collection of moisture in the trap throughout the cruise.

C.8. Radio- and Stable Carbon Isotopes – Collection and Analysis – Legs 1 and 2 (A. McNichol; R. Key)

Introduction and Objectives

The measurement of radio- and stable carbon isotopic abundances in oceanic dissolved inorganic carbon (DI13C and DI14C, respectively) provides information that can be used to study many aspects of the ocean carbon cycle. The distributions of both ¹³C and ¹⁴C in the ocean are governed by biological processes and carbonate chemistry, but the normalization of ¹⁴C to a constant ¹³C and time removes the biological effects and allows its distribution to be used as a physical tracer and source indicator while that of ¹³C can reveal information about biological processes and sources. In surface waters, both DI14C and DI13C can be used to assess the uptake of anthropogenic CO_2 (Peng et al., 1998; Gruber and Keeling, 1999; Sonnerup et al., 2000). The uptake of the thermonuclear bomb radiocarbon signal in DIC can be used to trace the movement of different water masses and to assess GCM models (Toggweiler 1989B; Guilderson et al. 2000; Broecker et al. 1985). In deeper waters, DI13C can be used to study oxidation of organic carbon and its impact on nutrient concentrations (Lynch-Stieglitz et al., 1995) and DI14C can be used to study the aging of the water and calculate pre-bomb surface water values (Toggweiler et al., 1989; Broecker et al. 1995; Schlosser et al. 1997; Key and Rubin, 2002). We present here a plan to ensure that measurement of both of these isotopes continues during the CLIVAR Repeat Hydrography cruises.

C.9. Chromophoric Dissolved Organic Matter (CDOM) – Legs 1 and 2

(D.A. Siegel, N.B. Nelson, C.A. Carlson)

Program Activities:

Our goal for P02 was to survey the distribution of chromophoric dissolved organic matter (CDOM) along the section, particularly in the upper 1000 m. CDOM is a dynamic component of the organic matter pool that is ubiquitous throughout the ocean. Because of its optical properties CDOM controls the penetration of ultraviolet radiation in the upper water column, and is therefore a major factor regulating photochemistry and photobiology. CDOM can also be quantified from space due to its impact upon ocean color. We also are evaluating the prospects for using CDOM as an ocean circulation tracer. On P02 we (in the person of Stacy Brown) collected seawater from profiles approximately once per day, approximately 12 depths per station. The samples were stored for absorption spectroscopy analysis at UCSB. CDOM is quantified in terms of absorption coefficient (1/m) and we are estimating this parameter as a continuous spectrum in the 290 nm to 700 nm wavelength range.

Data delivery:

Assuming no unexpected snags we should have the data available in 3-6 months.

Brief Notes on Methodology:

We prepared the seawater samples by filtration through 0.2um Nuclepore filters. The samples were stored refrigerated until analysis. Samples from Leg 1 were shipped to UCSB from Honolulu and have already been analyzed; Leg 2 analysis is underway now. We measured absorption coefficient spectra using a single beam liquid waveguide diode array spectrometer (WPI UltraPath), with a geometric path length of approximately 2 m. Milli-Q water was used as the reference. Absorption spectra (as optical density) were acquired over the 290-730 nm range, with an effective spectral resolution of 2 nm. Optical density spectra were converted to absorption coefficient after correction for baseline drift and the (salinity dependent) refractive index difference between seawater and Milli-Q water. We have a methods paper in progress describing the sample and data analysis used on P02 and previous sections.

D. Bottle Data – Leg 2

Bottle Sampling

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

- CFCs
- ³He
- O₂
- DIC/Total Alkalinity
- DOC/DON/DCNS/CDOM
- Tritium
- ¹⁴C
- Nutrients
- Salinity

The correspondence between individual sample containers and the rosette bottle from which the sample was drawn was recorded on the sample log for the cast. This log also included any observations and comments about the condition of 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 mistripped bottles.

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

Bottle Data Processing

Water samples collected and properties analyzed shipboard were managed centrally in a relational database (PostgreSQL-7.4.2) run on one of the Linux workstations. A web service (OpenAcs-5.1.1 and AOLServer-4.0.7) 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 secure data uploads and downloads.

The sample log (and any diagnostic comments) was 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.

D.1. Salinity Analysis

Equipment and Techniques

Two Guildline Autosal Model 8400A salinometers (S/N 48-266 & 57-396) located in the forward analytical lab were used for all salinity measurements. The salinometers were modified by ODF to contain an interface for computer-aided measurement. The water bath temperatures were set and maintained at a value near the laboratory air temperature. They were set to 24°C for the entire leg.

The salinity analyses were performed after samples had equilibrated to laboratory temperature, usually within 10-20 hours after collection. The salinometers were standardized for each group of analyses (usually 1-3 casts, up to ~80 samples) using at least one fresh vial of standard seawater per group. Salinometer measurements were made by computer, the analyst being prompted by software to change samples and flush.

Sampling and Data Processing

Salinity samples were drawn into 200 ml Kimax high-alumina borosilicate bottles, which were rinsed three times with sample prior to filling. The bottles were sealed with custom-made plastic insert thimbles and Nalgene screw caps. This assembly provides very low container dissolution and sample evaporation. Prior to sample collection, inserts were inspected for proper fit and loose inserts replaced to insure an airtight seal. The draw time and equilibration time were logged for all casts. Laboratory temperatures were logged at the beginning and end of each run.

PSS-78 salinity [UNES81] was calculated for each sample from the measured conductivity ratios. The difference (if any) between the initial vial of standard water and the next one run as an unknown was applied as a linear function of elapsed run time to the data. The corrected salinity data were then incorporated into the cruise database. 3275 salinity measurements were made and approximately 170 vials of standard water were used. Temperature control was somewhat problematic and a few runs were rendered unusable for calibration purposes because of a lack of temperature stability. Some samples were run without allowing adequate thermal equilibration time, resulting in systematically high and low runs. Standards were also sometimes run without adequate equilibration time, or without adequate flushing, systematically biasing entire runs. The estimated accuracy of bottle salinities run at sea is usually better than +/-0.002 PSU relative to the particular standard seawater batch used. The 95% confidence limit for residual differences between the bottle salinities and calibrated CTD salinity relative to SSW batch P-144 was +/-0.0076 PSU for all salinities, and +/-0.0015 PSU for salinities deeper than 1000db.

Laboratory Temperature

The temperature in the salinometer laboratory varied from 21.6 to 25.8°C, during the cruise. The air temperature change during any single run of samples was less than +/-1.5°C.

Standards

IAPSO Standard Seawater (SSW) Batch P-144 was used to standardize all salinity measurements.

D.2. Oxygen Analysis

Equipment and Techniques

Dissolved oxygen analyses were performed with an ODF-designed automated oxygen titrator using photometric end-point detection based on the absorption of 365nm wavelength ultra-violet light. The titration of the samples and the data logging were controlled by PC software. Thiosulfate was dispensed by a Dosimat 665 buret driver fitted with a 1.0 ml buret. ODF used a whole-bottle modified-Winkler titration following the technique of Carpenter [Carp65] with modifications by Culberson et al. [Culb91], but with higher concentrations of potassium iodate standard (~0.012N) and thiosulfate solution (~65 gm/l). Pre-made liquid potassium iodate standards were run at the beginning of each session of analyses, which typically included from 1 to 3 stations. Reagent/distilled water blanks were determined every other day or more often if a change in reagents required it to account for presence of oxidizing or reducing agents. The auto-titrator generally performed well.

Sampling and Data Processing

Samples were collected for dissolved oxygen analyses soon after the rosette was brought on board. Using a Tygon and silicone drawing tube, nominal 125ml volume-calibrated iodine flasks were rinsed 3 times with minimal agitation, then filled and allowed to overflow for at least 3 flask volumes. The sample drawing temperatures were measured with a small platinum resistance thermometer embedded in the drawing tube. These temperatures were used to calculate uM/kg concentrations, and as a diagnostic check of bottle integrity. Reagents were added to fix the oxygen before stoppering. The flasks were shaken twice (10-12 inversions) to assure thorough dispersion of the precipitate, once immediately after drawing, and then again after about 20 minutes.

The samples were analyzed within 1-6 hours of collection, and the data incorporated into the cruise database.

Thiosulfate normalities were calculated from each standardization and corrected to 20°C. The 20°C normalities and the blanks were plotted versus time and were reviewed for possible problems.

As samples warmed up to room temperature they would occasionally degas which would cause a noisy endpoint due to gas bubbles in the light path. The sample drawing temperature thermometer during this leg was intermittently functional and uncalibrated. 2816 oxygen measurements were made.

The blank volumes and thiosulfate normalities were smoothed (linear fits) at the end of the cruise and the oxygen values recalculated.

Volumetric Calibration

Oxygen flask volumes were determined gravimetrically with degassed deionized water to determine flask volumes at ODF's chemistry laboratory. This is done once before using flasks for the first time and periodically thereafter when a suspect bottle volume is detected. The volumetric flasks used in preparing standards were volume-calibrated by the same method, as was the 10 ml Dosimat buret used to dispense standard iodate solution.

Standards

Liquid potassium iodate standards were prepared and bottled in ODF's chemistry laboratory prior to the cruise. The normality of the liquid standard was determined at ODF by calculation from weight. A single standard batch was used during P2 2004 Leg 2. Potassium iodate was obtained from Acros Chemical Co. and was reported by the supplier to be >99.4% pure. All other reagents were "reagent grade" and were tested for levels of oxidizing and reducing impurities prior to use.

D.3. Nutrient Analysis

Equipment and Techniques

Nutrient analyses (phosphate, silicate, nitrate and nitrite) were performed on an ODF-modified 4-channel Technicon AutoAnalyzer II, generally within one hour after sample collection. Occasionally samples were refrigerated up to 4 hours at ~4°C. All samples were brought to room temperature prior to analysis.

The methods used are described by Gordon et al. [Gord92]. The analog outputs from each of the four colorimeter channels were digitized and logged automatically by computer (PC) at 2-second intervals.

Silicate was analyzed using the technique of Armstrong et al. [Arms67]. An acidic solution of ammonium molybdate was added to a seawater sample to produce silicomolybdic acid which was then reduced to silicomolybdous acid (a blue compound) following the addition of stannous chloride. Tartaric acid was also added to impede PO4 color development. The sample was passed through a 15mm flowcell and the absorbance measured at 660nm.

A modification of the Armstrong et al. [Arms67] procedure was used for the analysis of nitrate and nitrite. For the nitrate analysis, the seawater sample was passed through a cadmium reduction column where nitrate was quantitatively reduced to nitrite. Sulfanilamide was introduced to the sample stream followed by N-(1-naphthyl)ethylenediamine dihydrochloride which coupled to form a red azo dye. The stream was then passed through a 15mm flowcell and the absorbance measured at 540nm. The same technique was employed for nitrite analysis, except the cadmium column was bypassed, and a 50mm flowcell was used for measurement.

Phosphate was analyzed using a modification of the Bernhardt and Wilhelms [Bern67] technique. An acidic solution of ammonium molybdate was added to the sample to produce phosphomolybdic acid, then reduced to phosphomolybdous acid (a blue compound) following the addition of dihydrazine sulfate. The reaction product was heated to ~55°C to enhance color development, then passed through a 50mm flowcell and the absorbance measured at 820nm.

Sampling and Data Processing

Nutrient samples were drawn into 45 ml polypropylene, screw-capped "oak- ridge type" centrifuge tubes. The tubes were cleaned with 10% HCl and rinsed with sample 2-3 times before filling. Standardizations were performed at the beginning and end of each group of analyses (typically one cast, up to 36 samples) with an intermediate concentration mixed nutrient standard prepared prior to each run from a secondary standard in a low- nutrient seawater matrix. The secondary standards were prepared aboard ship by dilution from primary standard solutions. Dry standards were pre- weighed at the laboratory at ODF, and transported to the vessel for dilution to the primary standard. Sets of 6-7 different standard concentrations were analyzed periodically to determine any deviation from linearity as a function of concentrations when necessary.

After each group of samples was analyzed, the raw data file was processed to produce another file of response factors, baseline values, and absorbances. Computer-produced absorbance readings were checked for accuracy against values taken from a strip chart recording. The data were then added to the cruise database.

Nutrients, reported in micromoles per kilogram, were converted from micromoles per liter by dividing by sample density calculated at 1 atm pressure (0 db), in situ salinity, and a per-analysis measured laboratory temperature.

3278 nutrient samples were analyzed. The pump tubing was changed 3 times.

Standards

Primary standards for silicate (Na2SiF6) and nitrite (NaNO2) were obtained from Johnson Matthey Chemical Co.; the supplier reported purities of >98% and 97%, respectively. Primary standards for nitrate (KNO3) and phosphate (KH2PO4) were obtained from Fisher Chemical Co.; the supplier reported purities of 99.999% and 99.999%, respectively. The efficiency of the cadmium column used for nitrate was monitored throughout the cruise and ranged from 99-100%.

No major problems were encountered with the measurements. The temperature of the laboratory used for the analyses ranged from 21.6°C to 25.8°C, but was relatively constant during any one station (+/-1.5°C).

D.4. Total Dissolved Inorganic Carbon (DIC) – Leg 2 (D. Feely, C. Sabine)

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, middle, and end of each station with a set of the gas loop injections.

Secondary standards were run throughout the cruise on each analytical system; these standards are Certified Reference Materials (CRMs) consisting of poisoned, filtered, and UV irradiated seawater supplied by Dr. A. Dickson of Scripps Institution of Oceanography (SIO), and their accuracy is determined shoreside manometrically. On this cruise, the overall accuracy and precision for the CRMs on both instruments combined was 0.7±0.9 µmol/kg respectively (n=173). Preliminary DIC data reported to the database have not yet been corrected to the Batch 65 CRM value, but a more careful quality assurance to be completed shoreside will have final data corrected to the secondary standard on a per instrument basis.

Samples were drawn from the Niskin-type bottles into cleaned, pre-combusted 500-mL Pyrex bottles using Tygon 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 headspace, and 0.2 ml of saturated HgCl2 solution was added as a preservative. The sample bottles were sealed with glass stoppers lightly covered with Apiezon-L grease, and were stored at room temperature for a maximum of 24 hours prior to analysis.

Over 4000 samples were analyzed for discrete DIC; full profiles were completed at even numbered stations, with replicate samples taken from the surface, oxygen minimum, and bottom Niskin-type bottles. On the odd numbered stations, samples were drawn throughout the upper 1200m; occasionally only surface replicates were drawn due to equipment problems, resulting in a backlog of samples. The replicate samples were interspersed throughout the station analysis for quality assurance of the integrity of the coulometer cell solutions. No systematic differences between the replicates were observed.

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Dissolved Organic Carbon Analyses - Leg 2 P02_2004 line.

PI: Craig A. Carlson

Collection:

All samples were collected directly from the Niskin Bottles. Because particulate organic carbon (POC) concentrations in the surface waters can be elevated all samples collected from the upper 500 m were filtered. Water was filtered through a combusted GF/F housed in an acid washed polycarbonate filter cartridge attached directly the Niskin bottle spigot. Water below 500 m was not filtered because greater than 98% or the total organic carbon is DOC. All samples were collected directly into an acid washed and Nanopure flushed high density polyethylene (HDPE) bottles (60ml). Samples were immediately placed upright in a -20°C freezer and samples were shipped to shore laboratory packed in dry ice. All samples were kept frozen at -20°C in an organic (volatile) free environment.

Analysis:

All DOC samples were analyzed via high temperature combustion using Shimadzu TOC-V in shore based laboratory at the University of California, Santa Barbara. The operating conditions of the Shimadzu TOC-V were slightly modified from the manufacturer's model system. The condensation coil was removed and the head space of an internal water trap was reduced to minimize the system's dead space. The combustion tube contained 0.5 cm Pt pillows placed on top of Pt alumina beads to improve peak shape and to reduce alteration of combustion matrix throughout the run. CO_2 free carrier gas was produced with a Whatman® gas generator (Carlson et al. 2004). Samples were drawn into 5 ml injection syringe and acidified with 2M HCI (1.5%) and sparged for 1.5 minutes with CO_2 free gas. Three to five replicate 100 µl of sample were injected into combustion tube heated to 680° C. The resulting gas stream was passed though a several water and halide traps, the CO_2 in the carrier gas was analyzed with a non-dispersive infrared detector and the resulting peak area was integrated with Shimadzu chromatographic software. Injections continued until the at least three injection meet the system specified range of a SD of 0.1 area counts, CV ≤2% or best 3 of 5 injections.

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

DOC calculation:

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

References:

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D.5. Trace Metals; Dissolved and Aerosol Programs

(C. Measures; B. Landing)

Trace Metals Group:

Florida State University: Bill Landing, Cliff Buck, Paul Hansard University of Hawaii: Matt Brown, John Yeh

Summary

Sea water samples for on board trace metal determinations were collected using 12 L Go-Flo bottles on a 12-place rosette system equipped with a SeaBird 911 ctd and oxygen sensor and a Wet Labs FL-1 fluorometer. The rosette package was deployed from the stern of the ship with the Go-Flo bottles in the open configuration using a 4 conductor Kevlar cable sheathed in polyurethane. The package was lowered at ~ 40 m/min to 10-30m below the target depth of the deepest bottle. As the package was raised back through the water column the Go-Flo bottles were tripped individually at pre-assigned depths while the package was moving at ~ 10-20 m/min. The depths that the bottles were tripped was one of three sampling patterns that were designed to match the three sampling schemes used by the main hydrography program. Gary Klinkhammer (OSU) provided a photosynthetically-active radiation (PAR) sensor and a light scattering sensor for continuous profiling on the rosette/CTD at each station.

Upon package recovery the Go-Flo bottles were taken from the rosette into the trace metal sampling van for sub sampling. Unfiltered sub-samples were collected directly from each bottle for salinity and nutrient determinations and also to ensure that each Go-Flo bottle had closed at the correct depth. Filtered sub-samples were collected from each bottle through a 47mm in-line Nuclepore polycarbonate track-etched disc filters, 0.4 μ m, after attaching the bottles to a 10 psi filtered air supply. During leg 1 a total of 51 stations were occupied, yielding a total of 604 samples. During Leg 2 a total of 38 stations were occupied with a total of 456 samples. Cruise totals: 89 stations, 1060 samples.

Unfiltered and filtered subsamples were collected from each depth for return to FSU for analysis of iron by Fe-57 isotope dilution Inductively-Coupled Plasma Mass Spectrometry (ICPMS). Filtered samples were collected from each depth for ship-board analysis of dissolved Fe and Al using the University of Hawaii flow-injection system. Filtered subsamples were collected from each depth for ship-board analysis of Fe(II) and total dissolved Fe using the FSU FeLume chemiluminescent technique. Unfiltered samples were collected from each depth and analyzed on board. Subsamples were collected from each depth for Mark Altabet at the School for Marine Science and Technology, University of Massachusetts for shore-based analysis of nitrogen isotopes in dissolved nitrate. Subsamples (stored, frozen) were collected from each depth at 5 stations for shore-based analysis of dissolved Fe-binding ligands by Kristen Buck at UC Santa Cruz. Subsamples were collected from 5 sets of day/night station pairs for shore-based analysis of dissolved Mn by Gary Klinkhammer at Oregon State University.

Aerosol samples were collected each day (24-hour integrated) using the FSU aerosol sampling tower. Wind sector and wind speed control was used to immediately shut off the sampling when the wind brings ship's exhaust towards the bow. Bulk aerosols were collected on 47 mm, 0.4 µm polycarbonate filters for shore-based analysis of total trace elements using energy dispersive X-ray fluorescence (Joe Resing, University of Washington and NOAA/PMEL). Replicate samples on 0.45 µm polypropylene filter were leached with DI

water or surface seawater to measure soluble Fe(II) (ship-board), and for shore-based analysis of total soluble Fe and Al, and soluble anions and cations. Every other day, a sample of size-fractionated aerosols was collected using a Micro Orifice Uniform Deposition Impactor (MOUDI). Size cutoffs of 3.1, 1.0, 0.56, and 0.056 μ m were used. Those filters were also leached with DI water for shore-based analysis of total soluble Fe and Al, and soluble anions and cations.

A complete data set for dissolved Fe and AI was obtained from the UH FIA analytical system. Dissolved Fe concentrations compared very well with previously published data from the northeastern Pacific, ranging from a few tens of picomolar in the oligotrophic upper waters of the central gyre, to values of 500-1,000 pM from 500-1000 meters. Slight surface enrichment for dissolved Fe was seen as far east as Station 153. At station 167, we encountered an unusual plume of water (150-600 m) with very elevated dissolved Fe (1,000-2,000 pM) and dissolved reduced Fe(II) (50-100 pM) . Unusual hydrographic features were reported for other tracers as well, indicating that the feature was associated with an eddy that entrained water from the eastern tropical Pacific. High dissolved Fe concentrations are known from this region due to suboxic redox cycling where the oxygen minimum intersects the sediments. Concentrations of dissolved Fe in the 700-1000 m depth range increased steadily from 400-500 pM east of Hawaii to 800-1,000 pM approaching the eastern end of the section.

Dissolved AI also showed slight surface enrichment due to dust input (>3 nM) from Hawaii east to Station 151. Slightly elevated AI concentrations (3-4 nM) were also seen in the "mode water" from 175-250 m at stations between Hawaii and Station 141. The profiles are generally featureless east of Station 141, at around 2 nM. The eddy feature seen in dissolved Fe at Station 167 was not reflected in the AI profile.

Initial results of the on board Fe and Al determinations have already been submitted to the shipboard data base. Final data will be submitted to the data base by August 31st, 2005.

The dissolved Fe(II) profiles showed higher values in the surface waters (20-70 pM) and in the samples from between 750-1000 meters (20-40 pM). The elevated Fe(II) in surface waters has previously been attributed to photochemical reduction of dissolved Fe(III). The high Fe(II) concentrations in the deep samples were unexpected since the oxidation lifetime for photochemically produced Fe(II) should be as short as a few minutes to hours. The data suggest that a mechanism such as microbiological regeneration of Fe(II) from settling biogenic debris may be important here. The dissolved oxygen concentrations are not low enough to trigger inorganic Fe(II) reduction, but may contribute to the stabilization of the regenerated Fe(II).

The soluble aerosol Fe(II) concentrations ranged from 0.6-10 pmol/m³ of filtered air. These concentrations cannot be placed in perspective until after the shore-based analysis of total aerosol Fe and total soluble aerosol Fe has been completed. It is clear that the total aerosol loads in the atmosphere between Hawaii and San Diego were quite a bit lower than were observed on Leg 1 near Japan.

Comments from the Chief Scientist

(J. Swift)

Trace metal casts were carried out at every second station. The trace metal group had their own CTD, rosette, bottles (Go-Flo), cable (on a semi-portable winch supplied by SIO), laboratory van, and a full complement of personnel. No others from the ship's company, other than the mate on watch, had duties related to the over-the-side portion of trace metal casts. (The hydrographic team ran salinity and nutrient samples from the trace metal casts, and the hydrographic data processor included the trace metal casts in the integrated data system.)

The casts were carried out to 1000 meters, either immediately before of immediately after the principal CTD/rosette cast, at the choice of the trace metal group. The group was very well organized, and were always ready when it was time to launch their rosette. After a short period of familiarization during Leg 1 they were able to complete their operations within their allotted one-hour time window.

It should be noted that the CTD data produced by the trace metal program will become part of the archive of data from this expedition, and that those data appear poised to be valuable companion data to the core program. Furthermore, on these cruises with their tight data quality and availability requirements and inventory of specialized equipment to maintain there is typically a backlog of tasks to carry out, and the extra hour provided by the trace metal casts was put to good use in every case.

D.5.1. Aerosol Program

(W. Landing)

The role of iron as a limiting plant nutrient in the oceans is widely recognized, but still poorly understood. Atmospheric transport of mineral dust is the major mechanism by which Fe is supplied to the open ocean, and therefore has a major impact on upper ocean biogeochemical cycling of carbon and the major plant nutrients. There are very few data on the concentrations of total aerosol Fe and the percentage of soluble aerosol Fe over the open ocean. The aerosol sampling/analytical component of the CLIVAR Trace Metals research effort utilizes a 4-channel aerosol sampling system deployed on a 6.1 meter tower deployed near the bow of the ship. The sampling is automatically controlled by wind sector and wind speed to avoid stack exhaust contamination. We collect replicate bulk aerosol samples and size-fractionated aerosols on 47 mm diameter filters. The analyses of these samples is designed to help understand the processes responsible for solubilizing Fe and Al in mineral dust.

One of the bulk aerosol filters is analyzed for total aerosol Fe and AI (and other trace elements). A replicate filter is quickly leached with freshly-collected 0.2 μ m filtered surface seawater to measure soluble Fe(II) and total soluble Fe and AI. Another replicate filter is quickly leached with ultra-pure deionized water to measure DI-water soluble Fe and soluble anions (including excess sulfate and nitrate) and cations (sodium). The distribution of soluble aerosol Fe in various particle sizes is measured using a Micro Orifice Uniform Deposition cascade impactor (MOUDI).

Samples were collected (24-hour integrated) on 70 days from June 16-August 26, 2004 along the cruise track from Yokohama to San Diego.

Aerosol data is generally available within 12 months of the end of the cruise, in this case by August 31, 2005.

Instruments and Methods:

- a. Total aerosol Fe and Al is measured on 47 mm, 0.4 μm polycarbonate track-etched filters by energydispersive x-ray fluorescence by Dr. Joe Resing at the NOAA/PMEL lab in Seattle. In this method, secondary x-rays are used to excite the elements on the filter. The frequencies (energies) of the emitted x-rays are characteristic for each element, and the x-ray intensity at each frequency is roughly proportional to the amount of each element on the filter.
- b. Seawater-soluble Fe(II) is measured on freshly-collected 47 mm, 0.45 μm polypropylene aerosol filters. The loaded filter is placed in a clean polycarbonate vacuum filtration rig and 100 ml of 0.2 μm filtered surface seawater (natural pH) is pulled though the filter in 5-10 seconds. A small volume of ultra-pure hydrochloric acid is placed in the collection reservoir of the filtration rig prior to leaching the filter to stabilize the soluble Fe(II) at pH 6. These samples are immediately analyzed using a flow-injection chemiluminescent analytical method that is specific for dissolved Fe(II). After this, the samples are further acidified to pH 2 for storage and analysis of total dissolved Fe at FSU.
- c. Total soluble aerosol Fe is measured on the seawater and DI-water aerosol leaches by isotope dilution Inductively-coupled Plasma Mass Spectrometry (ICP-MS) and graphite furnace Atomic Absorption Spectrophotometry (GFAAS), respectively. The seawater leaching procedure is described above in section (b). For the DI-water solubility measurements, a replicate loaded aerosol filter is placed in a

clean polycarbonate vacuum filtration rig and 100 ml of ultra-pure deionized water (pH 5.6) is pulled though the filter in 5-10 seconds. These samples are immediately frozen for return to FSU. After thawing and analysis of the soluble anions and cations (section (d) below) the samples are acidified to pH 2 and stored for analysis of total soluble aerosol Fe and Al by GFAAS.

d. Soluble aerosol anions and cations are measured on the DI-water leaches using ion chromatography (chloride, nitrate, sulfate) and flame AAS (sodium).

D.5.2. Dissolved Fe(II) and Total Dissolved Fe in Seawater

(W. Landing)

It is expected that photochemical reactions between dissolved Fe and organic matter in surface waters can reduce Fe(III) to Fe(II). While the lifetime of Fe(II) with respect to re-oxidation can be as short as a few minutes, we expect that the Fe(II) could build up to measurable concentrations under the right conditions. Fe(II) is expected to form much weaker complexes than Fe(III) with dissolved Fe binding ligands, and may therefore be more bioavailable. Photochemical redox cycling may also serve to keep the total dissolved Fe concentrations in surface waters at higher levels than would be possible without such reactions. In addition, it is known that bacterial respiration inside fecal pellets and fecal aggregates can produce reducing micro-environments where Fe(III) may be released as Fe(II) during the bacterial oxidation of settling biogenic debris. If this mechanism is important, it might be possible to detect Fe(II) at the depths where sub-oxic respiration occurs. For these reasons, we made an effort to measure Fe(II) on seawater samples collected using our "trace metals clean" rosette system. We collected 12 samples (to 1000 meters) from each of 89 stations. Dissolved Fe(II) was measured on each sample from each station, with a few exceptions when we conducted special tests of the analytical system and the analytical conditions.

The analytical system used to measure Fe(II) can also be used to measure total dissolved Fe after the samples have been acidified and subjected to chemical reduction using a mild reducing agent; in this case disodium sulfite. This gives us an opportunity to compare the results to the FIA total dissolved Fe analysis conducted by the UH group. After confirming that direct analysis of the acidified samples was not accurate, we switched to the use of a cation chelating resin column to pre-concentrate the dissolved Fe(II), thereby eliminating the false positive "blank" that arises during direct analysis of the acidified samples. By pre-concentrating a 3 ml volume of sample on the column, this method has a detection limit on the order of 10-20 pM.

The dissolved Fe(II) and total dissolved Fe data should be available by August 31, 2005, 12 months after the end of the cruise.

Dissolved Fe(II) is measured on 0.2 μ m filtered seawater samples collected using the trace metals rosette system. Upon recovery of the rosette, the 12-liter GoFlo bottles are immediately transferred to the clean van. Samples are taken as quickly as possible using gravity filtration through a Pall AcroPak 0.2 μ m cartridge filter (polyethersulfone membrane) into 125 ml bottles that have been pre-charged with 20 μ L of 6M quartz-distilled HCI. This drops the pH to 6.0, the optimum pH for preserving the existing Fe(II) without inducing Fe(III) reduction. These samples are quickly analyzed for dissolved Fe(II) using a chemiluminescent reaction with luminol at pH 10.3. The analog signal from the photomultiplier tube is calibrated using Fe(II) standard additions to seawater at pH 6.0. The detection limit for dissolved Fe(II) using this method is on the order of 10-20 pM.

Total dissolved Fe is measured on 0.4 μ m filtered seawater samples following acidification to pH 2.3 (100 μ L 6M Q-HCl per 100 ml sample) and reduction for 24 hours with 20 μ M disodium sulfite. The samples are buffered back up to pH 5.3 with 40 mM ammonium acetate and extracted onto a 2 ml 8-hydroxyquinoline column at a flow rate of 2 ml per minute. This is followed by a rinse with 1 ml of DI-water, and elution with 2 ml of 0.14 M Q-HCl in DI-water. The acid elution is pumped into a stream of luminol at pH 9.4 in front of a

photomultiplier tube where the chemiluminescence from luminol oxidation is detected. The analysis is calibrated using Fe(II) and/or Fe(III) standard additions to acidified seawater in the range of 0-1.5 nM.

Additional Cooperative Sampling

Seawater samples were also collected with our trace metals rosette system for three other research groups collaborating with the UH/FSU trace metals team. Samples were collected from 12 depths (to 1000 meters) at 89 stations for Prof. Mark Altabet (University of Massachusetts) for analysis of nitrogen isotopes in dissolved nitrate. Samples were collected from 12 depths (to 1000 meters) at 10 stations for Kristen Buck (UC Santa Cruz) for analysis of dissolved Fe-binding ligands. Samples were collected from 12 depths (to 1000 meters) at 10 stations for Prof. Gary Klinkhammer (Oregon State University) for analysis of dissolved Mn.

E. CTD DATA - CLIVAR P02_2004 Leg 1

R/V Melville, VANC32MV

15 June 2004 - 25 July 2004 Yokohama, Japan - Honolulu, Hawaii Chief Scientist: Dr. Paul Robbins Scripps Institution of Oceanography Co-Chief Scientist: Dr. Andreas Thurnherr Lamont-Doherty Earth Observatory



P02_2004 Leg 1 Cruise Track 15 June - 25 July 2004

Preliminary Cruise Report mod. 4 October 2004

Data Submitted by:

Oceanographic Data Facility Scripps Institution of Oceanography La Jolla, Ca. 92093-0214

Summary

A hydrographic survey consisting of zonal LADCP/CTD/rosette sections in the western North Pacific was carried out June to July 2004. The R/V Melville departed Yokohama, Japan on 15 June 2004. A total of 107 LADCP/CTD/Rosette stations were occupied and 52 trace metals casts were made from 16 June - 22 July. Water samples (up to 36), LADCP and CTD data were collected in many cases to within 10 meters of the bottom. Salinity, dissolved oxygen and nutrient samples were analyzed from every bottle sampled on the rosette. The cruise ended in Honolulu, Hawaii. on 25 July 2004.

Introduction

A sea-going science team gathered from ten oceanographic institutions around the U.S. participated on the cruise. Several other science programs were supported with no dedicated cruise participant. The science party and their responsibilities are listed below:

Personnel

Duties	Name	Affiliation	email
CH SCI	Paul Robbins	UCSD/SIO	probbins@ucsd.edu
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Scientific Personnel P2 2004 Leg 1

Analysis	Institution	Principal Investigator	
CTDO/S/O ₂ /Nutrients	UCSD/SIO	Jim Swift	
Transmissometer	TAMU	Wilf Gardner	
CO ₂ -Alkalinity	UCSD/SIO	Andrew Dickson	
CO ₂ -DIC + Underway pCO ₂	NOAA	Dick Feely/Chris Sabine	
DOC/DON	RSMAS-UMiami/UCSB	Dennis Hansell/Craig Carlson	
CDOM	UCSB	Dave Siegel/Norm Nelson/Craig Carlson	
¹³ C/ ¹⁴ C	WHOI/Princeton Univ.	Ann McNichol/Robert Key	
CFCs	RSMAS-UMiami/LDEO	Rana Fine/Bill Smethie	
³ He/Tritium	WHOI	Bill Jenkins	
ADCP/LADCP	UHawaii/LDEO	Eric Firing/Martin Visbeck	
Trace Elements	UHawaii/FSU	Chris Measures/Bill Landing	
Aerosols	UCSD	Nicolas Patris	

Principal Programs

Principal Programs of P2 2004 Leg 1

Description of Measurement Techniques

E.1. CTD/Hydrographic Measurements Program

The basic CTD/hydrographic measurements consisted of salinity, dissolved oxygen and nutrient measurements made from water samples taken on CTD/rosette casts, plus pressure, temperature, salinity, dissolved oxygen and transmissometer from CTD profiles. A total of 107 CTD/rosette casts were made, usually to within 20 meters of the bottom. No major problems were encountered during the operation. The distribution of samples is illustrated in figures 1.0-1.2. Note that there was no station 41.



Figure 1.0 Sample distribution, stations 1-44.



Figure 1.1 Sample distribution, stations 44-75.



Figure 1.2 Sample distribution, stations 75-108.

E.1.1. Water Sampling Package

LADCP/CTD/rosette casts were performed with a package consisting of a 36-bottle rosette frame (ODF), a 36-place pylon (SBE32) and 36 10-liter Bullister bottles (ODF). Underwater electronic components consisted of a Sea-Bird Electronics (SBE) 9*plus* CTD (ODF #675) with dual pumps, dual temperature (SBE3*plus*), dual conductivity (SBE4), dissolved oxygen (SBE43), transmissometer (Wetlabs C-Star) and fluorometer (Seapoint Sensors); an SBE35RT Digital Reversing Thermometer, RDI LADCPs (Workhorse 300khz/Broadband 150khz) and a Simrad 807 altimeter.

The CTD was mounted vertically in an SBE CTD frame attached to the bottom center of the rosette frame. All SBE4 conductivity and SBE3*plus* temperature sensors and their respective pumps were

mounted vertically as recommended by SBE. Pump exhausts were attached to outside corners of the CTD cage and directed downward. The entire cage assembly was then mounted on the bottom ring of the rosette frame, offset from center to accommodate the pylon, and also secured to frame struts at the top. The SBE35RT temperature sensor was mounted vertically and equidistant between the T1 and T2 intakes. The altimeter was mounted on the inside of a support strut adjacent to the bottom frame ring. The transmissometer and fluorometer were mounted horizontally along the rosette frame adjacent to the CTD. The LADCPs were vertically mounted inside the bottle rings on the opposite side of the frame from the CTD with one set of transducers pointing down, the other up.

The rosette system was suspended from a UNOLS-standard three-conductor 0.322" electro-mechanical sea cable.

The R/V Melville's forward CTD winch ("Desh-5") was used for casts 1/1-50/1. It developed unresolvable level-wind problems and would have been put out of service earlier had weather conditions permitted moving the rosette and cart to the starboard A-frame. The aft CTD winch ("Desh-6") was used for the remaining casts (51/1-108/2).

Sea cable reterminations were made prior to casts 12/2, 19/1 and 51/1. CTD data dropouts occurring on the upcast of 25/1 were traced to a corroded slip ring termination which was repaired prior to 26/2. No casts were aborted.

The deck watch prepared the rosette 10-20 minutes prior to each cast. All valves, vents and lanyards were checked for proper orientation. The bottles were cocked and all hardware and connections rechecked. Once stopped on station, the LADCP was turned on and the rosette moved into position under the squirt boom (casts 1/1-50/1) or starboard A-Frame (51/1-108/2) via an air-powered cart and tracks. As directed by the deck watch leader, the CTD was powered-up and the data acquisition system started. Two stabilizing tag lines were threaded through rings on the rosette frame, and syringes were removed from the CTD sensor intake ports. The deck watch leader directed the winch operator to raise the package, the boom (A-Frame) and rosette were extended outboard and the package quickly lowered into the water. The tag lines were removed and the package was lowered to 10 meters. The CTD console operator then directed the winch operator to bring the package close to the surface, pause for typically 10 seconds and begin the descent.

Each rosette cast was usually lowered to within 20 meters of the bottom, or to 6000M, the operational limit for this package.

Each Bottle on the rosette had a unique serial number. This bottle identification was maintained independently of the bottle position on the rosette and was used for sample identification. No bottles were changed or replaced on this leg, although parts of a few of them were replaced or repaired.

Recovering the package at the end of the deployment was essentially the reverse of launching, with the additional use of poles and snap-hooks to attach tag lines for added safety and stability. The rosette was moved into the CTD hangar for sampling. The bottles and rosette were examined before samples were taken, and anything unusual noted on the sample log.

Routine CTD maintenance included soaking the conductivity and CTD DO sensors in fresh water between casts to maintain sensor stability. Rosette maintenance was performed on a regular basis. O-rings were changed as necessary and bottle maintenance was performed each day to insure proper closure and sealing. Valves were inspected for leaks and repaired or replaced as needed.

E.1.2. Underwater Electronics Packages

CTD data were collected with a SBE9*plus* CTD (ODF #675). This instrument provided pressure, dual temperature (SBE3), dual conductivity (SBE4), dissolved oxygen (SBE43), transmissometer (Wetlabs C-Star), fluorometer (Seapoint Sensors) and altimeter (Simrad 807) channels. CTD #675 supplied a standard Sea-Bird format data stream at a data rate of 24 frames/second (fps).

Sea-Bird SBE32 36-place Carousel Water Sampler	S/N 0187
Sea-Bird SBE35RT Digital Reversing Thermometer	S/N 0035
Sea-Bird SBE9 <i>plus</i> CTD	S/N 09P9852-0675
Paroscientifi c Digiquartz Pressure Sensor	S/N 88907
Sea-Bird SBE3plus Temperature Sensor	S/N 03P-4196 (Primary)
Sea-Bird SBE3plus Temperature Sensor	S/N 03P-4308 (Secondary)
Sea-Bird SBE4C Conductivity Sensor	S/N 04-2766 (Primary)
Sea-Bird SBE4C Conductivity Sensor	S/N 04-2569 (Secondary 1/1-57/1)
Sea-Bird SBE4C Conductivity Sensor	S/N 04-1880 (Secondary 58/1-108/2)
Sea-Bird SBE43 DO Sensor	S/N 43-0244 (1/1-103/1)
Sea-Bird SBE43 DO Sensor	S/N 43-0199 (104/1-108/2)
Wetlabs C-Star Transmissometer	S/N 507DR
Seapoint Sensors Fluorometer	S/N 2273
Simrad 807 Altimeter	S/N 4077
RDI Workhorse 300khz LADCP	S/N 754
RDI Broadband 150khz LADCP	S/N 1546
LADCP Battery Pack	

 Table 1.2.0 P2 2004 Leg 1 Rosette Underwater Electronics.

The CTD was outfitted with dual pumps. Primary temperature, conductivity and dissolved oxygen were plumbed on one pump circuit and secondary temperature and conductivity on the other. The sensors were deployed vertically. The primary temperature and conductivity sensors (T1 #4196 and C1 #2766) were used for reported CTD temperatures and conductivities on all casts. The secondary temperature and conductivity sensors (T2 #4308 and C2 #2569 casts 1/1-57/1, C2 #1880 casts 58/1-108/2) were used for calibration checks.

The SBE9*plus* CTD and the SBE35RT Digital Reversing Thermometer were both connected to the SBE32 36-place pylon providing for single-conductor sea cable operation. All three sea cable conductors were connected together for signal and power to improve reliability, the sea cable armor was used for the return. Power to the SBE9*plus* CTD (and sensors), SBE32 pylon, SBE35RT and Simrad altimeter was provided through the sea cable from the SBE11*plus* deck unit in the main lab.

E.1.3. Navigation and Bathymetry Data Acquisition

Navigation data were acquired (at 1-second intervals) from the ship's Trimble PCODE GPS receiver by one of the Linux workstations beginning June 15. Data from the ship's Knudsen 320B/R Echosounder (3.8 KHz transducer) were also acquired and merged with the navigation. The Knudsen bathymetry data were noisy and subject to washing out on station when the bow thrusters were engaged.

Bathymetric data from the ship's multibeam (Seabeam) echosounder system were also logged by the R/V Melville's underway system.

E.1.4. Real-Time CTD Data Acquisition System

The CTD data acquisition system consisted of an SBE-11*plus* deck unit and three networked generic PC workstations running Fedora 1 Linux. Each PC workstation was configured with a color graphics display, keyboard, trackball, 120 GB disk, and DVD+RW drives. Two of the three systems also had 8 additional RS-232 ports via a Rocketport PCI serial controller. The systems were networked through a 100BaseTX ethernet switch, which was also connected to the ship's network. These systems were available for real-time operational and CTD data displays, and provided for CTD and hydrographic data management and backup. Hardcopy capability was provided by an HP 1200C network printer and by the ship's networked printers.

One of the workstations was designated the CTD console and was connected to the CTD deck unit via RS-232. The CTD console provided an interface for controlling CTD deployments as well as real-time operational displays for CTD and rosette trip data, GPS navigation, bathymetry and the CTD winch.

CTD deployments were initiated by the console watch after the ship stopped on station. The watch maintained a console operations log containing a description of each deployment, a record of every attempt to close a bottle and any pertinent comments. The deployment software presented a short dialog instructing the operator to turn on the deck unit, to examine the on screen raw data display for stable CTD data, and to notify the deck watch that this was accomplished. When the deck watch was ready to put the rosette over the side, the console watch was notified and the CTD data acquisition started. The deployment software display changed to indicate that a cast was in progress. A processed data display appeared, as did a rosette bottle trip display and control for closing bottles. Various real-time plots were initiated to display the progress of the deployment. GPS time and position, and uncorrected Knudsen bottom depth were automatically logged at 1 second resolution during the cast. Both raw and processed (2 Hz time-series) CTD data were automatically backed up by one of the other workstations via ethernet.

Once the deck watch had deployed the rosette, the winch operator immediately lowered it to 10 meters. The CTD pumps were configured with an 8 second startup delay, and were on by the time the rosette reached 10 meters. The console operator checked the CTD data for proper sensor operation, then instructed the winch operator to bring the package to the surface, pause for 10 seconds, and descend to a target depth (wire-out). The lowering rate was normally 60 meters/minute for this package, depending on sea cable tension and 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 decided where to trip bottles on the up cast, noting this on the console log. The altimeter channel, CTD depth, wire-out and bathymetric depth were monitored to determine the distance of the package from the bottom. The on-screen winch and altimeter displays allowed the watch to refine the target wire-out relayed to the winch operator and safely approach to within 20 meters of the bottom.

Bottles were closed on the up cast by operating a "point and click" graphical trip control button. The data acquisition system responded with trip confirmation messages and the corresponding CTD data in a rosette bottle trip window on the display. All tripping attempts were noted on the console log. The console watch then directed the winch operator to raise the package up to the next bottle trip location. The console watch was also responsible for creating a sample log for the deployment which was used to record the correspondence between rosette bottles and analytical samples taken.

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

E.1.5. CTD Data Processing

ODF CTD processing software consists of over 30 programs running in a Linux/Unix run-time environment. The initial CTD processing program (ctdrtd/ctdba) is used either in real-time or with raw CTD data to:

- Convert raw CTD scans into scaled engineering units, and assign the data to logical data channels;
- Filter data channels according to specifi ed criteria;
- Apply sensor- or instrument-specifi c response-correction models;
- Decimate the data channels according to specifi ed criteria; and
- Store the output time-series in a CTD-independent format.

Once the CTD data are reduced to a standard format time-series, they can be manipulated in various ways. Channels can be additionally filtered. The time-series can be split up into shorter time-series or pasted together to form longer time-series. A time-series can be transformed into a pressure-series, or into a larger-interval time-series. The pressure, temperature and conductivity laboratory calibration coefficients are applied during the creation of the initial time-series. Adjustments to pressure, temperature and conductivity are maintained in separate files and are applied whenever the data are accessed.

The CTD data acquisition software acquired and processed the data in real-time, providing calibrated, processed data for interactive plotting and reporting during a cast. The 24 Hz data from the CTD were filtered, response-corrected and decimated to a 2 Hz time-series. Sensor correction and calibration models were applied to pressure, temperature, and conductivity. Rosette trip data were extracted from this time-series in response to trip initiation and confirmation signals. The calibrated 2 Hz time-series data, as well as the 24 Hz raw data, were stored on disk and were backed up via ethernet to a second system. At the end of the cast, various consistency and calibration checks were performed, and a 2 db pressure-series of the down cast was generated and subsequently used for reports and plots.

CTD data were examined at the completion of deployment for potential problems. Data from the two CTD temperature sensors were examined, compared with SBE35RT Digital Reversing Thermometer data and checked for sensor drift. CTD conductivity sensors were compared and calibrated by examining differences between CTD and check-sample conductivity values. The CTD dissolved oxygen sensor data were calibrated to check-sample data. Additionally, deep theta-salinity and theta- O_2 comparisons were made between down and up casts as well as with adjacent deployments.

Minor sea cable noise problems on this cruise did not significantly affect the CTD data, being filtered out during the data acquisition.

The initial 10 M yoyo in each deployment, where the package was lowered and then raised back to the surface to start the SBE pumps, was omitted during the generation of the 2 db pressure-series.

Density inversions can be induced in high-gradient regions by ship-generated vertical motion of the rosette. Detailed examination of the raw data shows significant mixing can occur in these areas because of "ship roll". To minimize density inversions, a "ship-roll" filter which disallowed pressure reversals was applied during the generation of the 2 db pressure-series down-cast data.

E.1.6. CTD Laboratory Calibration Procedures

Laboratory calibrations of the CTD pressure, temperature and conductivity sensors were used to generate Sea-Bird conversion equation coefficients applied by the data acquisition software at sea.

Pressure calibrations were last performed on CTD #675 at the ODF Calibration Facility (La Jolla) 19 March 2004. The Paroscientific Digiquartz pressure transducer (S/N 88907) was calibrated in a temperature-controlled water bath to a Ruska Model 2400 Piston Gauge Pressure Reference.

The SBE3*plus* temperature sensors (primary S/N 03-4196, secondary S/N 03-4308) were calibrated at ODF on 18 March 2004.

CTD #675 with pressure transducer #88907 was used for one 5-week cruise between the laboratory calibration and the beginning of P2 2004 Leg 1. The P2 2004 Leg 1 T1 sensor was used as the secondary temperature during that same cruise.

The SBE4 conductivity sensors (primary S/N 04-2766, secondary S/Ns 04-2569 and 04-1880) were all calibrated on 20 April 2004 at SBE.

The SBE35RT Digital Reversing Thermometer (S/N 0035) was calibrated on 15 March 2004 at SBE.

E.1.7. CTD Shipboard Calibration Procedures

CTD #675 (Pressure S/N 88907) was used for all P2 2004 Leg 1 casts. The CTD was deployed with all sensors and pumps aligned vertically, as recommended by SBE. Secondary temperature and conductivity (T2 & C2) sensors served as calibration checks for the reported primary temperature and conductivity (T1 & C1) on all casts. The SBE35RT Digital Reversing Thermometer (S/N 35-0035) served as an independent temperature calibration check. *In-situ* salinity check samples collected during each CTD cast were used to calibrate the conductivity sensors.

E.1.7.1. CTD Pressure

Pressure sensor conversion equation coefficients derived from the pre-cruise pressure calibration were applied to raw pressure data during each cast. No additional adjustments were made to the calculated pressures.

Residual pressure offsets (the difference between the first and last submerged pressures) were tabulated to check for calibration shifts. All were < 0.5db.

There was no apparent shift in pressure calibration during P2 2004 Leg 1. The CTD #675 post-cruise calibration is pending; repairs are required for damage caused by fboding during the second leg.

E.1.7.2. CTD Temperature

Temperature sensor conversion equation coefficients were derived from the pre-cruise calibrations and applied to raw primary and secondary temperature data. The primary (T1, S/N 03P-4196) and secondary (T2, S/N 03P-4308) SBE3*plus* temperature sensors were used the entire cruise without replacement.

Two independent metrics of calibration accuracy were examined. The primary and secondary temperatures were compared at each rosette trip, and the SBE35RT temperatures were compared to primary and secondary temperatures at each rosette trip.

The T1 sensor appeared to have a second-order pressure dependence, requiring a +0.00026 to -0.0005 °C correction from surface to 6200db. The T2 sensor did not appear to require any slope correction, only an offset; but the offset shifted occasionally, varying from 0 to 0.00086 °C during the leg.

The T1 and SBE35RT comparisons, after shipboard correction of T1, are summarized in figures 1.7.2.0 and 1.7.2.1.



Figure 1.7.2.0 T1 and SBE35RT temperature differences by pressure, all pressures.



Figure 1.7.2.1 T1 and SBE35RT temperature differences by cast, p>1000db.



Figures 1.7.2.2 and 1.7.2.3 show T1-T2 residual differences after shipboard corrections.

Figure 1.7.2.2 Primary and secondary temperature differences by pressure, all pressures.



Figure 1.7.2.3 Primary and secondary temperature differences by cast, p>1000db.

Preliminary results from post-cruise calibrations show T2 only required an offset of about +0.0008 °C. The T1 results appear to indicate a +0.0005 to 0 °C correction is required from 0 to 30 °C - the opposite of what was applied shipboard (-0.0005 to +0.00026 °C from 6200db to 0db). The laboratory calibrations only measure effects caused by temperature changes, since all are done at essentially surface pressure. The T1 shipboard corrections are about -0.001 °C deep and +0.0003 °C at the surface compared to post-cruise calibration results. This difference needs to be evaluated more carefully before fi nal temperature corrections are determined.

E.1.7.3. CTD Conductivity

Conductivity sensor conversion equation coefficients were derived from the pre-cruise calibrations and applied to raw primary and secondary conductivities.

One primary and two secondary SBE4 conductivity sensors were used on P2 2004 Leg 1: C1 S/N 04-2766 was used the entire cruise, and was used for all reported CTD conductivities. C2 S/N 04-2569 was used on casts 1/1-57/1. C2 S/N 04-1880 was used on 58/1-108/2. The secondary sensors were used as calibration checks on the primary sensor.

Comparisons between the primary and secondary sensors, and between sensors and check sample conductivities, were used to derive conductivity sensor corrections.

Comparisons between the primary and secondary sensors, and between sensors and check sample conductivities, were used to derive conductivity sensor corrections. A single first-order pressure-dependent slope (on the order of +0.002 mS/cm from 0 to 6200db) was applied to all C1 data. The C1 offset shifted by -0.0006 mS/cm from stations 1-57, then stabilized for the rest of the cruise (both legs). The two secondary sensors were corrected based on bottle salt differences.

Shipboard overlays of deep theta-salinity profiles were checked for cast-to-cast consistency. Most deep profiles of adjacent casts agreed to within 0.0001-2 mS/cm.

The comparison of the primary and secondary conductivity sensors by station, after applying shipboard corrections, is summarized in figure 1.7.3.0.



Figure 1.7.3.0 C1 and C2 conductivity differences by cast, p>1000db.

Salinity residuals after applying shipboard corrections are summarized in figures 1.7.3.1 through 1.7.3.3.



Figure 1.7.3.1 salinity residuals by pressure, all pressures.





Figure 1.7.3.3 salinity residuals by cast, p>1000db.

Figure 1.7.3.3 represents an estimate of the deep salinity accuracy of CTD #675. The 95% confi dence limit is ± 0.0024 PSU relative to bottle salts. The agreement between the C1/C2 sensors after shipboard corrections were applied is ± 0.0007 mS/cm deep (comparable to about ± 0.00085 PSU).

Post-cruise calibrations of the conductivity sensors by Sea-Bird are pending. These calibrations will not account for any pressure effects on the sensors.

E.1.7.4. CTD Dissolved Oxygen

Two SBE43 dissolved O_2 (DO) sensors were used for this cruise (S/N 43-0244 casts 1/1-103/1, S/N 43-0199 casts 104/1-108/2). Sensor 43-0244 was replaced when its response began to drop. The sensor was plumbed into the P1/T1/C1 intake line in a vertical confi guration after C1 and before P1 (as specifi ed by SBE).

The DO sensor calibration method used for this cruise was to match down-cast CTD O_2 data to up-cast bottle trips along isopycnal surfaces, then to minimize the residual differences between the *in-situ* check sample values and CTD O_2 using a non-linear least-squares fi tring procedure. Since this technique only calibrates the down-cast, only the 2 db pressure series down-cast data contain calibrated CTD O_2 .

Figures 1.7.4.0, 1.7.4.1 and 1.7.4.2 show the residual differences between bottle and calibrated CTD O_2 for all pressures. Figure 1.7.4.3 shows the residual differences for pressures deeper than 1000 db.



Figure 1.7.4.0 O_2 residuals by station number, all pressures.



Figure 1.7.4.1 O₂ residuals by pressure, all pressures.



Figure 1.7.4.2 O_2 residuals by temperature, all pressures.



Figure 1.7.4.3 O₂ residuals by station number, p>1000db.

The standard deviations of 0.050 ml/l for all oxygens and 0.021 ml/l for deep oxygens are only intended as indicators of how well the up-cast bottle O_2 and down-cast CTD O_2 match. ODF makes no claims regarding the precision or accuracy of CTD dissolved O_2 data.

The general form of the ODF O_2 conversion equation for Clark cells follows Brown and Morrison [Brow78] and Millard [Mill82], [Owen85]. ODF models membrane and sensor temperatures with lagged CTD temperatures and a lagged thermal gradient. *In-situ* pressure and temperature are filtered to match the sensor response. Time-constants for the pressure response τ_p , two temperature responses τ_{Ts} and τ_{Tf} , and thermal gradient response τ_{dT} are fitting parameters. The thermal gradient term is derived by low-pass filtering the difference between the fast response (T_f) and slow response (T_s) temperatures. This term is SBE43-specific and corrects a non-linearity introduced by analog thermal compensation in the sensor. The O_c gradient, dO_c/dt , is approximated by low-pass filtering 1st-order O_c differences. This gradient term attempts to correct for reduction of species other than O_2 at the sensor cathode. The time-constant for this filter, τ_{oq} , is a fitting parameter. Dissolved O_2 concentration is then calculated:

$$O_{2ml/l} = [c_1 O_c + c_2] \cdot f_{sat}(S, T, P) \cdot e^{(c_3 P_l + c_4 T_l + c_5 T_s + c_6 \frac{dO_c}{dt} + c_7 dT)}$$
(1.7.4.0)

where:

O _{2ml/l}	= Dissolved O_2 concentration in ml/l;
O _c	= Sensor current (μamps);
$f_{sat}(S,T,P)$	= O_2 saturation concentration at S,T,P (ml/l);
S	= Salinity at O ₂ response-time (PSUs);
Т	= Temperature at O ₂ response-time (° C);
Ρ	= Pressure at O ₂ response-time (decibars);
P _I	Low-pass fi Itered pressure (decibars);
T _f	= Fast low-pass fi Itered temperature (° C);
T _s	= Slow low-pass fi Itered temperature (° C);
$\frac{dO_c}{dt}$	= Sensor current gradient (µamps/secs);
dŤ	= low-pass fi Itered thermal gradient $(T_f - T_s)$.

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F. CTD Data - CLIVAR P02_2004 Leg 2

R/V Melville, VANC33MV





P02_2004 Leg 2 Cruise Track 28 July - 27 August 2004

Preliminary Cruise Report mod. 4 October 2004

Data Submitted by:

Oceanographic Data Facility Scripps Institution of Oceanography La Jolla, Ca. 92093-0214

Summary

A hydrographic survey consisting of a zonal LADCP/CTD/rosette section along latitude 30 north in the Eastern North Pacific was carried out July to August 2004. The R/V Melville departed Honolulu, Hawaii on 28 July 2004. A total of 82 LADCP/CTD/Rosette stations were occupied and 38 trace metals CTD/Rosette casts were made from 31 July - 27 August. Water samples (up to 36), LADCP and CTD data were collected in most cases to within 15 meters of the bottom. Salinity, dissolved oxygen and nutrient samples were analyzed from every bottle sampled on the rosette. Additional deployments included 12 ARGOS floats and 6 net tows. The cruise ended in San Diego, California on 27 August 2004.

Introduction

A sea-going science team gathered from ten oceanographic institutions around the U.S. participated on the cruise. Several other science programs were supported with no dedicated cruise participant. The science team and their responsibilities are listed below.

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Transmissometer	TAMU	Wilf Gardner
CO ₂ -Alkalinity	UCSD/SIO	Andrew Dickson
CO_2 -DIC + Underway p CO_2	NOAA	Dick Feely/Chris Sabine
DOC/DON	RSMAS-UMiami/UCSB	Dennis Hansell/Craig Carlson
CDOM	UCSB	Dave Siegel/Norm Nelson/Craig Carlson
¹³ C/ ¹⁴ C	WHOI/Princeton Univ.	Ann McNichol/Robert Key
CFCs	RSMAS-UMiami/LDEO	Rana Fine/Bill Smethie
³ He/Tritium	WHOI	Bill Jenkins
ADCP/LADCP	UHawaii/LDEO	Eric Firing/Martin Visbeck
Trace Elements	UHawaii/FSU	Chris Measures/Bill Landing
ARGO Floats	NOAA	Greg Johnson/Elizabeth Steffen
Aerosols	UCSD	Nicolas Patris
Net Tows	UCSD/SIO	John McGowan

Principal Programs

Principal Programs of P2 2004 Leg 2

Description of Measurement Techniques

F.1. CTD/Hydrographic Measurements Program

The basic CTD/hydrographic measurements consisted of salinity, dissolved oxygen and nutrient measurements made from water samples taken on CTD/rosette casts, plus pressure, temperature, salinity, dissolved oxygen and transmissometer from CTD profiles. A total of 84 CTD/rosette casts were made (two casts on stations 127 and 189), usually to within 15 meters of the bottom. No major problems were encountered during the operation. The distribution of samples is illustrated in fi gures 1.0-1.2.



Figure 1.0 Sample distribution, stations 109-137.



Figure 1.1 Sample distribution, stations 137-167.



Figure 1.2 Sample distribution, stations 167-190.

F.1.1. Water Sampling Package

LADCP/CTD/rosette casts were performed with a package consisting of a 36-bottle rosette frame (ODF), a 36-place pylon (SBE32) and 36 10-liter Bullister bottles (ODF). Underwater electronic components consisted of a Sea-Bird Electronics (SBE) 9*plus* CTD (ODF #675 or #474) with dual pumps, dual temperature (SBE3*plus*), dual conductivity (SBE4), dissolved oxygen (SBE43), transmissometer (Wetlabs C-Star) and fluorometer (Seapoint Sensors); an SBE35RT Digital Reversing Thermometer, RDI LADCPs (Workhorse 300khz/Broadband 150khz) and a Simrad 807 altimeter.

The CTD was mounted vertically in an SBE CTD frame attached to the bottom center of the rosette frame. All SBE4 conductivity and SBE3*plus* temperature sensors and their respective pumps were

mounted vertically as recommended by SBE. Pump exhausts were attached to outside corners of the CTD cage and directed downward. The entire cage assembly was then mounted on the bottom ring of the rosette frame, offset from center to accommodate the pylon, and also secured to frame struts at the top. The SBE35RT temperature sensor was mounted vertically and equidistant between the T1 and T2 intakes. The altimeter was mounted on the inside of a support strut adjacent to the bottom frame ring. The transmissometer and fluorometer were mounted horizontally along the rosette frame adjacent to the CTD. The LADCPs were vertically mounted inside the bottle rings on the opposite side of the frame from the CTD with one set of transducers pointing down, the other up.

The rosette system was suspended from a UNOLS-standard three-conductor 0.322" electro-mechanical sea cable.

The R/V Melville's aft CTD winch ("Desh-6") was used for the entire leg.

A single sea cable retermination made in Honolulu served for the entire leg, although a mechanical retermination was required after the winch operator two-blocked the rosette at the onset of (aborted) cast 184/2. *CTD #675 partially flooded near 1100M on the upcast of 127/2, which was aborted at 400M.* CTD #474 was used for all subsequent casts. No other casts were aborted.

The deck watch prepared the rosette 10-20 minutes prior to each cast. All valves, vents and lanyards were checked for proper orientation. The bottles were cocked and all hardware and connections rechecked. Once stopped on station, the LADCP was turned on and the rosette moved into position under starboard A-Frame via an air-powered cart and tracks. As directed by the deck watch leader, the CTD was powered-up and the data acquisition system started. Two stabilizing tag lines were threaded through rings on the rosette frame, and syringes were removed from the CTD sensor intake ports. The deck watch leader directed the winch operator to raise the package, the boom (A-Frame) and rosette were extended outboard and the package quickly lowered into the water. The tag lines were removed and the package was lowered to 10 meters. The CTD console operator then directed the winch operator to bring the package close to the surface, pause for typically 10 seconds and begin the descent.

Each rosette cast was usually lowered to within 20 meters of the bottom, or to 6000M, the operational limit for this package.

Each Bottle on the rosette had a unique serial number. This bottle identification was maintained independently of the bottle position on the rosette and was used for sample identification. Spots of blue paint were discovered on the upper and lower interior surfaces of bottle #8 and it was replaced by bottle #37 prior to 179/2. No other bottles were replaced on this leg, although parts of a few of them were changed or repaired.

Recovering the package at the end of the deployment was essentially the reverse of launching, with the additional use of poles and snap-hooks to attach tag lines for added safety and stability. The rosette was moved into the CTD hangar for sampling. The bottles and rosette were examined before samples were taken, and anything unusual noted on the sample log.

Routine CTD maintenance included soaking the conductivity and CTD DO sensors in fresh water between casts to maintain sensor stability. Rosette maintenance was performed on a regular basis. Orings were changed as necessary and bottle maintenance was performed each day to insure proper closure and sealing. Valves were inspected for leaks and repaired or replaced as needed.

F.1.2. Underwater Electronics Packages

CTD data were collected with a SBE9*plus* CTD (ODF #675 on 109/1-127/2, ODF #474 on 127/3-190/1). The instrument provided pressure, dual temperature (SBE3), dual conductivity (SBE4), dissolved oxygen (SBE43), transmissometer (Wetlabs C-Star), fluorometer (Seapoint Sensors) and altimeter (Simrad 807) channels. The CTD supplied a standard Sea-Bird format data stream at a data rate of 24 frames/second (fps).
Sea-Bird SBE32 36-place Carousel Water Sampler	S/N 0187
Sea-Bird SBE35RT Digital Reversing Thermometer	S/N 0035
Sea-Bird SBE9 <i>plus</i> CTD	S/N 09P9852-0675 (109/1-127/2)
Sea-Bird SBE9 <i>plus</i> CTD	S/N 09P9852-0474 (127/3-190/1)
Paroscientifi c Digiquartz Pressure Sensor	S/N 88907 (109/1-127/2)
Paroscientifi c Digiquartz Pressure Sensor	S/N 69008 (127/3-190/1)
Sea-Bird SBE3plus Temperature Sensor	S/N 03P-4196 (Primary)
Sea-Bird SBE3plus Temperature Sensor	S/N 03P-4308 (Secondary)
Sea-Bird SBE4C Conductivity Sensor	S/N 04-2766 (Primary)
Sea-Bird SBE4C Conductivity Sensor	S/N 04-1880 (Secondary 109/1-124/1)
Sea-Bird SBE4C Conductivity Sensor	S/N 04-2593 (Secondary 125/2-125/2)
Sea-Bird SBE4C Conductivity Sensor	S/N 04-2113 (Secondary 126/1-127/2)
Sea-Bird SBE4C Conductivity Sensor	S/N 04-2904 (Secondary 127/3-190/1)
Sea-Bird SBE43 DO Sensor	S/N 43-0199 (109/1-190/1)
Wetlabs C-Star Transmissometer	S/N 507DR
Seapoint Sensors Fluorometer	S/N 2273
Simrad 807 Altimeter	S/N 4077
RDI Workhorse 300khz LADCP	S/N 754
RDI Broadband 150khz LADCP	S/N 1546
LADCP Battery Pack	

 Table 1.2.0 P2 2004 Leg 2 Rosette Underwater Electronics.

The CTD was outfitted with dual pumps. Primary temperature, conductivity and dissolved oxygen were plumbed on one pump circuit and secondary temperature and conductivity on the other. The sensors were deployed vertically. The primary temperature and conductivity sensors (T1 #03P-4196 and C1 #04-2766) were used for reported CTD temperatures and conductivities on all casts. The secondary temperature and conductivity sensors were used for calibration checks.

The SBE9*plus* CTD and the SBE35RT Digital Reversing Thermometer were both connected to the SBE32 36-place pylon providing for single-conductor sea cable operation. All three sea cable conductors were connected together for signal and power to improve reliability, the sea cable armor was used for the return. Power to the SBE9*plus* CTD (and sensors), SBE32 pylon, SBE35RT and Simrad altimeter was provided through the sea cable from the SBE11*plus* deck unit in the main lab.

F.1.3. Navigation and Bathymetry Data Acquisition

Navigation data were acquired (at 1-second intervals) from the ship's Trimble PCODE GPS receiver by one of the Linux workstations beginning July 28. Data from the ship's Knudsen 320B/R Echosounder (3.8 KHz transducer) were also acquired and merged with the navigation. The Knudsen bathymetry data were noisy and subject to washing out on station when the bow thrusters were engaged.

Bathymetric data from the ship's multibeam (Seabeam) echosounder system were also logged by the R/V Melville's underway system.

F.1.4. Real-Time CTD Data Acquisition System

The CTD data acquisition system consisted of an SBE-11*plus* deck unit and three networked generic PC workstations running Fedora 1 Linux. Each PC workstation was configured with a color graphics display, keyboard, trackball, 120 GB disk, and DVD+RW drives. Two of the three systems also had 8 additional RS-232 ports via a Rocketport PCI serial controller. The systems were networked through a 100BaseTX ethernet switch, which was also connected to the ship's network. These systems were available for real-time operational and CTD data displays, and provided for CTD and hydrographic data management and backup. Hardcopy capability was provided by an HP 1200C network printer and by the ship's networked printers.

One of the workstations was designated the CTD console and was connected to the CTD deck unit via RS-232. The CTD console provided an interface for controlling CTD deployments as well as real-time operational displays for CTD and rosette trip data, GPS navigation, bathymetry and the CTD winch.

CTD deployments were initiated by the console watch after the ship stopped on station. The watch maintained a console operations log containing a description of each deployment, a record of every attempt to close a bottle and any pertinent comments. The deployment software presented a short dialog instructing the operator to turn on the deck unit, to examine the on screen raw data display for stable CTD data, and to notify the deck watch that this was accomplished. When the deck watch was ready to put the rosette over the side, the console watch was notified and the CTD data acquisition started. The deployment software display changed to indicate that a cast was in progress. A processed data display appeared, as did a rosette bottle trip display and control for closing bottles. Various real-time plots were initiated to display the progress of the deployment. GPS time and position, and uncorrected Knudsen bottom depth were automatically logged at 1 second resolution during the cast. Both raw and processed (2 Hz time-series) CTD data were automatically backed up by one of the other workstations via ethernet.

Once the deck watch had deployed the rosette, the winch operator immediately lowered it to 10 meters. The CTD pumps were configured with an 8 second startup delay, and were on by the time the rosette reached 10 meters. The console operator checked the CTD data for proper sensor operation, then instructed the winch operator to bring the package to the surface, pause for 10 seconds, and descend to a target depth (wire-out). The lowering rate was normally 60 meters/minute for this package, depending on sea cable tension and 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 decided where to trip bottles on the up cast, noting this on the console log. The altimeter channel, CTD depth, wire-out and bathymetric depth were monitored to determine the distance of the package from the bottom. The on-screen winch and altimeter displays allowed the watch to refine the target wire-out relayed to the winch operator and safely approach to within 20 meters of the bottom.

Bottles were closed on the upcast by operating a "point and click" graphical trip control button. The data acquisition system responded with trip confirmation messages and the corresponding CTD data in a rosette bottle trip window on the display. All tripping attempts were noted on the console log. The console watch then directed the winch operator to raise the package up to the next bottle trip location. The console watch was also responsible for creating a sample log for the deployment which was used to record the correspondence between rosette bottles and analytical samples taken.

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

F.1.5. CTD Data Processing

ODF CTD processing software consists of over 30 programs running in a Linux/Unix run-time environment.

Raw CTD data are initially converted to engineering units, filtered, response-corrected, calibrated and decimated to a more managable 0.5 second time-series. The laboratory calibrations for pressure, temperature and conductivity are applied at this time.

Once the CTD data are reduced to a standard format time-series, they can be manipulated in various ways. Channels can be additionally filtered. The time-series can be split up into shorter time-series or pasted together to form longer time-series. A time-series can be transformed into a pressure-series, or into a larger-interval time-series. Adjustments to pressure, temperature and conductivity determined from comparisons to other sensors and to check samples are maintained in separate files and are applied whenever the data are accessed.

The CTD data acquisition software acquired and processed the data in real-time, providing calibrated, processed data for interactive plotting and reporting during a cast. The 24 Hz CTD data were filtered, response-corrected and decimated to a 2 Hz time-series. Sensor correction and calibration models were applied to pressure, temperature, and conductivity. Rosette trip data were extracted from this time-series in response to trip initiation and confirmation signals. All data were stored on disk and were additionally backed up via ethernet to a second system. At the end of the cast, various consistency and calibration checks were performed and a 2 db pressure-series of the down cast was generated and subsequently

used for reports and plots.

CTD data were examined at the completion of deployment for potential problems. Data from the two CTD temperature sensors were examined, compared with SBE35RT Digital Reversing Thermometer data and checked for sensor drift. CTD conductivity sensors were compared and calibrated by examining differences between CTD and check-sample conductivity values. The CTD dissolved oxygen sensor data were calibrated to check-sample data. Additionally, deep theta-salinity and theta- O_2 comparisons were made between down and up casts as well as with adjacent deployments.

The initial 10 M yoyo in each deployment, where the package was lowered and then raised back to the surface to start the SBE pumps, was omitted during the generation of the 2 db pressure-series.

Density inversions can be induced in high-gradient regions by ship-generated vertical motion of the rosette. Detailed examination of the raw data shows significant mixing can occur in these areas because of "ship roll". To minimize density inversions, a "ship-roll" filter which disallowed pressure reversals was applied during the generation of the 2 db pressure-series down-cast data.

Minor sea cable noise problems on this cruise did not significantly affect the CTD data, being filtered out during the data acquisition.

Station 127 had a repeat cast to trip bottles in the top 1100M, after the CTD partially fboded at that depth during the first upcast. The station 189 cast was repeated because air vents on bottles were not closed prior to the first cast. Both CTD casts are reported for these two stations.

F.1.6. CTD Laboratory Calibration Procedures

Laboratory calibrations of the CTD pressure, temperature and conductivity sensors were used to generate Sea-Bird conversion equation coefficients applied by the data acquisition software at sea.

CTD #675 with pressure transducer #88907 was used for all of Leg 1 and stations 109/1-127/2 of Leg 2 of P2-2004. CTD #474 with pressure transducer #69008 was used for stations 127/3-190/1 on Leg 2.

Pressure calibrations were last performed on CTD #675 and CTD #474 at the ODF Calibration Facility (La Jolla) on 19 March 2004 and 4 December 2003, respectively. In both cases the Paroscientific Digiquartz pressure transducers (CTD #675 S/N 88907, CTD #474 S/N 69008) were calibrated in a temperature-controlled water bath to a Ruska Model 2400 Piston Gauge Pressure Reference.

The SBE3*plus* temperature sensors (primary S/N 03-4196, secondary S/N 03-4308) were calibrated at ODF on 18 March 2004.

The primary SBE4 conductivity sensor (S/N 04-2766) was calibrated on 20 April 2004 at SBE. The secondary conductivity sensors (S/N 04-1880, 04-2593, 04-2113, 04-2904) were calibrated at SBE on 20 Apr 2004, 1 Jul 2004, 1 Jan 2004 and 1 Aug 2003, respectively.

The SBE35RT Digital Reversing Thermometer (S/N 0035) was calibrated on 15 March 2004 at SBE.

F.1.7. CTD Shipboard Calibration Procedures

CTD #675 (109/1-127/2) and #474 (127/3-190/1) were used for all P2 2004 Leg 2 casts. The CTD was deployed with all sensors and pumps aligned vertically, as recommended by SBE. Secondary temperature and conductivity (T2 & C2) sensors served as calibration checks for the reported primary temperature and conductivity (T1 & C1) on all casts. The SBE35RT Digital Reversing Thermometer (S/N 35-0035) served as an independent temperature calibration check. *In-situ* salinity check samples collected during each CTD cast were used to calibrate the conductivity sensors.

F.1.7.1. CTD Pressure

Pressure sensor conversion equation coefficients derived from the pre-cruise pressure calibration were applied to raw pressure data during each cast. No additional adjustments were made to the calculated pressures for CTD #675 (Pressure S/N 88907). However, a -0.4db offset was applied to all pressures for CTD #474 (Pressure S/N 69008) in order to bring surface pressures closer to 0db.

Residual pressure offsets (the difference between the first and last submerged pressures) were tabulated to check for calibration shifts. All were < 0.5db.

The post-cruise CTD #474 pressure calibration showed about a +0.2db to +0.6db correction was needed from surface to 6200db. The offset applied shipboard was -0.4db, so there is a difference of up to -1.0db in the shipboard corrections as compared to post-cruise calibration results. The CTD #675 post-cruise calibration is pending; repairs are required for damage caused by fboding during station 127/2.

F.1.7.2. CTD Temperature

Temperature sensor conversion equation coefficients were derived from the pre-cruise calibrations and applied to raw primary and secondary temperature data. The primary (T1, S/N 03P-4196) and secondary (T2, S/N 03P-4308) SBE3*plus* temperature sensors were used the entire cruise without replacement.

Two independent metrics of calibration accuracy were examined. The primary and secondary temperatures were compared at each rosette trip, and the SBE35RT temperatures were compared to primary and secondary temperatures at each rosette trip.

The T1 sensor appeared to have a second-order pressure dependence, requiring a +0.00054 to -0.0005 °C correction from surface to 6200db. The T2 sensor did not appear to require any slope correction, only an offset; but the offset shifted occasionally, varying from 0 to 0.00086 °C over both legs of the cruise. Both T1 and T2 corrections changed slightly when the sensor was shifted from CTD #675 to CTD #474 during station 127, but each seemed to be fairly stable while attached to the same CTD.

The T1 and SBE35RT comparisons, after shipboard correction of T1, are summarized in figures 1.7.2.0 and 1.7.2.1.



Figure 1.7.2.0 T1 and SBE35RT temperature differences by pressure, all pressures.



Figure 1.7.2.1 T1 and SBE35RT temperature differences by cast, p>1000db.

Figures 1.7.2.2 and 1.7.2.3 show T1-T2 residual differences after shipboard corrections.



Figure 1.7.2.2 Primary and secondary temperature differences by pressure, all pressures.



Figure 1.7.2.3 Primary and secondary temperature differences by cast, p>1000db.

Preliminary results from post-cruise calibrations show T2 only required an offset of about +0.0008 °C. The T1 results appear to indicate a +0.0005 to 0 °C correction is required from 0 to 30 °C - the opposite of what was applied shipboard (-0.0005 to +0.0005 °C from 6200db to 0db). The laboratory calibrations only measure effects caused by temperature changes, since all are done at essentially surface pressure. The T1 shipboard corrections are about -0.001 °C deep and +0.0005 °C at the surface compared to post-cruise calibration results. This difference needs to be evaluated more carefully before fi nal temperature corrections are determined.

F.1.7.3. CTD Conductivity

Conductivity sensor conversion equation coefficients were derived from the pre-cruise calibrations and applied to raw primary and secondary conductivities.

One primary and four secondary SBE4 conductivity sensors were used on P2 2004 Leg 2. C1 S/N 04-2766 was used the entire cruise, and was used for all reported CTD conductivities. C2 S/N 04-1880 was used on 109/1-124/1, S/N 04-2593 on 125/2, S/N 04-2113 on 126/1-127/2 and S/N 04-2904 on 127/3-190/1. The secondary sensors were used as calibration checks on the primary sensor.

Comparisons between the primary and secondary sensors, and between sensors and check sample conductivities, were used to derive conductivity sensor corrections. A single first-order pressuredependent slope (on the order of +0.002 mS/cm from 0 to 6200db) was applied to all C1 data. The C1 offset shifted by -0.0006 mS/cm from stations 1-57 (during leg 1), then stabilized for the rest of the cruise (both legs). The four secondary sensors were corrected based on bottle salt differences.

Shipboard overlays of deep theta-salinity profiles were checked for cast-to-cast consistency. Only the first two stations of leg 2 (109 and 110) needed an additional +0.0002 mS/cm offset to C1, as compared to leg 1 casts at the same positions and nearby casts on the same leg. This was likely due to the 8.5-day idle period between the two legs. Most deep profiles of adjacent casts agreed to within $\pm 0.0001-2$ mS/cm.

The comparison of the primary and secondary conductivity sensors by station, after applying shipboard corrections, is summarized in fi gure 1.7.3.0.



Figure 1.7.3.0 C1 and C2 conductivity differences by cast, p>1000db.





Figure 1.7.3.1 salinity residuals by pressure, all pressures.



Salinity Residual (milliPSU)

Salinity Residual (milliPSU)

Figure 1.7.3.2 salinity residuals by cast, all pressures.





Figure 1.7.3.3 represents an estimate of the deep salinity accuracy for the CTDs/sensors used during P2-2004/Leg 2. The 95% confidence limit is ± 0.0015 PSU relative to bottle salts. The agreement between the C1/C2 sensors after shipboard corrections were applied is ± 0.00074 mS/cm deep (comparable to about ± 0.0009 PSU).

Post-cruise calibrations of the conductivity sensors by Sea-Bird are pending. These calibrations will not account for any pressure effects on the sensors.

F.1.7.4. CTD Dissolved Oxygen

A single SBE43 dissolved O_2 (DO) sensor was used for this cruise (S/N 43-0199). The sensor was plumbed into the P1/T1/C1 intake line in a vertical configuration after C1 and before P1 (as specified by SBE).

This DO sensor was installed near the end of Leg 1, and was the only dependable spare available for both legs. Its sensitivity decreased steadily as the cruise progressed, and its output voltage drifted a bit lower with each cast. After CTD O_2 data were fit to bottle data values, a residual "stepping" (as much as 0.02 ml/l on later casts) is noted in many deep gradient areas as a consequence of the lower sensitivity.

The DO sensor calibration method used for this cruise was to match down-cast CTD O_2 data to up-cast bottle trips along isopycnal surfaces, then to minimize the residual differences between the *in-situ* check sample values and CTD O_2 using a non-linear least-squares fitting procedure. Since this technique only calibrates the down-cast, only the 2 db pressure series down-cast data contain calibrated CTD O_2 . Bottle data from 127/3 were used to fit the shallower CTD O_2 data for 127/2. The coeffi cients for station 189/2 were used for 189/1, which had no bottle data.

Figures 1.7.4.0, 1.7.4.1 and 1.7.4.2 show the residual differences between bottle and calibrated CTD O_2 for all pressures. Figure 1.7.4.3 shows the residual differences for pressures deeper than 1000 db.



Figure 1.7.4.0 O₂ residuals by station number, all pressures.



Figure 1.7.4.1 O₂ residuals by pressure, all pressures.



Figure 1.7.4.2 O₂ residuals by temperature, all pressures.





The standard deviations of 0.0444 ml/l for all oxygens and 0.0167 ml/l for deep oxygens are only intended

as indicators of how well the up-cast bottle O_2 and down-cast CTD O_2 match. Preliminary CTD oxygen data used to generate these statistics were fit BEFORE post-cruise smoothed standard and blank values for bottle oxygen data were applied. Adjustments were made to shipboard CTD oxygen fits for any cast where bottle oxygen values changed more than ± 0.013 ml/l. Adjustments to all fits will need to be made before CTD oxygen data are considered final. ODF makes no claims regarding the precision or accuracy of CTD dissolved O_2 data.

The general form of the ODF O_2 conversion equation for Clark cells follows Brown and Morrison [Brow78] and Millard [Mill82], [Owen85]. ODF models membrane and sensor temperatures with lagged CTD temperatures and a lagged thermal gradient. *In-situ* pressure and temperature are filtered to match the sensor response. Time-constants for the pressure response τ_p , two temperature responses τ_{Ts} and τ_{Tf} , and thermal gradient response τ_{dT} are fitting parameters. The thermal gradient term is derived by low-pass filtering the difference between the fast response (T_f) and slow response (T_s) temperatures. This term is SBE43-specific and corrects a non-linearity introduced by analog thermal compensation in the sensor. The O_c gradient, dO_c/dt , is approximated by low-pass filtering 1st-order O_c differences. This gradient term attempts to correct for reduction of species other than O_2 at the sensor cathode. The time-constant for this filter, τ_{og} , is a fitting parameter. Dissolved O_2 concentration is then calculated:

$$O_{2m//l} = [c_1 O_c + c_2] \cdot f_{sat}(S, T, P) \cdot e^{(c_3 P_l + c_4 T_l + c_5 T_s + c_6 \frac{dO_c}{dt} + c_7 dT)}$$
(1.7.4.0)

where:

O _{2ml/l}	= Dissolved O_2 concentration in ml/l;
Oc	= Sensor current (μamps);
$f_{sat}(S,T,P)$	= O_2 saturation concentration at S,T,P (ml/l);
S	= Salinity at O ₂ response-time (PSUs);
Т	= Temperature at O ₂ response-time (° C);
Ρ	= Pressure at O ₂ response-time (decibars);
P	Low-pass fi Itered pressure (decibars);
T_f	= Fast low-pass fi Itered temperature (° C);
Ts	= Slow low-pass fi Itered temperature (° C);
$\frac{dO_c}{dt}$	= Sensor current gradient (μamps/secs);
dŤ	= low-pass filtered thermal gradient $(T_f - T_s)$.

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Date	Contact	Data Type	Data Status Summary
08/27/04	Landing	DOC	Submitted LADCP report
09/08/04	Johnson	DOC	Submitted CTD floats report
09/08/04	Carlson	DOC	Submitted DOM report
	Here is the information Carlson in this emain	ation you request ail.	ed from us. I am reporting for the DOM team of Hansell and
09/09/04	Swift	CTD/BTL/SUM	Submitted w/ known deficiencies
	This is information	regarding:	
	line:	P02	
	ExpoCode:	SEE	DATA
	Cruise Date:	2004	/06/13 - 2004/08/27
	From:	SWI	FT, JAMES
	Email address:	jswif	@ucsd.edu
	Institution:	UCS	D
	Country:	USA	
	The file:	WHF	P.P2-2004.tar.gz - 13181165 bytes
	has been saved as	s: 2004	0908.133032_SWIFT_P02_WHP.P2-2004.tar.gz
	in the directory:	2004	0908.133032_SWIFT_P02
	The bottle file has	the following para	meters:
	STNN	BR CASTNO	SAMPNO BTLNBR CTDRAW CTDPRS
	CTDT	MP CTDSAL	CTDOXY THETA SALNTY OXYGEN
	SILCA	T NITRAT	NITRIT PHSPHT CFC-11 CFC-12
	CFC11	13 TCO2	TALK QUALT1
	The data disposition	on is: Pul	
	The file format is:	Other: Var	lous
	The data type is	s. Zip s: Summary (na	vigation)
		Bottle Data (h	vd)
		CTD File(s)	<i>,</i> ,
	The file contains th	nese water sample	e identifiers:
		Cast Number	(CASTNO)
		Station Numb	er (STATNO)
		Bottle Numbe	r (BILNBR)
	SWIET LAMES W	Sample Numi	ving action(s) taken on the data:
		Place Data O	nline
	Any additional note	es are: file names	have known deficiencies; must add citation info to files
09/14/04	Muus	Cruise Data	Reformatting Needed; will combine data from both legs
	Jim and Lynne bo separate files for thetrace metal dat where two legs on	oth want P02_20 the trace metal a and p02_2004 the same line wil	04 legs 1 & 2 combined into single files but there will be data and the regular data. I am using p02_2004tm for for the regular data. I assume this will not be the only cruise be combined.
09/15/04	Measures	DOC	Submitted trace metals report
09/15/04	Roberts	DOC	Submitted DIC pdf doc

Date	Contact	Data Type	Data Status Summary		
09/22/04	Muus	CTD/BTL	Data Files Relocated		
	The P02_2004	data files are in: /usr/	/export/html-public/data/co2clivar/pacific/p02/		
	p02_2004a/p /p02_2004ah /p02_2004ac /p02_2004a_ /p02_2004a_	02_2004asu.txt F y.txt t.zip hy1.csv ct1.zip	Regular ODF deep rosette		
	p02_2004atn /p02_2004atr	p02_2004atm/p02_2004atm_ct1.zip Trace metal rosette /p02_2004atm_hy1.csv			
	together with appropriate f	ogether with other files added by Danie. Trace metal directory can be placed where appropriate for website.			
	1. EXPOCODE	changed to 318M200	0406 vs. 318MVANC32MV		
	2. Quality Flags (Transmissor Oxygen and	"1"s left unchanged to neter and fluorometer fluorometer in the trac	for now. r in the regular(deep) CTD casts. ce metal CTD casts.)		
	3. No WOCE format trace metal data. Trace metal CTD and bottle data given as exchan format only. Tried Bren's backward formatting without success. If we need WOCE format believe it will be easier to work from ODF data when available.				
	4. Summary file	has no trace metal c	asts.		
	5. Cannot get a 1-159 okay. Needed 6 _c Can add first	II 190 CTD stations in t1.zip files to load to 6 five .joa files but not	one .joa file. 6 _ctd1.joa files. the sixth (160-190). iter or could be a problem for evenyone.		
10/04/04	Johnson	CTD/BTL/SUM	Final Data Avaliable at ODF website		
	A zip-file containing the updated documentation and bottle + CTD data for BOTH P2-2004 legs are available on the odf ftp site: README.P2 description of data release P2-2004.zip zip file containing all the				
10/5/04	McNichol	DOC	Submitted C13/C14 report		
10/5/04	Nelson	DOC	Submitted CDOM report		
	Final CDOM Da	ita from 2003's A20 a	nd A22 lines.		
10/05/04	McNichol	Cruise Report	Submitted C13/C14 report		
10/5/04	Johnson	DOC	ODF cruise reports submitted		
10/12/04	Swift	DOC	Submitted chi. sci. report		
	narrative Leg 2				
10/13/04	Robbins	DOC	Submitted chi. sci. report		
	narrative Leg 1				
10/20/04	Landing	DOC	Submitted new report		
	merged both leg	gs into one report			
10/28/04	Landing	DOC	Submitted new report		
	merged both leg	gs into one report			

Date	Contact [Data Type	Data Status Summary
10/28/04	Kozyr 1	FCO2/ALK	Not yet submitted
	The final TCO2, TAL Feely, Wanninkhof co QC work will be perfo done I will forward the	K, and pH data w priversation last m prmed, new qualit new numbers to	vill be submitted to CDIAC during next few months (per nonth). The data will be adjusted for CRMs and the QA- y flags will be assigned. As soon as all this work will be CCHDO.
11/01/04	Kappa (Cruise Report	Assembled Preliminary Cruise Report from:
	 Leg 1 Summary, Bot 	ttle Data Report, 0	CTD Data Report: Ocean Data Facility / SIO
	 Leg 2 Summary, Bot 	ttle Data Report, 0	CTD Data Report: Ocean Data Facility / SIO
	Leg 1 Cruise Narrati	ve: Paul Robbins	/ UCSD-SIO; Leg 1 Chief Scientist
	Leg 2 Cruise Narrati	ve: James Swift /	UCSD-SIO; Leg 2 Chief Scientist
	Radiocarbon Report CECs: lim Happoll /		WHOI
	Trace Metals Report	Rolling Cli	ff Buck, Paul Hansard / II Hawaii
	Dissolved Organic C	arbon and Nitroge	en Report: Craig Carlson / UCSB
	Chromophoric Disso	lved Organic Mat	ter Report: Norm Nelson / UCSB
	• Floats Report: Greg	Johnson / NOAA/	PMEL
	LADCP Report: Etha	an Coon / Columb	ia University
	 HBSCE Report: And 	lreas Thurnherr / l	_DEO
	These Data Process	ing Notes	
12/17/04	Kozyr T	CO2/ALK/PH	DQE Begun
	The final TCO2, TAL Feely, Wanninkhof co QA-QC work will be p be done I will forward	K, and pH data w onversation last r performed, new qu the new numbers	vill be submitted to CDIAC during next few months (per month ?). The data will be adjusted for CRMs and the uality flags will be assigned. As soon as all this work will to CCHDO.
01/21/05	Kozyr E	DIC/ALKALI	DIC DQE Begun, ALKALI not yet available
	We also have receive TALKs from these cru	ed the final DIC d ises the files will b	ata from A20_2003 and P02_2004. As soon as we get be available to public through CDIAC.
02/17/05	Kozyr T	CARBN	Submitted; Data are Public
	This is information reg	arding line: P02_2	2004
	ExpoCode:	318M200406	
	Cruise Date:	2004/06/15 - 20	04/07/25
	From: Email address:	KUZYR, ALEX	AV.
	Institution.	CDIAC/ORNI	v
	Country:	USA	
	The file:	p02_2004a_nev	v_TCO2.txt - 478429 bytes
	has been saved as:	20050217.1119	19_KOZYR_P02_2004_p02_2004a_new_TCO2.txt
	in the directory:	20050217.1119	19_KOZYR_P02_2004
	The data disposition is	s: Public	
	I he bottle file has the	tollowing parame	
	The file format is:	WOCE Format	(ASCII)
	The archive type is	NONE - Individu	Jal File
	The data type(s) is:		

Date	Contact	Data Type	Data Status Summary
02/17/05	Kozyr	TCARBN	Submitted; Data are Public (continued)
	Bottle Da	ata (hyd)	
	The file contains	these water sample id	entifiers:
	Cast Nu	mber (CASTNO)	
	Station N	Number (STATNO)	
	Bottle N	umber (BTLNBR)	
	Sample	Number (SAMPNO)	
	KUZIR, ALEX W	vould like the following	action(s) taken on the data:
	Any additional no	otes are:	
	These d	lata are the new TCO	2 (TCARBN) and flags numbers I've just received from
	Feely/Roberts (F soon as I get th	PMEL), note that ALKA	LI data are still not public in your files for this cruise. As A. Dickson (SIO) I will send it to you after evaluation.
	Thank you, Alex	(.	
04/04/05	Willey	CFCs	Submitted stns 109-190
	This is information	on 	
	regarding line:	P02	
	ExpoCode:	318M200406	07
	Cruise Date:	2004/06/16 - 2004/08/	27
	From: Email address:	dwillev@rsmas miami	edu
	Institution:	UNIVERSITY	
	Country:	USA	
	The file:	P02_2004_CFCs_stns	s109-190.csv - 81958 bytes
	has been saved	as: 20050404.112	915_WILLEY_P02_P02_2004_CFCs_stns109-190.csv
	in the directory:	20050404.112915_WI	LLEY_P02
	The data disposi	tion is:	
	Public		
	The bottle file ha	is the following parame	ters:
	CFC-11 The file format is	, CFC-12, CFC-113	
		ychange	
	The archive type	e is:	
	NONE -	Individual File	
	The data type(s)	is:	
	Bottle D)ata (hyd)	
	The file contains	these water sample id	entifiers:
	Cast Nu	umber (CASTNO)	
	Station	Number (STATNO)	
	Bottle N	lumber (BTLNBR)	
	WILLEY, DEBRA	A would like the followir	ng action(s) taken on the data:
	Merge L	Jata Noto Onlino	
	Place D Any additional or	ntes are:	
	I am su	ubmitting 2 separate f	iles for P02 CFCs: one for stns1-108 and another for

Date	Contact	Data Type	Data Status Summary	
04/04/05	Willey	CFCs	Submitted stns 1-108	
	This is informati	on		
	regarding line:	P02		
	ExpoCode:	318M200406		
	Cruise Date:	2004/06/16 - 2004/08/2	27	
	From:	WILLEY, DEBRA		
	Email address:	dwilley@rsmas.miami.	edu	
	Institution:	UNIVERSITY		
	Country:	USA		
	The file:	02_2004_CFCs_stns2	I-108.csv - 125134 bytes	
	has been saved	as: 20050404.112	547_WILLEY_P02_P02_2004_CFCs_stns1-108.csv	
	In the directory:	20050404.112547_WI	LLEY_P02	
	The data dispos	ition is:		
	PUDIIC The bettle file by	as the following peremo	toro:	
	The file format is	, 01 0-12, 01 0-113		
	WHP F	s. xchange		
	The archive type	e is:		
	NONE -	· Individual File		
	The data type(s) is:		
	Bottle D) Data (hyd)		
	The file contains	s these water sample ide	entifiers:	
	Cast Nu	umber (CASTNO)		
	Station	Number (STATNO)		
	Bottle N	lumber (BTLNBR)		
	WILLEY, DEBR	A would like the followin	g action(s) taken on the data:	
	Merge I	Data		
	Place D	ata Online		
	Any additional n	otes are:		
	for stns	109-190.	s for P02 CFCs: one file for stns1-108 and another file	
04/20/05	Nelson	CDOM	Submitted	
	This is informati	on regarding		
	line:	P02		
	ExpoCode:	318M200406	_	
	Cruise Date:	2004/06/16 - 2004/08/2	27	
	From:	NELSON, NORM		
	Email address:			
	Country:			
	The file	n02cdom final txt - 51	217 bytes	
	has been saved	as: 20050420 172	247 NELSON P02 p02cdom final txt	
	in the directory:	20050420.172247 NF	ELSON PO2	
	The data dispos	ition is:	— •	
	Public			
	The file format is	5:		
	Plain T	ext (ASCII)		

Data	Proce	essing	Notes
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Date	Contact	Data Type	Data Status Summary
04/20/05	Nelson	CDOM	Submitted (continued)
	The archive type is	:	
	NONE - Ir	ndividual File	
	I ne data type(s) is	:	
	Bottle Dat	a (other)	
	The file contains th	ese water sample ide	entifiers:
	Cast Num	ber (CASTNO)	
	Station Nu Bottle Nur	umber (STAINO)	
	Sample N	umber (SAMPNO)	
	NELSON, NORM V	vould like the followir	ng action(s) taken on the data:
	Place Data	a Online	
05/26/05	Anderson TCO2 submitted 2/	TCARBN/CFCs 17/05 &	Website Updated: CFCs stns 109-190 online
	Merged new TCO2	submitted by Koyzr	on 20050217 into online file 20040915WHPOSIODM.
	Merged new CFC Willey's file had or the other samples, cfc values for this at this level in Wil exchange and net	C-11, CFC-12, and the apparent error. S /bottles for sta. 102 level. The .sum file lley's file into the or cdf files. and put all fil	CFC-113 submitted by Willey on 20050404 into file. Station 102, sample/bottle 4 had the cast as 1 when all were cast 2. Also the online .hyd file had cast 2 but no indicates only a cast 2 for sta. 102. I merged the values line file, but did not correct her original file.Made new les online.
06/03/05	Anderson	CFCs	Website Updated:
	new data, stas 10 data for stas. 109-2	9-190 online June 3 190 from file	, 2005 p02_2004a 318M200406 Merged the new cfc
	20050527.134017_	_ WILLEY_P02_P02	_2004_CFCs_stns109-190.csv
	sent by D. Willey o	n May 27, 2005 into	online file 20050526WHPOSIOSA.
06/22/05	Kozyr	TCO2/ALK/PH	Estimated Data Submission Soon
	The final TCO2, T Feely, Wanninkho QA-QC work will b be done I will forwa	ALK, and pH data w f conversation last r re performed, new qu ard the new numbers	vill be submitted to CDIAC during next few months (per month ?). The data will be adjusted for CRMs and the uality flags will be assigned. As soon as all this work will to CCHDO.
11/02/05	Johnson	THETA-S	Clarification Request: float data
	I downloaded the relation ("deep" fo profiling CTD floa somewhat surprise fresh of the neares same batch of SS (closer than 0.005 data on the web s P2	2004 reoccupation or the floats - betwe the that reported pro- ed to see that the fir st P2 CTD profiles, of W (P144) used on F) comparison result, ite final? I tried to c	of the P2 data recently to compare the deep theta-S en about 1600 and 2000 dbar) to the 10 Argo Project ofiles close in space and time to those data. I was st float CTDs were on average about 0.009 (+/- 0.002) despite the fact that the floats were calibrated using the P2. I would have expected a somewhat better float-CTD even if different SSW batches were used. Are the P2 heck this question at the data history & updates link for
	(http:// cchdo.ucsd.	.edu/data/co2clivar/p	acific/p02/p02_2004a/datahist.htm)
	but it appears to b profiles of the 12 P16S agree to wit floats and the secti	e broken.In contrast Argo Project profiling hin 0.000 (+/-0.001) on CTDs appear to h	to P2, the "deep" theta-S from stations nearest the first g CTD floats deployed during the 2005 reoccupation of ! This was rather better than I expected. Again, both have been calibrated with SSW batch P144.

Date	Contact	Data Type	Data Status Summary
11/07/05	Johnson I notice the P2 data post-cruise data documentation; poi ASAP. Thanks.(T Greg Johnson's pro mine?)	CTD/BTL/SUM a on the CCHDO we until Oct. 4. Sta tentially some bottle he changes were s oblem, but it was the	Clarification Needed: online data latest? ebsite are dated Sept. 16, 2004 - but I didn't submit the ations 170-190 were updated, and so was all the e data as well. Please see that these files are updated mall enough that they are unlikely to be the source of e first thing I checked - do the cchdo website files match
02/03/06	Carlson	DOC	Submitted leg 2 DOC data & report
	Attached are DOC Attached also is do there is a gap betw contaminated durin were re-washed a remaining profiles good. All DOC ana	data from the sec ocumentation of how een the first and se g collection. We th nd contaminated at which have a quality lyses for this leg we	ond leg of P2. DOC data are reported in umol C/L . <i>w</i> samples were collected and processed. You will see cond leg. The samples collected up to station 127 were ink this was related to a batch of collections bottles that sea during that leg. There are a few "bad" data in the y flag of 4 associated with them otherwise the data are re performed at UCSB in our DOM lab.
02/07/06	Jenkins	HELIUM	May be avail. early april, 2006
	We are currently at by early April. At measurement mode May or June of th summer. We are w should be able to s mid April).	bout half way throug that point the m e, and we will comn his year. We hope working on data red submit the helium re	h the helium analyses on P02, and expect to finish them ass spectrometer will be converted over to tritium nence tritium measurement on those samples starting in to complete the tritium measurements sometime this uction for the helium analyses as we go along, so we esults shortly after completion of the analyses (probably
05/19/06	Kozyr	DOC	Final Data Submitted; not online yet
	On March 15 this A16S_2005 I rece merged in the hydr the DOC data me merged.	year I submitted th ived from Dennis H ographic file at CCH rging status at CCI	he final DOC data for repeat sections P02_2004 and Hansell of RSMAS. I don't see these data have been IDO for each above cruise yet. Could you please tell me HDO and let me know as soon as these data will be
05/22/06	Kozyr	DOC	Final Data Submitted; not online yet
	I submitted the DC received the A20 a not see the DOC n files for DOC data if you received thes	C data from P02_2 nd A22 DOC data f umbers for these cri from P02_2004, A1 e files OK and when	004 and A16N_2005 using CCHDO submission page. I illes from you, so I guess you have these files, but I did uises were merged at CCHDO yet. Here are attached 3 6N_2003, and A16S_2005 cruises. Please, let me know are you planning to merge these data.
05/22/06	Kozyr	DOC	Data Update previous file incorrect
	I've sent you a wror	ng file for P02_2004	DOC data. please use one attached here.
06/21/06	Карра	Cruise Rprt	Website Updated:
	Added new DOC re Updated these data	port, Leg 2 processing notes.	