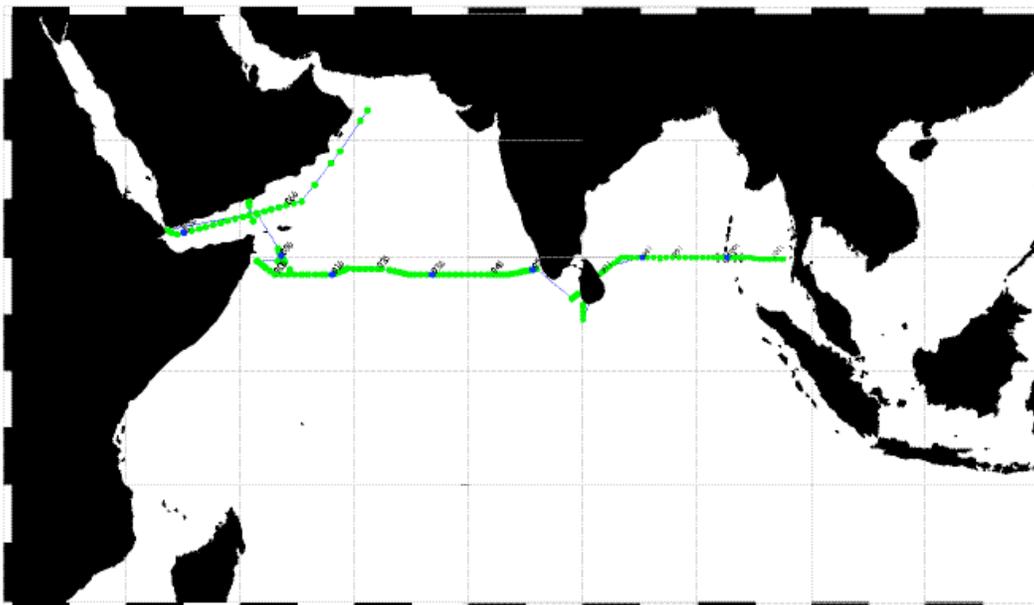


# Cruise report: I01

(Updated JUN 2008)

## A. Highlights



### A.1. Cruise Summary Information

WOCE section designation	<b>I01</b>
Expedition designation (ExpoCodes)	<b>316N145_11-12</b>
Chief Scientist	<b>Dr. John M. Morrison / NCSU</b> (Leg 1)
Co-Chief Scientist	<b>Dr. Harry L. Bryden / SOC</b> (Leg 2)
Dates	1995 AUG 29 – 1995 SEP 28 (Leg 1) 1995 SEP 30 – 1995 OCT 16 (Leg 2)
Ship	<i>R/V KNORR</i>
Ports of call	Muscat, Oman to Colombo, Sri Lanka (Leg 1) Colombo, Sri Lanka to Singapore (Leg 2)
Station geographic boundaries	22° 28.17' N 43° 41.67' W 97° 33' E 4° 0.30' N
Stations	158
Floats and drifters deployed	16 ALACE floats
Moorings deployed or recovered	0
Contributing Authors	Sarah Zimmerman, Maggie Cook, Marshall Swartz

#### **Dr. John M. Morrison**

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#### **Dr. Harry L. Bryden**

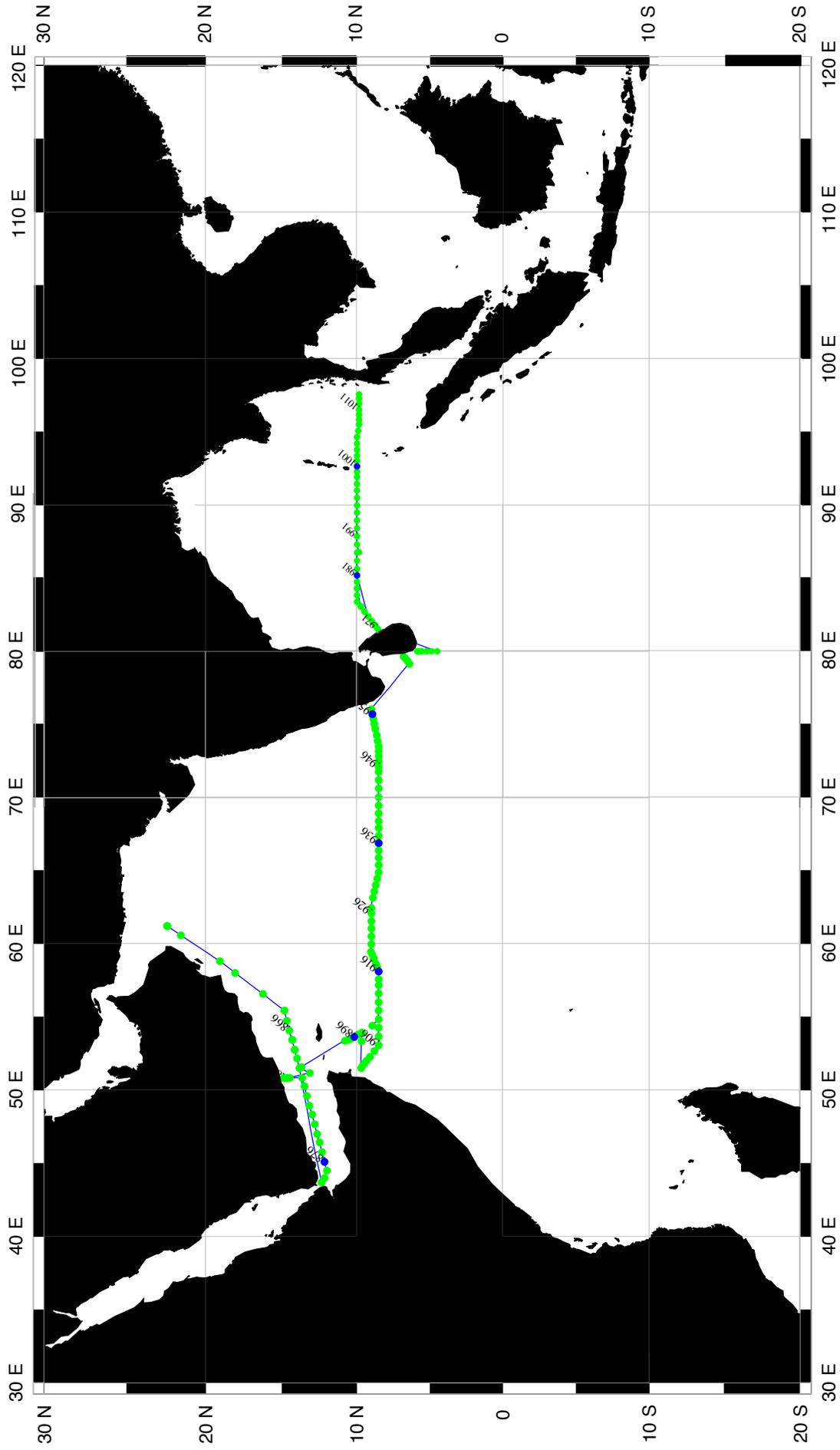
Southampton Oceanography Centre • Empress Dock • Southampton S014 3ZH • UK  
Ph: 44-1703-596436 • Fax: 44-1703-596204 • Email: h.bryden@soc.soton.ac.uk

## Cruise and Data Information

Links to text locations. Shaded sections are not relevant to this cruise or were not available when this report was compiled

Cruise Summary Information	Hydrographic Measurements
<a href="#">Description of Scientific Program</a>	<b>CTD Data:</b>
<a href="#">Geographic Boundaries</a>	<a href="#">Acquisition</a>
<a href="#">Cruise Track (Figure):</a> <a href="#">PI</a> <a href="#">CCHDO</a>	<a href="#">Processing</a>
<a href="#">Description of Stations</a>	<a href="#">Calibration</a>
<a href="#">Description of Parameters Sampled</a>	<a href="#">Salinities</a> <a href="#">Temperature</a>
<a href="#">Bottle Depth Distributions (Figure)</a>	<a href="#">Oxygens</a> <a href="#">Pressure</a>
<a href="#">Floats and Drifters Deployed</a>	<b>Bottle Data</b>
<a href="#">Moorings Deployed or Recovered</a>	<a href="#">Oxygen</a>
<a href="#">Principal Investigators</a>	<a href="#">Nutrients</a>
<a href="#">Cruise Participants</a>	<a href="#">Carbon System Parameters</a>
<a href="#">Problems and Goals Not Achieved</a>	<a href="#">Helium Tritium</a>
<a href="#">Other Incidents of Note</a>	<a href="#">Radiocarbon</a>
	<a href="#">CFCs</a>
Underway Data Information	References
<a href="#">Navigation</a> <a href="#">Bathymetry</a>	<a href="#">CTD</a>
<a href="#">Acoustic Doppler Current Profiler (ADCP)</a>	<a href="#">Radiocarbon</a>
<a href="#">Thermosalinograph</a>	<a href="#">Carbon System Parameters</a>
<a href="#">XBT and/or XCTD</a>	
<a href="#">Meteorological Observations</a>	<b>Acknowledgments</b>
<a href="#">Atmospheric Chemistry Data</a>	
Data Processing Notes	Data Quality Evaluations

# Station locations for I01 • Morrison/Bryden • R/V Knorr • 1995



(Produced by CCHDO)

## A.2 Cruise Summary

### A.2.a Geographic boundaries

#### Cruise Track

The cruise went across the North Indian Ocean at a nominal latitude of 8°N. From Muscat, the ship headed for the entrance to the Red Sea before starting the main section off the coast of Somalia. The section across the Arabian Sea ended on the continental shelf of India. After a brief port stop in Colombo, the section was continued from the Sri Lankan continental shelf across the Bay of Bengal and ended on the Myanmar continental shelf.

### A.2.b Number of Stations

A total of 158 hydrographic stations were taken during the cruise, which includes three test stations to check instrument performance. A list of station positions including a brief chronology of notable events is in [Table 1](#).

#### Sampling

On each hydrographic station, a continuous CTD profile of temperature, salinity and oxygen versus pressure is measured throughout the water column from the sea surface down to the ocean bottom; 36 water samples are then collected during the upcast and analysed in the laboratory for salinity, oxygen, nutrients (nitrate+nitrite, nitrite, silica and phosphate), chlorofluorocarbons (CFC-11, CFC-12), CO<sub>2</sub> components (total CO<sub>2</sub> and alkalinity); on selected stations water samples were collected for later analysis for helium, tritium, <sup>14</sup>C, <sup>13</sup>C and barium; finally, an LADCP was mounted on the CTD/Rosette frame on nearly every station to measure continuous profiles of horizontal velocity from the sea surface to the bottom and back to the sea surface. While underway and on station, continuous measurements were made of bottom depth, surface currents by a ship-mounted ADCP instrument with associated P-code GPS navigation, and meteorological variables with the ship-mounted IMET system.

Equipment used aboard KNORR for the basic CTD/Rosette system was provided by both Woods Hole Oceanographic Institution CTD Operations Group, and the Scripps Institution of Oceanography's Shipboard Technical Services/Ocean Data Facility (SIO STS/ODF). Four CTDs were brought for the cruise, two of which were used for the majority of the stations. Underwater equipment included:

*Primary Sensors:* Two Falmouth Scientific (FSI) ICTDs with Sensormedics oxygen sensors. Each has a Sensormedics oxygen sensor assembly and a titanium pressure transducer with temperature monitor.

*Secondary Sensors:* Two Neil Brown Mk-3 CTDs. Each has a Sensormedics oxygen sensor assembly and a titanium pressure transducer with temperature monitor.

In addition to the principal section across 8N-10N from Somalia to India, Sri Lanka to Myanmar, this station list contains:

1. a section along the axis of the Gulf of Aden
2. a meridional section across the Gulf of Aden from Yemen coastline
3. a section following German mooring line south of Socotra
4. a short section up onto the Sri Lanka continental shelf near Colombo
5. a short section south of the southern tip of Sri Lanka along 80°E to 4.5°N, repeating 18 stations 6 months later

**Table 1:** Hydrographic Station Positions and Brief Chronology for WOCE Section I1, R/V KNORR, 29 August to 16 October 1995, Muscat to Singapore

Sta #	WOCE #	Lat (N)	Lon (E)	Depth (m)	Comments	CTD Used
Start		23 37	58 38		Muscat Dep 8/29 0600	
1	857	22 28	61 12	3215	Station 841 on I7N	CTD38
2	858	22 28	61 12	3190	and	CTD09
3	859	22 28	61 12	3190	JGOFS station	CTD44
4	860	21 35	60 35		Water sample test 300m	
5	861	19 05	58 48	3285	Station 808 on I7N	
6	862	18 05	58 00	2815	JGOFS station	
7	863	16 16	56 33	3710	CTD test	CTD09
8	864	14 50	55 25	2440	CTD12	
9	865	14 40	54 45	2205	CTD44	
10	866	14 30	54 05	2595		
11	867	14 20	53 25	2970	Terminated at 700db	
12	868	14 20	53 25	2960	ALACE deployed	
13	869	14 10	52 45	1880	Terminated at 500bd	
14	870	14 10	52 45	1895		CTD38
15	871	14 00	52 10	2195		
16	872	13 50	51 30	1790	Repeated as 35	
17	873	12 22	43 42	300	Exit of Red Sea	
18	874	12 10	44 00	495		
19	875	12 00	44 30	1410		
20	876	12 10	45 05	815		
21	877	12 20	45 45	1390		
22	878	12 30	46 25	1770		
23	879	12 40	47 00	2005		
24	880	12 50	47 40	2350		
25	881	13 00	48 20	1995	ALACE deployment	
26	882	13 10	48 55	2640		
27	883	13 20	49 35	1950		
28	884	13 30	50 15	1955		
29	885	13 40	50 50	2470		
30	886	14 55	50 50	190	Yemen Shelf	
31	887	14 49	50 50	560		
32	888	14 40	50 50	1230	ALACE deployment	
33	889	14 30	50 50	1955		
34	890	14 10	51 10	2200		
35	891	13 50	51 30	1825		
36	892	13 43	51 34	4000	Proceed around Socotra	
37	893	10 48	53 22	3905	Pegasus German	CTD44
38	894	10 34.2	53 26	4020	mooring K14	
39	895	10 21	53 32	4185	Pegasus mooring	
40	896	10 09.9	53 38	4280	mooring K15	
41	897	9 54	53 48	4460	Pegasus line	
42	898	9 38.1	53 56	4580	mooring K16	
43	899	9 39	53 19	4580	Test station for	CTD12

Sta #	WOCE #	Lat (N)	Lon (E)	Depth (m)	Comments	CTD Used
43	900	9 42	51 30	760	Somalia	CTD44
44	901	9 35	51 40	1480	Fast ALACE deployment	
45	902	9 28	51 50	2325		
46	903	9 20	52 00	3650	Fast ALACE deployment	
47	904	9 06	52 17	4540		
48	905	8 48	52 41	4900	Fast ALACE deployment	
49	906	8 30	53 05	5035		
50	907	8 30	53 40	4970		
51	908	8 30	54 15	5025	mooring K17 8 43,54 20	
52	909	8 56	54 25	4800	Halfway between 908+909	
53	910	8 30	54 50	4660		
54	911	8 30	55 25	4730	Fast ALACE deployment	
55	912	8 30	56 00	3800		
56	913	8 30	56 35	4380		
57	914	8 30	57 10	4385		
58	915	8 30	57 34	3105		
59	916	8 30	58 06	3905	Section	
60	917	8 37	58 24	3700	Perpendicular to	
61	918	8 42	58 37	2305	Carlsberg Ridge	
62	919	8 51	59 00	3150	ALACE deployment	
63	920	8 57	59 14	3525		
64	921	9 01	59 25	3615		
65	922	9 01	59 57	3540		
66	923	9 01	60 29	3345		
67	924	9 01	61 01	3965		
68	925	9 01	61 33	4380		
69	926	9 01	62 05	4530		
70	927	9 01	62 37	4545	ALACE deployment	
71	928	8 54	63 08	4535		
72	929	8 48	63 34	4535	17 station 782	
73	930	8 42	64 00	4530		
74	931	8 36	64 26	4560		
75	932	8 30	64 52	4550		
76	933	8 30	65 23	4535		
77	934	8 30	65 53	4525	ALACE deployment	
78	935	8 30	66 23	4530		
79	936	8 30	66 53	4555		
80	937	8 30	67 23	4560		
81	938	8 30	67 53	4575		
82	939	8 30	68 23	4575		
83	940	8 30	68 54	4590	ALACE deployment	
84	941	8 30	69 25	4615	Pick up Indian Officer	
85	942	8 30	70 00	4465		
86	943	8 30	70 35	4165		
87	944	8 30	71 10	3910		
87	945	8 30	71 45	3475		
88	946	8 30	72 05.7	2685	ALACE deployment	

Sta #	WOCE #	Lat (N)	Lon (E)	Depth (m)	Comments	CTD Used
89	947	8 30	72 26	2125		
90	948	8 30	72 47	2190		
91	949	8 30	73 08	2250		
92	950	8 30	73 28	1910		
93	951	8 34	73 50	2650		
94	952	8 39	74 15	2750		
95	953	8 44	74 40	2750		
96	954	8 48	75 00	2695		
97	955	8 52	75 20	1665		
98	956	8 56	75 40	345		
99	957	9 00	76 00	95		
Way	012	6 58	78 25		Disembark Indian Off	
100	958	6 25	79 06	2685	Baldrige station	
101	959	6 33	79 18	2345	Baldrige station	
102	960	6 42	79 30	1630	Baldrige station	
103	961	6 48	79 36	705	Baldrige station	
	Colombo	6 55	79 52		Colombo Arr 9/28 0500	
	Colombo	6 55	79 52		Colombo Dep 9/30 0300	
104	962	5 53	80 00	155	Short Section	
105	963	5 49	80 00	1110	Across Boundary	
106	964	5 45	80 00	2215	Current South of	
107	965	5 40	80 00	3235	Sri Lanka	
108	966	5 35	80 00	4030	18 Station 284	
109	967	5 15	80 00	4135	Along 80 E	
110	968	4 55	80 00	4225	ALACE in 6C mode water	
111	969	4 30	80 00	4285	Down to 4.5°N	
112	970	8 31	81 28	55		
113	971	8 37	81 36	2695		
114	972	8 46	81 48	3740	ALACE deployed	
115	973	8 58	82 04	3750		CTD38
116	974	9 13	82 24	3730		CTD44
117	975	9 28	82 44	3695		
118	976	9 43	83 04	3650		
119	977	9 58	83 24	3620		
120	978	9 58	83 51	3610		CTD38
121	979	9 58	84 18	3580	ALACE deployed	CTD44
122	980	9 58	84 45	3570		CTD38
123	981	9 58	85 12	3565		
124	982	9 13	82 24	3725	Redo 974	
125	983	9 28	82 44	3695	Redo 975	
126	984	9 43	83 04	3645	Redo 976	
127	985	9 58	84 18	3585	Redo 979	
128	986	9 58	85 39	3540		
129	987	9 58	86 12	3505		
130	988	9 58	86 45	3495		
131	989	9 50	86 47	3510	I9 station 268	
132	990	9 58	87 18	3480		

Sta #	WOCE #	Lat (N)	Lon (E)	Depth (m)	Comments	CTD Used
133	991	9 58	87 51	3425	ALACE	
134	992	9 58	88 24	3405		
135	993	9 58	88 57	3375		
136	994	9 58	89 28	3350		
137	995	9 58	89 59	3310		
138	996	9 58	90 30	3330	Pick up Ind. Navy Off	
139	997	9 58	91 00	3470	I9 station 234	
140	998	9 58	91 27	3405		
141	999	9 58	91 54	1285		
142	1000	9 58	92 16	845		
143	1001	9 58	92 38	990	Ten Degree Channel	
144	1002	9 58	93 00	1435		
145	1003	9 58	93 22	3065		
146	1004	9 58	93 46	4235		
147	1005	9 58	94 12	3180		
148	1006	9 58	94 38	2855		
149	1007	9 54	95 04	1775	Disembark Indian Off	
150	1008	9 50	95 30	2620		
151	1009	9 50	95 50	2475		
152	1010	9 50	96 10	1315		
153	1011	9 50	96 30	430		
154	1012	9 50	96 55	325		
155	1013	9 50	97 17	260		
156	1014	9 50	97 33	83		
End		1 20	103 50		Singapore Arr10/15 1100	

General Oceanics (GO) model 1016-36 pylon with 36-bottle frame with 10-liter bottles manufactured by SIO STS/ODF and Ocean Instrument Systems 10-kHz pinger.

### A.2.c. Floats: ALACE Deployments

Autonomous Lagrangian Circulation Explorer (ALACE) floats are intended to map absolute velocity of large-scale currents for use with geostrophic shears from historical and WOCE Hydrographic Programme sampling. The floats drift at 800 to 1000 m depth, surfacing periodically to report their position by satellite. To avoid diffusion bias, the horizontal coverage is intended to be relatively uniform but the density for this cruise was augmented a bit near the western boundary of the Somalia coast

Two floats could not be launched as planned because they were in the territorial waters of India. Permission for such deployments had not been requested from the Government of India and the official Indian observer insisted that no ALACE deployments were allowed. One of the resulting two extra floats was deployed in a thermostad feature south of Sri Lanka at about 1000 m depth at 4 44 N, 80 E. Most of the ALACE floats have a 26-day cycle time, drifting for 26 days at 800 to 1000 m depth, then rising to the sea surface to report position to a satellite, before returning to depth to repeat the cycle for another 26 days. Design lifetime for these floats is 5 years. Four of the ALACE floats deployed in the region of the Somali Current (denoted by  $\text{O}^{\circ}\text{O}^{\circ}$ ) have 15-day cycle times. Each ALACE float was prepared in the laboratory during the downcast of a CTD station and launched from the stern of KNORR at the

completion of a hydrographic station just as the ship set out for the next station. The launch information is shown in Table 2.

**TABLE 2:** WOCE I1 ALACE FLOAT LAUNCH INFORMATION

S/N	START TIME OF LAST SELFTEST	DEPLOYMENT TIME	DEPLOYMENT POSITION
536	950903 0230Z	950903 0357Z	14:20.03N, 53:25.11E
534	950907 0413Z	950907 0557Z	13:00.34N, 48:19.81E
539	950908 0912Z	950908 1302Z	14:38.08N, 50:49.52E
523F	950912 0944Z	950912 1126Z	09:36.95N, 51:40.11E
521F	950912 1547Z	950912 1944Z	09:21.39N, 51:58.86E
522F	950913 0527Z	950913 0857Z	08:50.95N, 52:41.39E
524F	950914 1555Z	950915 0234Z	08:27.02N, 55:24.39E
540	950916 1452Z	950916 2328Z	09:49.95N, 59:00.22E
546	950918 2142Z	950919 0148Z	09:00.87N, 62:36.73E
545	950921 0131Z	950921 0323Z	08:29.95N, 65:53.15E
542	950922 1955Z	950922 2217Z	08:29.80E, 68:53.85E
541	950924 0841Z	950924 1022Z	08:30.14N, 72:04.99E
543	951001 1615Z	951001 1940Z	04:55.10N, 79:59.93E
544	951003 0318Z	951003 0530Z	08:35.22N, 81:36.64E
533	951005 0413Z	951005 0626Z	09:58.81N, 84:17.46E
532	951008 2001Z	951008 2206Z	09:58.18N, 87:51.67E

**A.2.d Mooring deployed or recovered**

**A.3 List of Principle Investigators**

The list of Principal Investigators, their institution and the measurement program that they are responsible for is shown in Table 3.

**Table 3:** WOCE I1 Principal Investigators

Measurement	Principal Investigator	Institution
Chief Scientist	John M. Morrison	North Carolina State University
co-Chief Scientist	Harry Bryden	Southampton Oceanography Centre
Salinity, oxygen, CTD/O2	John Toole	Wood Hole Oceanographic Institution
Nutrients	Louis Gordon	Oregon State University
Chlorofluorocarbons	Mark Warner	University of Washington
Shallow He/Tr	William Jenkins	Wood Hole Oceanographic Institution
Deep He/Tr	Zafer Top	University of Miami
AMS C-14	Robert Key	Princeton University
Barium	Kelly Falkner	Oregon State University
TCO2	Catherine Goyet	Wood Hole Oceanographic Institution
ADCP/LADCP	Teresa Chereskin	Scripps Institution of Oceanography
Underway PCO2	Robert Key	Princeton University
IMET	Barrie Walden	Wood Hole Oceanographic Institution
Thermosalinograph	Barrie Walden	Wood Hole Oceanographic Institution
ALACE Floats	Russ Davis	Scripps Institution of Oceanography

#### A.4 Scientific Programme and Methods

The transindian hydrographic section I1 is the northernmost of the zonal sections to be carried out during the US WOCE Indian Ocean Expedition in 1994-1996. It crosses the southern boundaries of both the Bay of Bengal in the east and the Arabian Sea in the west. This section effectively completes the circumnavigation of the ocean with high quality hydrographic sections at latitudes between 8°N and 11°N, started by the 10°N transpacific and the 11°N transatlantic section carried out in 1989.

Section I1 encloses two areas of the northern Indian Ocean, the Arabian Sea and the Bay of Bengal. From I1 we should be able to compute separate heat, salt and water-mass budgets for each of these basins. This is of interest because the Arabian Sea is an important source of salt to the world ocean, while the Bay of Bengal is an important source of fresh water. In addition to helping define the thermohaline circulation of the Indian Ocean in conjunction with the overall survey of the Indian Ocean Expedition, the specific objectives of the Principal Investigators (PIs) are:

1. To determine the meridional heat and freshwater transports across 8°N in the Indian Ocean and to combine the new estimates with existing Atlantic and Pacific estimates in order to determine the total global ocean heat and freshwater transports across 10°N for comparison with the atmospheric and satellite-based estimates of energy transport;
2. To make a detailed analysis of the freshwater budget of the Bay of Bengal, into which 2 of the world's largest rivers empty, in order to understand the effects of this freshwater source on the Indian Ocean circulation;
3. To estimate the nutrient (and possibly the carbon transport) into and out of the Arabian Sea across its southern boundary at 8°N in order to estimate the size of the overall biological productivity and of the "biological pump" in the Arabian Sea for comparison with JGOFS results.
4. To cooperate with the PIs of the other WOCE Indian Ocean Expedition on the preparation of a new "atlas" describing the first order circulation of the basin and to present and catalog the data collected in a systematic fashion.
5. To coordinate the results of our survey with the JGOFS Arabian Sea Process Study. JGOFS is carrying out 7 cruises within the Arabian Sea, encompassing an entire monsoonal cycle. The JGOFS data will be used to investigate the representativeness of the WOCE sections in the Arabian Sea, where there is large seasonal variability associated with monsoonal forcing. In addition, comparison of data collected during the JGOFS efforts near the mouth of the Arabian Sea with the hydrographic properties at Section I1 may allow us to estimate the percentage of Persian Gulf Water that actually escapes into the Indian Ocean. Finally, estimates of the amount of Arabian Sea Water leaving the basin at the end of the Southwest Monsoon will be made.
6. To determine the extent of eastward penetration of high salinity Arabian Sea waters during the boreal winter that displace the low salinity waters normally carried westward by the North Equatorial Current (NEC).
7. To describe the deep water properties of the Adaman Basin, which is an enclosed basin below approximately 1500 m depth.

In addition, there are a number of questions that will be addressed using data from a combination of multiple sections, VOS XBT data, Lagrangian drifter data, etc. We will actively share the I1 measurements with other scientists working on such objectives and questions.

## Preliminary Results

KNORR departed Muscat, Oman, on schedule on 29 August 1995. We proceeded westward down the coast of Oman, reoccupying a joint JGOFS and I7 station (841) at 22° 28' N, 61° 12' E, an I7 station (808) at 19° 05' N, 58° 48' E and a JGOFS station at 18° 05' N, 58° 00' E. Preliminary inter-comparisons of the data show excellent agreement. We then proceeded to carry out our Gulf of Aden Section. This section has 20 stations along a line from 12° 22' N, 43° 44' E to 14° 50' N, 55° 22' E. This section shows considerable variability, but gives us a good endpoint for Red Sea Water for water mass analysis. Satellite imagery from the JGOFS receiving station in Oman will aid in interpreting this data.

Because of the threat of pirates, we were forced to cancel the southern half of our planned section across the mouth of the Gulf of Aden. Instead, we proceeded to the position of a German current meter array south of Socotra. Once again because of the threat of pirates, we were forced to cancel any work around the moorings within 60 nm of Socotra. In discussions with Dr. F. Schott via Imarsat, we determined that we were just ahead of METEOR on this section. We coordinated our efforts with Schott to make a more densely spaced section along his array. In addition, we occupied 3 of his Pegasus sites for intercomparison of our LADCP velocities with his Pegasus velocity profiles.

We then proceeded to 9° 42' N, 51° 30' E to begin the main I1 line across the Arabian Sea. We took 6 closely spaced stations across the Somali Current, angling down to our main section latitude of 8° 30' N. The main section is across the basin at 8° 30' N, except for a short diagonal section perpendicular to the Carlsberg Ridge at about 58° E and a diversion to reoccupy another I7 station (782) at 8° 48' N, 63° 54' E.

On Monday, 18 September, we received word that the Government of India has decided to give a one-time exemption to carry out work in their waters at 20 nm spacing and to allow use of the ADCP and LADCP. Fortunately, the State Department and WOCE Office had been able to give us a heads-up on the clearance about a week earlier. We picked up the Indian Observer at 8° 30' N, 69° 25' E on Saturday, 23 September. We then continued our line through the Laccadive Islands at the 8 Degree Channel and into the coast at 9° 00' N, 76° 00' E. In all we took 58 stations along the main I1 section of which 17 stations were within the Indian EEZ.

From the end of the main section, we disembarked the Indian Observer while transiting to Sri Lankan waters. We then reoccupied the 4 inshore stations of the BALDRIDGE I1 Pre-peat section onto the Sri Lankan shelf. We arrived in Colombo, Sri Lanka, on the morning of 28 September, having completed 103 stations on Leg 1. The final station on this leg was WOCE station 961.

KNORR departed Colombo, Sri Lanka, on schedule at 0800 on 30 September 1995 and proceeded south of Sri Lanka where 8 stations of Section I8 was reoccupied along 80° E to 4° 30' N. Currents were weak along this section, showing little sign of the Indian Monsoon Current. Time had been scheduled to occupy 2 stations in the Trincomalee Canyon at about 8° 30' N, 81° 20' E on the coast of Sri Lanka at the request of Kamal Tennakoon of National Aquatic Resources Agency in Sri Lanka. The Sri Lankan Naval Observer informed us that the Tamal Tigers were active in this area and advised us not to take these stations. KNORR then proceeded to the endpoint of the main line at 8° 31' N, 81° 28' E (just off the coast of Sri Lanka). Even though this station was in sight of land in the vicinity of the city of Trincomalee (where there is a major Sri Lankan Naval Base), the Sri Lankan Navy was so concerned about the potential threat of the Tamal Tigers, that they requested that we occupy this station during the daylight hours. They also escorted us with 4 gunboats as we came up the coast from the south to the location of this station. KNORR began the main line across the Bay of Bengal without incident. The first 8 stations were along a SW to NE line from the coast of Sri Lanka to the latitude of the proposed section, 9° 58' N, across the Bay of Bengal. As KNORR proceeded along the main line, a 2 - 3 knot current

flowing to the south out to about 75 nm (at least to the 4000 m isobath) was observed in the shipboard ADCP record. We then proceeded along the main line to 9° 58' N, 85° 12' E, where a problem with the CTD occurred. Fortunately, we had been processing the data with about a 24 hour delay. Because we had time, we decided to backtrack and redo 4 of the stations along the main line. We proceeded back to 9° 58' N, 85° 12' E, and continued to the east along the main line. We diverted slightly off the main line to reoccupy I9 Station 268. We picked up the Indian Naval Observer at 9° 58' N, 88° 58' E on Monday morning, 9 October 1995. We then proceeded with our section across the Adaman Sea. The Indian observer disembarked just prior to our entry into the waters of Myanmar. The last 4 stations of the line were within the waters of Myanmar. We completed the section at station 1014 and deadheaded to Singapore, anchoring in the harbour for the night of 15 October 1995 before docking on 16 October.

#### **A.5 MAJOR PROBLEMS ENCOUNTERED ON THE CRUISE**

Because of the threat of pirates, we were forced to cancel the southern half of our planned section across the mouth of the Gulf of Aden. Also, because of the threat of pirates, we were forced to cancel any work around the German current meter moorings within 60 nm of Socotra. Finally, because of the threat of pirates we were not able to begin the section as close to Somalia as we would have liked; our most inshore station was in about 850 meters of water; the ADCP data shows that the most inshore hydrographic station was in the core of the Somali Current; hence we were not able to sample completely across to the inshore side of the Somali Current.

##### **Potential problem with Standard Seawater Batch P-124.**

Suspicion that salinity samples drawn after long times on deck might be changed due to condensation in the warm moist air in the head space of cold, deep-water bottles.

LADCP equipment failure for a section of the first leg leaves a portion of the section across the mouth of the Arabian Sea without absolute velocities.

#### **A.6 OTHER OBSERVATIONS OF NOTE**

Preliminary data were supplied to the foreign observers of India, Sri Lanka and Myanmar prior to their departure from the ship.

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**OUTLINE OF DATA PROCESSING DOCUMENTATION**

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Figure 3 Leg 1 CTD-bottle salts uptrace stns 878 to 981.

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Figure 9 Leg 1 stations (857-961) CTD-bottle oxygen by station and by pressure.

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Figure 11 example of results of oxygen current digitizer change in CTD.

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CRUISE INTERPOLATION DOCUMENTATION

WOCE EXPOCODES 316N145-11 (West leg), 316N145-12 (East leg);  
Knorr Cruise 145 Leg 11; WHOI Internal code "KA45".

Document written by Sarah Zimmerman -July 1998; Document revised by Maggie Cook – December 1998.

Final version revised by Marshall Swartz - July 1999.

## INTRODUCTION

The WHOI CTD Group supported PIs Harry Bryden and John Morrison in the occupation of WOCE Hydrographic Program line I1 across the N. Indian Ocean from 8/29/95 to 10/16/95. The cruise was conducted as two legs, with stations 857 to 961 done on leg 1 and stations 962 to 1014 occupied on leg 2. Although the cruise completed the planned set of stations, multiple instrumental difficulties and failures plagued the voyage. This report summarizes those problems and outlines the steps taken in the data reduction effort.

A synopsis of the instrument problems is given in the [ATSEA.DOC](#). Instrument failures meant that ICTDs from FSI constituted the primary instruments on the I1 cruise, the first time they have been so used by the WHOI Group. In some respects, this cruise highlighted shortcomings in this new instrument. Despite the difficulties, the data set produced by cruise end is of fair quality. Pre-to-post laboratory temperature calibration analyses were quite consistent (differences of only 0.002 C) suggesting the absolute temperatures in the data are reasonable. Calibrated CTD salinity profiles are quite consistent with the water sample salts, with residual salinity discrepancies with pressure between bottles and the profile data ranging between about +0.004 to -0.001 pss with depth. CTD oxygen calibrations are not as good, owing in large part to bad sensor units (that were changed repeatedly during the cruise in search of a well-functioning sensor. The sensor problems have been traced to manufacturing difficulties experienced by the producer combined with the company's poor quality control.) Noise levels in the dataset are somewhat larger than scientists are used to working with. A general 0.002 pss salt noise level is present, about a factor of 2 larger than the norm. CTD oxygen noise levels are 0.04ml/l, worsening to 0.06 for individual stations (ship roll/weather or bad sensor?). Between legs 1 and 2, modifications were made to the ICTD giving the oxygen current more resolution. The general noise level was reduced to 0.03ml/l; better, but still slightly higher than the 0.02ml/l noise level typical of the MKIII CTD.

## DATA DOCUMENTATION

Table of CTDs used by station number:

ICTD1338: stations 857, 863, 870 through 892, 978, 980 through 1014.

ICTD1344: stations 859 through 862, 865 through 869, 893 through 898, 900 through 977 and 979.

CTD09: station 858.

CTD12: stations 864 and 899.

There are no bottle files for stations 858, 867 and 869 due to the pressure signal having dropped out requiring the cast to be aborted. Station 859 has bottles up to 800 dbars only due to fouling of the pylon. Other station by station events are noted in the station by station log (file [ATSEA.RPT](#) submitted along with this document).

Final processed WOCE-format CTD files are named in the form KA45Dnnn.WC1, where nnn is the station number. Note that stations 000 to 014 are actually stations 1000 through 1014 respectively.

Documentation files for this cruise are listed below:

[I1FINAL.DOC](#) this report.

[INTERP.DOC](#) list of linear interpolations performed in final processing of the data.

[ATSEA.DOC](#) a station by station description of CTD issues.

Final-revision CTD data files have been submitted with this data report.

### **INSTRUMENT CONFIGURATION:**

Four CTDs were available on the cruise: two MkIII (CTDs 9 and 12) and two FSI ICTDs (1338 and 1344), with multiple deck units (MkIII and FSI). The CTDs were mounted in an SIO-designed 36-bottle frame fitted with a General Oceanics model 1016-36 36-position rosette pylon, driven through an SIO-modified controller.

The MkIII CTDs both experienced failures early in the cruise, making the two FSI ICTDs the primary instruments by default. Roughly 100 stations were made with ICTD 1344 as primary CTD and 50 stations with ICTD 1338 as primary CTD. Most commonly, the underwater frame was set up with two ICTD instruments: one sending data up the wire using its normal FSK configuration, and one set to record data internally, so that at the end of the station the data could be downloaded.

Significant signal interaction problems were encountered with the ICTDs and the General Oceanics pylon operating on a 10-km seacable, which resulted in data dropouts from the CTD and loss of confirmation of bottle closure from the pylon. A temporary solution was achieved through electrical modifications to both the CTDs and the pylon deck controller to accommodate the long seacable, and data quality improved substantially.

### **ACQUISITION AND PROCESSING METHODS**

Data from ICTD1338 were acquired at 26.0 Hz and processed with a temperature lag of 630 ms. Data from ICTD 1344 were acquired at 26.0 Hz and with a temperature lag of 500 ms. The temperature lag was checked by comparing density reversals in theta salinity (TS) plots (Giles and McDonald, 1986). It was found that the aforementioned lags showed the least amount of looping or density reversals.

For the first 9 stations (857-865) CTD data were acquired using an FSI DT-1050 deck unit to demodulate the data. From station 866 and beyond, data were acquired by an EG&G Mk-III deck unit to demodulate the data. The deck units fed serial data to two personal computers running EG&G version 5.2 rev. 2 CTD acquisition software (EG&G, Oceansoft Acquisition Manual, 1990), one providing graphical data to screen and plotter, and the other a running listing output. Approach to seafloor of the CTD package was controlled by monitoring the pinger trace made by the direct and bottom return signals on the ship-provided PDR.

After each station, the CTD data were forwarded to another set of personal computers running both EG&G CTD post-processing 5.2 rev. 2 software and custom-built software from WHOI (Millard and Yang, 1993). The data were first-differenced, lag corrected, pressure sorted, and centered into 2 dbar bins for final data quality control and analysis, including fitting to water sample salinity and oxygen results.

**SUMMARY OF LABORATORY CALIBRATIONS FOR CTDs**

Maren Tracy Plueddemann and Marshall Swartz calibrated the pressure, temperature, and conductivity sensors at the Woods Hole Oceanographic Institution CTD Calibration Laboratory pre and post-cruise. The results are given below.

**LABORATORY PRESSURE CALIBRATIONS****ICTD 1338:****PRE CRUISE CAL**

Date: August 1995

Notes: 1338 and 1344 kept together in cold bath for pressure calibration.

1338, 1344 and CTD1 received temperature calibration at same time.

Bath temperature during pressure calibration = 1.85 deg C

Resulting polynomial coefficients for a third order fit:  $(A+Bx+Cx^2+Dx^3)$ :

A = 0.337188E+01

B = 0.100040E+00

C = -0.989186E-08

D = 0.121806E-12

Standard deviation of fit = 0.757851E+00

**POST CRUISE CAL**

Date: November 1995

Notes: 1338 and 1344 received pressure and temperature calibrations at the same time.

Bath temperature during pressure calibration = 1.67 deg C

Resulting polynomial coefficients for a third order fit:  $(A+Bx+Cx^2+Dx^3)$ :

A = 0.299558E+01

B = 0.999477E-01

C = -0.646358E-08

D = 0.900392E-13

Standard deviation of fit = 0.635441E+00

Bath temperature during pressure calibration = 29.80 deg C

Resulting polynomial coefficients for a third order fit:  $(A+Bx+Cx^2+Dx^3)$ :

A = 0.300466E+01

B = 0.999851E-01

C = -0.785380E-08

D = 0.103497E-12

Standard deviation of fit = 0.740938E+00

**COMBINED PRE- and POST-CRUISE CAL**

- Due to pressure bias shifts, a combination of the pre- and post-cruise pressure calibrations was selected for post cruise processing.

Bath temperature during pressure calibrations were 1.85 and 1.67 deg C

Resulting polynomial coefficients for a third order fit:  $(A+Bx+Cx^2+Dx^3)$ :

A = 0.326823E+01

B = 0.999882E-01

C = -0.798407E-08

D = 0.103679E-12

Standard deviation of fit = 0.766984E+00

**ICTD 1344:**

**PRE CRUISE CAL**

Date: August 1995

Notes: 1338 and 1344 kept together in cold bath for pressure calibration.

1338, 1344 and CTD1 received temperature calibration at same time.

Bath temperature during pressure calibration = 1.85 deg C

Resulting polynomial coefficients for a third order fit:  $(A+Bx+Cx^2+Dx^3)$ :

$$A = 0.203003E+01$$

$$B = 0.999794E-01$$

$$C = -0.166617E-08$$

$$D = 0.175895E-13$$

$$\text{Standard deviation of fit} = 0.490572E+00$$

**POST CRUISE CAL**

Date: November 1995

- This post cruise calibration was selected for post-cruise processing.

Notes: 1338 and 1344 received pressure and temperature calibrations at the same time.

Bath temperature during pressure calibration = 1.67 deg C

Resulting polynomial coefficients for a third order fit:  $(A+Bx+Cx^2+Dx^3)$ :

$$A = 0.162374E+01$$

$$B = 0.999549E-01$$

$$C = -0.293230E-09$$

$$D = 0.372714E-14$$

$$\text{Standard deviation of fit} = 0.341575E+00$$

Bath temperature during pressure calibration = 29.80 deg C

Resulting polynomial coefficients for a third order fit:  $(A+Bx+Cx^2+Dx^3)$ :

$$A = 0.167806E+01$$

$$B = 0.999615E-01$$

$$C = -0.720102E-09$$

$$D = 0.938970E-14$$

$$\text{Standard deviation of fit} = 0.462750E+00$$



**LABORATORY TEMPERATURE CALIBRATIONS**

ICTD 1338 had a small change, less than 0.002 deg C. The pre and post temperature calibrations were averaged to be used with the post cruise processing. The ICTD 1344 temperature calibration changed pre to post cruise with a bias shift of +0.002 deg C. CTD reading warmer at the post cruise calibration. The point at where the temperature shift occurred was looked for but not found. The most reliable search was to look at data from the same station where both primary and internal recording CTDs were used. They did not show where the jump occurred. The fast thermistor channel data were also compared at points where the salinity calibration changed. There was not enough proof to point to a spot where the jump occurred, so an average of the pre and post cruise calibrations was used to process the data.

**ICTD 1338 SLOW PLATINUM THERMOMETER CHANNEL****PRE CRUISE CAL**

Resulting polynomial coefficients for a third order fit:  $(A+Bx+Cx^2+Dx^3)$ :

$$A = 0.285975E-02$$

$$B = 0.500231E-03$$

$$C = -0.177714E-10$$

$$D = 0.194501E-15$$

$$\text{Standard deviation of fit} = 0.373642E-03$$

**POST CRUISE CAL**

Resulting polynomial coefficients for a third order fit:  $(A+Bx+Cx^2+Dx^3)$ :

$$A = 0.918509E-03$$

$$B = 0.500358E-03$$

$$C = -0.190649E-10$$

$$D = 0.192328E-15$$

$$\text{Standard deviation of fit} = 0.352686E-03$$

**COMBINED PRE AND POST CRUISE CAL**

- A combined calibration was used for post cruise processing as noted above.

Resulting polynomial coefficients for a third order fit:  $(A+Bx+Cx^2+Dx^3)$ :

$$A = 0.186857E-02$$

$$B = 0.500298E-03$$

$$C = -0.185827E-10$$

$$D = 0.195224E-15$$

$$\text{Standard deviation of fit} = 0.594841E-03$$

**ICTD 1338 FAST THERMISTOR CHANNEL**

Note: ICTD1338 fast thermistor temperature data was used to check for temperature shifts during cruise, but did not contribute to the final processed temperature data.

**PRE CRUISE CAL**

Note: the second order fit was used during the cruise. The third order fit was used post cruise to compare changes pre to post cruise for the fast thermistor channel.

Resulting polynomial coefficients for a second order fit:  $(A+Bx+Cx^2)$ :

$$A = 0.915609E-01$$

$$B = 0.495852E-03$$

$$C = 0.333829E-10$$

$$\text{Standard deviation of fit} = 0.693632E-01$$

Resulting polynomial coefficients for a third order fit:  $(A+Bx+Cx^2+Dx^3)$ :

$$A = -0.187870E-01$$

$$B = 0.524023E-03$$

$$C = -0.116195E-08$$

$$D = 0.129201E-13$$

$$\text{Standard deviation of fit} = 0.168422E-02$$

**POST CRUISE CAL**

Resulting polynomial coefficients for a third order fit:  $(A+Bx+Cx^2+Dx^3)$ :

$$A = -0.186425E-01$$

$$B = 0.524085E-03$$

$$C = -0.116322E-08$$

$$D = 0.129201E-13$$

$$\text{Standard deviation of fit} = 0.175345E-02$$

**ICTD 1338 OXYGEN TEMPERATURE CHANNEL****PRE CRUISE CAL**

Resulting polynomial coefficients for a second order fit:  $(A+Bx+Cx^2)$ :

$$A = -0.216281E+01$$

$$B = 0.160633E+00$$

$$C = -0.121723E-03$$

$$\text{Standard deviation of fit} = 0.158769E+00$$

**POST CRUISE CAL**

- This post-cruise calibration was used with the oxygen algorithms to produce the final dataset.

Resulting polynomial coefficients for a third order fit:  $(A+Bx+Cx^2+Dx^3)$ :

$$A = -0.277188E+01$$

$$B = 0.183254E+00$$

$$C = -0.324103E-03$$

$$D = 0.503239E-06$$

$$\text{Standard deviation of fit} = 0.361886E-01$$

**ICTD 1344 SLOW PLATINUM THERMOMETER****PRE CRUISE CAL**

Resulting polynomial coefficients for a third order fit:  $(A+Bx+Cx^2+Dx^3)$ :

$$A = -0.639595E-02$$

$$B = 0.500576E-03$$

$$C = -0.219271E-10$$

$$D = 0.227245E-15$$

$$\text{Standard deviation of fit} = 0.260050E-03$$

**POST CRUISE CAL**

Resulting polynomial coefficients for a third order fit:  $(A+Bx+Cx^2+Dx^3)$ :

$$A = -0.853971E-02$$

$$B = 0.500625E-03$$

$$C = -0.235555E-10$$

$$D = 0.243046E-15$$

$$\text{Standard deviation of fit} = 0.668181E-03$$

**COMBINED PRE AND POST CRUISE CAL**

- A combined calibration was used for final post cruise processing.

Resulting polynomial coefficients for a third order fit:  $(A+Bx+Cx^2+Dx^3)$ :

$$A = -0.748166E-02$$

$$B = 0.500600E-03$$

$$C = -0.226875E-10$$

$$D = 0.234567E-15$$

$$\text{Standard deviation of fit} = 0.940009E-03$$

**ICTD 1344 FAST PLATINUM THERMOMETER CHANNEL**

Note: The fast platinum thermometer channel was used as a secondary reference to judge changes to the ICTD 1344 slow platinum thermometer channel during the cruise. These measurements did not contribute to the final processed data.

**PRE CRUISE CAL**

Resulting polynomial coefficients for a second order fit:  $(A+Bx+Cx^2)$ :

$$A = -0.164421E-02$$

$$B = 0.499960E-03$$

$$C = 0.832749E-12$$

$$\text{Standard deviation of fit} = 0.146257E-02$$

Resulting polynomial coefficients for a third order fit:  $(A+Bx+Cx^2+Dx^3)$ :

$$A = -0.390910E-02$$

$$B = 0.500535E-03$$

$$C = -0.235454E-10$$

$$D = 0.263094E-15$$

$$\text{Standard deviation of fit} = 0.356128E-03$$

**POST CRUISE CAL**

Resulting polynomial coefficients for a third order fit:  $(A+Bx+Cx^2+Dx^3)$ :

$$A = -0.707179E-02$$

$$B = 0.500630E-03$$

$$C = -0.267632E-10$$

$$D = 0.294216E-15$$

$$\text{Standard deviation of fit} = 0.585656E-03$$

**ICTD 1344 FAST THERMISTOR CHANNEL**

Note: ICTD1344 fast thermistor temperature data was used to check for temperature shifts during cruise, but did not contribute to the final processed temperature data.

**PRE CRUISE CAL**

Resulting polynomial coefficients for a second order fit:  $(A+Bx+Cx^2)$ :

$$A = 0.889859E-01$$

$$B = 0.496237E-03$$

$$C = 0.282361E-10$$

$$\text{Standard deviation of fit} = 0.677849E-01$$

Resulting polynomial coefficients for a third order fit:  $(A+Bx+Cx^2+Dx^3)$ :

$$A = -0.188737E-01$$

$$B = 0.523767E-03$$

$$C = -0.113985E-08$$

$$D = 0.126255E-13$$

$$\text{Standard deviation of fit} = 0.182910E-02$$

**POST CRUISE CAL**

Resulting polynomial coefficients for a third order fit:  $(A+Bx+Cx^2+Dx^3)$ :

$$A = -0.181959E-01$$

$$B = 0.523798E-03$$

$$C = -0.113971E-08$$

$$D = 0.126209E-13$$

$$\text{Standard deviation of fit} = 0.171024E-02$$

**ICTD 1344 OXYGEN TEMPERATURE CHANNEL****PRE CRUISE CAL**

Resulting polynomial coefficients for a second order fit:  $(A+Bx+Cx^2)$ :

$$A = -0.336502E+01$$

$$B = 0.146252E+00$$

$$C = -0.637599E-04$$

$$\text{Standard deviation of fit} = 0.293626E+00$$

**POST CRUISE CAL**

- The post-cruise oxygen temperature calibration was used with the oxygen algorithms for the final dataset.

Resulting polynomial coefficients for a third order fit:  $(A+Bx+Cx^2+Dx^3)$ :

$$A = -0.477833E+01$$

$$B = 0.194995E+00$$

$$C = -0.466521E-03$$

$$D = 0.921395E-06$$

$$\text{Standard deviation of fit} = 0.714265E-01$$

**SALINITY CALIBRATIONS**

The CTD conductivity sensor data were fit to the water sample conductivity as described in Millard and Yang (1993). The stations were fit by groups according to the drift of the conductivity sensor over time.

Plot results of deep water  $\theta/S$  revealed that there was a difference between CTDs:

1338: \*.PRS CTD salt read too high  $\sim 0.002$  psu or temperature was too low compared to \*.SEA file.

1344: \*.PRS CTD salt read too low  $\sim 0.001$  psu or temperature was too high compared to \*.SEA file.

The consistency of the bias between stations indicates it was probably not a real ocean measurement such as measuring internal waves, but some kind of instrument, package dynamic or bottle artifact. All ICTD 1338 stations have a significant bias, with the downtrace always saltier than the bottles. The uptrace has been fit well, but the uptrace is fresher than the downtrace. To correct for the difference, the downtrace salinity data for the group of stations 978 and 980 through 1014 were fit to the bottle data. This was accomplished by processing the 2-decibar averaged downtrace CTD data against the bottle data, and provided a more acceptable fit for these stations. [Figures 1 and 2](#) demonstrate the CTD salt to bottle salt fits for stations 982 through 1000 using downtrace data, and [figures 3 and 4](#) demonstrate the same fits using uptrace data as is normally done.

ICTD 1338 stations 870 through 892 seemed to fit well after forcing the CTD salt data to agree with the bottom bottle data, and so were not refit using the downtrace. ICTD 1344 downtraces trend toward being fresher than the bottles. The uptrace and downtrace agree, but the fits were not working well. Some of the fits were recalculated, with emphasis on matching up the CTD and salts in the bottom water.

CTD comparisons were made with the primary CTD and memory CTD data from the same stations. Pressure agreed very well, with bottom depths agreeing within 1dbar on the stations checked. Temperature would stray,  $\pm 0.002$  at the bottom, sometimes ICTD 1338 being warmer, and sometimes ICTD 1344 was warmer. This is most likely a factor of the location of the telemetering CTD on the sampler frame being different than the position of the memory mode CTD and thus in a different waterpath. Both CTDs could have thermal contamination of the temperature signal from the frame while sampling at a bottle stop.

Notes for particular stations' salinity calibrations

Stations 936-938, 940-941:

A pressure dependent difference between bottle and CTD salinities could not be removed without changing the conductivity cell geometry correction terms for pressure (ALPHA) and temperature (BETA). After station 942, the conductivity cell was cleaned due to slime buildup. The difficult calibrations from stations 936 to 942 could have been induced by fouling or buildup of slime on the conductivity cell.

Stations 936, 937 and 938:

BETA was changed from  $1.5e-8$  to  $0.75e-8$

Stations 940 and 941 have BETA changed from  $1.5e-8$  to  $0.75e-8$ , and

ALPHA changed from  $-6.5e-6$  to  $-9.75e-6$ .

Station 923 and 954:

Salt changes that looked questionable until the uptrace was overlaid and followed the shape of the downtrace. Station 923 freshens around 2 deg C. Station 954 has spikes and a shift at 1750dbar, 1900dbar and 2250 dbar that are clearly repeated in the uptrace.

**Table 1. Final conductivity coefficients applied by station number**

The coefficients used to scale downtrace conductivity data for the II stations are listed below.

stn	bias	slope	stn	bias	slope	stn	bias	slope
857	0.269148E-02	0.999756E-03	910	-1.06344E-02	0.100004E-02	963	-3.90173E-02	0.100009E-02
858	0.148422E-01	0.997105E-03	911	-1.06344E-02	0.100004E-02	964	-5.19660E-02	0.100021E-02
859	0.758850E-02	0.999569E-03	912	-1.06344E-02	0.100004E-02	965	-5.19660E-02	0.100021E-02
860	0.758850E-02	0.999569E-03	913	-1.06344E-02	0.100004E-02	966	-5.19660E-02	0.100021E-02
861	0.758850E-02	0.999569E-03	914	-1.06344E-02	0.100004E-02	967	-5.19660E-02	0.100021E-02
862	0.758850E-02	0.999569E-03	915	-1.06344E-02	0.100004E-02	968	-5.19660E-02	0.100019E-02
863	0.269148E-02	0.999816E-03	916	-1.06344E-02	0.100004E-02	969	-5.19660E-02	0.100021E-02
864	0.187740E-01	0.100097E-02	917	-1.06344E-02	0.100004E-02	970	-5.19660E-02	0.100019E-02
865	0.758850E-02	0.999569E-03	918	-1.28407E-03	0.100004E-02	971	-5.19660E-02	0.100019E-02
866	0.758850E-02	0.999569E-03	919	-1.28407E-03	0.100004E-02	972	-5.19660E-02	0.100019E-02
867	0.758850E-02	0.999569E-03	920	-1.28407E-03	0.100004E-02	973	-5.19660E-02	0.100019E-02
868	0.758850E-02	0.999649E-03	921	-1.28407E-03	0.100004E-02	974	-5.19660E-02	0.100019E-02
869	0.758850E-02	0.999569E-03	922	-1.28407E-03	0.100004E-02	975	-5.19660E-02	0.100019E-02
870	0.269148E-02	0.999795E-03	923	-1.28407E-03	0.100004E-02	976	-5.19660E-02	0.100019E-02
871	0.269148E-02	0.999795E-03	924	-1.28407E-03	0.100004E-02	977	-3.90173E-02	0.100007E-02
872	0.269148E-02	0.999795E-03	925	-1.28407E-03	0.100004E-02	978	0.419290E-03	0.999988E-03
873	0.269148E-02	0.999795E-03	926	-1.28407E-03	0.100004E-02	979	-3.90173E-02	0.100015E-02
874	0.269148E-02	0.999795E-03	927	-1.28407E-03	0.100004E-02	980	0.419290E-03	0.999994E-03
875	0.269148E-02	0.999795E-03	928	-1.28407E-03	0.100004E-02	981	0.419290E-03	0.999994E-03
876	0.269148E-02	0.999795E-03	929	-2.96800E-03	0.100006E-02	982	0.419290E-03	0.999994E-03
877	0.269148E-02	0.999795E-03	930	-2.96800E-03	0.100006E-02	983	0.419290E-03	0.999994E-03
878	0.269148E-02	0.999795E-03	931	-2.96800E-03	0.100006E-02	984	0.419290E-03	0.999994E-03
879	0.269148E-02	0.999795E-03	932	-2.96800E-03	0.100006E-02	985	0.419290E-03	0.999994E-03
880	0.269148E-02	0.999795E-03	933	-2.96800E-03	0.100006E-02	986	0.419290E-03	0.999994E-03
881	0.269148E-02	0.999795E-03	934	-2.96800E-03	0.100014E-02	987	0.419290E-03	0.999994E-03
882	0.269148E-02	0.999795E-03	935	-2.96800E-03	0.100006E-02	988	0.419290E-03	0.999994E-03
883	0.269148E-02	0.999795E-03	936	0.141056E-02	0.100005E-02	989	0.419290E-03	0.999994E-03
884	0.269148E-02	0.999795E-03	937	0.141056E-02	0.100005E-02	990	0.419290E-03	0.999994E-03
885	0.269148E-02	0.999795E-03	938	0.141056E-02	0.100005E-02	991	0.419290E-03	0.999994E-03
886	0.269148E-02	0.999795E-03	939	0.141056E-02	0.100005E-02	992	0.419290E-03	0.999994E-03
887	0.269148E-02	0.999795E-03	940	-5.14493E-02	0.100032E-02	993	0.419290E-03	0.999994E-03
888	0.269148E-02	0.999795E-03	941	-5.14493E-02	0.100032E-02	994	0.419290E-03	0.999994E-03
889	0.269148E-02	0.999795E-03	942	-5.14493E-02	0.100030E-02	995	0.419290E-03	0.999994E-03
890	0.269148E-02	0.999795E-03	943	-8.91709E-03	0.100003E-02	996	0.419290E-03	0.999994E-03
891	0.269148E-02	0.999795E-03	944	-8.91709E-03	0.100003E-02	997	0.419290E-03	0.999994E-03
892	0.269148E-02	0.999795E-03	945	-8.91709E-03	0.100003E-02	998	0.419290E-03	0.999994E-03
893	-8.23240E-03	0.999989E-03	946	-8.91709E-03	0.100004E-02	999	0.419290E-03	0.999994E-03
894	-8.23240E-03	0.999989E-03	947	-8.91709E-03	0.100004E-02	000	0.419290E-03	0.999994E-03
895	-8.23240E-03	0.999989E-03	948	-8.91709E-03	0.100004E-02	001	0.419290E-03	0.999994E-03
896	-8.23240E-03	0.999989E-03	949	-8.91709E-03	0.100004E-02	002	0.419290E-03	0.999994E-03
897	-8.23240E-03	0.999989E-03	950	-8.91709E-03	0.100004E-02	003	0.419290E-03	0.999994E-03
898	-8.23240E-03	0.999989E-03	951	-8.91709E-03	0.999983E-03	004	0.419290E-03	0.999994E-03
899	0.187740E-01	0.100097E-02	952	-8.91709E-03	0.100004E-02	005	0.419290E-03	0.999994E-03
900	-0.823240E-03	0.999992E-03	953	-8.91709E-03	0.100004E-02	006	0.419290E-03	0.999994E-03
901	-0.823240E-03	0.999992E-03	954	-8.91709E-03	0.100004E-02	007	0.419290E-03	0.999994E-03
902	-0.823240E-03	0.999992E-03	955	-8.91709E-03	0.100004E-02	008	0.419290E-03	0.999994E-03
903	-0.823240E-03	0.999992E-03	956	-8.91709E-03	0.100004E-02	009	0.419290E-03	0.999994E-03
904	-0.823240E-03	0.999992E-03	957	-8.91709E-03	0.100004E-02	010	0.419290E-03	0.999994E-03
905	-0.823240E-03	0.999992E-03	958	-8.91709E-03	0.999997E-03	011	0.419290E-03	0.999994E-03
906	-0.823240E-03	0.999992E-03	959	-8.91709E-03	0.100004E-02	012	0.419290E-03	0.999994E-03
907	-0.823240E-03	0.999992E-03	960	-8.91709E-03	0.100008E-02	013	0.419290E-03	0.999994E-03
908	-0.823240E-03	0.999992E-03	961	-8.91709E-03	0.100008E-02	014	0.419290E-03	0.999994E-03
909	-8.23240E-03	0.999989E-03	962	-3.90173E-02	0.100009E-02			

The coefficients used to scale uptrace conductivity data for selected I1 stations are listed below.

<b>stn</b>	<b>bias</b>	<b>slope</b>	<b>stn</b>	<b>bias</b>	<b>slope</b>
978	0.216462E-02	0.999940E-03	997	0.216462E-02	0.999975E-03
980	0.216462E-02	0.999940E-03	998	0.216462E-02	0.999975E-03
981	0.216462E-02	0.999940E-03	999	0.216462E-02	0.999975E-03
982	0.216462E-02	0.999940E-03	000	0.216462E-02	0.999975E-03
983	0.216462E-02	0.999975E-03	001	0.216462E-02	0.999975E-03
984	0.216462E-02	0.999975E-03	002	0.216462E-02	0.999975E-03
985	0.216462E-02	0.999975E-03	003	0.216462E-02	0.999975E-03
986	0.216462E-02	0.999975E-03	004	0.216462E-02	0.999975E-03
987	0.216462E-02	0.999975E-03	005	0.216462E-02	0.999975E-03
988	0.216462E-02	0.999975E-03	006	0.216462E-02	0.999975E-03
989	0.216462E-02	0.999975E-03	007	0.216462E-02	0.999975E-03
990	0.216462E-02	0.999975E-03	008	0.216462E-02	0.999975E-03
991	0.216462E-02	0.999975E-03	009	0.216462E-02	0.999975E-03
992	0.216462E-02	0.999975E-03	010	0.216462E-02	0.999975E-03
993	0.216462E-02	0.999975E-03	011	0.216462E-02	0.999975E-03
994	0.216462E-02	0.999975E-03	012	0.216462E-02	0.999975E-03
995	0.216462E-02	0.999975E-03	013	0.216462E-02	0.999975E-03
996	0.216462E-02	0.999975E-03	014	0.216462E-02	0.999975E-03

Note: Uptrace CTD conductivity data was fit to the bottle salts for stations 978 and 980 through 1014 as described in the preceding documentation to achieve a better fit.

**SALINITY FITTING RESULTS:**

The following plots show the differences between the rosette and CTD salts across legs one and two. It is important to note that these plots cover both CTDs, each of which were opened on several occasions potentially causing calibration changes. In the beginning of the cruise many mechanical problems were encountered. (see [ATSEA.doc](#)).

**Figure 1: Leg 1 - Difference between calibrated downtrace CTD salts and the rosette salinity data**

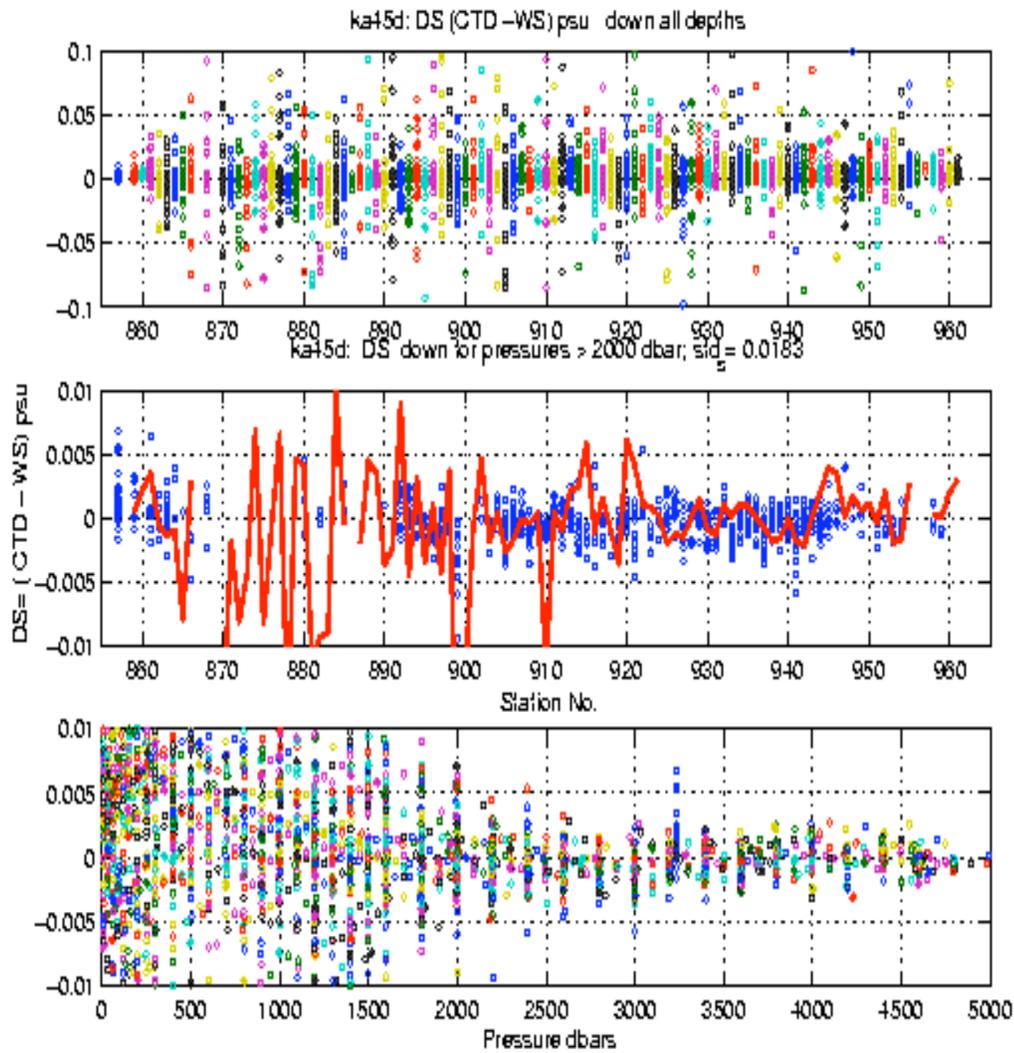
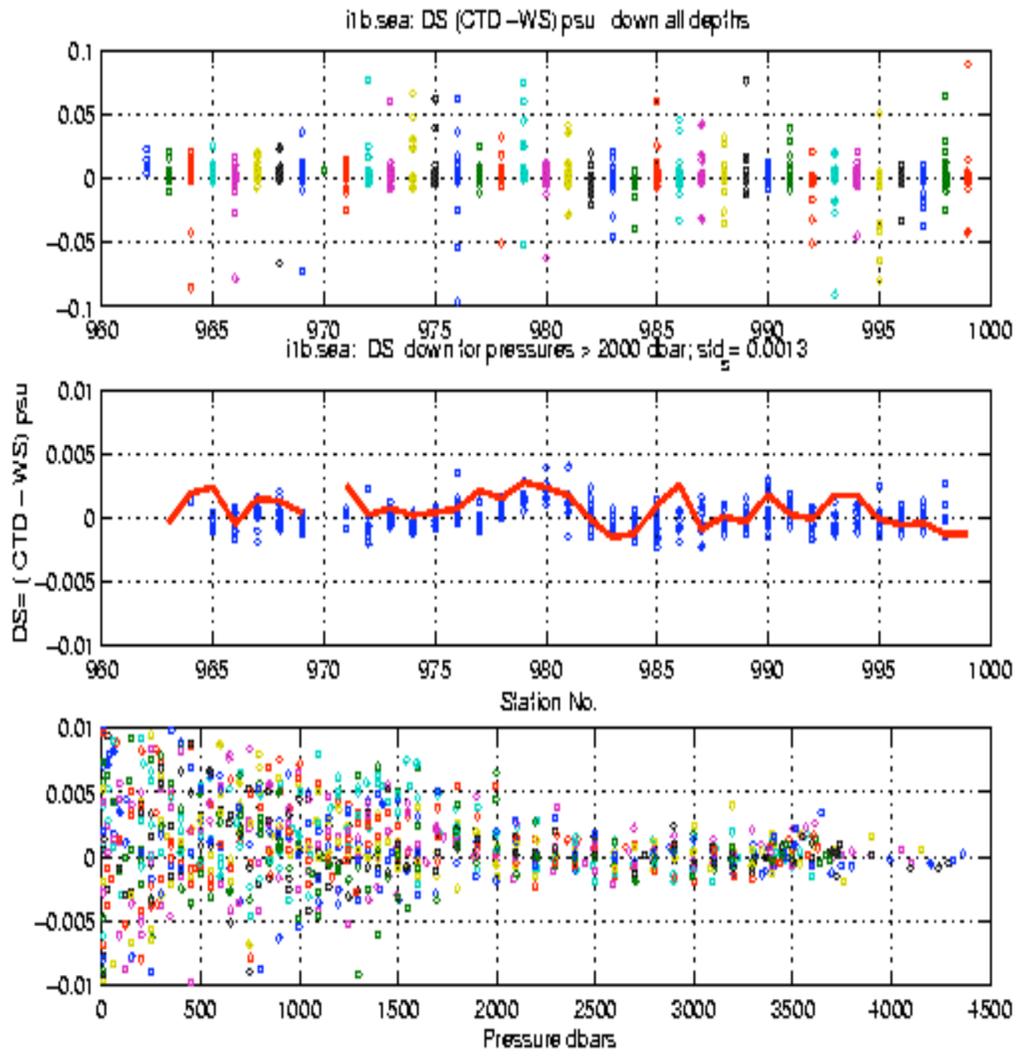


Figure 2: Leg 2 - Difference between calibrated downtrace CTD salts and rosette salinity data



**Figure 3: Leg 1 Differences between calibrated uptrace CTD salts in rosette file (scaled with separate multiple regression fit from down salinities) and rosette salts. Note that the residuals are significantly better for the uptrace data. Fits to the uptrace data were applied to the uptrace CTD data in the rosette file. Due to hysteresis, fits to the downtrace data needed to be applied to the downtrace CTD data files for stations 978 to 1014.**

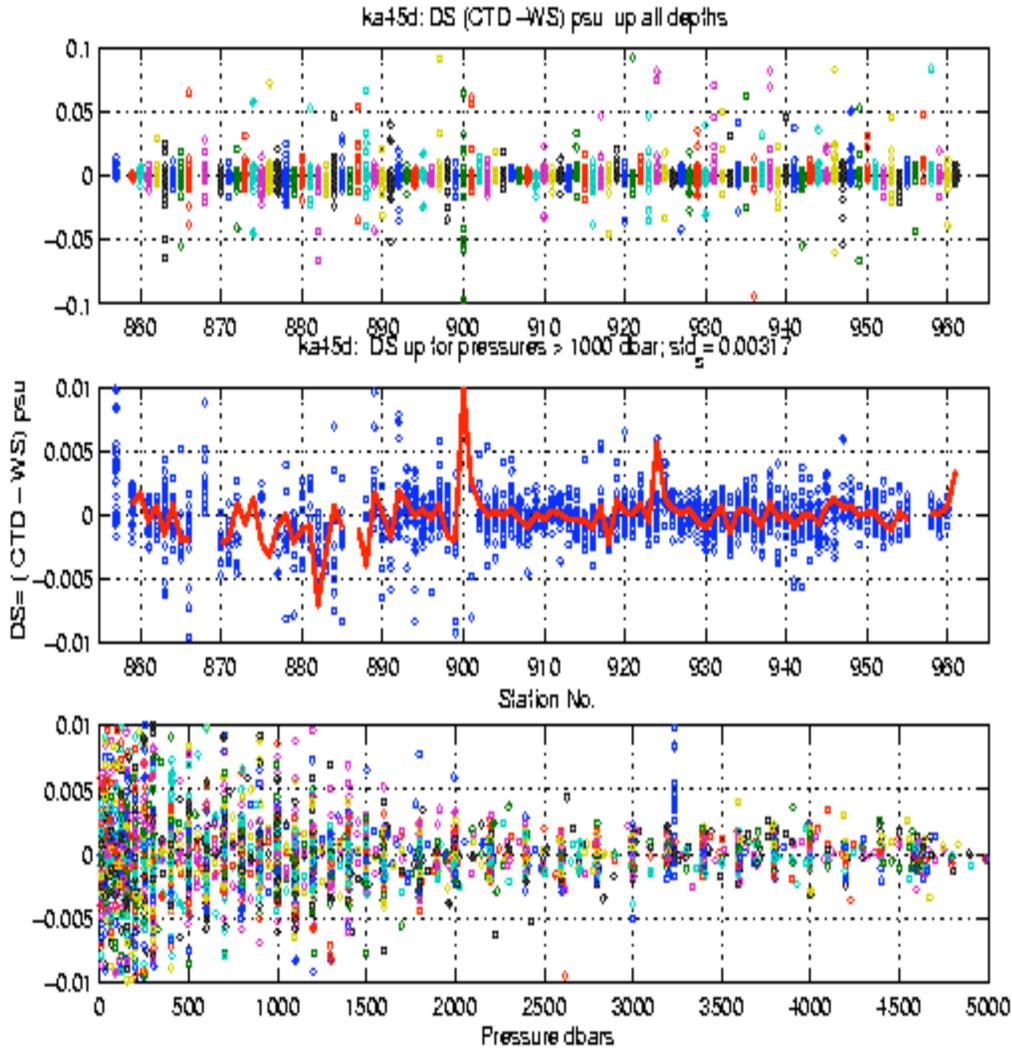
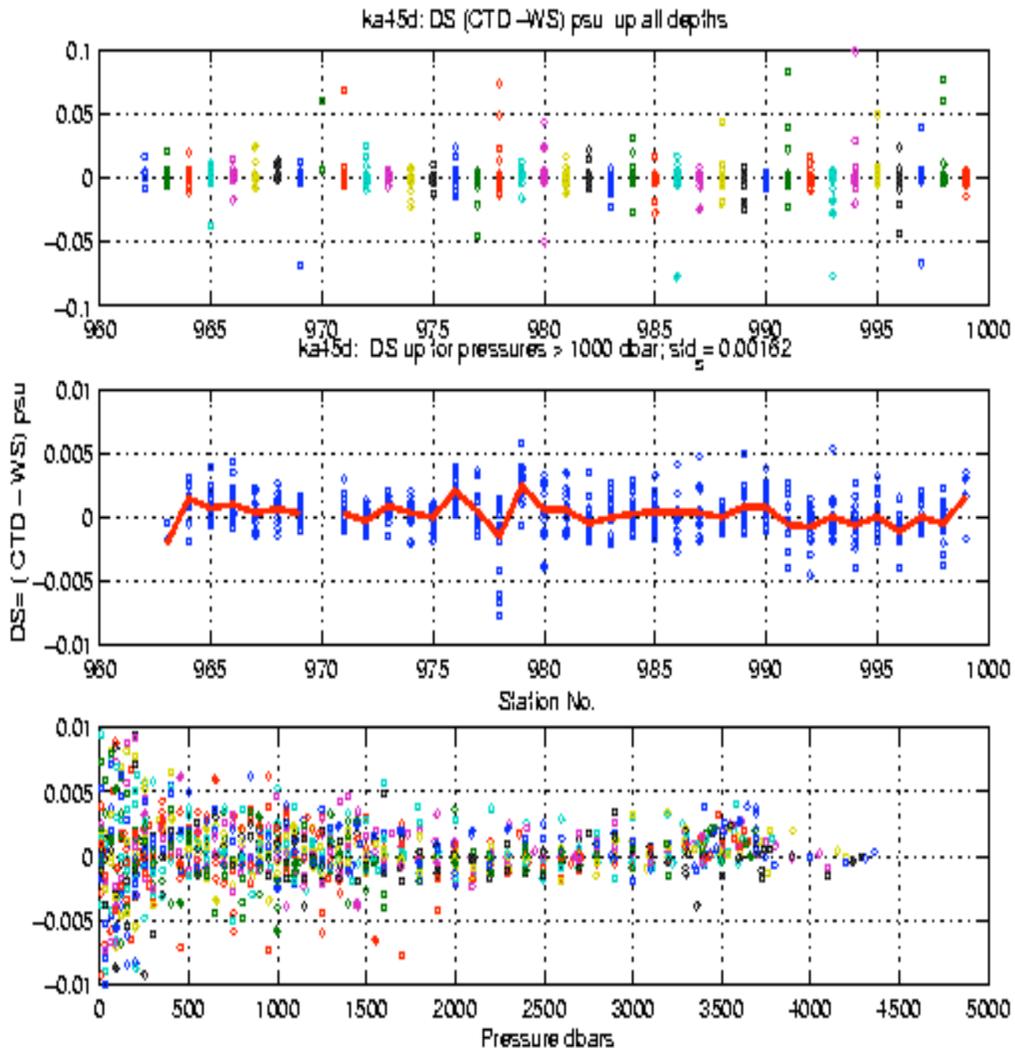


Figure 4: Leg 2: Differences between scaled uptrace CTD salts in the rosette file (separate multiple regression fit from down salinities) and the rosette salt data.



**OXYGEN CALIBRATIONS:****SENSOR FAILURES**

The CTD oxygen data presented special problems from the beginning. While all four CTDs were initially fitted with new oxygen sensors, and spares were brought on the cruise, the stations were plagued with sensor failures and erratic sensor data. The CTDs all used Sensormedics brand polarographic oxygen sensors, and due to recent experience of failures, it was expected that sensor changes would have to be made. However, the failure rate exceeded our low expectations, with seven replacement sensors being used.

Oxygen sensors were replaced following the stations listed below:

Station	CTD	Sensor s/n
865	1344	5-06-03
910	1344	5-06-02
923	1344	5-07-02
930	1344	4-10-2
980	1344	4-12-04
991	1344	5-06-01

The CTDs used interchangeable sensor assemblies, which permitted the oxygen thermistor and sensor module to simply be unplugged and a new one installed if a problem was found. This speeded up the changeout of failed oxygen sensors. However, since each CTD's oxygen temperature channel is calibrated to a specific module, swapping a module out changes the oxygen temperature calibration. Due to the large number of failures of sensors, modules were interchanged between the ICTDs on several occasions, and necessitated special attention to fitting of the data.

**OXYGEN DATA FITTING**

Some stations fit well using normal fitting routines, while others had a definite pressure dependent shape in the residuals. A similar shape recurred in different groups. The shape was more pronounced in some groups than others. A weight of 0.8 and lag of 1 was consistent from a few of the larger groups. Most of the groups had this weight and lag held during the fits since many groups came up with weights over 1 and lags below 0 when allowed to fit for those parameters. For the groups with the pressure dependent shape in the residuals, tcor was held at some value lower than the fit originally came up with. Usually tcor was adjusted by -0.002 and the group refit. The resulting residuals between 2000 to 5000 dbars would be centered around 0 with a spread reduced from +/-0.1 to +/-0.04 but the shape would remain in the upper 2000 dbars.

Special notes for fitting oxygen data for particular stations:

The oxygen temperature (OT) coefficients were changed for the post processing. There were several instances of the CTD profile not reaching the oxygen minimum, or overshooting the minimum. This may have been due to not having the proper OT coefficients in the at-sea station header files. These were corrected during post-processing so all calibration files now have the proper OT coefficients for each CTD.

OT coefficient changes:

Station applied to	Change made
857, 870-892	replaced wrong 38 bias with right 38 bias.
859-862	replaced 38 OT cal with 44 OT cal.
865-869	left as is.
893-979, 899, 978	replaced 38 OT wrong bias with 44 OT cal.
979	replaced wrong 38 bias with right 38 bias.
980	replaced wrong 38 bias with right 38 bias.
981-004	replaced wrong 38 bias with right 38 bias.
005-014	replaced wrong 38 bias with right 38 bias.

Stations 859 to 862 were taken with ICTD 1344 but used ICTD1338's oxygen assembly. 1344's OT calibration terms were put into the cal file.

Stations 877, 878, 879 and 004 were scaled using the at-sea OT and oxygen current (OC) terms. With the new OT terms, it was not possible to get as good a fit as the at-sea results. The terms arrived at had unrealistic numbers such as a negative lag but was used anyway for the resulting good fit.

Stations 857 and 858, test stations, had the oxygen quality word flagged '4' (bad) in the downtrace. All the bottles were deep and not useful for finding a fit for the whole profile.

Station 859, the next station in the same locations as 857 and 858, had bottles except for the top 800dbar due to a pylon failure. Even with a better fit this top should be labeled '3' (questionable).

Station 860, a test station for water sampling. The downtrace oxygen was labeled '4' due to all bottles fired deep.

Stations 906 to 904 have clear shape in the bottom water that may or may not be real. The uptrace looks as if it follows the shapes loosely, not really until the larger features around 2000dbar does it really follow the downtrace. Station 937 had extra bottles taken deep to watch the +/- 0.05ml/l variation in oxygen. The bottles do look like they agree with the oxygen.

Station 987, a -0.04 ml/l shift in oxygen at 2711dbar does not look real, and does not agree with bottle or following stations. It has been flagged '3' (questionable).



**SPECIAL OXYGEN ALGORITHM FITTING**

Fifty-three stations had the problem of fitting the CTD oxygen profile to the bottle data. Bob Millard revised the oxygen algorithm in an attempt to improve the oxygen data from ICTD stations with pressure dependent oxygen residuals using the original Owens & Millard oxygen algorithm:

$$oc = (ocr+lag*docr/dt)*slope+bias$$

Two changes to the oxygen algorithm of Owens & Millard (1985) result in the equation below:

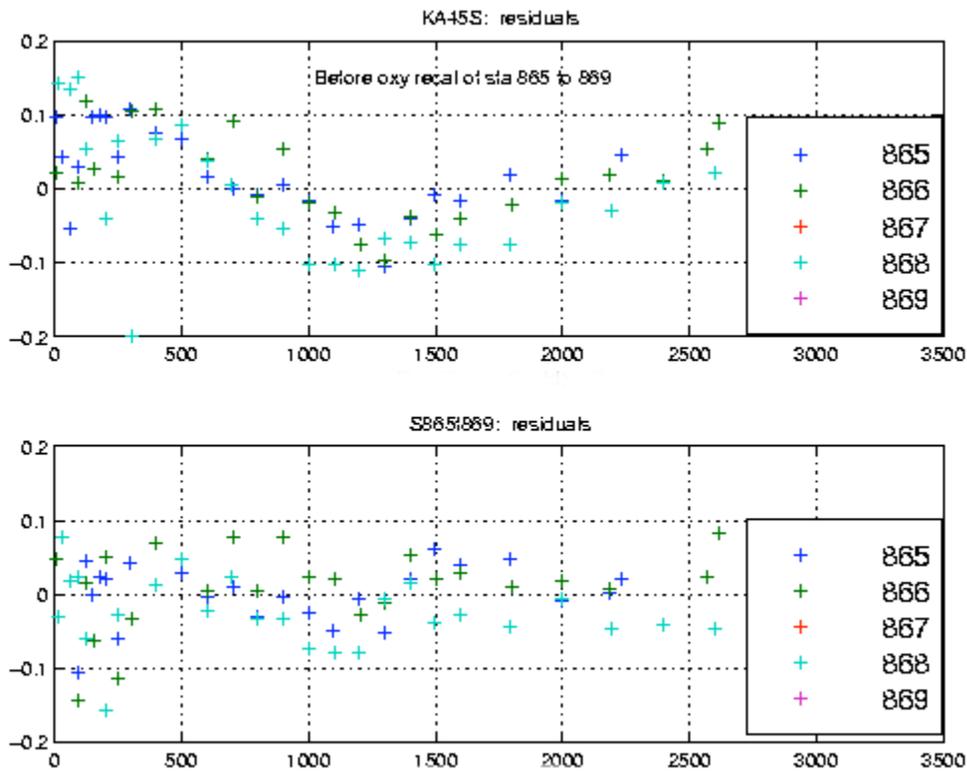
$$ox = oc*oxsat* \exp(tc\text{or}*(T+wt*(OT-T)+p\text{cor}*P)$$

First is the uncoupling of the temperature parameters in the exponential of the algorithm ( $tc\text{or}*wt$ ). This becomes particularly helpful if the oxygen temperature (OT) term does not have a valid calibration. A new term involving the cross-term between pressure and temperature has been added to the algorithm as it picks up additional variance. Note that the oxygen lag term is negative for a number of station groups listed in [table 3](#) below. In recognition of the inadequate performance of the oxygen sensor modules used for these stations, we opted for the best fit to the water sample oxygen data even though the terms may not be physically realistic.

$$ox = oc*oxsat* \exp(tc\text{or}1*T+tc\text{or}2*OT+p\text{cor}*P+pt\text{cor}*P*T)$$

The following figures demonstrate how well the adjusted algorithm has done in fitting two station groups that could not be fit with the original algorithm.

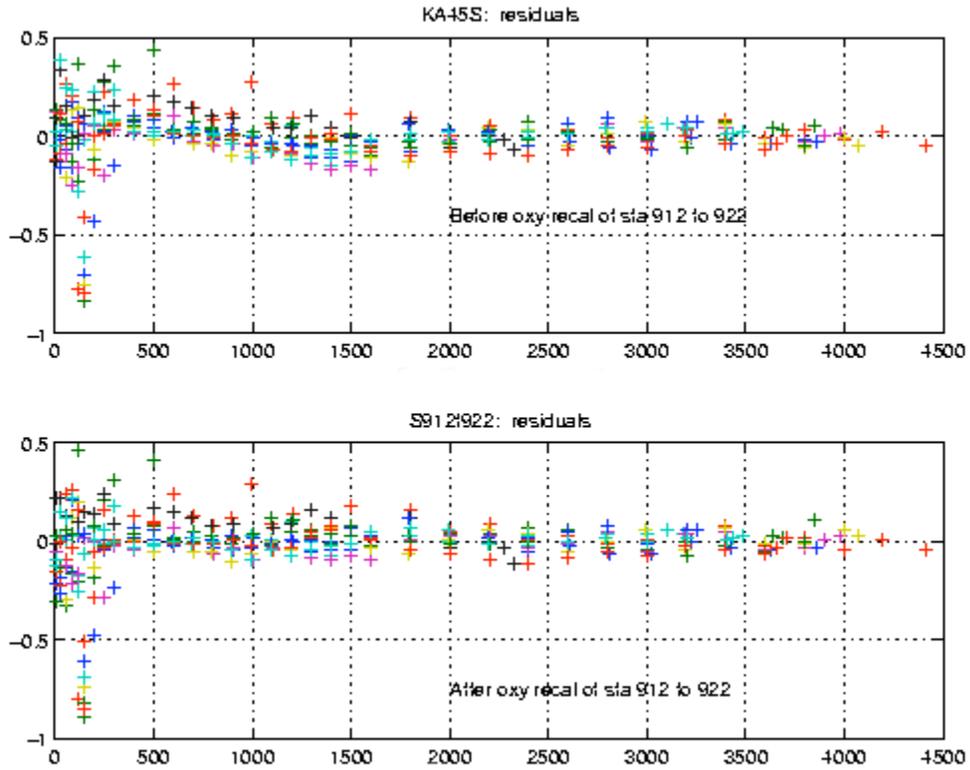
**Figure 5: Oxygen fitting with new algorithm: Stations 865 to 869: Original fit shows distinct pressure dependent shape as opposed to fit with new algorithm.**



plots display differences of bottle to CTD oxygen ml/l by pressure in decibars.

Above

Figure 6: Oxygen fitting with new algorithm: Stations 912 to 922: Fit with new algorithm removes pressure dependent shape of residuals.



Above plots display differences of bottle to CTD oxygen ml/l by pressure in decibars.

Figure 7: Refit of station group 912 to 922 (notice that shallow station 918 rosette data are bad).

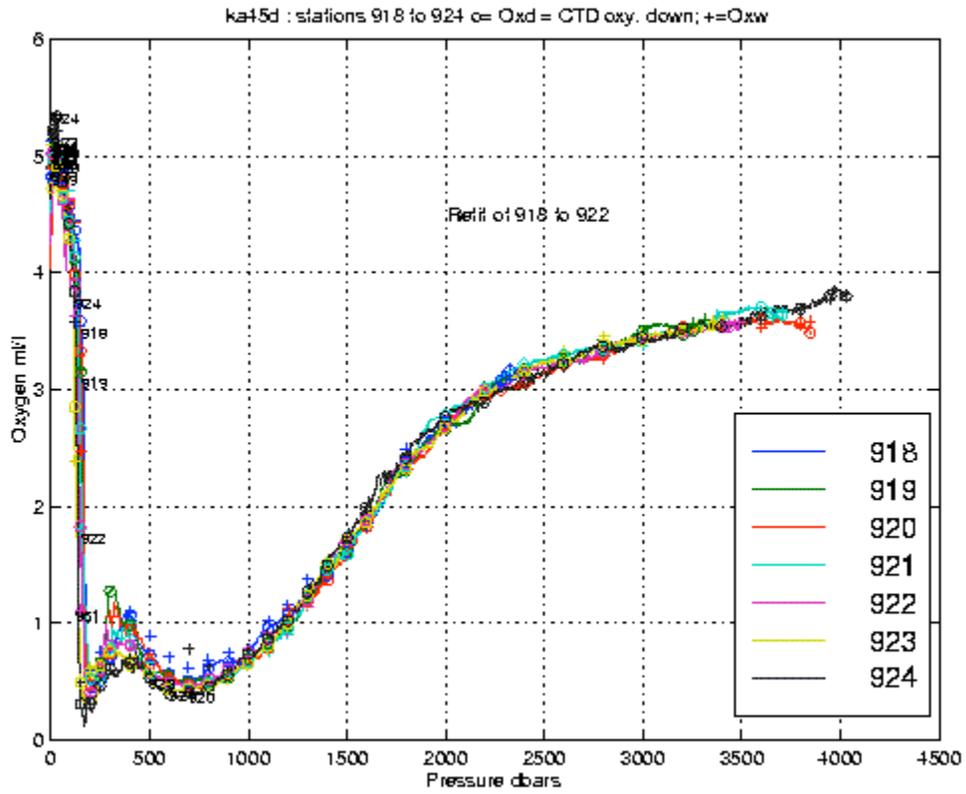
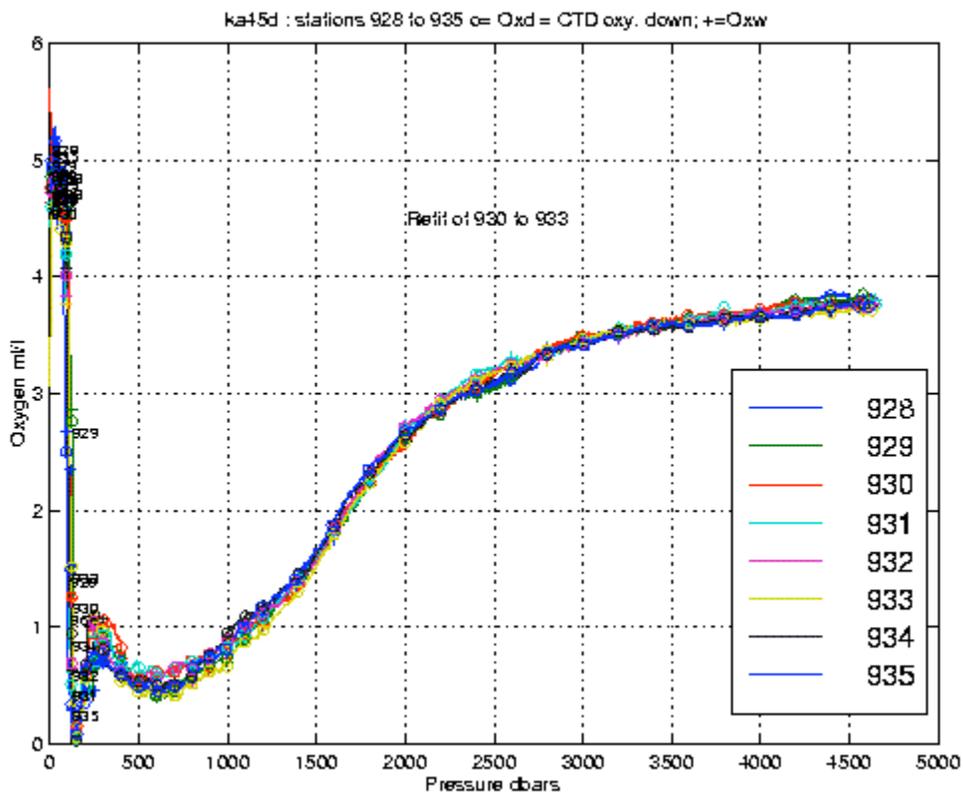


Figure 8: Refit of stations 930 to 933 in comparison to surrounding stations.



**Table 3 OXYGEN DATA FITTING COEFFICIENTS FOR REVISED ALGORITHM**

The following is a table of coefficients used to scale the oxygen data in the 53 stations that exhibited oxygen fitting problems. Note that some of the terms (i.e. lag) are unrealistic; they do, however, allow these data to be fit to the rosette water sample values. These are the data that could not be fit with the standard oxygen algorithm.

stn	bias	slope	pcor	tcor1	tcor2	lag	ptcor
860	-0.007971	0.001741	0.000156	-0.118095	0.050579	-4.17	-0.00006604
861	-0.007971	0.001741	0.000156	-0.118095	0.050579	-4.17	-0.00006604
862	-0.007971	0.001741	0.000156	-0.118095	0.050579	-4.17	-0.00006604
865	0.016388	0.001236	0.000163	-0.027216	-0.007340	-0.82	-0.00003362
866	0.016388	0.001236	0.000163	-0.027216	-0.007340	-0.82	-0.00003362
867	0.016388	0.001236	0.000163	-0.027216	-0.007340	-0.82	-0.00003362
868	0.016388	0.001236	0.000163	-0.027216	-0.007340	-0.82	-0.00003362
869	0.016388	0.001236	0.000163	-0.027216	-0.007340	-0.82	-0.00003362
880	0.157432	0.000496	0.000439	0.077879	-0.080973	-3.74	-0.00011072
881	0.052984	0.000207	0.001009	0.073267	-0.044510	-11.85	-0.00010797
882	0.046955	0.001134	0.000207	-0.011526	-0.015070	0.03	-0.00004038
883	0.046955	0.001134	0.000207	-0.011526	-0.015070	0.03	-0.00004038
884	0.046955	0.001134	0.000207	-0.011526	-0.015070	0.03	-0.00004038
885	0.046955	0.001134	0.000207	-0.011526	-0.015070	0.03	-0.00004038
886	0.046955	0.001134	0.000207	-0.011526	-0.015070	0.03	-0.00004038
887	0.046955	0.001134	0.000207	-0.011526	-0.015070	0.03	-0.00004038
888	0.046955	0.001134	0.000207	-0.011526	-0.015070	0.03	-0.00004038
889	0.046955	0.001134	0.000207	-0.011526	-0.015070	0.03	-0.00004038
890	0.046955	0.001134	0.000207	-0.011526	-0.015070	0.03	-0.00004038
891	0.046955	0.001134	0.000207	-0.011526	-0.015070	0.03	-0.00004038
892	0.046955	0.001134	0.000207	-0.011526	-0.015070	0.03	-0.00004038
912	0.018098	0.001265	0.000161	-0.011542	-0.016859	-0.84	-0.00002167
913	0.018098	0.001265	0.000161	-0.011542	-0.016859	-0.84	-0.00002167
914	0.018098	0.001265	0.000161	-0.011542	-0.016859	-0.84	-0.00002167
915	0.018098	0.001265	0.000161	-0.011542	-0.016859	-0.84	-0.00002167
916	0.018098	0.001265	0.000161	-0.011542	-0.016859	-0.84	-0.00002167
917	0.018098	0.001265	0.000161	-0.011542	-0.016859	-0.84	-0.00002167
918	0.018098	0.001265	0.000161	-0.011542	-0.016859	-0.84	-0.00002167
919	0.018098	0.001265	0.000161	-0.011542	-0.016859	-0.84	-0.00002167
920	0.018098	0.001265	0.000161	-0.011542	-0.016859	-0.84	-0.00002167
921	0.018098	0.001265	0.000161	-0.011542	-0.016859	-0.84	-0.00002167
922	0.018098	0.001265	0.000161	-0.011542	-0.016859	-0.84	-0.00002167
930	-0.028873	0.001555	0.000177	-0.016931	-0.010603	-5.01	-0.00003549
931	-0.028873	0.001555	0.000177	-0.016931	-0.010603	-5.01	-0.00003549
932	-0.028873	0.001555	0.000177	-0.016931	-0.010603	-5.01	-0.00003549
933	-0.028873	0.001555	0.000177	-0.016931	-0.010603	-5.01	-0.00003549
963	-0.013299	0.001418	0.000157	-0.009204	-0.015968	1.10	-0.00002067
964	-0.013299	0.001418	0.000157	-0.009204	-0.015968	1.10	-0.00002067
965	-0.013299	0.001418	0.000157	-0.009204	-0.015968	1.10	-0.00002067
966	-0.013299	0.001418	0.000157	-0.009204	-0.015968	1.10	-0.00002067
967	-0.013299	0.001418	0.000157	-0.009204	-0.015968	1.10	-0.00002067
968	-0.013299	0.001418	0.000157	-0.009204	-0.015968	1.10	-0.00002067
969	-0.013299	0.001418	0.000157	-0.009204	-0.015968	1.10	-0.00002067
971	-0.019304	0.001652	0.000148	-0.011510	-0.019372	1.83	-0.00004173
972	-0.019304	0.001652	0.000148	-0.011510	-0.019372	1.83	-0.00004173
973	-0.019304	0.001652	0.000148	-0.011510	-0.019372	1.83	-0.00004173
974	-0.019304	0.001652	0.000148	-0.011510	-0.019372	1.83	-0.00004173
975	-0.019304	0.001652	0.000148	-0.011510	-0.019372	1.83	-0.00004173
976	-0.019304	0.001652	0.000148	-0.011510	-0.019372	1.83	-0.00004173
977	-0.019304	0.001652	0.000148	-0.011510	-0.019372	1.83	-0.00004173
978	0.411273	0.000324	0.000045	0.266932	-0.283316	102.98	-0.00008445
979	-0.035108	0.001632	0.000151	-0.018120	-0.012538	-2.50	-0.00003505

The quality of the final oxygen data is documented by the residual plots below:

Figure 9: Leg 1: Differences between final calibrated down oxygen data and rosette water sample data.

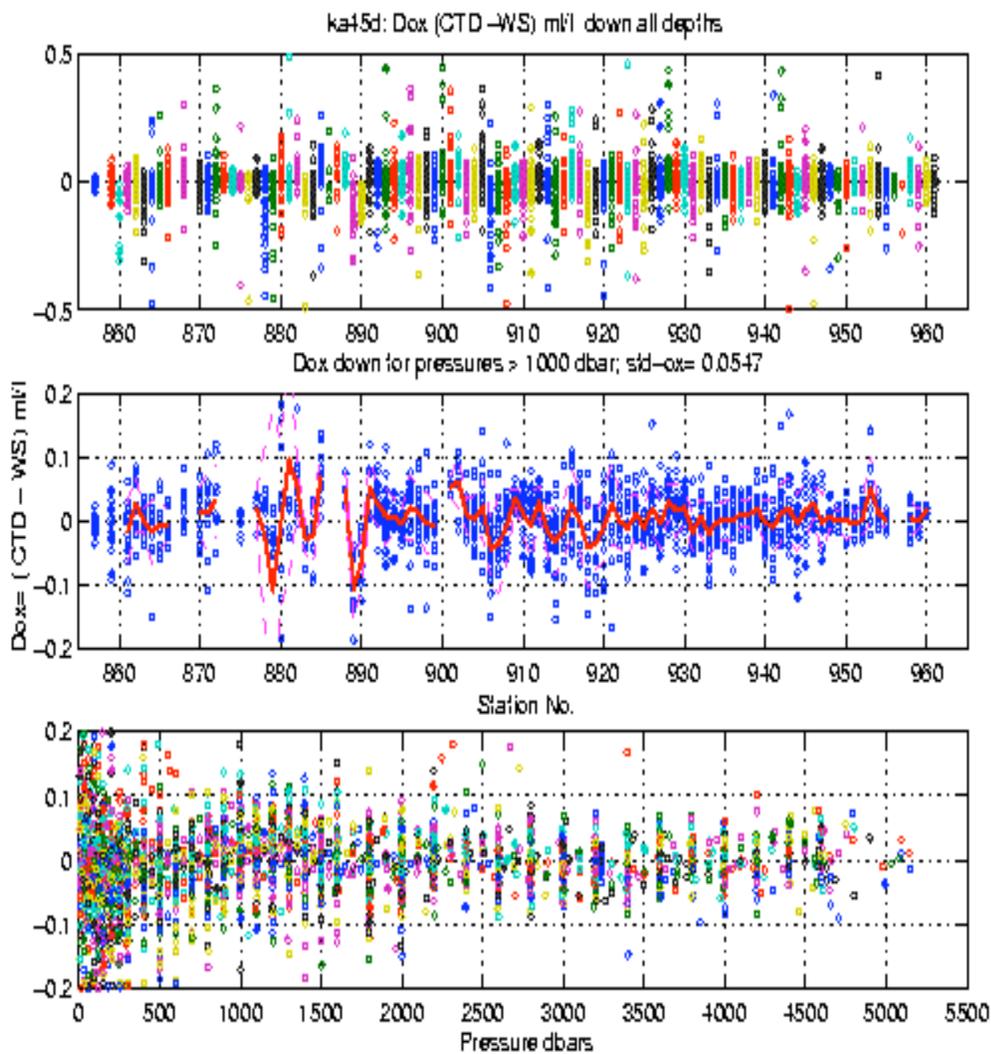


Figure 10: Leg 2: Differences between calibrated down oxygen data and rosette water sample data

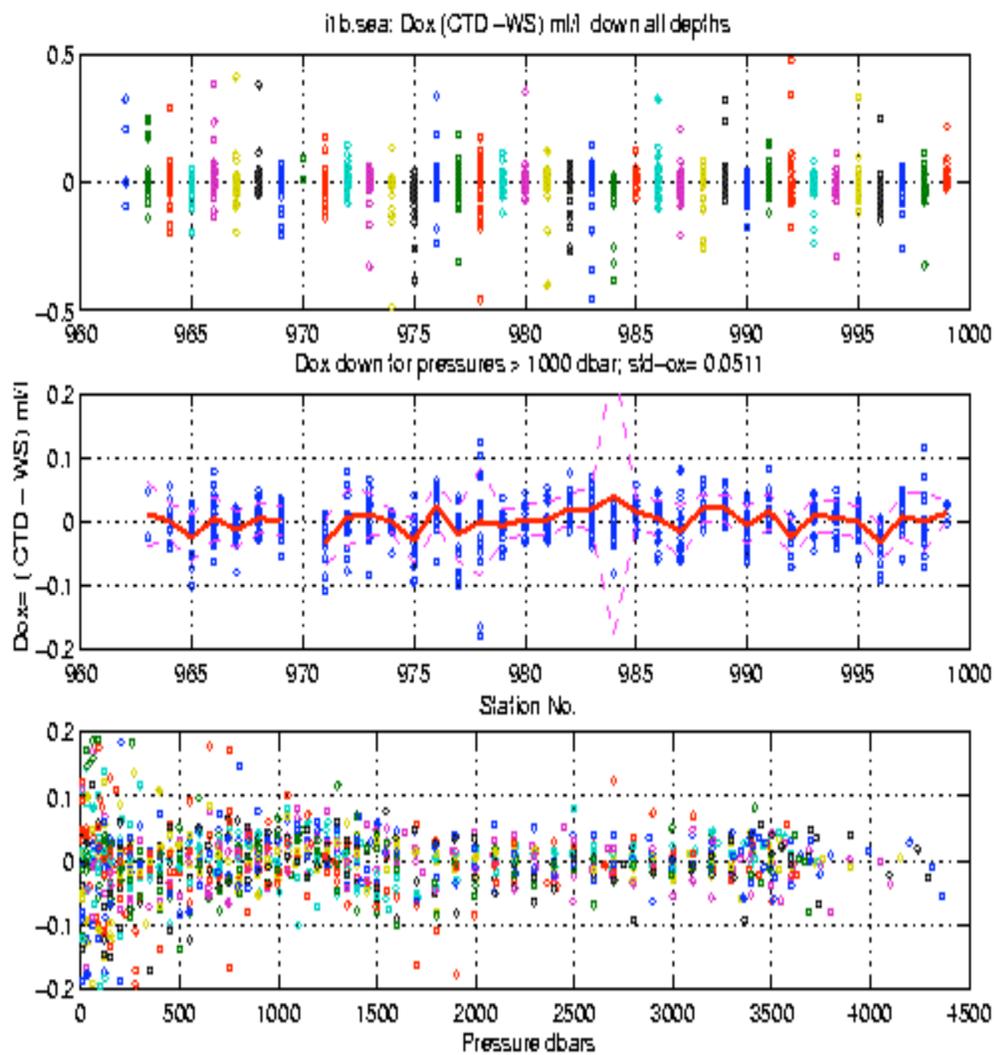
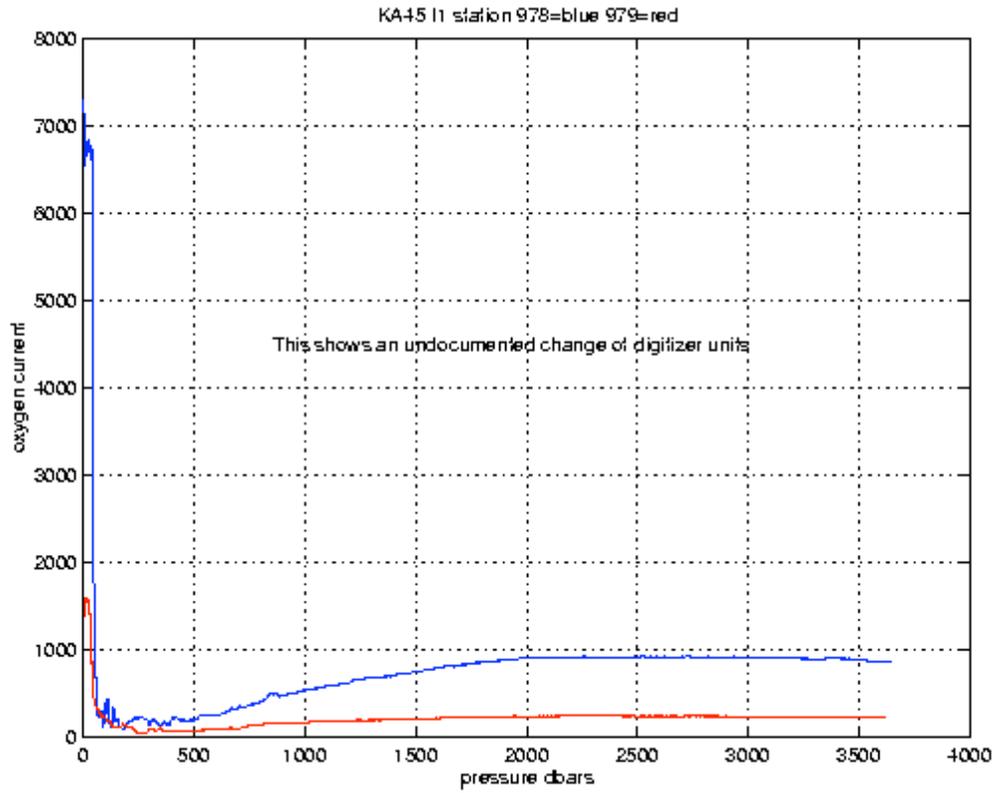


Figure 11: Stations 978 and 979 demonstrate that there were times during the cruise when the CTD was opened up and the oxygen current digitizer changed, resulting in a scaling change.



The following notes document instances where the quality word flag of the CTD oxygen in the CTD downtrace files was changed to 4 to signify bad data.

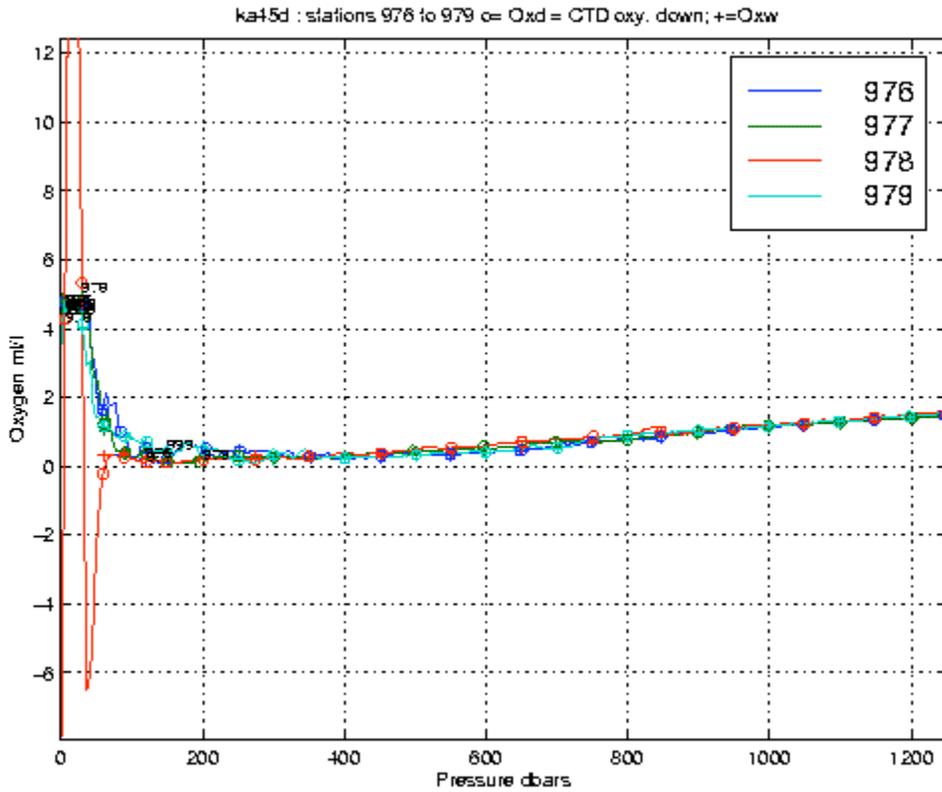
Stations 920-922, 915, 918:

Set flag of 1<sup>st</sup> oxygen value to 4 because oxygen current value is low by 0.8 ml/l.

Station 858: Oxygen bad between 237 to 241 and 275 dbars; set quality word =4.

Station 978: From the surface to 71 dbars the CTD oxygen is flagged bad.

Figure 12: Station 978 oxygen data unsalvageable above 71 dbar.



**DATA PROCESSING DETAIL NOTES:**

STATION 863:

Made the internally recording (IR) backup CTD, CTD 1338, the primary data for the station instead of CTD 9. CTD9's oxygen and salinity in the down profile were bad due to noisy pressure requiring heavy interpolation. ICTD 1338 data were used to make the down 2-dbar file. CTD 9's info was left with the bottle file. There were problems making the bottle file from the IR CTD. Note, there are different up and down cal, one for CTD1338, the other for CTD9.

STATION 909:

ICTD1344 jumped in salinity by -0.002psu at 3453dbar. Profile continued down at this lower salinity until reaching the bottom when it jumped back +0.001psu. The uptrace bottles and surrounding stations did not support this feature. The salinity below 3453 was replaced with the uptrace salinity.

STATIONS 973 to 979:

ICTD 1344 conductivity sensor was jumping low, away from the profile and then back to the real value over these set of stations. The problem appeared to be a loose mounting on the conductivity sensor that was epoxied into place after station 981.

STATION 973:

Replaced the bad downtrace salinity with uptrace salinity over the pressure ranges 1191 to 1641 dbar and 1707 to 2747 dbar.

STATION 974:

Replaced the bad downtrace salinity with uptrace salinity over the pressure range 1921 to 3773 dbar (bottom).

STATION 975:

Large interpolations over bad sections. The ranges are listed in the interpolation file:

Station, Start pressure, 3=salinity, Ending pressure

975,939,3,1127

975,1447,3,1453

975,1455,3,1457

975,1479,3,1485

975,1781,3,1833

975,2083,3,2157

STATION 976:

Interpolate over the bad section. The range is listed in the interpolation file:

Station, Start pressure, 3=salinity, Ending pressure

976,2191,3,2251

STATION 977:

Leave as is, there is some odd shape in the 900 to 1100 dbar range but it is loosely mimicked by the uptrace.

STATION 979:

Interpolate over bad section. The range is 2683 to 3151 dbar. There is some shape in the 800 to 1200 dbar section but again, it is loosely copied by the uptrace data.

STATION 978, 980 to 014:

ICTD1338 downtrace salinity was fit to bottles for downtrace scaling term. Uptrace left as it was. There are two cal files for each station, one for uptrace data \*.CU8 and one for downtrace data \*.C08.

The \*.CTD files of 2 dbar pressure averaged and centered downtrace profiles and the \*.SEA bottle file both refer to stations 1000 to 1014 as 0 to 14.

The \*.SEA files (one for leg1 and one for leg2) have been updated with new CTD pressure, temperature, potential temperature, salinity and oxygen data produced from the latest set of calibration coefficients.

Final nutrient data has been merged into the \*.SEA files as well.

A distinct processing sequence of events occurred after rescaling oxygen data for the 53 "problem oxygen " stations.

The following was done using Matlab:

1. The WOCE format files submitted in July 1998 were the starting point.
2. For those stations requiring revised CTD oxygen data, the new oxygen data were overwritten into the original files.
3. The original CTD oxygen data in the SEA file were also overwritten with the newest oxygen data.

The bottle file pressures were used to merge the 2 dbar down-profile CTD oxygen data from the stations reprocessed into the bottle file.

The SEA file was also put through an initial pass at setting quality flags for both CTD salt and oxygen:

The quality word of both the CTD oxygen and CTD salinity were compared to the bottle values using a screening criteria that varied with pressure.

Within the following pressure levels, differences  $\text{abs}(\text{Oxw}-\text{Oxcw})$  exceeding the value given are marked questionable.

Pressure less than 500 dbars Dox > 0.5 ml/l.

Pressure between 500 and 1500 dbars Dox > 0.2 ml/l.

Pressure greater than 1500 dbars and Dox > 0.1 ml/l.

All CTD oxygen values equal to -9.0 have had their quality word set equal to 9.

The original bottle file I1A.SEA had newly calibrated down CTD oxygen data merged into it and CTD salinity and oxygen data quality control edited. The resultant file is I1AA.SEA.

The original bottle file I1B.SEA was output to file I1BB.SEA.

The file I1B.SEA had a second set of four header records that were found to be inserted between station 999 and 0 (ie, station 1000). These headers were removed from file I1aa.SEA.

#### **RESOLVED DATA ISSUES:**

Concern over possible pressure hysteresis in ICTD 1338 found to be caused by internal wave signal.

Issue was looked at by Bob Millard and determined not to be instrumental hysteresis but the signal of vertical heaving by internal waves.

Non-compliant IOS standard water, batch P-124 from box 2.

Standard water believed to be .002 fresh. Problem recognized immediately, only two stations resulted in questionable water sample salts from using this batch of standard water.

Spikes and jumps in all data fields throughout the cruise caused extensive editing.

The entire dataset has been edited and spikes, jumps, etc have been removed.

Pre- to post-cruise laboratory temperature calibrations of CTD 1344 and CTD 1338 showed changes.

A combined pre and post cruise temperature calibration has been selected for the ICTDs as described in the calibration summary section.

Oxygen fitting problems due to oxygen sensor failures and change-outs.

Several factors slowed the CTD oxygen fitting. Poor quality oxygen sensors necessitated frequent changes of sensors: 7 changes total. This resulted in at least as frequent changes in oxygen calibration coefficients. Swapped oxygen assemblies for stations 859 to 862 altered the oxygen temperature calibrations, another

complication to the data fitting. Concentrations at the oxygen minimum come close to zero for 35 stations. It took substantially more time than usual to find a calibration that resulted in CTD oxygen data consistent with the water sample data but without going negative.

As noted in the oxygen calibration section, a revision to the Owens-Millard algorithm was tried and found to provide an acceptable fit for the oxygen data for 53 stations that were previously not able to be fit with the original algorithm.

CTD equipment failures caused extra processing to fit data to water samples and improve data.

Stations that had trouble with the primary instrument took extra time to correct. Such trouble includes segments of unreadable data or individual sensors not responding. Because two CTDs were usually on the frame, along with a second, independent temperature sensor, these problem stations were recovered by using data from the other instrumentation. For example, in the case of station 973, data from both primary and backup was used to construct the final hydrographic profile.

**Reference:**

Owens, W. B. and R. C. Millard Jr. (1985). A new algorithm for CTD oxygen calibration. *Journal of Physical Oceanography*, 15, 621-631.

**ATSEA.DOC**

**NOTES ON WORK DONE TO PARTICULAR STATIONS: EXTRACTS FROM AT-SEA WATCH-STANDERS' LOG HIGHLIGHTING DATA PROBLEMS AND FIXES.**

Station 858: CTD 9

Pressure dropout and cast aborted- no water samples. CTD9 subsequently found to have failed pressure sensor, apparently due to corrosion in sensing element. CTD cannot be fixed at sea.

Station 859: ICTD1344.

Pylon failure, at bottle 18 pylon homed itself with message error was 242. Problem due to interfering telemetry of CTD and pylon.

AFTER Station 862: ICTD1338

ICTD1338 opened to switch from FSK to memory mode, and will be used as second CTD on frame.

Station 863: CTD9 with ICTD1338 in Memory mode.

After Test station for CTD9, CTD 9 opened and found dessicant packs to be caught btw boards, causing components on board to short out. Thought was fixed, but everything dropped out twice during this station.  
-USE ICTD1338 DATA FOR THIS STATION

Station 864:CTD12,

Test station for CTD12, after shipping got complete garbage trying to run through seacable at 180 ma, switched to running at 250 ma seemed to run fine on deck, so tried a test station.

-down trace- cond jumps

-uptrace- large TMR error that was counted as btl tags scan # 47614, 1297 dbar 55 btl tags 11-37 taken out, and 12

Station 865: ICTD1344

with new oxygen sensor 5-06-03.

CHANGED TO MKIII DECK UNIT ON UP CAST

-a lot of noise in cast, changed over deck unit to MarkIII from FSI DT-1050, seemed to cleanup data.

Station 867:ICTD1344

loss of signal during down cast, fsk was still there but pressure pegged out at 6552. Put power supply in standby and switched to DT1050, no response. Put power supply back in standby, swapped back to MKIII DU and voila data returned.

CAST ABORTED

Down trace- weird pressure jump in beginning of cast complete pressure dropout at scans 26466-29569, 647 dbar

Station 869:ICTD1344

on down trace pressure pegged at 6552, FSK ok. Tried powering down for 5 min then back up- no luck, package brought back to 400m powered down then back up- no luck. Brought package to 200m powered down then backup - no luck, Tried firing 3 btl- no effect.

CAST ABORTED- BROUGHT BACK TO SURFACE

downcast- complete pressure drop out at 27832 used this as cut off scan number in header.

After station 869:

ICTD1338 OPENED TO CHANGE TO FSK MODE

After station 870:

I ICTD1344 opened up, found un-insulated wires, sloppy wiring.  
Problems repaired. ICTD1344 memory card now installed.

SALINOMETER 10 BLEW POWER SUPPLY, CHANGED OUT OK

After station 872: ICTD1338, ICTD1344 memory.

ICTD1344 SURGERY, ICTD OPENED. Power board replaced with spare.

Station 875:ICTD1338

fter finished station tried to send pylon home, received  
comm errors, pylon draws .280 A, pylon trying to move  
to home, but seemed stuck, helped move and washed out,  
pylon them seemed to be ok, drew .1 A.

Station 884:ICTD1338

-down trace PRESSURE JUMP  
pressure jumped from 5.9 to 7.7 and did not jump  
back. scan # 14458  
interped btw 5.9 dbar.  
-uptrace- cast started on deck and not erased  
fast temperature jump

Station 886:ICTD1338

-Pylon problems- computer return after firing 1 01 7  
2 02 7  
tried to position to 3- comm error  
reinitialized and positioned to 2 success  
-CTD powered up at 0725

After station 888:

\*\*\*\*\*ICTD1344 OPENED \*\*\*\*\*  
ICTD not used since last opening to replace power board.

After station 892:

\*\*\*\*\*ICTD1344 AND ICTD1338 BOTH OPENED TO SWAP OUTMEMORY CARD\*\*\*\*\*

Station 900:ICTD1344, P1484, SIOSCI, MKIII DU, FRAME B

ICTD 1338 INTERNALLY RECORDING  
Cast one aborted, sensor covers left on package  
CTD harness replaced and connectors re-greased, still  
a problem- a lot of synch errors from CTD  
Problem found to be in termination, swapped to port sea cable  
problem still continued. Turned off pylon power and synch error  
went away.

Station 907:ICTD1344

MODEM CARD ON SIOSCI MODIFIED TO REDUCE  
TRANSMIT LEVEL, HOPING  
TO AVOID SYNCH ERRORS- lower surf xmit

Station 910:ICTD1344

NEW OXYGEN SENSOR 5-06-02

Station 913:BACKUP ICTD1338 ON FRAME, BUT NOT RECORDING  
IN MEM MODE-  
bat died

Station 915:BACKUP ICTD1338 INTERNALLY RECORDING- new  
battery  
-down trace-clean

Station 923:ICTD1344  
NEW OXYGEN SENSOR (5-07-02)  
FAWL CONNECTOR ON IRICTD1338 FAILED, ICTD1338  
WAS REMOVED AND  
A 3 PIN BULKHEAD CONNECTOR WAS PUT IN PLACE.

Station 925:ICTD1344  
ICTD1338 INTERNALLY RECORDING, POWERED DOWN  
SEACABLE  
PORT SEACABLE  
lots o' synch errors, pylon turned off during down trace  
winch stopped at 4350 dbar to check level wind of winch  
pylon problems trying to fire bottle 35, tried turning off and  
on pylon, reinitializing it, kept saying 02 7. When brought on  
deck found pylon to be at position 7. Reinitialized on deck  
and seemed to work fine.  
-down trace- very noisy in conductivity, fast temp, oxtemp jumps  
pressure -150 jumps  
synch errors- 55 errors  
-uptrace- cleaned up only around btl tags  
took out btl tag 33.

Station 903:ICTD1344  
NEW OXYGEN SENSOR 4-10-2

After station 942:  
\*\*\*\*\*CONDUCTIVITY SENSOR ON BOTH ICTD1338 AND 1344 WERE CLEANED\*\*\*\*\*

Station 948:ICTD1344  
pylon problems in beginning of cast, reinitialized, retried  
re-initialized and retried again, worked on third attempt.

After station 955:  
\*\*\*\*\*PROBLEMS WITH INTERNALLY RECORDING ICTD  
1338\*\*\*\*\*

Station 958:ICTD1344  
BOTTOM CONTACT WITH PACKAGE  
pylon problems, comm errors with pylon, however all  
bottles were fired

After station 961:  
\*\*\*\*\*ICTD1338 UPDATED EEPROM VERSION 1.9SMF \*\*\*\*\*  
\*\*\*\*\*CHANGED OUT POWER SUPPLY AND PUT A NEW ONE IN\*\*\*\*\*

Station 973:ICTD1344

PRIOR TO STATION TOOK OUT MECCA WYE, AND 2 PIN  
CONNECTOR TO MECCA, CHANGED OUT THE HARNESS  
\*\*\*\*IN FINAL DATA USE ICTD1344 OXYGEN TRACE w/ ICTD1338  
CONDUCTIVITY TRACE\*\*\*\*

STATION 973 \*.prs file currently has oxygens from iCTD1344 and  
salts  
from IRICTD1338. M-file s973sal.m can be used to replace the  
the salt column from kj45d973.prs.

Station 975:ICTD1344

PRIOR TO STATION, SWAPPED FSKICTD CONDUCTOR  
TO MEM ICTD  
CONDUCTOR

Station 977:ICTD1344

CLEANED CONDUCTIVITY SENSOR ON ICTD1344,  
CHECKED FOR ROTATION

Station 978: ICTD1344

\*\*\*\*\*IN FINAL DATA SET USE IRICTD1338 DATA, THIS WAS DONE OCT95\*\*\*\*  
\*\*\*\* ICTD1344 DATA BACKED UP ONTO POSTPROC DISKS AS WELL AS \*\*\*\*  
\*\*\*\* ICTD1338 DATA \*\*\*\*

Station 980: ICTD1344, ICTD1338 in Memory mode.

New oxgen sensor on ICTD1344 #4-12-04  
ICTD1338 IN MEMORY w/ OTM 1372, POWER DOWN SEA CABLE.  
For final dataset use ICTD1338 data - note this was done in Oct95.  
ICTD1338 data backed up in POSTPR data, ICTD1344 only backed up raw data.  
Water sample salts flagged as 3, appear to be .002 fresh, problem with standard water.

Station 981: ICTD1338

Water sample salts flagged as 3, appear to be 0.002 fresh, problem with standard water was subsequently  
found to be cause.

After station 981: ICTD1344

ICTD1344 FIRMWARE UPGRADED to version 1.9SMF providing 14 bits of oxygen digitization.  
CONDUCTIVITY SENSOR STEM EPOXIED IN PLACE SO IT WILL NOT ROTATE.  
OTM CHANGED TO VARIABLE 16, AND REDUNDANT TEMP TO VARIABLE 17, TO MATCH  
PAST CRUISES.

Station 991: ICTD1344

IN MEMORY w/ OTM 1372- new oxygen sensor (5-06-01)

Station 1005:ICTD1338

\*\*\*\*\*RECORD LAYOUT CHANGED TO INCLUDE PRSTEMP VAR#14\*\*\*\*  
Stopped cast at 1000m on down cast to see how pressure temp reacts, also stopped at approx 2750m.

Station 1012:ICTD1338,

Fast thermistor stem is not tight, tech did not repair anything; damage might result.

= end of Watchstander's log =

**CRUISE INTERPOLATION DOCUMENTATION**

List of interpolations applied after the pressure averaging and centering. The columns are for station number, the starting bad pressure, the column to be interpolated over (3=salinity, 4=oxygen), and the ending bad pressure. This does not list the edits done to the raw data using the EG&G software's ctdpost editor.

**SALINITY INTERPOLATIONS**

002	1291	3	1297
002	1353	3	1367
002	1405	3	1413
005	2773	3	2779
005	1001	3	1015
005	881	3	885
864	2407	3	2413
872	9	3	9
964	1995	3	1999
964	2243	3	2255
964	1127	3	1137
964	1429	3	1435
975	939	3	1127
975	1447	3	1453
975	1455	3	1457
975	1479	3	1485
975	1781	3	1833
975	2083	3	2157
976	2191	3	2251
979	2683	3	3151
986	1535	3	1545
987	671	3	697
987	1043	3	1051
987	1395	3	1399
988	1321	3	1328
988	1419	3	1423
990	1187	5	1195
991	1241	3	1245
995	937	3	947
997	1755	3	1771
999	921	3	931
999	1063	3	1081

**OXYGEN INTERPOLATIONS**

984	2321	4	2341
984	2559	4	2575
984	2871	4	2885
984	2981	4	2991
984	3087	4	3091
987	2717	4	2725
988	2125	4	2131
988	3357	4	3361
989	2977	4	2983
990	3353	4	3357

## POST CRUISE PROCESSING DOCUMENTATION

(July 1998)

### SUMMARY OF STATIONS

CTD 1338 857,863,870-892,978,980,981-1014

CTD 1344 859-862,865-869, 893-898,900-978

CTD 9 858

CTD 12 864,899

There are no bottle files for stations 858,867 and 869 due to the pressure signal having dropped out requiring the cast to be aborted. Station 859 had bottles up to 800db until a jellyfish got caught up in the pylon causing the pylon to home itself.

### PRE V POST CALIBRATIONS

#### PRESSURE

ICTD 1338 changed by 1.5 db, chose to use an average of the pre and post cruise cal.

#### TEMPERATURE

The ICTD 1344 temperature calibration changed pre to post cruise laboratory calibration with a bias shift of +.002 deg C. CTD reading warmer at the post cruise cal than at the pre cruise cal. The point at where the temperature shift occurred was looked for but not found. The most reliable search was to look at same station primary and internal recording CTDs. They did not show where the jump occurred. The fast thermister's were also compared and points where the salinity cal changed. There was not enough proof to point to a spot where the jump occurred so instead an average of the pre and post cruise calibrations was used to process the data.

ICTD 1338 had a small change, less than .002 deg C. The pre and post temperature cal were averaged to be used with the post cruise processing.

#### SALT

Plot results of deep water revealed that there was a CTD dependent bias: 1338: \*.PRS CTD salt read too high ~.002psu or temperature was too low compared to \*.SEA file. 1344: \*.PRS CTD salt read too low ~.001 psu or temperature was too high compared to \*.SEA file. The consistency of the bias between stations indicates it was probably not a real ocean measurement such as measuring internal waves, but some kind of instrument, package dynamic or bottle artifact.

All ICTDS 1338 stations have a sig. bias, with the downtrace always saltier than the bottles. The uptrace has been fit well, but the uptrace is fresher than the downtrace. To correct for the difference, the downtrace salinity, the group of station 978 to 1014, was fit to the bottle data. The results looked good. The earlier group of 1338 stations seemed to fit well after forcing the bottom bottles to be met by the CTD so were not refit using the downtrace.

ICTD 1344 downtrace trends toward being fresher than the bottles. The uptrace and downtrace agree, but the fits were not working well. Rework some of the fits, concentrating on matching up the CTD and salts in the bottom water.

CTD comparisons were made with the primary and backup data from the same stations. Pressure agreed very well, bottom depths were within 1db on the stations checked. Temperature would stray, +/- .002 at the bottom, sometimes ictd 1338 being warmer, sometimes ictd 1344. probably a factor of where they were located on the frame.

Stations 936-938,940-941

A Pressure dependant shape could not be removed without changing beta (and alpha) conductivity terms. After station 942, the conductivity cell was cleaned although no specific reason is given. The difficult calibrations from station 936 to 942 could have been induced by fouling or buildup on the conductivity cell. Stations 936, 937 and 938 have BETA changed from 1.5e-8 to .75e-8 Stations 940 and 941 have BETA changed from 1.5e-8 to .75e-8 and ALPHA changed from -6.5e-6 to -9.75e-6.

Station 923 and 954 both have salt changes that looked questionable until the uptrace was overlaid and followed the shape of the downtrace. Station 923 freshens around 2 deg C. Station 954 has spikes and a shift at 1750db, 1900db and 2250 db that are clearly repeated in the uptrace.

## OXY

The oxygen temperature (OT) coefficients were changed for the post processing. Found that there were several instances of the CTD profile not reaching the oxygen minimum, or overshooting the minimum. This may have been due to not having the proper OT coefficients so decided to remake calibrations files that have the proper pre cruise OT coefficients for each CTD.

OT coefficient changes:

Sta,	Apply to,	Change made
857	857,870-892	replaced wrong 38 bias with right 38 bias.
859	859-862	replaced 38 OT cal with 44 OT cal.
865	865-869	left as is.
893	893-979 x899,978	replaced 38 OT +wrong bias with 44 OT cal.
978	978	replaced wrong 38 bias with right 38 bias.
980	980	replaced wrong 38 bias with right 38 bias.
981	981-004	replaced wrong 38 bias with right 38 bias.
005	005-014	replaced wrong 38 bias with right 38 bias.

Stations 859 to 862 were taken with ICTD 1344 but used ICTD1338's oxygen assembly. 44's ot term were put into the cal file.

## Fitting

Some stations fit just fine and others had a definite pressure dependant shape in the residuals. It was a similar shape that reoccured in different groups. The shape was more pronounced in some groups than others. A weight of .8 and lag of 1 was consistant from a few of the larger groups. Most of the groups had this weight and lag held during the fits since many groups came up with weights over 1 and lags below 0 when allowed to fit for those parameters. For the groups with the pressure dependant shape in the residuals, tcor was held at some value lower than the fit originally came up with. Usually tcor was

adjusted  $-.002$  and the group refit. The resulting residuals between 2000 to 5000 db would be centered around 0 with a spread reduced from  $\pm .1$  to  $\pm .04$  but the shape would remain in the upper 2000 db.

Groups with the pressure dependant shape:

859-862  
865-869  
911-922  
930-933  
934  
935  
937-946  
962-969  
971-979

Stations 877,878,879 and 004 were scaled using the atsea ot and oc terms. With the new OT, it was not possible to get as good a fit as the atsea results. The terms arrived at had unrealistic numbers such as a negative lag but was used anyway for the resulting good fit.

50 stations had the problem of fitting to the top water or fitting to the bottom but not both at once. Bob Millard agreed to try his method of coming up with two fits for a single station and then blend them together at the middle. The stations have '4's (bad) in the quality word of the CTD files.

The stations are:

859,861-862  
865-869  
880-881  
882-892  
912-922  
933  
963-969  
971-977  
978-979

Stations 857-858, test stations, had the oxygen quality word flagged '4' (bad) in the downtrace. All the bottles were deep and not useful for finding a fit for the whole profile.

Station 859, the next station in the same locations as 857 and 858, had bottles except for the top 800db due to a pylon failure. Even with a better fit this top should be labeled '3' (questionable).

Station 860, a test station for water sampling. The downtrace oxygen was labeled '4' due to all bottles fired deep.

Stations 906 to 904 have clear shape in the bottom water that may or may not be real. The uptrace looks as if it follows the shapes loosely, not really until the larger features around 2000db does it really follow the downtrace. Station 937 had extra bottles taken deep to watch the  $\pm .05$ ml/l variation in oxygen. The bottles do look like they agree with the oxygen.

Station 987, a  $-.04$  ml/l shift in oxygen at 2711db does not look real, and does not agree with bottle or following stations. It has been flagged '3' (questionable).

**NOTES ON WORK DONE TO PARTICULAR STATION:**

STATION 863

Made the internally recording (IR) backup CTD, CTD 1338, the primary data for the station instead of CTD 9. CTD9's oxygen and salinity in the down profile were bad due to noisy pressure requiring heavy interpolation. ICTD 1338 data was used to make the down 2-db file. CTD 9's info was left with the bottle file. There were problems making the bottle file from the IR CTD. Note, there are different up and down calcs!, one for CTD1338, the other for CTD9.

STATION 909

CTD1344 had jumped in salinity -.002psu at 3453db. Profile continued down at this lower salinity until reaching the bottom it jumped back +.001psu. The uptrace, bottles and surrounding stations did not support this feature. The salinity below 3453 was replaced with the uptrace salinity.

STATIONS 973 to 979

CTD 1344 conductivity sensor was jumping low, away from the profile and then back to the real value over these set of stations. The problem appeared to be a loose conductivity sensor that was epoxied into place after station 981.

STATION 973

Replace the bad salinity with uptrace salinity over the pressure ranges 1191 to 1641 db and 1707 to 2747 db.

STATION 974

Replace the bad salinity with uptrace salinity over the pressure range 1921 to 3773 db (bottom).

STATION 975

Large interpolations over bad sections. The ranges are listed in the interpolation file: Station, Start pressure, 3=salinity, Ending pressure

975,939,3,1127

975,1447,3,1453

975,1455,3,1457

975,1479,3,1485

975,1781,3,1833

975,2083,3,2157

STATION 976

Interpolate over the bad section. The range is listed in the interpolation file:

Station, Start pressure, 3=salinity, Ending pressure 976,2191,3,2251

STATION 977

Leave as is, there is some odd shape in the 900 to 1100 db range but it is loosley mimicked by the uptrace

STATION 979

Interpolate over bad section. The range is 2683 to 3151 db. There is some shape in the 800 to 1200 dbar section but again, it is loosely copied by the uptrace data.

STATION 978, 980 to 014

CTD1338, the downtrace salinity was fit to bottles for downtrace scaling term. Uptrace left as it was. There are two cal files for each station, one for uptrace data \*.CU8 and one for downtrace data \*.C08.

The \*.CTD files of 2 db pressure averaged and centered downtrace profiles and the \*.SEA bottle file both refer to stations 1000 to 1014 as 0 to 14.

The \*.SEA files (one for leg1 and one for leg2) have been updated with the new CTD pressure, temperature, potential temperature, salinity and oxygen data produced from the latest set of calibration coefficients. The individual quality of the CTD salt and oxygen observations within the \*.SEA file has not been checked. The quality words for these two parameters has been left as '3' (questionable) simply to show they have not been looked at.

Final nutrient data has been merged into the \*.SEA files as well.

## BOTTLE DATA

### CFC-11 and CFC-12 Measurements - WOCE II

Leg 1: Muscat, Oman to Colombo, Sri Lanka

Analysts: Mr. Steven Covey, University of Washington  
Ms. Sabine Mecking, University of Washington

Leg 2: Colombo, Sri Lanka to Singapore

Analysts: Mr. Steven Covey, University of Washington  
Ms. Wenlin Huang, University of Washington

### Sample Collection and Analysis

Samples for CFC analysis were drawn from the 10-liter Niskins into 100-cc ground glass syringes fitted with plastic stopcocks. These samples were the first aliquots drawn from the particular Niskins. The samples were analyzed using a CFC extraction and analysis system of Dr. Ray F. Weiss of Scripps Institution of Oceanography. The analytical system was set up in a portable laboratory, belong to Dr. John Bullister, on the fantail of the R/V Knorr. The analytical procedure and data analysis are described by Bullister and Weiss (1988). One syringe, Becton-Dickinson 9882, was found to be a source of contamination for CFC-11. A separate sampling blank was applied to this syringe. These samples have been flagged as "questionable" (WOCE flag 3) and are listed below (Table 4). The CFC concentrations in air (Table 3) were measured approximately every two days during this expedition. Air was pumped to the portable laboratory from the bow through Dekabon tubing.

### Calibration

A working standard, calibrated on the SIO1993 scale, was used to calibrate the response of the electron capture detector of the Shimadzu Mini-2 GC to the CFCs. This standard, Airco cylinder CC88110, contained gas with CFC-11 and CFC-12 concentrations of 275.61 parts per trillion (ppt) and 496.49 ppt, respectively.

### Sampling Blanks

We have attempted to estimate the level of contamination by taking the mode of measured CFC concentration in samples which should be CFC-free. In this region, measurements of other transient tracers such as carbon-14 indicate that the deep waters are much older than the CFC transient. We have used all samples deeper than 2000 meters to determine the blanks of 0.002 picomoles per kilogram (pmol/kg) for CFC-12 and 0.004 pmol/kg for CFC-11. These concentrations have been subtracted from all the reported dissolved CFC concentrations. Syringe 9882 had a much higher sampling blank for CFC-11 (0.010 +/- 0.010 pmol/kg) based on the mean of a few samples. Since there is a large uncertainty in the contamination level, all of the samples collected using this syringe during the first leg have been flagged as questionable. The stopcock (likely source of the contamination) appears to have been changed for leg 2.

### Data

In addition to the CFC concentrations which have merged with the .hyd file, the following three tables have been included to complete the data set. The first two are tables of the duplicate samples. The third is a table of the measured atmospheric CFC concentrations listed with time and position.

**Table 1:** CFC-11 Concentrations in Replicate Samples

STATION NUMBER	SAMP NO.	CFC-11 pM/kg	WOCE Flag
859	1	10 0.003	2
859	1	10 0.007	2
862	1	24 0.812	2
862	1	24 0.822	2
863	1	25 0.100	2
863	1	25 0.098	2
864	1	15 0.135	2
864	1	15 0.136	2
866	1	25 0.972	2
866	1	25 0.965	2
870	1	12 0.071	2
870	1	12 0.072	2
871	1	19 0.402	2
871	1	19 0.410	2
872	1	20 0.816	2
872	1	20 0.830	2
873	1	1 0.661	2
873	1	1 0.670	2
877	1	17 0.701	2
877	1	17 0.703	2
885	1	20 0.501	2
885	1	20 0.492	2
889	1	15 0.147	2
889	1	15 0.146	2
899	1	1 0.002	2
899	1	1 0.003	2
902	1	16 0.208	2
902	1	16 0.211	2
909	1	21 0.026	2
909	1	21 0.025	2
912	1	9 -0.004	2
912	1	9 -0.001	2
925	1	2 0.000	2
925	1	2 0.000	2
925	1	21 0.005	2
925	1	21 0.003	2
929	1	1 0.008	2
929	1	1 0.008	2
936	1	24 0.010	2
936	1	24 0.013	2
940	1	29 0.355	2
940	1	29 0.348	2

STATION NUMBER	SAMP NO.	CFC-11 pM/kg	WOCE Flag
941	1	1 0.000	2
941	1	1 0.002	2
952	1	16 0.010	2
952	1	16 0.014	2
954	1	5 -0.002	2
954	1	5 -0.003	2
1012	1	7 1.441	2
1012	1	7 1.425	2

**Table 2:** CFC-12 Concentrations in Replicate Samples

STATION NUMBER	SAMP NO.	CFC-11 pM/kg	WOCE Flag
859	1	10 0.005	2
859	1	10 0.011	2
862	1	24 0.476	2
862	1	24 0.482	2
863	1	25 0.054	2
863	1	25 0.044	2
864	1	15 0.070	2
864	1	15 0.070	2
866	1	25 0.543	2
866	1	25 0.545	2
868	1	22 0.186	2
868	1	22 0.172	2
870	1	12 0.034	2
870	1	12 0.038	2
871	1	19 0.220	2
871	1	19 0.224	2
872	1	20 0.429	2
872	1	20 0.427	2
873	1	1 0.370	2
873	1	1 0.380	2
877	1	17 0.395	2
877	1	17 0.392	2
885	1	20 0.275	2
885	1	20 0.266	2
889	1	15 0.080	2
889	1	15 0.078	2
896	1	33 1.006	2
896	1	33 1.012	2
899	1	1 -0.002	2
899	1	1 -0.002	2
902	1	16 0.111	2
902	1	16 0.111	2
909	1	21 0.014	2
909	1	21 0.013	2

912	1	9 0.000	2
912	1	9 -0.002	2
925	1	2 0.002	2
925	1	2 0.002	2
925	1	21 0.004	2
925	1	21 0.000	2
929	1	1 0.003	2
929	1	1 0.001	2
936	1	24 0.004	2
936	1	24 0.007	2
940	1	29 0.188	2
940	1	29 0.184	2
941	1	1 0.001	2
941	1	1 0.000	2
952	1	16 0.006	2
952	1	16 0.006	2
954	1	5 0.001	2
954	1	5 -0.001	2
1012	1	7 0.840	2
1012	1	7 0.831	2

**Table 3:** Atmospheric CFC Concentrations

AIRNBR	LAT N	LON E	DATE	TIME	CFC-11	CFC-12	STNNBR
	dec deg	dec deg	gmt	gmt	ppt	ppt	(approx.)
1	19.082	58.797	950831	657	262.0	526.2	861
1	19.082	58.797	950831	707	261.9	523.8	861
1	19.082	58.797	950831	717	261.5	527.3	861
1	19.082	58.797	950831	726	262.1	528.8	861
2	16.267	56.555	950901	825	262.2	527.0	863
2	16.267	56.555	950901	840	262.6	527.3	863
2	16.267	56.555	950901	850	262.6	525.8	863
2	16.267	56.555	950901	900	262.4	523.7	863
2	16.267	56.555	950901	918	262.1	522.5	863
3	14.167	52.753	950903	1001	262.0	523.9	870
3	14.167	52.753	950903	1010	262.0	521.4	870
3	14.167	52.753	950903	1020	261.9	523.3	870
3	14.167	52.753	950903	1029	261.8	523.5	870
4	12.375	43.812	950905	1721	266.0	531.1	873
4	12.375	43.812	950905	1730	264.8	531.2	873
4	12.375	43.812	950905	1740	265.2	529.7	873
4	12.375	43.812	950905	1749	265.1	532.7	873
5	12.333	45.753	950906	904	263.9	531.0	877
5	12.333	45.753	950906	914	263.6	530.9	877
5	12.333	45.753	950906	923	263.7	529.3	877
5	12.333	45.753	950906	933	263.7	528.5	877
6	13.065	48.568	950907	1701	265.3	536.2	883
6	13.065	48.568	950907	1711	264.6	536.0	883

AIRNBR	LAT N	LON E	DATE	TIME	CFC-11	CFC-12	STNNBR
	dec deg	dec deg	gmt	gmt	ppt	ppt	(approx.)
6	13.065	48.568	950907	1720	264.7	533.4	883
7	13.717	51.568	950909	1118	262.6	523.5	892
7	13.717	51.568	950909	1128	261.6	523.1	892
7	13.717	51.568	950909	1137	262.7	522.5	892
7	13.717	51.568	950909	1147	262.3	523.4	892
8	9.898	53.800	950911	32	262.8	524.7	897
8	9.898	53.800	950911	43	261.5	521.1	897
8	9.898	53.800	950911	52	261.9	522.3	897
8	9.898	53.800	950911	102	261.4	521.8	897
9	8.823	52.690	950913	802	261.9	525.6	904
9	8.823	52.690	950913	812	261.8	525.0	904
9	8.823	52.690	950913	822	261.6	523.9	904
9	8.823	52.690	950913	832	262.3	524.4	904
10	8.930	54.417	950914	1151	262.6	523.6	908
10	8.930	54.417	950914	1201	262.5	523.8	908
10	8.930	54.417	950914	1212	262.3	524.7	908
11	8.490	58.110	950916	603	262.0	525.5	916
11	8.490	58.110	950916	613	262.1	523.6	916
11	8.490	58.110	950916	624	262.3	523.4	916
11	8.490	58.110	950916	634	262.2	523.1	916
12	9.008	61.552	950918	941	262.4	524.5	925
12	9.008	61.552	950918	951	263.1	525.6	925
12	9.008	61.552	950918	1001	263.1	525.7	925
12	9.008	61.552	950918	1010	263.5	524.9	925
13	8.500	65.883	950921	258	262.9	528.6	934
13	8.500	65.883	950921	308	263.1	528.5	934
13	8.500	65.883	950921	318	263.1	526.4	934
13	8.500	65.883	950921	328	262.8	528.8	934
14	8.497	68.900	950922	2130	263.9	526.4	940
14	8.497	68.900	950922	2140	262.7	524.3	940
14	8.497	68.900	950922	2151	263.7	525.1	940
14	8.497	68.900	950922	2202	262.5	525.4	940
14	8.497	68.900	950924	40	261.9	520.6	940
14	8.497	68.900	950924	55	260.2	522.8	940
15	8.503	71.215	950924	130	262.7	528.6	944
15	8.503	71.215	950924	140	262.2	526.8	944
15	8.503	71.215	950924	149	262.0	525.0	944
15	8.503	71.215	950924	200	262.9	526.5	944
16	8.568	73.832	950925	906	262.9	525.4	951
16	8.568	73.832	950925	916	263.0	523.7	951
16	8.568	73.832	950925	926	262.7	526.5	951
17	6.417	79.100	950927	1418	263.7	527.1	958
17	6.417	79.100	950927	1428	263.7	526.7	958
17	6.417	79.100	950927	1438	264.0	526.7	958
18	5.633	79.997	950930	1242	262.9	529.2	963
18	5.633	79.997	950930	1251	261.5	528.3	963
18	5.633	79.997	950930	1301	262.7	526.9	963
19	9.963	83.847	951004	2220	265.1	532.5	978

<b>AIRNBR</b>	<b>LAT N</b>	<b>LON E</b>	<b>DATE</b>	<b>TIME</b>	<b>CFC-11</b>	<b>CFC-12</b>	<b>STNNBR</b>
	dec deg	dec deg	gmt	gmt	ppt	ppt	(approx.)
19	9.963	83.847	951004	2231	264.8	530.5	978
19	9.963	83.847	951004	2241	265.0	528.9	978
19	9.963	83.847	951004	2252	264.4	530.6	978
20	9.828	86.788	951008	920	262.5	529.3	989
20	9.828	86.788	951008	930	264.1	531.8	989
20	9.828	86.788	951008	940	263.8	528.7	989
21	9.855	95.332	951012	230	263.2	526.8	1008
21	9.855	95.332	951012	239	263.6	526.2	1008
21	9.855	95.332	951012	250	262.8	525.0	1008
21	9.855	95.332	951012	302	263.1	526.2	1008
22	9.627	97.442	951013	21	263.9	530.7	1014
22	9.627	97.442	951013	30	263.9	528.9	1014
22	9.627	97.442	951013	41	264.1	527.8	1014
22	9.627	97.442	951013	53	263.8	526.7	1014

**Table 4 - Samples Collected Using Syringe 9882**

The following samples were collected with syringe 9882. Since deep samples taken with this syringe showed some contamination, a higher blank of 0.01 pmol/kg is subtracted from the samples collected during the first leg of the cruise (up to station 861). All of the samples from the first leg are also flagged as questionable (3) or bad (4).

NOTE: The sample number is 100\*Cast plus the bottle number.

<b>STA NBR</b>	<b>SAMPLE</b>	<b>Nominal Depth</b>	
857	127	3195	
861	106	2600	
862	106	2000	
863	123	800	
864	120	250	
868	122	300	% part of dupl.
874	114	120	
879	127	30	
881	110	1000	
882	126	90	
883	121	180	
884	114	600	
885	122	200	
887	116	20	
889	128	0	
891	112	700	
892	136	5	
893	110	2400	
894	110	2600	
895	128	300	
896	133	90	% part of dupl.
898	111	2800	
899	109	3200	
900	119	60	
902	110	1100	
903	123	600	
904	126	500	
905	110	3400	% depth may be off
906	109	3800	
907	109	3600	
908	109	3800	
909	130	200	
910	124	700	
911	109	3400	
912	122	700	
913	126	400	
914	112	2400	
915	123	250	
917	110	2600	

<b>STA NBR</b>	<b>SAMPLE</b>	<b>Nominal Depth</b>	
918	114	800	
919	116	1100	
920	131	90	
921	124	500	
922	136	5	
923	119	800	
924	119	1100	
925	101	4450	
926	120	1100	
927	121	100	
928	101	4625	
929	115	2000	
930	116	1800	
931	119	1200	
932	104	4200	
933	125	600	
934	124	700	
935	108	3400	
936	108	3700	
937	123	900	
938	107	3700	
941	135	30	
948	124	165	
949	126	30	
950	122	90	
951	127	250	
952	108	1550	
953	126	90	
955	110	800	
958	127	30	
964	108	1350	
965	128	90	
966	128	350	
967	128	300	
968	128	350	
969	123	800	
971	124	150	
972	125	450	
974	128	150	
975	114	1500	
976	129	250	
977	126	300	
979	129	150	
980	125	350	
981	125	300	
986	110	2100	
987	126	250	
989	131	120	

<b>STA NBR</b>	<b>SAMPLE</b>	<b>Nominal Depth</b>	
990	114	1900	
991	128	120	
992	128	100	
993	126	200	
994	122	450	
995	129	90	
996	122	450	
997	122	600	
998	126	200	
1000	112	150	
1002	113	350	
1003	128	90	
1004	126	500	
1005	127	120	
1008	121	200	
1009	116	650	

## Data Quality Evaluations

### DQE of WOCE I01E hydrographic data

(Arnold W. Mantyla, Sept. 27, 2001)

This fall cruise started out with a short section south of Sri Lanka, repeating stations occupied six months earlier on I08; and then completed a section along 10N latitude across the southern Bay of Bengal and across the Andaman Sea. The Andaman Basin was quite uniform in characteristics and provided an excellent "calibration tank" for assessment of data precision. Salinity, oxygen and nutrients all easily met WOCE precision goals: salinity standard deviations to within .001 PSU, and oxygen and nutrient to better than 0.6%. In general, the data quality on this cruise was quite good. The following is a list of problems that were noticed, some of which may be corrected by the data originator.

I did not see any description in the DOC file on the analytical methods used to analyze the water sample salinity, oxygen or nutrient samples. Those descriptions should be added to the cruise documentation file.

1. Errors in the .sum file:  
 Sta. 966 EN - had the wrong month and day - had 0930, changed to 1001  
 Sta. 1007 BO - latitude was 9 04.00 - changed to 9 54.00
2. The CTD salinities and oxygens assigned to the bottle tip levels were flagged as questionable on the last 29 stations. I understand that there were problems with some of the CTD oxygen sensors and apparently the up and down CTD salinity profiles had different offsets. However, from the fairly consistent bottle minus up CTD salinity differences of just a few thousandths, it appears that the up CTD salinities could be fixed to match the bottle data reasonably well and accepted as ok. It is useful to have good CTD salinity data for levels where the water sample salinity is either missing or bad. Both T and S needed for density when O<sub>2</sub> or nutrients are used with respect to density surfaces.
3. The water sample salinities for stations 980 and 981 were all flagged questionable, apparently on the basis of a presumed faulty ampule of Standard Sea Water (P124). Comparison of the T/S curves for these stations with a pair of stations to the west (979 and 985) and a pair of stations to the east (986 and 987) showed differences of only about .001 to .002, station 980 and 9891 slightly lower. Station 981 also agrees with the CTD salinity to typically .001 except for samples 2 to 4, which appear to have been drawn out of 1 bottle deeper than the depth assigned to the sample. I suggest that station 981 salinities be accepted as ok, except for samples 2-4, which should be left as uncertain. On Station 980, the water samples appear to be slightly low, while the CTD salinities appear to be slightly high, but I would tend to accept the uncertain flags on the water samples as done by the originators.
4. Twenty-seven different bottles were flagged as leakers at least once during the cruise; but for the most part, the water samples appeared to be ok and were not flagged. Bottles 1, 2, 23, 31, and 37 leaked more than 10 times. It would be of interest to know what caused the bottles to be flagged and add a comment in the cruise documentation report noting what was seen to result in such an unusually large number of leaking rosette bottles.
5. Several stations had some nitrite data fields filled with "-9.00", but with the data quality flag set to "2", meaning acceptable measurement. I've changed those flags to "5" to indicate data not reported. (Stas. 972,976,992, and 993.)
6. Stations 982 to 985 were repeats or overlaps of stations 974 to 979. The silicates on station 974 were about 4% higher than on sta. 982, both at the same position. The silicate profile appeared to jump on

sta. 973 and then came back down on sta. 975. I suggest the data originators re-check the standard factors compared to the other stations to see if there might be a calibration error that resulted in the silicates being higher on stas. 973 and 974. For now, I would consider the silicates for those two stations to be questionable.

7. The bottom 12 silicates on sta. 996 appear to be high compared to adjacent stations and also the nearby station from I09, sta. 234. Suggest flag them uncertain unless the data originators can identify a problem with the end calibration standard.
8. Although the oxygen precision was good in the Andaman Basin stations, there are other indications that the oxygens might be suspect on this cruise. On other cruises with more than one bottle tripped in the surface mixed layer, the multiple trips agree to within the measurement precision (O<sub>2</sub> to within 0.5um/kg). Except for oxygen that was also true for the ten or so stations on this cruise that had two bottles tripped in the mixed layer. Here, the O<sub>2</sub>'s differed by 3 to 8um/kg. Also, the I01E repeats of I08 were high by about 4% (I01E higher). The mixed layer oxygen percent saturation was also unusually high for this time of year, 107.5% +/-2.6%, compared to historical values of 101 to 104%. Even a conversion error from ml/l to um/l instead of um/kg would only result in a 2.5% error. I recommend that the data originators re-check the ml/l to um/kg conversion to verify the conversion was done correctly. As the data stands now, I would regard the O<sub>2</sub> data for this cruise as suspicious.
9. Station 969 has a temperature inversion of 0.02 deg. in the top 2 bottles while the salinities are uniform, resulting in an instability. I recommend the temperature calculations be re-examined to see if one might include a spike in the average and a better value calculated.
10. Station 976: samples 8 and 9 O<sub>2</sub> are about the same, while the CTD O<sub>2</sub> profile shows a gradient. It appears that both O<sub>2</sub> samples may have been collected from the 8th bottle, so sample 9 was flagged "u".
11. Station 988: sample 8 salt and O<sub>2</sub> are missing; the nutrients are unlikely for this depth, so were flagged "u".
12. Station 995: An O<sub>2</sub> inversion at 401db was flagged "u", but the CTD O<sub>2</sub> profile also shows an inversion at this depth, so it appears the O<sub>2</sub> should be accepted as ok unless the originators have some other reason for questioning that value. The bottle was not flagged as a leaker on this station, although it was 13 other times on this leg.
13. Station 1004: Sample 36 at the surface clearly mistripped, the water samples clearly are from some other depth. The oxygen and nutrients were flagged "bad", but the bottle and salinity were accepted as ok. Both should be flagged questionable as well.
14. Station 1005: Sample 23 salt and bottle flagged doubtful, but the O<sub>2</sub> and nutrients were accepted as ok. They should also be flagged "u".
15. Station 1009: The bottom salinity appears to be about .005 low and should be "u'ed", it would be ok if the last 2 digits had mistakenly been transposed.
16. Station 1010: From the silica profile compared to adjacent stations, it appears that samples 5 and 6 both came from the number 6 depth, and samples 3 and 4 were also assigned to one depth too deep. Therefore samples 3, 4, and 5 nutrients were flagged "u".

**DQE of WOCE I01W Hydrographic Data**

(Arnold W. Mantyla, Nov. 1, 2001)

This cruise started in the northwest Arabian Sea with a few stations along the coast of Oman; there they did a line of stations in the Gulf of Aden to the Red Sea entrance; followed by the main line of stations across the southern Arabian Sea from Somalia to India.

The first test station tripped all 36 bottles at about 3200db. The oxygen and nutrient precision were excellent, better than 0.5% S.D., but the salinities included a few poor samples that made the precision apparently not up to WOCE specifications. However, this station was early in the cruise and I suspect that inexperienced help may have resulted in a few sampling errors. The salinities for the majority of the cruise were fine. The overall data quality was generally quite good, except for some curiously poor mixed layer oxygens. The following text lists a few problems that were noticed during the data examination.

## 1. Problems in the .sum file:

Many stations are listed with identical positions for the BE, BO, and EN of a cast, and all 3 were coded as having been derived from a GPS fix. Only the cast time closest to the GPS fix should have that code, the rest that are assumed should have some other lower quality code, perhaps the one for dead reckoning.

Sta. 890 BE Position off by 1 deg. Changed to 14 deg. Sta. 927 BE Position differs from BO and EN by 10'. Changed BE to agree with BO and EN Sta. 941 BE, BO, and EN Dates off by one day, had 0922, changed to 0923.

## 2. The CTD salinities and oxygens assigned to the bottle trips have all been flagged as "3, questionable measurement", or "1 analysis not received", but data are listed for all trips. Should resolve the "1" flags on this and on the following leg, as either OK or questionable.

## 3. Sta. 859 - NO DATA - 0-800db, all of the deep cast nutrients were poor, so I flagged them as questionable. I suggest that the nutrient standardization be re-checked to see if the data can be recovered.

Sta. 863, 2db: Surface temperature is bad, need to get a good one. There are no flags for temperature. Should either get a good temperature, or delete this one.

Sta. 893 - There were 4 bottles tripped in the surface mixed layer, with good agreement in all samples except for dissolved oxygen. The 3rd one was 12 micro mols higher than the other 3, so I flagged it "u". Station O2's seemed erratic at times on this and on the following leg (see comment in the I01E DQE report).

Sta. 899 and 900 - The surface temperatures are unlikely cooler than the next depth down, while the salinities are uniform, resulting in instabilities. The difference is 0.2 deg C on sta. 900. Suggest re-check surface temperatures to see if the average includes any spurious data.

Sta. 900, 499db - Double trip, data do not agree very well, "u'd" bottle 5 data.

Sta. 901, 33db - Temperature minimum, though salts are uniform 8 to 61 db. Suggest re-check temperature calculation, would "u" it if there were a flag for temperature.

Sta. 918 - Two trips at 5db, oxygens differ by 5%, can't tell which is better, so left both as ok.

Sta. 934 - 3 NO2's listed as -9.00, but flagged ok. Changed flag to not reported. Problem occurs on other stations on this leg and on the next leg as well.

Sta. 940 - Poor mixed layer O<sub>2</sub> agreement, don't know which is most likely, so accepted both as is.

Sta. 943 - Deep silicates are unlikely high compared to other stations. "u'd" the bottom 14 silicates, but suggest re-check end standard calculations to see if these can be salvaged.

Sta. 961 - Sample 1 was listed 13 times. Deleted 12 of them.

**WOCE CTD Data Consistency Check: I01E**

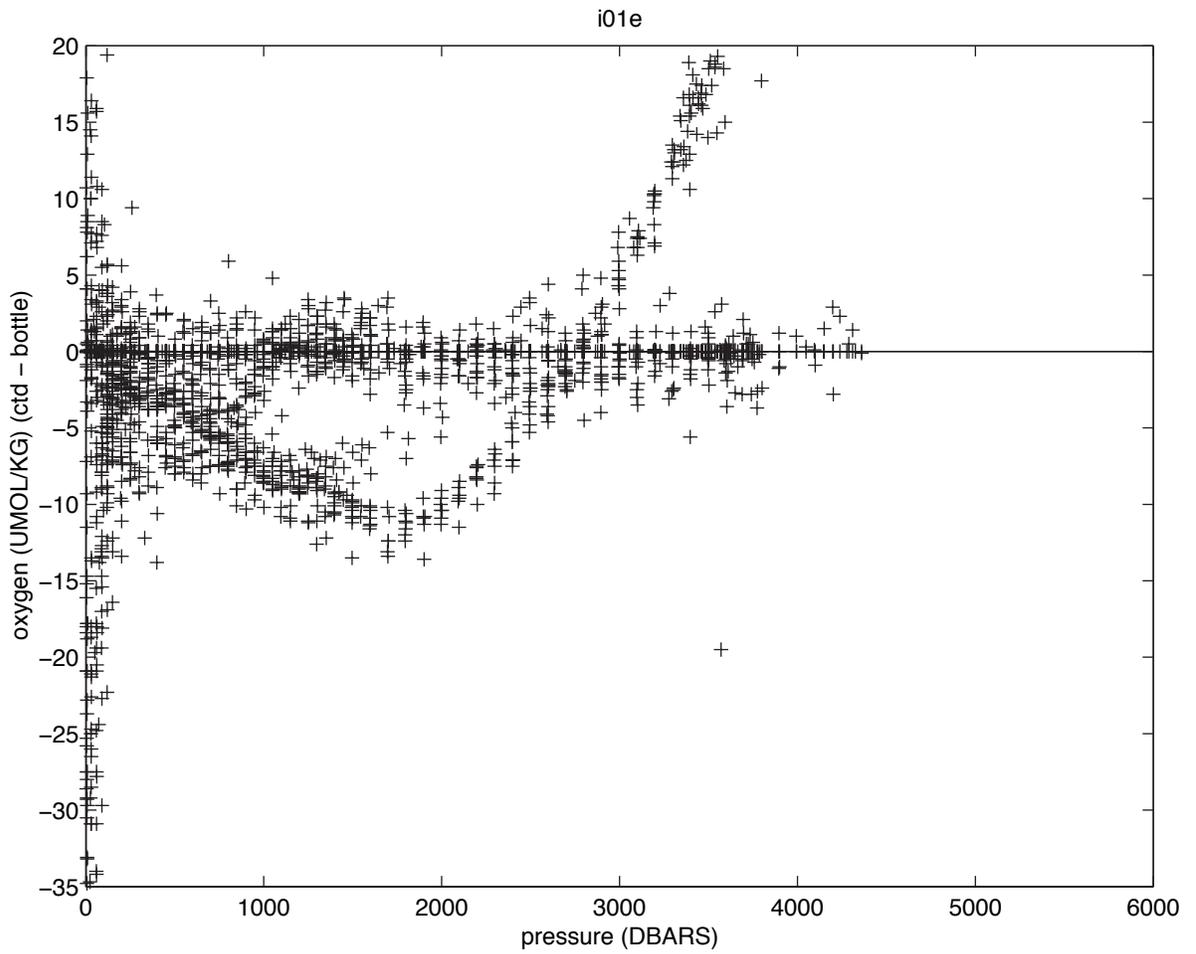
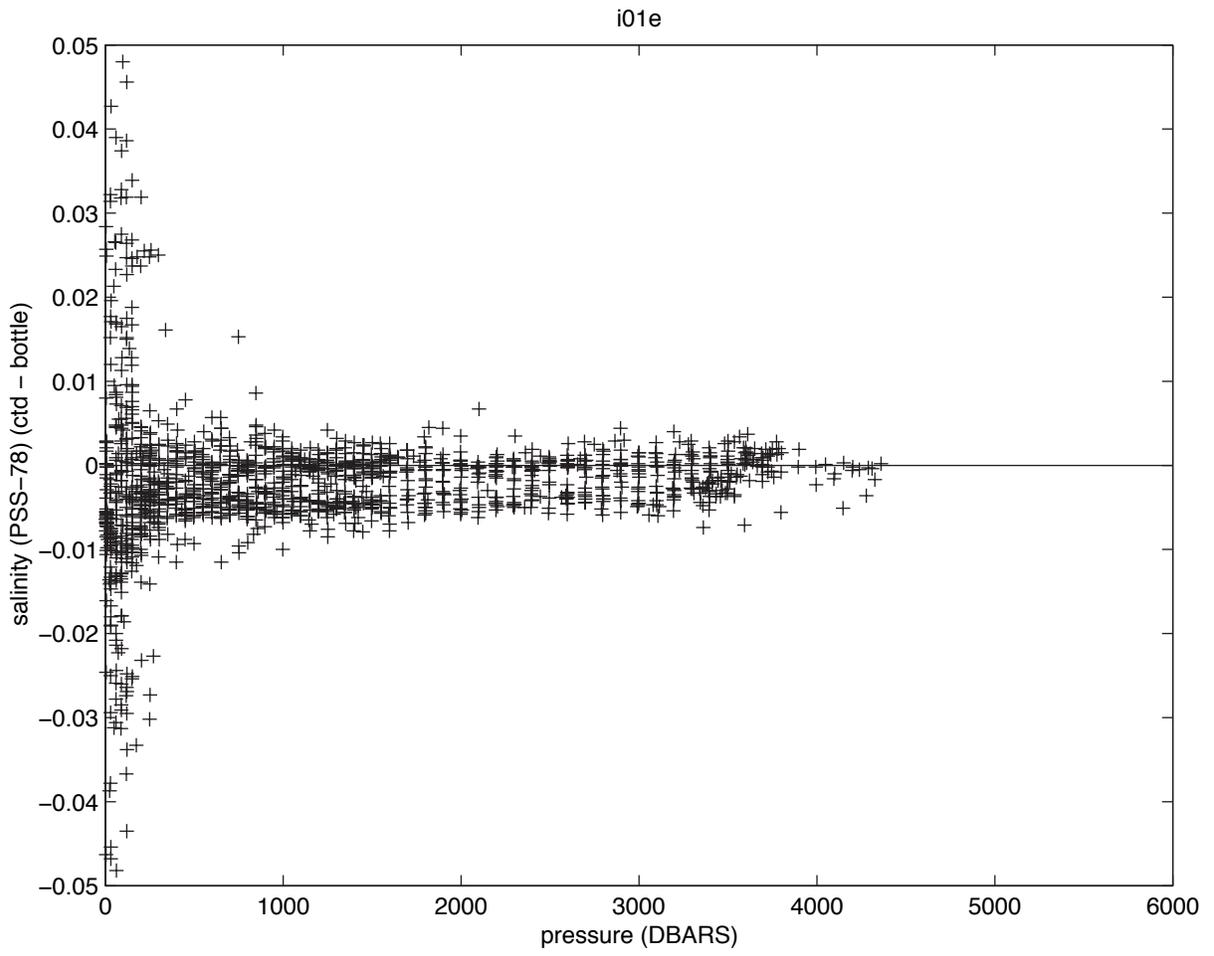
About the '\_check.txt', '\_sal.ps' and '\_oxy.ps' files:

The WHP-Exchange format bottle and/or CTD data from this cruise have been examined by a computer application for contents and consistency. The parameters found for the files are listed, a check is made to see if all CTD files for this cruise contain the same CTD parameters, a check is made to see if there is a one-to-one correspondence between bottle station numbers and CTD station numbers, a check is made to see that pressures increase through each file for each station, and a check is made to locate multiple casts for the same station number in the bottle data. Results of those checks are reported in this '\_check.txt' file. When both bottle and CTD data are available, the CTD salinity data (and, if available, CTD oxygen data) reported in the bottle data file are subtracted from the corresponding bottle data and the differences are plotted for the entire cruise. Those plots are the '\_sal.ps' and '\_oxy.ps' files.

Following parameters found for bottle file:

EXPCODE	SALNTY	CFC-12
SECT_ID	SALNTY_FLAG_W	CFC-12_FLAG_W
STNNBR	CTDOXY	TRITUM
CASTNO	CTDOXY_FLAG_W	TRITUM_FLAG_W
SAMPNO	OXYGEN	HELIUM
BTLNBR	OXYGEN_FLAG_W	HELIUM_FLAG_W
BTLNBR_FLAG_W	SILCAT	DEL14
DATE	SILCAT_FLAG_W	DEL14_FLAG_W
TIME	NITRAT	TCARBN
LATITUDE	NITRAT_FLAG_W	TCARBN_FLAG_W
LONGITUDE	NITRIT	ALKALI
DEPTH	NITRIT_FLAG_W	ALKALI_FLAG_W
CTDPRS	PHSPHT	CTDRAW
CTDTMP	PHSPHT_FLAG_W	THETA
CTDSAL	CFC-11	
CTDSAL_FLAG_W	CFC-11_FLAG_W	

- All ctd parameters match the parameters in the reference station.
- All stations correspond among all given files.
- No bottle pressure inversions found.
- Bottle file pressures are increasing.
- No multiple casts found in bottle data.



**WOCE CTD Data Consistency Check: I01W**

About the '\_check.txt', '\_sal.ps' and '\_oxy.ps' files:

The WHP-Exchange format bottle and/or CTD data from this cruise have been examined by a computer application for contents and consistency. The parameters found for the files are listed, a check is made to see if all CTD files for this cruise contain the same CTD parameters, a check is made to see if there is a one-to-one correspondence between bottle station numbers and CTD station numbers, a check is made to see that pressures increase through each file for each station, and a check is made to locate multiple casts for the same station number in the bottle data. Results of those checks are reported in this '\_check.txt' file.

When both bottle and CTD data are available, the CTD salinity data (and, if available, CTD oxygen data) reported in the bottle data file are subtracted from the corresponding bottle data and the differences are plotted for the entire cruise. Those plots are the '\_sal.ps' and '\_oxy.ps' files.

Following parameters found for bottle file:

EXPCODE	SALNTY	CFC-12
SECT_ID	SALNTY_FLAG_W	CFC-12_FLAG_W
STNNBR	CTDOXY	TRITUM
CASTNO	CTDOXY_FLAG_W	TRITUM_FLAG_W
SAMPNO	OXYGEN	HELIUM
BTLNBR	OXYGEN_FLAG_W	HELIUM_FLAG_W
BTLNBR_FLAG_W	SILCAT	DEL14
DATE	SILCAT_FLAG_W	DEL14_FLAG_W
TIME	NITRAT	TCARBN
LATITUDE	NITRAT_FLAG_W	TCARBN_FLAG_W
LONGITUDE	NITRIT	ALKALI
DEPTH	NITRIT_FLAG_W	ALKALI_FLAG_W
CTDPRS	PHSPHT	CTDRAW
CTDTMP	PHSPHT_FLAG_W	THETA
CTDSAL	CFC-11	
CTDSAL_FLAG_W	CFC-11_FLAG_W	

- All ctd parameters match the parameters in the reference station.

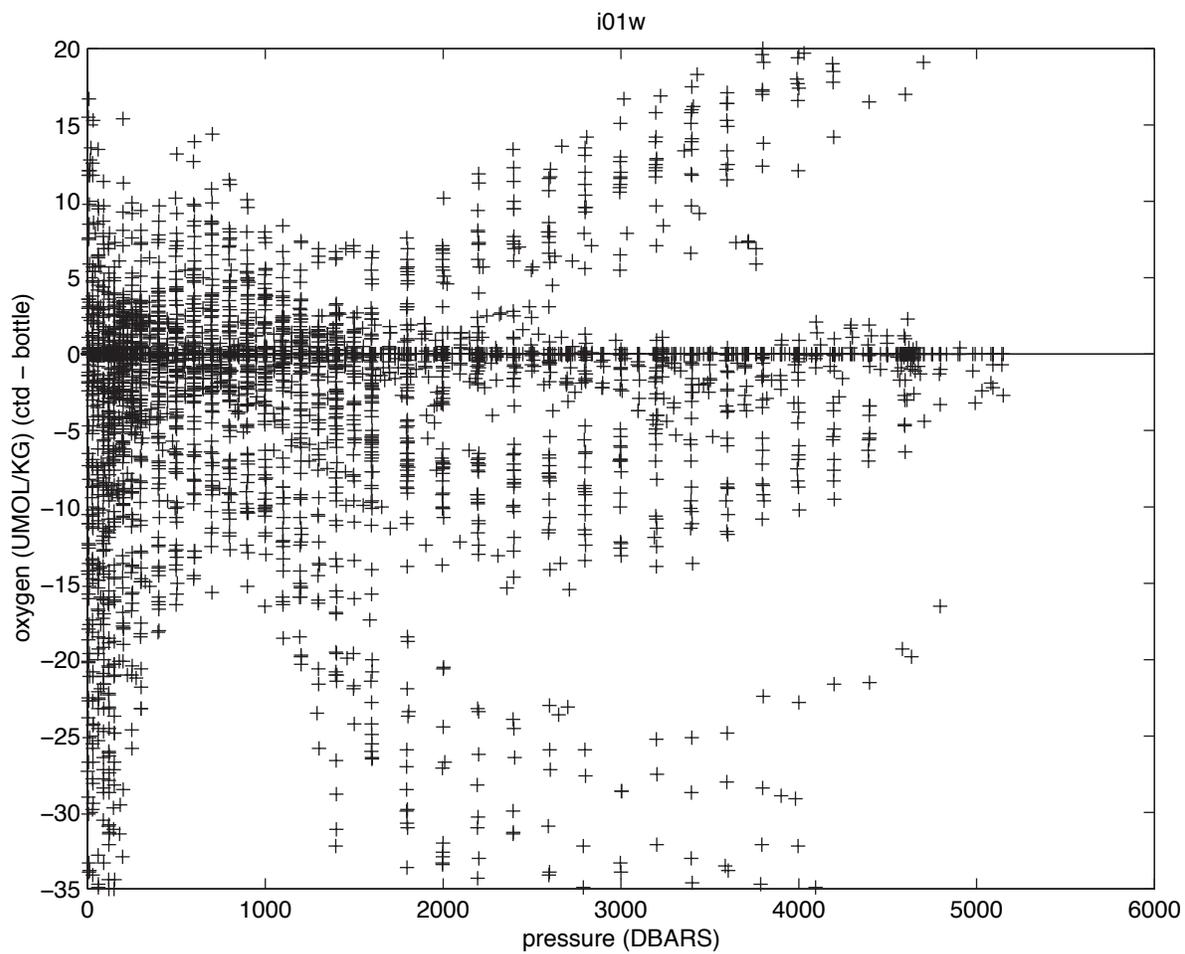
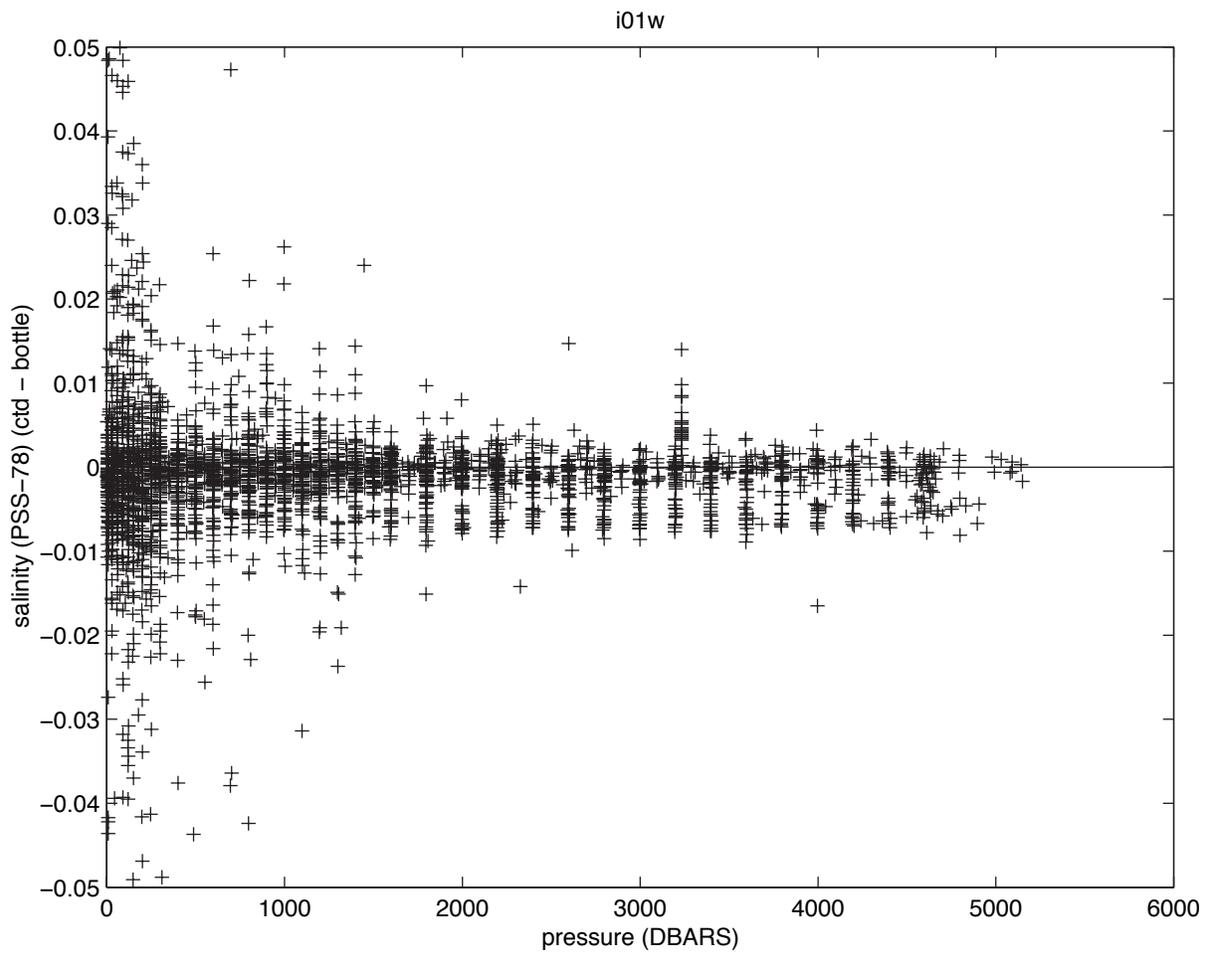
Station #858 has a CTD file, but does not exist in i01w\_hy1.csv.

Station #867 has a CTD file, but does not exist in i01w\_hy1.csv.

Station #869 has a CTD file, but does not exist in i01w\_hy1.csv.

Station #882 exists in i01w\_hy1.csv, but does not have a corresponding CTD file.

- No bottle pressure inversions found.
- Bottle file pressures are increasing.
- No multiple casts found in bottle data.



## **APPENDIX A:**

### **REPRINT OF PERTINENT LITERATURE**

Johnson K. M., A. G. Dickson, G. Eiseid, C. Goyet, P. R. Guenther, R. M. Key, K. Lee, E. R. Lewis, F. J. Millero, D. Purkerson, C. L. Sabine, R. G. Schottle, D. W. R. Wallace, R. J. Wilke, and C. D. Winn. 2002. Carbon Dioxide, Hydrographic and Chemical Data Obtained During the Nine R/V Knorr Cruises Comprising the Indian Ocean CO<sub>2</sub> Survey (WOCE Sections I8SI9S, I9N, I8NI5E, I3, I5WI4, I7N, I1, I10, and I2; December 1, 1994 - January 22, 1996), Ed. A. Kozyr. ORNL/CDIAC-138, NDP-080. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee.

**CARBON DIOXIDE, HYDROGRAPHIC, AND CHEMICAL DATA OBTAINED  
DURING THE NINE R/V *KNORR* CRUISES COMPRISING THE INDIAN OCEAN  
CO<sub>2</sub> SURVEY (WOCE SECTIONS I8SI9S, I9N, I8NI5E, I3, I5WI4, I7N, I1, I10, and  
I2;  
DECEMBER 1, 1994–JANUARY 19, 1996)**

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## ACRONYMS

A/D	analog-to-digital
ADCP	acoustic Doppler current profiler
ALACE	autonomous Lagrangian circulation explorer
BOD	biological oxygen demand
BNL	Brookhaven National Laboratory
<sup>14</sup> C	radiocarbon
CALFAC	calibration factor
CDIAC	Carbon Dioxide Information Analysis Center
CFC	chlorofluorocarbon
CO <sub>2</sub>	carbon dioxide
CTD	conductivity, temperature, and depth sensor
CRM	certified reference material
d.f.	degree of freedom
DIW	deionized water
DOE	U.S. Department of Energy
EEZ	Exclusive Economic Zone
emf	electro-magnetic fields
EXPOCODE	expedition code
FSI	Falmouth Scientific Instruments
<i>f</i> CO <sub>2</sub>	fugacity of CO <sub>2</sub>
FTP	file transfer protocol
GO	General Oceanics
GMT	Greenwich mean time
GPS	global positioning system
Hcl	hydrochloric acid
IAPSO	International Association for the Physical Sciences of the Ocean
IMET	Improved METeorology
I/O	input-output
JGOFS	Joint Global Ocean Flux Study
kn	knots
LADCP	lowered ADCP
LDEO	Lamont-Doherty Earth Observatory
MATS	Miami University alkalinity titration systems
NBIS	Neil Brown Instrument system
NCSU	North Carolina State University
NDP	numeric data package
NOAA	National Oceanic and Atmospheric Administration
nm	nautical mile
NSF	National Science Foundation
ODF	Ocean Data Facility
ONR	Office of Naval Research
OSU	Oregon State University
PC	personal computer
PI	principal investigator
POC	particulate organic carbon

PMEL	Pacific Marine Environmental Laboratory
PU	Princeton University
QA	quality assurance
QC	quality control
R/V	research vessel
RSMAS	Rosenstiel School of Marine and Atmospheric Sciences
SIO	Scripps Institution of Oceanography
SOMMA	single-operator multiparameter metabolic analyzer
SSW	standard seawater
TAMU	Texas A&M University
TALK	total alkalinity
TCO <sub>2</sub>	total carbon dioxide
TD	to-deliver
UH	University of Hawaii
UM	University of Miami
UW	University of Washington
VFC	voltage to frequency converter
WHOI	Woods Hole Oceanographic Institution
WHPO	WOCE Hydrographic Program Office
WOCE	World Ocean Circulation Experiment
WHP	WOCE Hydrographic Program

## ABSTRACT

Johnson K. M., A. G. Dickson, G. Eiseheid, C. Goyet, P. R. Guenther, R. M. Key, K. Lee, E. R. Lewis, F. J. Millero, D. Purkerson, C. L. Sabine, R. G. Schottle, D. W. R. Wallace, R. J. Wilke, and C. D. Winn. 2002. *Carbon Dioxide, Hydrographic and Chemical Data Obtained During the Nine R/V Knorr Cruises Comprising the Indian Ocean CO<sub>2</sub> Survey (WOCE Sections I8SI9S, I9N, I8NI5E, I3, I5WI4, I7N, I1, I10, and I2; December 1, 1994–January 22, 1996)*, Ed. A. Kozyr. ORNL/CDIAC-138, NDP-080. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee, 59 pp.

This document describes the procedures and methods used to measure total carbon dioxide (TCO<sub>2</sub>) and total alkalinity (TALK) at hydrographic stations taken during the R/V *Knorr* Indian Ocean cruises (Sections I8SI9S, I9N, I8NI5E, I3, I5WI4, I7N, I1, I10, and I2) in 1994–1996. The measurements were conducted as part of the World Ocean Circulation Experiment (WOCE). The expedition began in Fremantle, Australia, on December 1, 1994, and ended in Mombasa, Kenya, on January 22, 1996. During the nine cruises, 12 WOCE sections were occupied.

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

The R/V *Knorr* Indian Ocean data set is available as a numeric data package (NDP) from the Carbon Dioxide Information Analysis Center (CDIAC). The NDP consists of 18 oceanographic data files, two FORTRAN 77 data retrieval routine files, a readme file, and this printed documentation, which describes the contents and format of all files as well as the procedures and methods used to obtain the data. Instructions for accessing the data are provided.

**Keywords:** carbon dioxide; TCO<sub>2</sub>; total alkalinity; coulometry; gas chromatography; World Ocean Circulation Experiment; Indian Ocean; hydrographic measurements; carbon cycle.

## 1. BACKGROUND INFORMATION

The World Ocean Circulation Experiment (WOCE) Hydrographic Program (WHP) was a major component of the World Climate Research Program. The primary WOCE goal was to understand the general circulation of the global ocean well enough to be able to model its present state and predict its evolution in relation to long-term changes in the atmosphere. The impetus for the carbon system measurements arose from concern over the rising atmospheric concentrations of carbon dioxide (CO<sub>2</sub>). Increasing atmospheric CO<sub>2</sub> may intensify the earth's natural greenhouse effect and alter the global climate.

The carbon measurements, which were carried out on the U.S. WOCE Indian Ocean cruises, were supported as a core component of the Joint Global Ocean Flux Study (JGOFS). This coordinated effort received support in the United States from the U.S. Department of Energy (DOE), the National Oceanic and Atmospheric Administration (NOAA) and the National Science Foundation (NSF). Goals were to estimate the meridional transport of inorganic carbon in a manner analogous to the estimates of oceanic heat transport (Bryden and Hall 1980; Brewer, Goyet, and Drysen 1989; Holfort et al. 1998; Roemmich and Wunsch 1985) and to build a database suitable for carbon-cycle modeling and the estimation of anthropogenic CO<sub>2</sub> in the oceans. The global data set includes approximately 23,000 stations. Wallace (2001) recently reviewed the goals, conduct, and initial findings of the survey.

This report discusses the CO<sub>2</sub> science team effort to sample the entire Indian Ocean for inorganic carbon (Fig. 1). The total CO<sub>2</sub> (TCO<sub>2</sub>) and total alkalinity (TALK) were measured in the water column and the fugacity of CO<sub>2</sub> (*f*CO<sub>2</sub>) in the surface waters [see Sabine and Key (1998) for a description of the *f*CO<sub>2</sub> methods and data]. The TCO<sub>2</sub> analytical systems were furnished and set up by Brookhaven National Laboratory under the supervision of D. W. R. Wallace and K. M. Johnson, and the alkalinity titrators were furnished and set up by the University of Miami under the supervision of F. J. Millero. During the survey, certified reference material (CRM) was used to ensure measurement accuracy. All shipboard measurements followed standard operating procedures (DOE 1994). This report focuses on TCO<sub>2</sub> and TALK measurements. Because the team shared equipment throughout all nine cruises and so much material, including quality assessments of the data, has already appeared in the refereed literature, it will be limited to a brief summary. Published documentation appears in appendices.

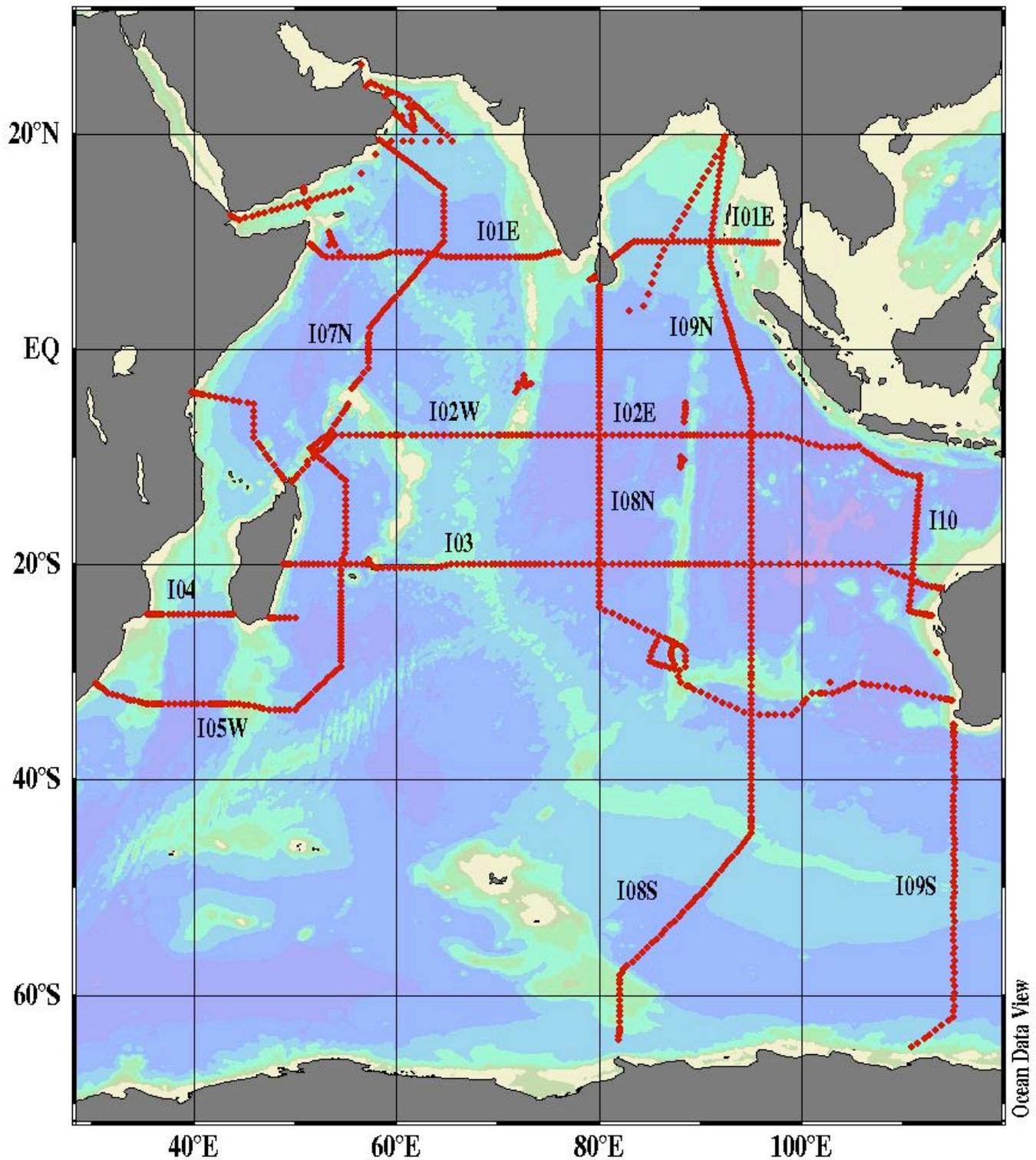


Fig. 1. The cruise track during the R/V Knorr expeditions in the Indian Ocean along WOCE Sections I8SI9S, I9N, I8NI5E, I3, I5WI4, I7N, I1, and I2.

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

## 2. DESCRIPTION OF THE EXPEDITION

### 2.1 R/V *Knorr*: Technical Details and History

The R/V *Knorr*, built in 1969 by the Defoe Shipbuilding Company in Bay City, Michigan, is owned by the U.S. Navy. It was turned over to the Woods Hole Oceanographic Institution in 1971 for operation under a charter agreement with the Office of Naval Research. It was named for E. R. Knorr, a hydrographic engineer and cartographer who in 1860 held the title of Senior Civilian and Chief Engineer Cartographer of the U.S. Navy Office. Its original length and beam were 245 and 46 ft, respectively. Beginning on February 6, 1989, it underwent a major midlife retrofit or “jumbo-izing” at the McDermott Shipyard in Amelia, Louisiana. A midsection was added to the ship to stretch its length by 34 ft, to 279 ft, and fore and aft azimuthing propulsion systems were added to make it one of the most maneuverable and stable ships in the oceanographic fleet. By the time it was returned to the Woods Hole Oceanographic Institution in late 1991, the retrofit had taken 32 months. The P6 Section was the vessel’s first scientific cruise after the retrofit. The R/V *Knorr* was designed for a wide range of oceanographic operations and possesses antiroll tanks and a strengthened bow for duty in icy waters. Like its sister ship, the R/V *Melville*, it is used for ocean research and routinely carries scientists from many different countries. [Table 2](#) provides individual cruise information, parameters measured, and responsible personnel with their institutional affiliations.

## 2.2 The Indian Ocean CO<sub>2</sub> Survey Cruises Information

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

**Table 2. Dates, ports of call, expedition codes (EXPOCODEs), and names of chief scientists during Indian Ocean CO<sub>2</sub> survey cruises**

Section	Start date	Finish date	From	To	EXPOCODE	Chief scientist (affiliated institution) <sup>a</sup>
I8SI9S	12/01/94	01/19/95	Fremantle	Fremantle	316N145_5	M. McCartney (WHOI)
I9N	01/24/95	03/06/95	Fremantle	Colombo	316N145_6	A. Gordon (LDEO)
I8NI5E	03/10/95	04/16/95	Colombo	Fremantle	316N145_7	L. Talley (SIO)
I3	04/20/95	06/07/95	Fremantle	Port Louis	316N145_8	W. Nowlin (TAMU)
I5WI4	06/11/95	07/11/95	Port Louis	Port Louis	316N145_9	J. Toole (WHOI)
I7N	07/15/95	08/24/95	Port Louis	Muscat	316N145_10	D. Olson (RSMAS)
I1	08/29/95	10/18/95	Muscat	Singapore	316N145_11,12	J. Morrison (NCSU)
Dry Dock	10/19/95	11/05/95	Dampier			
I10	11/06/95	11/24/95	Dampier	Singapore	316N145_13	N. Bray (SIO)
I2	11/28/95	01/22/96	Singapore	Mombasa	316N145_14,15	G. Johnson (PMEL)

<sup>a</sup>Participating institutions:

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

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

**Table 3. WOCE measurement programs and responsible institutions during Indian Ocean CO<sub>2</sub> survey cruises**

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

<sup>a</sup>Participating institutions:

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

<sup>b</sup>conductivity, temperature, and depth sensor

<sup>c</sup>chlorofluorocarbons

<sup>d</sup>helium

<sup>e</sup>tritium

<sup>f</sup>carbon-14

<sup>g</sup>acoustic Doppler current profiler

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

**Table 4. Principal investigators and senior at-sea personnel responsible for WOCE measurement programs during Indian Ocean CO<sub>2</sub> survey cruises**

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

[Table 5](#) contains a summary of the personnel responsible for the discrete carbonate system measurements.

**Table 5. Personnel responsible for carbonate system parameter measurements, number of CTD stations, and number of TCO<sub>2</sub> and TALK analyses made during Indian Ocean CO<sub>2</sub> survey cruises**

<b>Section</b>	<b>Institution</b>	<b>PI(s)</b>	<b>Group leader</b>	<b>Stations (No.)</b>	<b>TCO<sub>2</sub> (No.)</b>	<b>TALK (No.)</b>
I8SI9S	BNL	D. Wallace K. Johnson	K. Johnson	147	2184	1910
I9N	PU	R. Key C. Sabine	C. Sabine	131	2511	2504
I8NI5E	UH	C. Winn	C. Winn	166	2419	2421
I3	RSMAS	F. Millero	D. Purkerson	120	1734	1810
I5WI4	BNL	D. Wallace K. Johnson	R. Wilke	136	1991	1831
I7N	UH	C. Winn	R. Schottle	156	2235	2577
I1	WHOI	C. Goyet	G. Eiseid	158	2400	2387
I10	PU	R. Key C. Sabine	C. Sabine	61	927	926
I2	UH	C. Winn	R. Schottle	168	2562	2562
Total				1244	18963	18928

### 2.3 Brief Cruise Summary

Unlike other CO<sub>2</sub> survey cruises where a single institution was responsible for all phases of the work, these cruises were a group effort in which the measurement groups used the same ship and instrumentation for a 14-month period. BNL supplied two single-operator multiparameter metabolic analyzers (SOMMA) systems [S/N 004(I) and 006(II)] that were certified at BNL. A complete back-up system (S/N 023) was supplied by WHOI. The alkalinity titrators were supplied by RSMAS. Preparation began with a 4-day workshop held in September 1994 at RSMAS under the direction of and in the laboratory of F. J. Millero. Cruise participants and group leaders from BNL, LDEO, SIO, RSMAS, PU, WHOI, and UH were instructed in the use of the alkalinity titrators by F. J. Millero and D. Campbell and in the use of the SOMMA-coulometer systems by K. M. Johnson and R. W. Wilke. The day after Thanksgiving the BNL and RSMAS TCO<sub>2</sub> groups left for Australia. Setup of the alkalinity and coulometric titration systems began on November 28, 1994. The I8SI9S cruise began on December 1, 1994.

The first of the nine cruises on the R/V *Knorr* was the longest continuous cruise during the survey. It occupied a series of CTD stations along two north-south tracks essentially proceeding from Australia to the ice edge (**I8S**) along 90° E and then back again to Australia (**I9S**) at approximately 110° E. Station spacing ranged from 5 to 40 nautical miles (nm). Testing and selection of the best of the available titration systems and components was completed during I8S. The alkalinity and especially the coulometric titration systems benefited from this “shake-out” period. Components damaged during transit were identified and repaired or replaced. By the beginning of the I9S, operations were more or less routine. Except for one approximately 12-h period when high winds of ~60 knots (kn) made sampling impossible, work proceeded pretty much on schedule during the 50-day cruise. During the cruise the ability of a team of four marine mammal and bird observers onboard from PMEL, under the direction of C. Tynan, to remain in the cold weather and identify whales that were little more than blips on the horizon amazed all participants of the expedition. Both Christmas and New Year holidays were celebrated aboard the ship. The fine Christmas dinner was highlighted by the appearance of three humpback whales, who put on a spectacular display, jumping and passing under and about the ship. The ship docked in Fremantle, to the relief of the CO<sub>2</sub> team members, on January 19, 1995, after 147 stations were occupied. Measurement crews were exchanged, and the new team brought along some badly needed spare parts and components.

The ship departed Fremantle for I9N on January 24 with A. Gordon as Chief Scientist and a CO<sub>2</sub> measurement group from PU. This section was basically a northward continuation of I8S. The weather was perfect during all 43 days of the cruise. The participants celebrated the equator crossing on February 14. This cruise ended on March 5 in Colombo, Sri Lanka, with 131 stations logged. During the stopover, the carrier gas supply for the coulometric titrators was shifted from bottled high purity nitrogen to a calibration gas generator (Peak Scientific), which supplied CO<sub>2</sub>-free carrier gas for the remaining of the cruises.

I8NI5E began in Colombo on March 10 with L. Talley as chief scientist and a CO<sub>2</sub> measurement group from UH on board. No problems were noted for the sampling program, and the weather remained excellent for most of this leg. The ship track proceeded southward from Sri Lanka along 88° E to 24° S, then angled southeastward to the junction of the Ninety-East Ridge and Broken Ridge. Next, the ship followed a 1987 section along approximately 32° S. This zonal section included the Central Indian Basin, and crossed the northward flow of deep water just west of Australia. Due to the good weather, some extra sampling was carried out, and by the time the ship docked in Fremantle on April 15, 166 stations had been occupied. On station 296, the rosette accidentally hit bottom at 3630 m, but the cast was successfully completed. A postcruise inspection

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

On April 23, the R/V *Knorr* departed Fremantle for section I3 with W. Nowlin as chief scientist and a  $\text{CO}_2$  measurement group from RSMAS. The ship had to detour almost immediately back to Fremantle for a medical emergency. The injured analyst was able to rejoin the ship in Port Louis, Mauritius. In addition to the CTD work, this cruise included the deployment of current meters, drifters, and autonomous Lagrangian circulation explorer (ALACE) floats. The cruise track ran along  $20^\circ$  S from Australia to Mauritius to Madagascar, crossing the West Australian Basin, Ninety-East Ridge, Central Indian Basin, and Central Indian Ridge before veering southward to  $22^\circ$  S around Rodrigues Island. After this, it proceeded to the east coast of Mauritius, where a 2-day port stop was made in Port Louis. Returning to sea, the ship continued sampling westward along  $20^\circ$  S from the continental shelf to Madagascar. Weather was characterized by southeasterly winds of 10–20 kn, mostly sunny skies, occasional rain squalls, and 4–6 ft swells with slightly higher winds and seas in mid-May. The *Knorr* returned to Port Louis, Mauritius, on June 5 with 120 stations logged.

The next cruise, I4I5W, began on June 11 with J. Toole as chief scientist and a  $\text{CO}_2$  measurement group from BNL on board. This leg focused on major circulation features of the southwest region of the Indian Ocean, including the region where the Agulhas Current originates and where dense waters filtering through fractures in the Southwest Indian Ridge form a northward deep boundary current east of Madagascar. The cruise track formed a closed box to aid in deducing the absolute circulation. A stop was made in Durban, South Africa, on June 21 to pick up a replacement drum of CTD wires. Attempts were also made to repair the ship's bow thruster, which had failed very early in the leg; although the repair was not successful, the lack of a bow thruster had no effect on the scientific work. The R/V *Knorr* departed Durban on June 22 and began I5W including reoccupation of stations where data had been taken in 1987. Bad weather was experienced on June 30 when wind gusts of 40–50 kn and high seas slowed winch operations. As the ship moved across the Madagascar Basin toward port, station spacing was decreased to 20 nm. When the ship arrived in port on July 11, 136 stations had been occupied—20 more than planned.

After four days in port, the R/V *Knorr* departed on I7N with D. Olson as chief scientist and a  $\text{CO}_2$  measurement group from UH. The director of the U.S. WOCE office, Piers Chapman, was aboard and served as a salt analyst during the section. I7N was designed to define the water mass properties and transports across the Mascarene Basin and to measure water mass properties and baroclinic structure on a short section across the Amirante Passage, located between the Mascarene and Somali Basins. It included a cross-equatorial section and a reoccupation of stations previously sampled to confirm water mass flows. This work included sampling along  $65^\circ$  E in the central Arabian Basin. The concluding phase of the cruise was a deep line of stations up the center of the Gulf of Oman. The last station of this phase was in the Strait of Hormuz, and it identified inflows of Arabian (Persian) Gulf water into the Arabian Basin. The cruise terminated on August 24 in Muscat, Oman, with 156 stations occupied.

After a 5-day layover, the R/V *Knorr* departed Muscat on I1 with J. Morrison as chief scientist and a  $\text{CO}_2$  measurement group from WHOI. I1 was the northernmost Indian Ocean section. It enclosed the Arabian Sea and Bay of Bengal, which are important sources of salt and fresh water, respectively. The *Knorr* proceeded from Muscat to the southern end of the Red Sea and then to the coast of Somali, where the zonal section started at a nominal latitude of  $8^\circ$  N. The section crossed the Arabian Sea, in part to study the carbon transport in and out of the Arabian Sea,

and ended on the continental shelf of India. After a brief port stop in Colombo, Sri Lanka, on September 28–30, the leg continued from the Sri Lankan shelf across the Bay of Bengal to the Myanmar continental shelf. CTD problems caused considerable difficulty for the scientific party and resulted in a somewhat noisy hydrographic data set compared to data obtained from the other sections. After the last station on the Myanmar shelf, the *Knorr* deadheaded to Singapore, arriving on October 16 with 158 stations logged. I1 was not only the northernmost section, it was clearly the most adventurous. ALACE float deployments had to be canceled in the territorial waters of India because the Indian observer on board refused to allow them, and then the threat of pirates caused the cancellation of a planned section across the Gulf of Aden. In the vicinity of Colombo, the ship had to be escorted by four Sri Lankan gunboats, and planned stops at stations over the Trincomalee Canyon could not be taken because of the threat of attack by the Tamil Tigers. Nevertheless, the *Knorr* was able to coordinate scientific activities and physical oceanographic measurements with the nearby R/V *Meteor* (F. Schott, chief scientist) in an area of German current meter moorings near Socotra. Sampling during I1 enabled comparison of bottle and TCO<sub>2</sub> data with earlier JGOFS results and *Meteor* Pegasus and *Knorr* lowered acoustic Doppler current profiler (LADCP) horizontal velocities. From Singapore, the *Knorr* proceeded to Dampier, Australia, where it was placed in dry dock from October 19 until November 5.

With the R/V *Knorr* back in the water, the I10 CO<sub>2</sub> measurement group from PU arrived. This group was required to do some additional work not normally part of the crew exchange routine. During the dry dock period, the CO<sub>2</sub> instrumentation had been depowered, and the measurement group had to repower and check the instrumentation. Some minor repairs were required for the coulometric titrators, including the replacement of one or two solenoid valves (the only valves replaced during the cruises). In addition, the sample pipettes and coolant lines were dismantled and cleaned of algal growth.

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

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

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

For inorganic carbon, the principal analytical problems for the cruise centered on the breakage of glass components in the alkalinity titrators; resupply; accumulation of bubbles in the acid lines of the alkalinity titrators; damaged coulometric cathode electrodes; algal growth in the sample lines, baths, pipettes, and alkalinity cells; wide swings in laboratory temperature (19–33°C), and the failure of the TCO<sub>2</sub> glassware drying oven. Fortunately, glassware drying oven was repaired. Temperature swings (21–29°C ) were also noted for the salinometer and nutrient laboratories. The most vexing problem for the inorganic carbon analysts was the failure of the refrigerated baths used by both the alkalinity and coulometric titration systems. The baths had to be constantly jury-rigged so that one bath did the work of two, repaired by ship's technicians when possible, or replaced when possible. The two groups used almost 12 different baths, and by the time the work ended, not one could be considered in reliable condition. Some were never repaired, while others were repaired and used for the North Atlantic survey in 1997.

### 3. DESCRIPTION OF VARIABLES AND METHODS

#### 3.1 Hydrographic Measurements

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

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

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

##### 3.1.1 SIO/ODF Methods and Instrumentation

Hydrographic measurements consisted of salinity, dissolved oxygen, and nutrient (nitrite, nitrate, phosphate, and silicate) samples collected from Niskin bottles filled during CTD/rosette casts, and temperature, pressure, salinity, and dissolved oxygen from the CTD. At 5- to 40-m intervals, depending on the topography, hydrographic casts were made to within 5–20 m of the bottom with a 36-bottle Rosette frame belonging to ODF. This unit consisted of a 36-bottle frame, thirty six 10-L bottles, and a 1016 General Oceanics (GO) 36-place pylon. The GO pylon was used in conjunction with an ODF-built deck unit and power supply. The underwater components comprising the CTD included an ODF-modified Neil Brown Instrument Systems (NBIS) Mark III CTD with conductivity, pressure, oxygen, and temperature sensors. The underwater package also consisted of a SeaTech transmissometer, an LADCP, a Sormedics dissolved oxygen sensor, a Falmouth Scientific Instruments (FSI) secondary PRT sensor, a Benthos altimeter, and a Benthos pinger. The CTD was mounted horizontally along the bottom of the frame, while the LADCP was vertically mounted inside the bottle rings. The system was suspended from and powered by a three-conductor 0.322-in. electromechanical cable. The Rosette was deployed from the starboard side using either the port side Markey CTD or the starboard side Almon Johnson winch. Standard CTD practices (i.e., soaking the conductivity and O<sub>2</sub> sensors in distilled water between casts and protecting the sensors against sunlight and wind by storing the rosette in the hanger between casts) were observed throughout the cruises. Regular CTD maintenance included the replacement of O-rings when needed, bottle inspections, and a regular cleaning of the transmissometer windows. At the beginning of each station the time, position, and bottom depth were logged. The CTD sensors were powered and control was transferred to the CTD acquisition and control system in the ship's laboratory. The CTD was lowered to within 10 m of the bottom if bottom returns were adequate. Continuous profiles of horizontal velocity from the sea surface to the bottom were made for most CTD/rosette casts using the LADCP.

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

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

After the CTD was on deck, the acquisition system, the CTD, the pylon, and video recording were turned off and the sensor protective measures were completed before sampling began. If a full suite of samples was drawn, the sampling order was CFCs,  $^3\text{He}$ ,  $\text{O}_2$ ,  $\text{TCO}_2$ , TALK,  $^{14}\text{C}$ ,  $^3\text{H}$ , nutrients, and salinity. Only salinity,  $\text{O}_2$ , and nutrients were measured at every station. A deck log was kept to document the sampling sequence and to note anomalies (e.g., status of bottle valves, leaks, etc.). One member of the sampling crew was designated the “sample cop,” and it was his or her responsibility to maintain this log and to ensure that the sampling order was followed. Oxygen sampling included measurement of the temperature, which proved useful for determining leaking or mis-tripped bottles. Following the cruises, WHP quality flags were assigned according to the WOCE Operations Manual (Joyce and Corry 1994) to each measured quantity.

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

Bottle **salinity** samples were collected in 200-mL Kimax high alumina borosilicate bottles, sealed with custom-made plastic insert thimbles and Nalgene screw caps. Salinity was determined after equilibration in a temperature-controlled laboratory, usually within 8–20 h of collection. Salinity was measured with two ODF-modified Guildline Autosol Model 8400A salinometers, normally at 21 or 24°C, depending on the prevailing temperature of the salinometer laboratory. The salinometers included interfaces for computer-aided measurements (e.g., acquiring the measurements, checking for consistency, logging results, and prompting the analyst). The salinometers were standardized with International Association for the Physical Sciences of the Ocean (IAPSO) Standard Seawater (SSW) Batches P-124, P-126, or P-128 using at least one fresh vial per cast (usually 36 samples). The accuracy of the determination was normally 0.002 relative to the SSW batch used. PSS-78 was then calculated for each sample (UNESCO 1981). On some stations (e.g., on Section I5E18N), bottle salinity exhibited small offsets (0.002–0.004) compared to the corresponding CTD results and bottle salinity from nearby stations, and corrections of this magnitude need to be applied to the bottle salinity. Errors of this magnitude have no practical effect on the calculated  $\text{TCO}_2$  or TALK values. Hence, bottle salinity is sufficiently accurate to express inorganic carbon results in  $\mu\text{mol/kg}$ .

Bottle **oxygen** was determined by rinsing 125-mL iodine flasks twice and then filling to overflowing (3x-bottle volume) with a draw tube. Sample temperature was measured immediately with a thermometer imbedded in the draw tube. The Winkler reagents were added; and the flask was stoppered, shaken, and then shaken again 20 min later to ensure that the dissolved  $\text{O}_2$  was completely fixed. Oxygen was determined within 4 h of collection using a whole-bottle modified Winkler titration following the technique of Carpenter (1965) and incorporating the modifications of Culberson et al. (1991) on an SIO/ODF-designed automated oxygen titrator. A Dosimat 665 burette driver fitted with a 1.0-mL burette was used to dispense thiosulfate solution (50 g/L).

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

Phosphate, nitrate, nitrite, and silicate samples were collected in 45-mL high-density polypropylene, narrow-mouth, screw-capped centrifuge tubes which were cleaned with 10% hydrochloric acid (HCl) and then rinsed three times with sample before filling. The samples were analyzed on an ODF-modified four-channel Technicon AutoAnalyzer II, usually within 1 h of the cast, in a temperature-controlled laboratory. If the samples were stored for longer than 1 h prior to analysis, they were stored at 2–6°C (for no more than 4 h). The AutoAnalyzer incorporates the method of Armstrong, Stearns, and Strickland (1967) for silicate, this same method as modified for nitrate and nitrite, and the method of Bernhardt and Wilhelms (1967) for phosphate. The last method is described by Gordon and coworkers (Atlas et al. 1971; Hager et al. 1972; and Gordon et al. 1992). Standards were analyzed at the beginning and end of each group of sample analyses, with a set of secondary intermediate concentrations prepared by diluting preweighed primary standards. Replicates were also drawn at each station for measurement of short-term precision. For reagent blanks, deionized water (DIW) from a Barnstead Nanopure deionizer fed from the ship’s potable water supply was analyzed. An aliquot of deep seawater was run with each set of samples as a substandard. The primary standard for silicate was  $\text{Na}_2\text{SiF}_6$ ; and for nitrate, nitrite, and phosphate the standards were  $\text{KNO}_3$ ,  $\text{NaNO}_2$ , and  $\text{KH}_2\text{PO}_4$ , respectively. Chemical purity ranged from 99.97% ( $\text{NaNO}_2$ ) to 99.999% ( $\text{KNO}_3$ ).

Most hydrographic data sets met or exceeded the WHP requirements. Some exceptions for silicate were noted when differences between overlapping stations on I3 (Station 548) and I415W (Stations 705 and 574) approached 3%; these silicate data (Stations 702–707) were corrected by adding 3% to the original results. Instrument problems also caused difficulties for the nitrite and silicate analyses on many of the I2 cruise stations. Silicate problems were noted at some 30% of these stations, with errors typically being on the order of 2–4%. This required considerable post-cruise evaluation and workup before the desired between-station precision for deep water values of 1% was attained. However, users of the I2 silicate data are urged to use caution or to contact the analysts for assistance. Because of the difficulties with the nutrient analyses on the I2 cruise, the post-cruise I2 precision is given in Table 7 as a “worst case” for comparison with the WHP standards shown in Table 6. Short-term precision is the absolute mean difference between replicates analyzed within a sample run; the standard deviation of the differences is also shown. The authors know of no remaining CTD problems, that would affect the quality of the carbonate system data.

Table 6. Required WHP accuracy for deep water analyses

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

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

**Table 7. The short-term precision of the nutrient analyses for Indian Ocean Section I2**

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

### 3.1.2 WHOI Methods and Instrumentations

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

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

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

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

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

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

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

### 3.1.3 Underway Measurements

Navigational data (heading, speed, time, date, and position) were acquired from the ship's Magnavox MX global positioning system (GPS) receiver via RS-232 and logged automatically at 1-min intervals on a SunSPARC station. Underway bathymetry was logged manually at 5-min intervals from the hull-mounted 12-kHz echo sounder and a Raytheon recorder corrected according to methods described by Carter (1980). These data were merged with the navigation data to provide a time-series of underway position, course, speed, and bathymetry data that were used for all station positions, depths, and vertical sections. The Improved METeorology (IMET) sensors logged meteorological data—which included air temperature, barometric pressure, relative humidity, sea surface temperature, and wind speed and direction—at 1-min intervals. Underway shipboard measurements were made throughout the work to document the horizontal velocity structure along the cruise tracks using a 150-kHz hull-mounted acoustic Doppler current profiler (ADCP) manufactured by RD Instruments. The ADCP was mounted at a depth of 5 m below the sea surface. Underway chemical measurements in water and air included salinity,  $\text{pCO}_2$  (PU and SIO),  $\text{pN}_2\text{O}$  (SIO), and  $\text{CH}_4$  (SIO). Two different systems were used for  $\text{pCO}_2$ ; the PU group used a rotating disk equilibrator and infrared detector, while the Scripps group used a shower type equilibrator and gas chromatograph for the detection of  $\text{CO}_2$ . The  $\text{pCO}_2$  measurements, including a comparison of the shower and disk equilibrator results, were described by Sabine and Key (1998).

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

### 3.2 Total Carbon Dioxide Measurements

TCO<sub>2</sub> was determined on 18,963 samples using two automated single-operator multiparameter metabolic analyzers (SOMMA) with coulometric detection of the CO<sub>2</sub> extracted from acidified samples. A description of the SOMMA-coulometry system and its calibration can be found in Johnson et al. 1987; Johnson and Wallace 1992; and Johnson et al. 1993. A schematic diagram of the SOMMA analytical sequence and a complete description of the sampling and analytical methods used for discrete TCO<sub>2</sub> on the Indian Ocean WOCE sections appear in [Appendix B](#) (Johnson et al. 1998). Further details concerning the coulometric titration can be found in Huffman (1977) and Johnson, King, and Sieburth (1985). The measurements for the Indian Ocean Survey were made on two systems provided by BNL (S/Ns 004 and 006) and a backup by WHOI (S/N 023).

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

Seawater introduced from an automated “to-deliver” (TD) pipette into a stripping chamber was acidified, and the resultant CO<sub>2</sub> from continuous gas extraction was dried and coulometrically titrated on a model 5011 UIC coulometer. The coulometer was adjusted to give a maximum titration current of 50 mA, and it was run in the counts mode [the number of pulses or counts generated by the coulometer’s voltage-to-frequency converter (VFC)] during the time the titration was displayed and acquired by the computer. In the coulometer cell, the acid (hydroxyethylcarbamic acid) formed from the reaction of CO<sub>2</sub> and ethanolamine was titrated coulometrically (electrolytic generation of OH<sup>-</sup>) with photometric endpoint detection. The product of the time and the current passed through the cell during the titration was related by Faraday’s constant to the number of moles of OH<sup>-</sup> generated and thus to the moles of CO<sub>2</sub> that reacted with ethanolamine to form the acid. The age of each titration cell was logged from its birth (time that electrical current was applied to the cell) until its death (time when the current was turned off). The age was measured from birth (chronological age) and in mass of carbon (mgC) titrated since birth (carbon age). The systems were controlled with PCs equipped with RS232 serial ports for the coulometer and the barometer, a 24-line digital input/output (I/O) card for the solid state relays and valves, and an analog-to-digital (A/D) card for the temperature, conductivity, and pressure sensors.

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

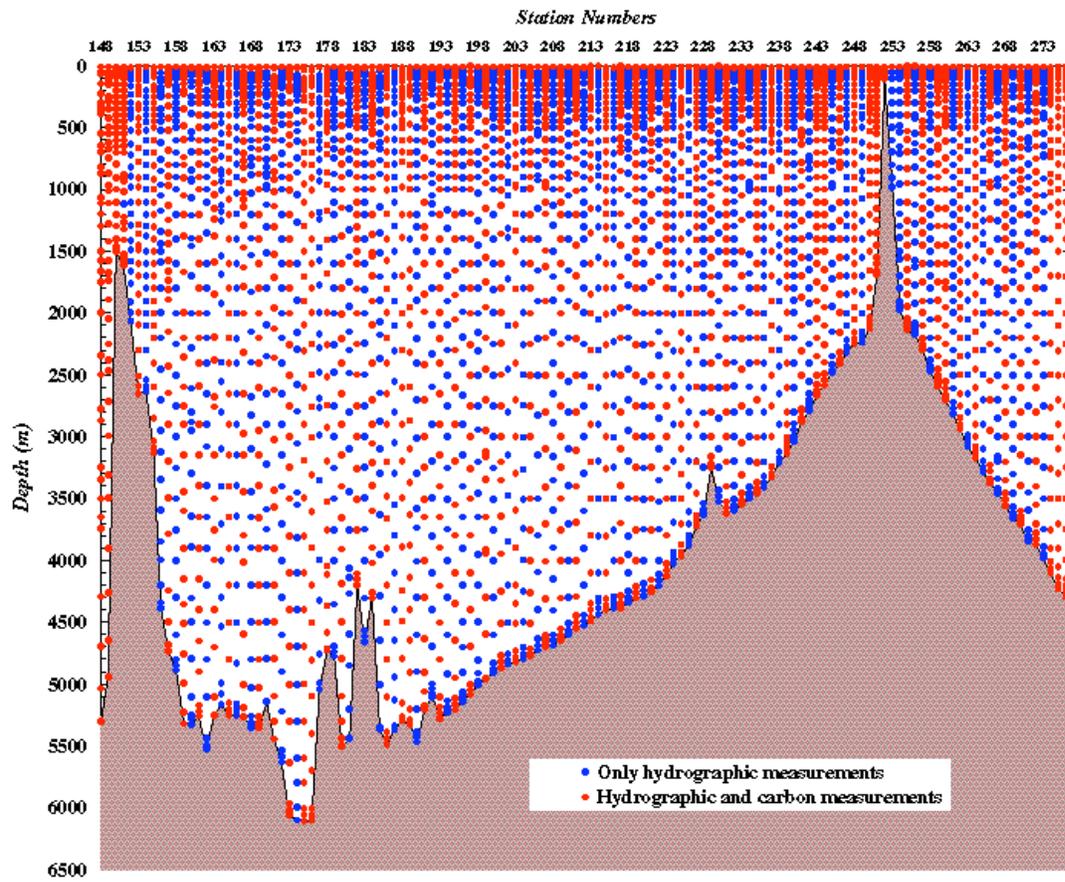


Fig. 2. Sampling depths at all hydrographic stations occupied during the R/V *Knorr* Indian Ocean survey along WOCE Section I9N

The TD volume ( $V_{cal}$ ) of the sample pipettes was determined gravimetrically prior to the cruise and periodically during the cruise by collecting aliquots of deionized water dispensed from the pipette into pre-weighed serum bottles which were sealed and re-weighed on shore. The apparent weight of water collected ( $W_{air}$ ), corrected to the mass in vacuo ( $M_{vac}$ ), was divided by the density of the calibration fluid at the calibration temperature to give  $V_{cal}$ . The sample volume ( $V_t$ ) at the pipette temperature was calculated from the expression

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

where  $a_v$  is the coefficient of volumetric expansion for Pyrex-type glass ( $1 \times 10^{-5}/^{\circ}\text{C}$ ), and  $t$  is the temperature of the pipette at the time of a measurement.  $V_{cal}$  for the Indian Ocean CO<sub>2</sub> survey cruises and a chronology of the pipette volume determinations appear in [Appendix B](#).

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

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

where 4824.45 (counts/ $\mu\text{mol}$ ) was the scaling factor obtained from the factory calibration,  $T_t$  was the length of the titration in minutes, *Blank* is the system blank in  $\mu\text{mol}/\text{min}$ , and  $T_t$  the time of continuous current flow in minutes.

The SOMMA-coulometry systems were calibrated daily with pure CO<sub>2</sub> (calibration gas) by titrating the mass of CO<sub>2</sub> contained in two stainless steel gas sample loops of known volume and by analyzing CRM samples supplied by Dr. Andrew Dickson of the SIO. The ratio of the calculated (known) mass of CO<sub>2</sub> contained in the gas sample loops to the mass determined coulometrically was the CALFAC ( $\sim 1.004$ ). A complete history of the calibration results appears in [Appendix B](#). For water and CRM samples, TCO<sub>2</sub> concentration in  $\mu\text{mol}/\text{kg}$  was

$$\text{TCO}_2 = M \times \text{CALFAC} \times [1 / (V_t \times \rho)] \times d_{Hg},$$

where  $\rho$  is the density of seawater in  $\text{g}/\text{mL}$  at the analytical  $t$  and  $S$  calculated from the equation of state given by Millero and Poisson (1981), and  $d_{Hg}$  is the correction for sample dilution with bichloride solution (for the cruises  $d_{Hg} = 1.000666$ ).

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

Three CRM batches were used for the Indian Ocean Survey. The certified TCO<sub>2</sub> concentrations were determined by vacuum-extraction/manometry in the laboratory of C. D. Keeling at SIO and are given in [Table 8](#).

**Table 8. Certified salinity, TALK, and TCO<sub>2</sub> for CRM supplied for Indian Ocean CO<sub>2</sub> survey**

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

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

The quality control-quality assurance (QC-QA) of the coulometric TCO<sub>2</sub> determinations was assessed from analyses of 983 CRM samples during the nine Indian Ocean CO<sub>2</sub> survey cruises. For both coulometric titration systems (004 and 006) the average ΔTCO<sub>2</sub> (measurement minus CRM value) for the whole survey was -0.86 μmol/kg and the standard deviation was ±1.21 μmol/kg. A cruise-by-cruise breakdown of the accuracy and precision of the CRM analyses is given in [Appendix B](#).

The small mean difference between the analyzed and certified TCO<sub>2</sub> and the very high precision (±1.21 μmol/kg) of the differences indicates that the two systems gave very accurate and virtually identical results over the entire survey (see also [Fig. 6](#) in [Appendix B](#)).

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

**Table 9. Precision of discrete TCO<sub>2</sub> analyses during Indian Ocean CO<sub>2</sub> survey**

Section	$S_p^2$ (K, n, d.f)
I8SI9S	1.26 (15, 30, 15)
I4I5W	0.91 (21, 42, 21)
CRM	1.21

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

**Table 10. Mean Difference [ $\Delta\text{TCO}_2(\text{s-sio})$ ] and standard deviation of the differences [S.D. $_{(\text{s-sio})}$ ] between at-sea  $\text{TCO}_2$  by coulometry and on-shore  $\text{TCO}_2$  by manometry on aliquots of the same sample from Indian Ocean  $\text{CO}_2$  survey, and the mean replicate precision [S.D. $_{(\text{sio})}$ ] of the manometric analyses**

Section	Pairs Analyzed (n)	$\Delta\text{TCO}_2(\text{s-sio})$ ( $\mu\text{mol/kg}$ )	S.D. $_{(\text{s-sio})}$ ( $\mu\text{mol/kg}$ )	S.D. $_{(\text{sio})}$ <sup>a</sup> ( $\mu\text{mol/kg}$ )
I8SI9S	23	-4.14	1.80	0.82
I9N	24	-1.96	1.67	0.80
I8NI5E	17	-4.80	2.87	1.31
I3	29	-3.29	1.26	0.82
I4I5W	16	-2.95	1.40	1.30
I7N	13	-5.37	1.92	1.40
I1	26	-5.59	1.38	1.05
I10	8	-4.94	1.52	1.28
I2	10	-4.42	1.50	0.83
n	166	9	9	9
Mean		-4.16	1.70	1.07
S.D.		1.21	0.49	0.25

<sup>a</sup>Each on-shore  $\text{TCO}_2$  by manometry is always the mean of two analyses (see text).

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

everywhere, but the magnitude of the Indian Ocean difference is clearly the largest observed to date. Even if the consistent and slightly negative difference for the CRM is taken into account ( $-0.86 \mu\text{mol/kg}$ ), the at-sea coulometric measurements are approximately  $2 \mu\text{mol/kg}$  lower than the manometric method. A suite of samples from the 1997 North Atlantic sections remains to be analyzed. Until these analyses are completed and a thorough statistical evaluation of the entire  $\text{CO}_2$  survey data set is made, the explanation of the at-sea and on-shore differences, including those found for the Indian Ocean, is not possible.

An additional step in the QA-QC was also undertaken. Inspection of [Fig. 1](#) shows points where the cruise tracks cross or nearly cross. The agreement between  $\text{TCO}_2$  measurements made at these crossover locations ( $\pm 100 \text{ km}$ ) on different cruises was examined by assuming that the temporal and spatial variations in deep-ocean  $\text{TCO}_2$  are small relative to the measurement accuracy and precision. Hence, deep ocean waters should have the same  $\text{TCO}_2$  at different times in the absence of internal vertical motion, and because deep ocean motion probably occurs along constant density surfaces (isopycnals), the comparisons of  $\text{TCO}_2$  measurements were made with reference to density and not depth. [Appendixes B and D](#) (Johnson et al. 1998 and Sabine et al. 1999) give a complete description of the statistical procedures used to make the crossover comparisons. Briefly, crossover points were selected for comparison of water samples collected below 2500 m. A smooth curve was fit through the  $\text{TCO}_2$  data as a function of the density anomaly referenced to 3000 dbar ( $\sigma - 3$ ) using Cleveland's LOESS smoother (Cleveland and Devlin 1988). A separate fit was performed for the data collected at each of the two intersecting crossover points, but the same tension parameter was used for all of the crossover points so that the smoothing function was consistently applied to all crossover locations. The difference between the two smoothed curves was evaluated at 50 evenly spaced points covering the density range where the two data sets overlapped. A mean and standard deviation for the 50 comparisons was calculated for each crossover point. For  $\text{TCO}_2$ , differences never exceeded  $3 \mu\text{mol/kg}$ , and the overall mean and standard deviation of the differences was  $-0.78 \pm 1.74 \mu\text{mol/kg}$ . The latter differences were consistent with the overall precision of the CRM analyses ( $\pm 1.2 \mu\text{mol/kg}$ ).

Tables 8–10 show an internally consistent  $\text{TCO}_2$  data set for the Indian Ocean with excellent accuracy with respect to the CRM certified values, consistently good precision, no analytical bias between the coulometric titration systems, and crossover agreement to within the precision of the method. However, the agreement between the at-sea and on-shore analyses is not as good as for earlier WOCE sections from other oceans (i.e., the Pacific and the South Atlantic). Based on the accuracy of the CRM analyses and the high precision of the sample analyses, the  $\text{TCO}_2$  data were not corrected in any way and were deemed to meet survey criteria for accuracy and precision.

### 3.3 Total Alkalinity Measurements

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

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

A Lab Windows C program was used to run the titrators, record the volume of titrant added, and record the measured electromagnetic fields (emf) of the electrodes through RS232 serial interfaces. Two electrodes were used in each cell: a ROSS glass pH electrode (Orion, Model 810100) and a double-junction Ag/AgCl reference electrode (Orion, Model 900200). The specific electrodes used during the Indian Ocean survey were selected after careful screening for non-Nernstian behavior. Only those electrodes which gave  $\text{TCO}_2$  results in good agreement with  $\text{TCO}_2$ , as determined coulometrically, were used (Sect. 3.2).

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

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

While CRM samples were available to the  $\text{TCO}_2$  analysts from the beginning of the measurement program in 1990, the Indian Ocean cruises were the first to have a certified alkalinity standard as well. Hence, the accuracy of the method was checked in the laboratory by analyzing CRM samples from batches 23, 24, 26, 27, 29, and 30 and comparing the analyzed values with the certified TALK determined by A. Dickson at SIO (in the same manner as for  $\text{TCO}_2$ ). These results are summarized in [Table 11](#) (see also [Appendix C](#)). The mean difference between the MATS measurements in the laboratory and the certified TALK values was  $-0.8$   $\mu\text{mol/kg}$  for CRM samples with a concentration range approximately one-half as large as the range of a typical seawater profile. The excellent agreement indicated that the CRM concept for alkalinity was valid and that the methodology for TALK was ready for the Indian Ocean survey. The results for the at-sea measurements of the CRM samples have been extracted from [Table 2](#) of [Appendix C](#), summarized, and are given in [Table 12](#).

**Table 11. Mean analytical difference (TALK) between analyzed and certified TALK for CRM used during Indian Ocean CO<sub>2</sub> survey**

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

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

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

and the corrected TALK (TALK<sub>c</sub>) was

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

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

The overall precision of TALK determinations during the Indian Ocean survey was ± 4.2 μmol/kg. The precision of the potentiometric pH and TCO<sub>2</sub> measurements are given in [Table 3](#) of Appendix C.

**Table 12. Mean analytical difference ( $\Delta$ TALK) between analyzed and certified TALK for each section during Indian Ocean CO<sub>2</sub> survey**

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

TALK was also checked at the crossover locations of two cruises in the same way as TCO<sub>2</sub>. The agreement between the corrected TALK measurements made at the crossover locations ( $\pm 100$  km) on different cruises was examined by assuming that the temporal and spatial variations of the deep-ocean TALK were small relative to measurement accuracy and precision. Hence, deep ocean waters should have the same TALK at different times in the absence of internal vertical motion, and because deep ocean motion probably occurs along constant-density surfaces (isopycnals), the comparisons of TALK measurements were made with reference to density and not depth. [Appendixes C and D](#) give a description of the statistical procedures used to make the crossover comparisons. For water samples collected below 2500 m, a smooth curve was fit through the TALK data as a function of the density anomaly referenced to 3000 dbar ( $\sigma_3$ ) using Cleveland's LOESS smoother (Cleveland and Devlin 1988). A separate fit was performed on the data collected at each of the two intersecting crossover points, with the same tension parameter being used for all of the crossovers so that the smoothing function was consistently applied. The difference between the two smoothed curves was evaluated at 50 evenly-spaced points covering the density range where the two data sets overlapped. Mean and standard deviations for the differences at the 50 points were calculated for each crossover point. For TALK, differences never exceeded 6  $\mu\text{mol/kg}$ , and the overall mean and standard deviation of the differences was 2.1

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

Table 13 is a final summation of the inorganic carbon analytical work completed during the Indian Ocean CO<sub>2</sub> survey from 1994 to 1996.

**Table 13. Final count of carbonate system parameter (CSP) analyses during Indian Ocean CO<sub>2</sub> survey**

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

### 3.4 Carbon Data Synthesis and Analysis

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

### 3.5 Radiocarbon Measurements

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

## 4. DATA CHECKS AND PROCESSING PERFORMED BY CDIAC

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

The following information summarizes the data processing and QA checks performed by CDIAC on the data obtained during the R/V *Knorr* cruise along WOCE Sections I8SI9S, I9N, I8NI5E, I3, I5WI4, I7N, I1, I10, and I2 in the Indian Ocean.

1. The final carbon-related data were provided to CDIAC by the ocean carbon measurement PIs listed in [Table 5](#). The final hydrographic and chemical measurements and the station information files were provided by the WOCE Hydrographic Program Office (WHPO) after quality evaluation. A FORTRAN 90 retrieval code was written and used to merge and reformat all data files.
2. Every measured parameter for each station was plotted vs. depth (pressure) to identify questionable outliers using the Ocean Data View (ODV) software (Schlitzer 2001) Station Mode ([Fig. 3](#)).
3. The section plots for every parameter were generated using the ODV's Section Mode in order to map a general distribution of each property along all Indian Ocean sections ([Fig. 4](#)).
4. To identify "noisy" data and possible systematic, methodological errors, property-property plots for all parameters were generated ([Fig. 5](#)), carefully examined, and compared with plots from previous expeditions in the Indian Ocean.
5. All variables were checked for values exceeding physical limits, such as sampling depth values that are greater than the given bottom depths.
6. Dates, times, and coordinates were checked for bogus values (e.g., values of MONTH < 1 or > 12; DAY < 1 or > 31; YEAR < 1994 or > 1996; TIME < 0000 or > 2400; LATITUDE < -70.000 or > 60.000; LONGITUDE < 19.000 or > 119.000).
7. Station locations (latitudes and longitudes) and sampling times were examined for consistency with maps and cruise information supplied by PIs.
8. The designation for missing values, given as -9.0 in the original files, was changed to -999.9 for the consistency with other oceanographic data sets.

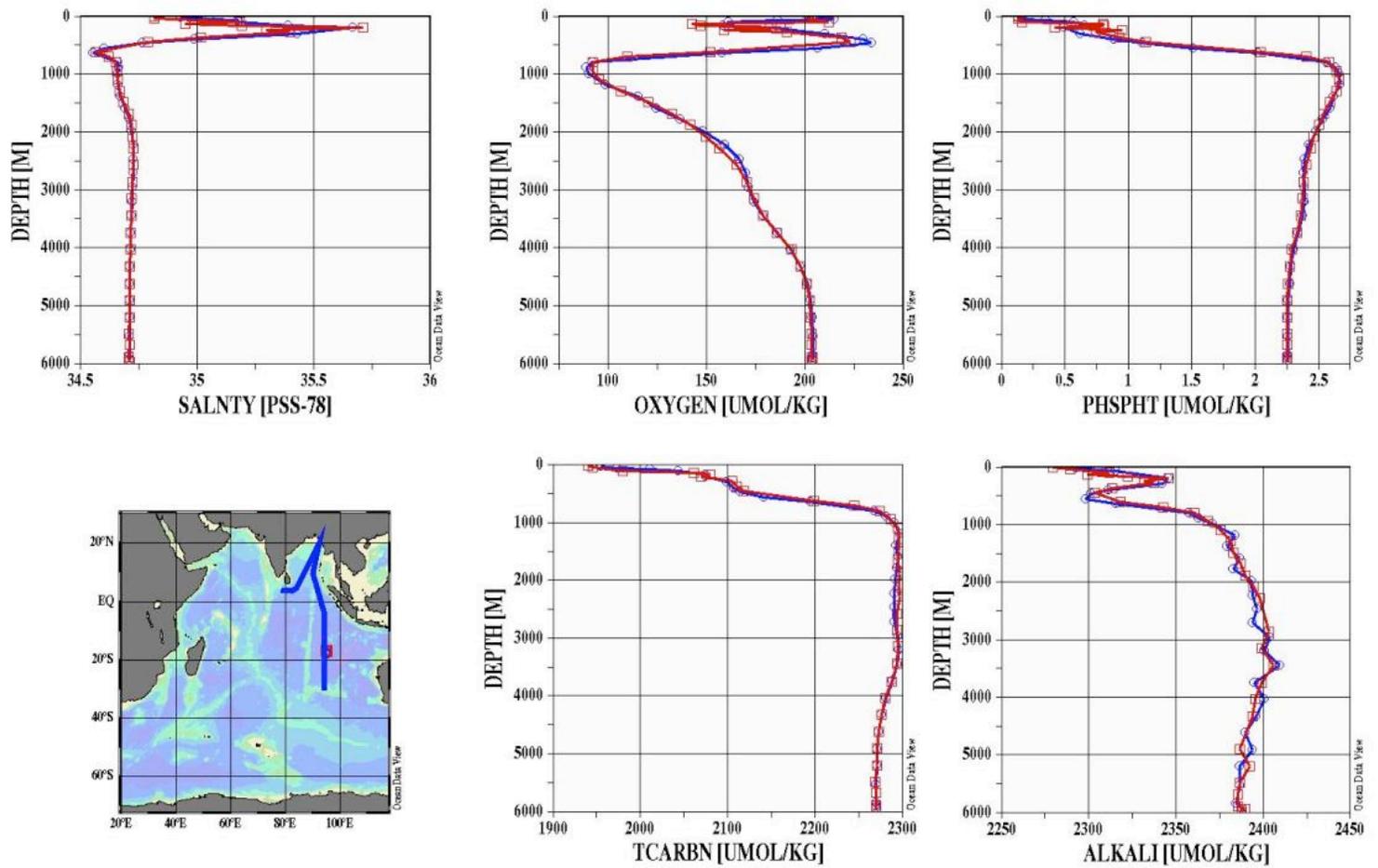


Fig. 3. Example of ODV station mode plot: measurements vs depth for Stations 172-174 of Section I9N

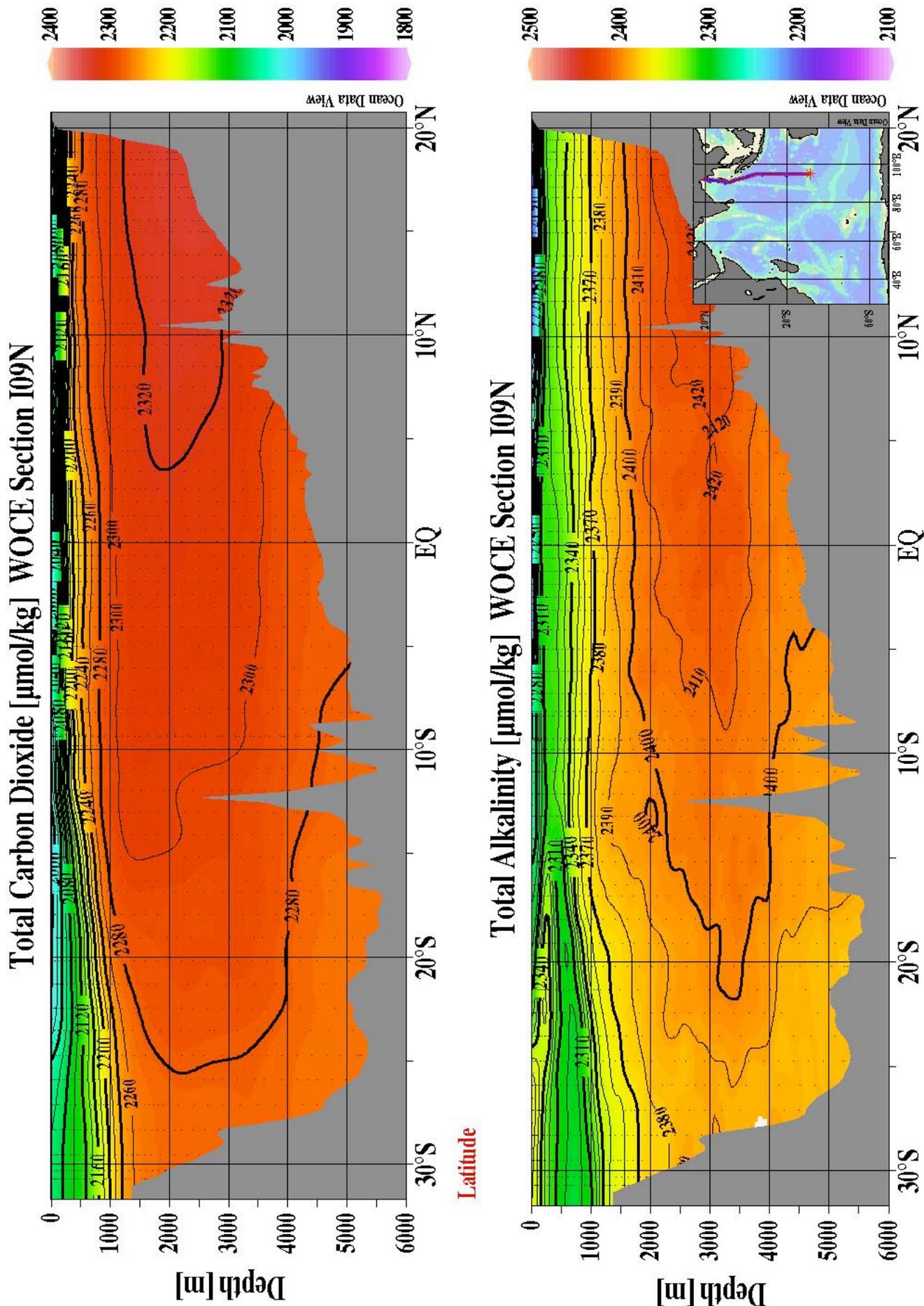


Fig. 4. Distribution of the TCO<sub>2</sub> and TALK in seawater along WOCE Section I09N

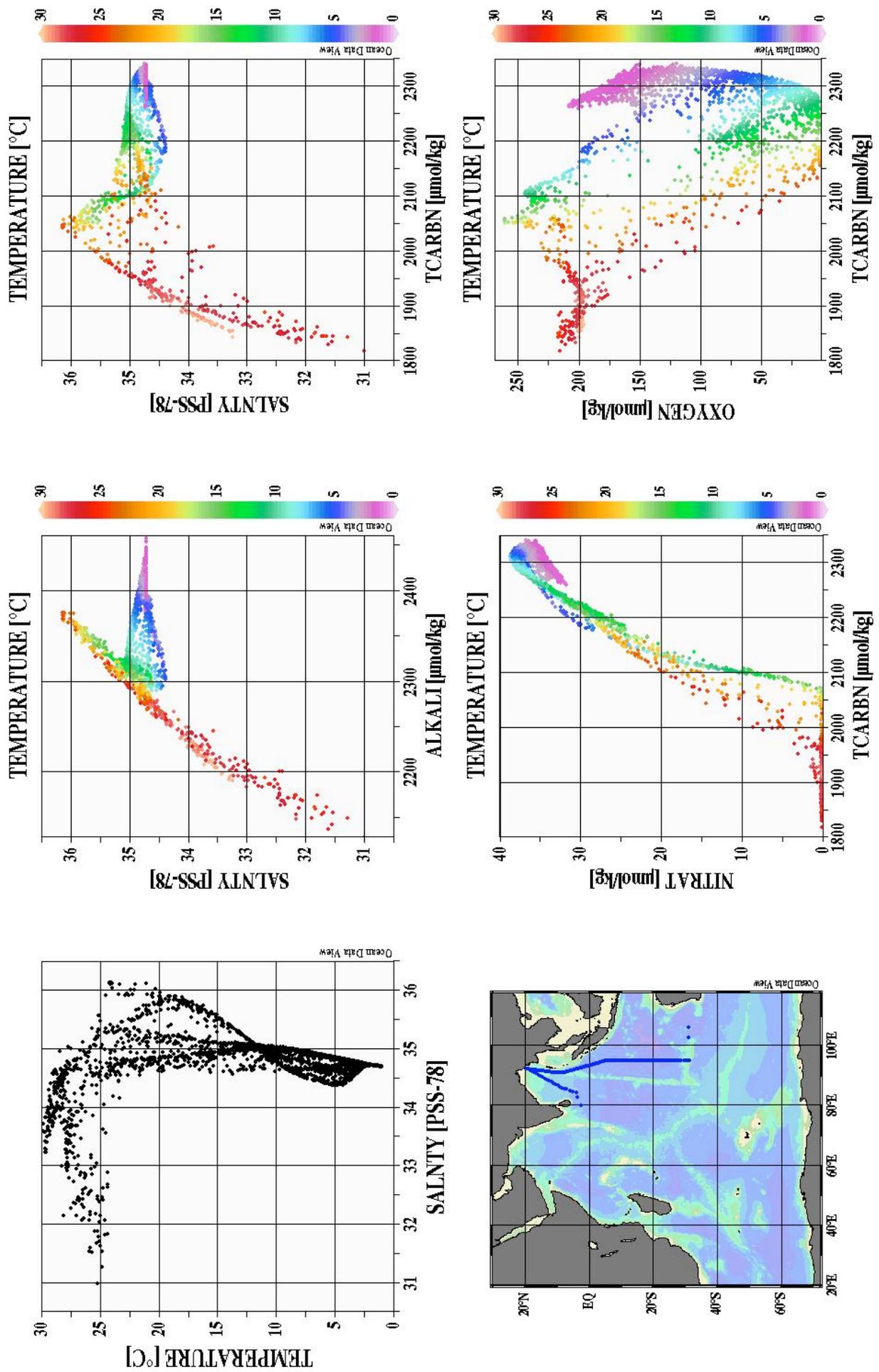


Fig. 5. Property-property plots for all stations occupied during the R/V Knorr cruise along WOCE Section 19N

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**List of CO<sub>2</sub> measurement group members participating in the Indian Ocean CO<sub>2</sub> Survey  
aboard the R/V *Knorr* in 1994–1996**

(CO<sub>2</sub> group leaders for each section are given in [Table 4](#) in the text)

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

Participating institutions:

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

## **APPENDIX B:**

### **REPRINT OF PERTINENT LITERATURE**

Johnson, K. M., A. G. Dickson, G. Eiseid, C. Goyet, P. R. Guenther, R. M. Key, F. J. Millero, D. Purkerson, C. L. Sabine, R. G. Schotle, D. W. R. Wallace, R. J. Wilke, and C. D. Winn. 1998. Coulometric total carbon dioxide analysis for marine studies: Assessment of the quality of total inorganic carbon measurements made during the U.S. Indian Ocean CO<sub>2</sub> Survey 1994–1996. *Marine Chemistry* 63:21–37.

## Coulometric total carbon dioxide analysis for marine studies: assessment of the quality of total inorganic carbon measurements made during the US Indian Ocean CO<sub>2</sub> Survey 1994–1996

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Peter Guenther <sup>b</sup>, Robert M. Key <sup>d</sup>, Frank J. Millero <sup>e</sup>, David Purkerson <sup>e</sup>,  
Christopher L. Sabine <sup>d</sup>, Rolf G. Schottle <sup>f</sup>, Douglas W.R. Wallace <sup>a</sup>,  
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### Abstract

Two single-operator multiparameter metabolic analyzers (SOMMA)-coulometry systems (I and II) for total carbon dioxide (TCO<sub>2</sub>) were placed on board the R/V Knorr for the US component of the Indian Ocean CO<sub>2</sub> Survey in conjunction with the World Ocean Circulation Experiment-WOCE Hydrographic Program (WHP). The systems were used by six different measurement groups on 10 WHP Cruises beginning in December 1994 and ending in January 1996. A total of 18,828 individual samples were analyzed for TCO<sub>2</sub> during the survey. This paper assesses the analytical quality of these data and the effect of several key factors on instrument performance. Data quality is assessed from the accuracy and precision of certified reference material (CRM) analyses from three different CRM batches. The precision of the method was 1.2 μmol/kg. The mean and standard deviation of the differences between the known TCO<sub>2</sub> for the CRM (certified value) and the CRM TCO<sub>2</sub> determined by SOMMA-coulometry were  $-0.91 \pm 0.58$  ( $n = 470$ ) and  $-1.01 \pm 0.44$  ( $n = 513$ ) μmol/kg for systems I and II, respectively, representing an accuracy of 0.05% for both systems. Measurements of TCO<sub>2</sub> made on 12 crossover stations during the survey agreed to within 3 μmol/kg with an overall mean and standard deviation of the differences of  $-0.78 \pm 1.74$  μmol/kg ( $n = 600$ ). The crossover results are therefore consistent with the precision of the CRM analyses. After 14 months of nearly continuous use, the accurate and the virtually identical performance statistics for

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the two systems indicate that the cooperative survey effort was extraordinarily successful and will yield a high quality data set capable of fulfilling the objectives of the survey. © 1998 Elsevier Science B.V. All rights reserved.

**Keywords:** total carbon dioxide (TCO<sub>2</sub>); single-operator multiparameter metabolic analyzers (SOMMA) coulometry; marine studies

## 1. Introduction

Between 1990 and 1997 an international effort was made to determine the global oceanic distribution of inorganic carbon in conjunction with the World Ocean Circulation Experiment (WOCE) Hydrographic Programme (WHP). This effort is referred to as the Global Survey of CO<sub>2</sub> in the oceans, and it is an integral part of the Joint Global Ocean Flux Study (JGOFS). The goals of this survey are to:

1. Accurately determine the oceanic distribution of dissolved inorganic carbon,
2. Quantify the uptake of anthropogenic carbon dioxide by the oceans to better predict future atmospheric carbon dioxide levels,
3. Provide a global description of anthropogenic carbon dioxide in the oceans to aid development of a 3-dimensional model of the oceanic carbon cycle,
4. Characterize the transport of carbon dioxide between the ocean and the atmosphere and the large scale (e.g., meridional) transports of carbon dioxide within the ocean.

The survey has acquired a global data set of profile measurements of dissolved carbon dioxide parameters on both zonal and meridional oceanographic transects throughout the world's oceans. With reference to program goals, Bates et al. (1996) found that for mixed layer waters the average rate of increase in CO<sub>2</sub> concentration due to the uptake of anthropogenic CO<sub>2</sub> was 1.7 μmol/kg/yr (< 0.1%). This rate of increase establishes a natural target for the accuracy of the TCO<sub>2</sub> measurements. The distribution of this 'excess' CO<sub>2</sub> signal is not uniform spatially, and it is masked by variability in CO<sub>2</sub> concentrations arising from natural biological and physicochemical processes. Hence, the goals of the program imply that measurements must be extremely accurate (0.1% or better) and spatially extensive. A large part of the US contribution to this survey has been conducted by a team of investigators supported by the US Department of Energy (DOE). This team has developed certified reference materials (Dickson, 1990), instrumentation (Johnson and Wallace, 1992),

a set of standard operating procedures (DOE, 1994) and, to a large extent, shared a common approach to the measurement program.

This paper presents the DOE team effort which sampled the Indian Ocean for inorganic carbon during the course of approximately 1 year. All the measurements were made aboard a single research vessel during sequential cruises which allowed the investigators to share equipment and procedures to an unprecedented extent. This paper concentrates on estimating the accuracy of the shipboard determinations of the total dissolved inorganic carbon concentration of seawater. This parameter was established at the onset of the survey as the primary carbonate system parameter because its concentration should change in response to anthropogenic CO<sub>2</sub> uptake and it had the highest potential for measurement accuracy. Our results highlight some factors which affect the accuracy of this measurement. The Indian Ocean Survey aboard the R/V Knorr encompassed the cruise legs shown in Fig. 1 in the sequence given in Table 1. Fig. 1 also gives the location of the crossover

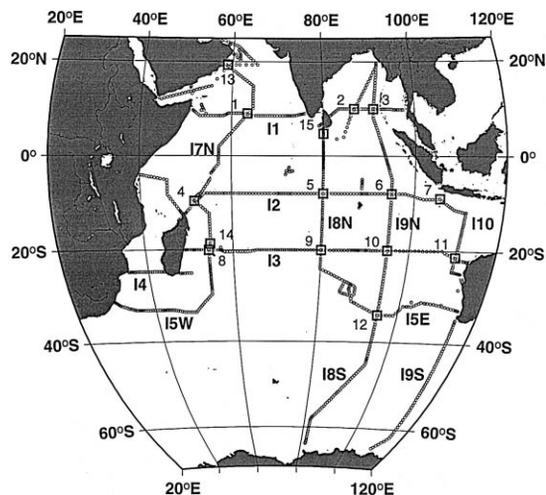


Fig. 1. The cruise tracks for the nine legs of the US Indian Ocean WOCE Survey 1994–1996. Crossover points between the various legs are marked with a square and numbered. These intersection points and crossovers are referred to in Table 4.

Table 1

Approximate dates and ports of call for the 9 legs of the Indian Ocean CO<sub>2</sub> Survey, and the measurement groups responsible for the determination of the carbonate system parameters

Leg	Dates		From	To	Group	Duration (days)
	Start	End				
I8SI9S	12/1/94	1/19/95	Fremantle	Fremantle	BNL	50
I9N	1/24/95	3/6/95	Fremantle	Colombo	Princeton U.	42
I8NI5E	3/10/95	4/16/95	Colombo	Fremantle	U. of Hawaii	38
I3	4/20/95	6/7/95	Fremantle	Port Louis	U. of Miami	49
I5WI4	6/11/95	7/11/95	Port Louis	Port Louis	BNL	31
I7N	7/15/95	8/24/95	Port Louis	Matrah	U. of Hawaii	41
I1	8/29/95	10/18/95	Matrah	Singapore	WHOI	51
Dry Dock	10/19/95	11/5/95	Singapore			17
I10	11/6/95	11/24/95	Singapore	Singapore	Princeton U.	19
I2	11/28/95	1/19/96	Singapore	Mombasa	U. of Hawaii	53

Abbreviations: BNL, Brookhaven National Laboratory; U, University; WHOI, Woods Hole Oceanographic Institution.

points (cruise track intersections) where comparisons of the reproducibility of the TCO<sub>2</sub> analyses were made. The six survey groups measured two water column carbonate system parameters, total dissolved carbon dioxide (TCO<sub>2</sub>) and total alkalinity (TA), and assisted with the operation of an underway pCO<sub>2</sub> (surface) system. This paper focuses on TCO<sub>2</sub> by coulometry, while the total alkalinity (TA) and partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) measurements are the subject of companion papers and reports (Millero et al., 1998; Sabine and Key, 1998).

## 2. Materials and methods

### 2.1. Preparations

The total carbon dioxide concentration (TCO<sub>2</sub>) was determined using two single-operator multiparameter metabolic analyzers (SOMMA) each connected to a Model 5011 coulometer (UIC, Joliet, IL 60434). Descriptions of the SOMMA-coulometer system and its calibration can be found in the works of Johnson (1995), Johnson and Wallace (1992), and Johnson et al. (1987, 1993). A schematic diagram of the SOMMA is shown in Fig. 2, and further details concerning the coulometric titration can be found in the works of Huffman (1977) and Johnson et al. (1985). Briefly, seawater fills an automated to-deliver sample pipette. The contents of the pipette are

pneumatically injected into a stripping chamber containing approximately 1.2 cm<sup>3</sup> of 8.5% (v/v) phosphoric acid, and the resultant CO<sub>2</sub> is extracted, dried, and coulometrically titrated. Calibration is performed by titrating known masses of pure CO<sub>2</sub> and checked by analyzing certified reference material (CRM). The coulometers were adjusted to give a maximum titration current of 50 mA, and they were run in the counts mode (the number of pulses or counts generated by the coulometer's voltage to frequency converter during the titration is displayed). In the coulometer cell, the acid (hydroxyethylcarbamic acid) formed from the reaction of CO<sub>2</sub> and ethanolamine is titrated coulometrically (electrolytic generation of OH<sup>-</sup>) with photometric endpoint detection. The systems were equipped with conductance cells (Model SBE-4, Sea-Bird Electronics, Bellevue, WA) for measuring salinity as described by Johnson et al. (1993).

The DOE supported the construction of nine SOMMA-coulometer systems for the US CO<sub>2</sub> Survey Measurement Groups in the early 1990's (Johnson and Wallace, 1992), and two of these systems from the DOE instrument pool were set up aboard the R/V Knorr in Fremantle, Australia on November 28, 1994. Before they were shipped to Australia, the temperature sensors were calibrated, the glassware was chemically cleaned and gravimetrically calibrated, the gas sample loop volumes were calibrated according to the procedure of Wilke et al. (1993), the coulometers were electronically cali-

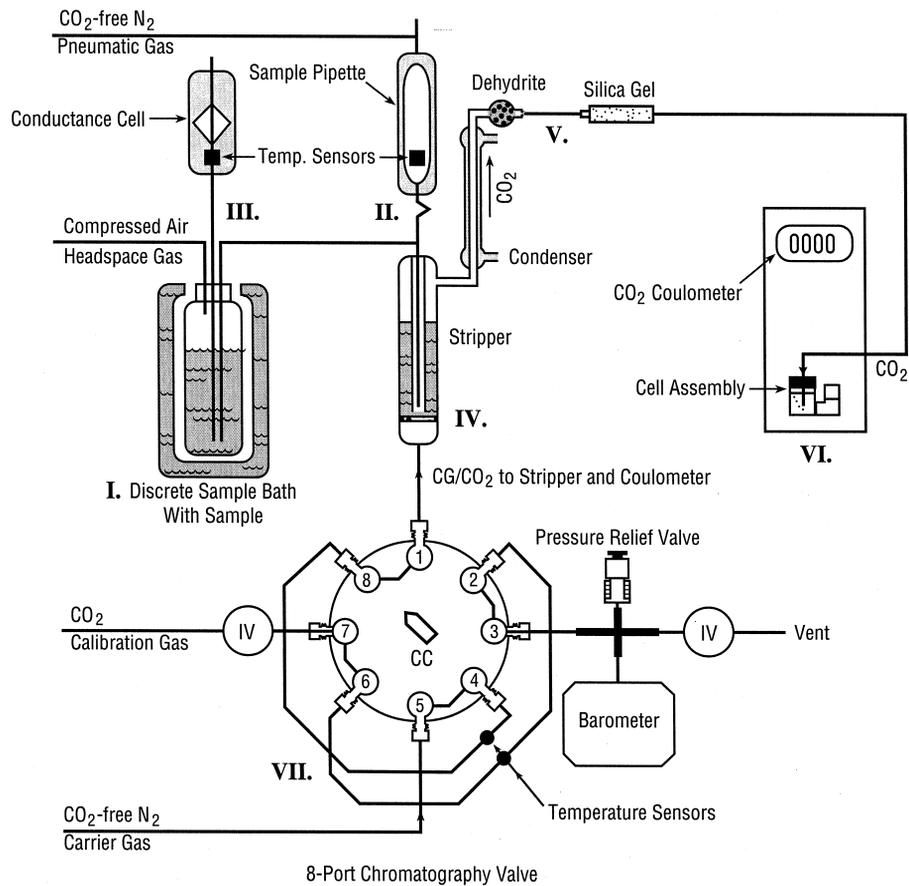


Fig. 2. SOMMA-coulometer system schematic. Carbon dioxide extracted from a water sample (I) or from volume-calibrated gas sample loops filled at a known pressure and temperature is degassed from the stripper (IV), dried (V), and coulometrically titrated (VI). The water sample is pneumatically injected from the pipette (II) into the stripper, and the pure CO<sub>2</sub> contained in the gas loops is delivered to the stripper from an 8-port chromatography valve (VII) equipped with pressure and temperature sensors. Salinity is measured using a conductance cell (III) integrated into the SOMMA chassis. The pipette and conductance cell are thermostatted and equipped with temperature sensors.

brated (Johnson et al., 1993; DOE, 1994), and system accuracy was verified with CRM at Brookhaven National Laboratory (BNL). The same two systems (hereafter called I and II) were used by all measuring groups. A backup system (from Woods Hole Oceanographic Institution) was onboard but was not used. Pre-cruise preparations also included a training session for participants at the University of Miami in September 19–23, 1994.

Referring to Fig. 2, the analytical gases included UHP nitrogen (99.998%) for carrier and pneumatic gases, compressed air for the headspace gas, and analytical grade CO<sub>2</sub> (99.995%) from Scott Special-

ity Gases (South Plainfield, NJ) for the calibration gas. The survey began with the use of compressed gases, but prior to leg I8N in April 1995, a N<sub>2</sub> generator (TOC Model 1500, Peak Scientific, Chicago, IL) was placed into service. The generator provided N<sub>2</sub> (99.9995%, hydrocarbons < 0.1 ppm, CO<sub>2</sub> < 1.0 ppm) for carrier and pneumatic gases to both systems for the remainder of the survey. Unless otherwise stated, all other reagents remain as described by Johnson et al. (1993).

The BNL measurement group supplied 7 side-arm type glass titration cells (UIC, PN 200-034), 7 silver electrodes (PN 101-033), and 5 rubber cell

caps (PN 192-005). A platinum electrode (PN 101-034), temperature sensor (PN LM34CH, National Semiconductor, Santa Clara, CA), and a teflon inlet tube were mounted in each cap. Together, the cell and cap comprise the cell assembly shown in Fig. 3. For this paper, each cell assembly is assigned an ‘age’ or lifetime which is measured in minutes (chronological age) or by the mass of carbon titrated in mg C (carbon age) from the time when current is first applied to the assembly (cell birth) until the current is turned off (cell death). The software continuously records the chronological and carbon ages.

## 2.2. Selection of cell assemblies

The performance of individual cell assemblies (Fig. 3) varies widely (K.M. Johnson, unpublished data). Unacceptable assemblies exhibit high blanks, prolonged blank determinations (> 2 h), reduced accuracy or precision, or become noisy early in their lifetime. Acceptable assemblies stabilize quickly

(within 60 min) and function well for periods exceeding 24 h. Cell behavior will be discussed elsewhere, but our experience suggests several factors play a role: quality of the reagents; quality (purity) of the carrier gases; damage to the platinum electrode; and perhaps the porosity of the cell frit. Therefore, a systematic effort was made at the beginning of leg I8SI9S to select satisfactorily performing cell assemblies using pretested reagents and carrier gas sources known to be uncontaminated. During this first leg, the assemblies on hand were evaluated for conformance to the following empirical criteria.

(1) Cell assemblies should attain a blank of  $\leq 0.005 \mu\text{mol C}/\text{min}$  within 90 min of cell birth. Satisfactory assemblies usually exhibit a 15–25% decline in the blank with each successive determination.

(2) The gas calibration factor, which is the ratio of an accurately known mass of  $\text{CO}_2$  to the mass of this gas determined coulometrically, should be  $1.004 \pm 0.0015$  (recoveries of  $\sim 99.6\%$ ).

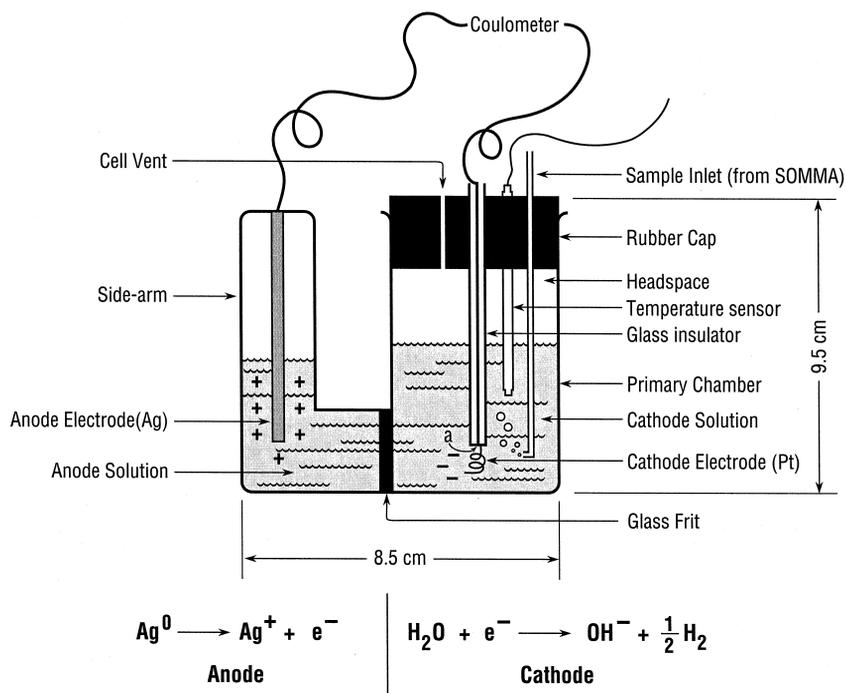


Fig. 3. The titration cell assembly and the cathodic and anodic half reactions for the coulometric titration of the  $\text{H}^+$  from the acid formed by the reaction of  $\text{CO}_2$  and ethanolamine.

(3) Titrations of  $\text{CO}_2$  extracted from gas sample loops (gas calibration) or pipettes of  $20 \text{ cm}^3$  (sample analysis) should take 9–12 min.

(4) Cell assemblies, which repeatedly exhibit titrations longer than 20 min (no endpoint) before their carbon age reached 30 mg C titrated, were considered defective. An occasional failure to attain an endpoint after the carbon age exceeds 30 mg C was interpreted to mean that the cell frit required cleaning with 6 N  $\text{HNO}_3$  and retesting.

Based on these criteria, three assemblies (2 primary and a third as backup) were found to be acceptable during the first leg, and these assemblies were used throughout the survey (at the midpoint of the survey an additional assembly was placed into service).

### 2.3. At-sea operations

The following  $\text{TCO}_2$  sampling and measurement practices were followed throughout the survey.

(1) The daily sequence of analytical operations for each system as described in the SOMMA operator's manual (Johnson, 1995) consisted of changing the cells and drying agents, determining the blank, running test seawater samples, calibrating the system using pure  $\text{CO}_2$  (gas calibration), analyzing samples, and analyzing certified reference material (CRM) at the beginning and end of the cell lifetime.

(2) A complete deep vertical profile for  $\text{TCO}_2$  and TA consisted of 36 samples. A lesser number of samples were drawn at shallower stations. Complete profiles were taken at every other station, and if time permitted, additional truncated profiles (0–1000 m) were taken.  $\text{TCO}_2$  samples always coincided with  $^{14}\text{C}$  samples. Samples were drawn from 10-l Niskin bottles according to DOE (1994).

(3) Samples for  $\text{TCO}_2$  were collected in  $300 \text{ cm}^3$  BOD-type glass bottles. They were poisoned with a saturated  $\text{HgCl}_2$  solution (200–400  $\mu\text{l}$ ) upon collection. The appropriate correction factors for dilution were applied by the measurement groups according to DOE (1994).

(4) Sample bottles were rinsed and then allowed to overflow by at least 1/2 volume before poisoning. Prior to April 1995, a glass stopper was inserted into the full BOD bottle. After April 1995, a headspace of approximately  $4 \text{ cm}^3$  was created be-

fore poisoning and stoppering. This was done in a reproducible manner by squeezing the filling tube shut before withdrawing it from the bottle. This change was made to ensure that no  $\text{HgCl}_2$  was displaced by the stopper, and to allow for water expansion. The gas–liquid phase ratio was approximately 1.3%. A correction ( $\pm 0.5 \mu\text{mol}/\text{kg}$ ) for the reequilibration of the liquid with the gas phase was applied by the measurement groups according to DOE (1994).

(5) To estimate sample precision, duplicate samples were normally collected at surface, mid depth, and at the deepest depth. The duplicate analyses were interspersed with the analysis of the other profile samples with a minimum of 2 h and up to 12 h between duplicate analyses. Because the duplicate analyses were separated in time, these data could potentially detect drift (decreased precision) as the cell aged. Every effort was made to run each station profile on a single cell assembly, and to limit the cell lifetime to  $\leq 35 \text{ mg C}$ .

(6) Although salinity was determined by the SOMMA-coulometer systems, post-cruise sample density was calculated using bottle salinities supplied by the chief scientists. However, SOMMA-based salinities were often compared to the real-time CTD salinities to spot bottle mistrips during the taking of the vertical profiles. The agreement between SOMMA-based and CTD salinities was  $\pm 0.02$  or better.

(7) To monitor the volume of the SOMMA pipettes, they were periodically filled with deionized water at known temperatures, and their output collected in preweighed serum bottles. The bottles were sealed immediately and stored until they were reweighed at BNL on a model R300S (Sartorius, Göttingen, Germany) balance. The mass of water corrected for buoyancy was used to calculate the to-deliver pipette volume ( $V_{\text{cal}}$ , Eq. (3)) according to DOE (1994).

(8) After use, cells were cleaned with deionized water followed by an acetone rinse of the glass frit. Before reuse, they were dried at  $55^\circ\text{C}$  for at least 12 h. Cell caps and the platinum electrodes were thoroughly washed with deionized water and dried at  $55^\circ\text{C}$  for at least 6 h before reuse.

(9) Duplicate samples from approximately 3000 m and 20 m were regularly collected for shore-based

reference analyses of TCO<sub>2</sub> by vacuum extraction/manometry by C.D. Keeling at the Scripps Institution of Oceanography (SIO). Between 2 and 5% of the samples analyzed at sea will be analyzed at SIO and reported elsewhere.

#### 2.4. Calculation of results

For the coulometric determination, the mass of carbon titrated from CO<sub>2</sub> extracted from the gas sample loops or a water sample in μmol of carbon is given by  $M$  according to:

$$M = [\text{Counts}/4824.45 - (\text{Blank} \times t_i) - (\text{Int}_{\text{ec}} \times t_i)] / \text{Slope}_{\text{ec}}, \quad (1)$$

where Counts is the coulometer display, i.e., the number of pulses accumulated by the coulometer's voltage to frequency circuit (VFC); 4824.45 (counts/μmol) is a scaling factor derived from the factory calibration of the VFC and the value of the Faraday (96,485.309 C/mol); Blank is the system blank in μmol/min;  $t_i$  is the length of the titration in minutes;  $\text{Int}_{\text{ec}}$  is the intercept from the electronic calibration of the coulometer;  $t_i$  is the duration (min) of continuous current flow, and  $\text{Slope}_{\text{ec}}$  is the slope from electronic calibration (Johnson et al., 1993; DOE, 1994). Electronic calibration serves as a check of the factory calibration. If the coulometer was perfectly calibrated, the slope and intercept would be 1 and 0, respectively. Typically, minor deviations from the theoretical slope (0.998–0.999) and intercept (0.001–0.01) are observed. The water sample TCO<sub>2</sub> concentration in μmol/kg is calculated from:

$$\text{TCO}_2 = M \times \text{Calibration Factor} \times (1/(V_T p)) D + \Delta\text{TCO}_2, \quad (2)$$

where  $V_T$  is the sample volume (to-deliver volume of the SOMMA pipette) calculated from:

$$V_T = V_{\text{cal}} [1 + a_v (T - T_{\text{cal}})], \quad (3)$$

and  $T$  is the analytical temperature;  $V_{\text{cal}}$  is the calibrated volume of the pipette at the calibration temperature,  $T_{\text{cal}}$ ;  $a_v$  is the coefficient of volumetric expansion for Pyrex glass ( $1.0 \times 10^{-5}/\text{deg}$ ). In Eq. (2), Calibration Factor is the gas calibration factor (see Eq. (4));  $p$  is the density of seawater from the seawater equation of state (Millero and Poisson,

1981) at the sample salinity and  $T$ ;  $D$  is the correction due to dilution of the sample with HgCl<sub>2</sub> preservative;  $\Delta\text{TCO}_2$  is the correction for the repartitioning of CO<sub>2</sub> into the sample headspace according to DOE (1994). Note that correction factors  $D$  and  $\Delta\text{TCO}_2$  (Eq. (2)) are not incorporated into the SOMMA software and were applied post cruise by the individual measurement groups.

The gas calibration factor (Calibration Factor) is the ratio of:

$$M_{\text{calc}}/M, \quad (4)$$

where  $M_{\text{calc}}$  is the mass of CO<sub>2</sub> contained in the gas sample loop calculated according to DOE (1994), and  $M$  is the coulometric determination of that same mass from Eq. (1).

#### 2.5. Assessment of analytical accuracy

Analytical accuracy was assessed by analyzing certified reference materials (CRMs). The CRMs are filtered seawater poisoned with HgCl<sub>2</sub>. They are prepared in 500 cm<sup>3</sup> bottles at the Scripps Institution of Oceanography (SIO) according to procedures given by Dickson (1990). The certified TCO<sub>2</sub> value is obtained by analyzing a representative number of samples by vacuum extraction/manometry in the laboratory of C.D. Keeling at SIO. For this paper, the term analytical difference refers to the difference between the analyzed (by coulometry) and the certified value of the CRM (by manometry), i.e., at-sea accuracy is estimated from the analyzed TCO<sub>2</sub>-certified TCO<sub>2</sub> differences.

#### 2.6. Data distribution

The complete data set has been submitted to the Carbon Dioxide Information Analysis Center (CDIAC) at the Oak Ridge National Laboratory (ORNL). CDIAC will issue a final data report which will detail the procedures for retrieving the data. The overall accuracy given below is considered final at this time, and the estimated precision is expected to remain unchanged. The CDIAC web address is <http://cdiac.esd.ornl.gov>.

### 3. Results

During the survey, approximately 18,828 separate samples (not counting duplicates) for  $\text{TCO}_2$ , and 983 CRM were analyzed on the two systems (A. Kozyr, personal communication, November 1997).

#### 3.1. To-deliver pipette volume

Some 103 gravimetric determinations of the sample pipette volume were made on 28 separate occasions during the survey (14 on each system). Four of the determinations were rejected; two because they were exactly  $1 \text{ cm}^3$  too high with respect to the survey mean (likely due to failure to correctly note the tare weight determined prior to the cruise), and

two because they were inexplicably 0.3% lower than the survey mean volumes (probably due to faulty sealing and evaporation). There were no results from leg I8N because the gravimetric samples were collected incorrectly. Volume determinations should have been made at the start, middle, and at the end of each leg, or at least at the beginning and end of each leg. However, for a variety of reasons, this was not always the case. In order to consistently assign a pipette volume to each leg, a leg-specific volume ( $V_{\text{cal}}$ ) was obtained by averaging the volume determinations made closest to the beginning and end of the leg along with any made during that leg. Table 2 presents the results for  $V_{\text{cal}}$ , and the chronological order of the pipette determinations used to calculate  $V_{\text{cal}}$  are plotted in Fig. 4a for system I and Fig. 4b for

Table 2

The leg-specific to-deliver pipette volume ( $V_{\text{cal}}$ ) and the calibration temperature ( $T_{\text{cal}}$ ) for SOMMA-coulometer systems I and II during the Indian Ocean Survey 1994–1996

Leg	<i>n</i>	$V_{\text{cal}}$ ( $\text{cm}^3$ )	S.D. ( $\pm \text{cm}^3$ )	R.S.D. (%)	$T_{\text{cal}}$ (C)	Determinations averaged (legs)
<i>System I</i>						
I8S19S	2	21.4609	0.0037	0.02	20.00	see text, 8S9S <sub>e</sub>
I9N	9	21.4543	0.0112	0.05	20.97	8S9S <sub>e</sub> , 9N <sub>e</sub>
Gas generator introduced as CG source						
I8N15E	9	21.4443 *	0.0021	0.01	20.97	9N <sub>e</sub> , 3 <sub>m</sub>
I3	15	21.4471	0.0042	0.02	20.57	9N <sub>e</sub> , 3 <sub>m</sub> , 4 <sub>s</sub>
Gas generator output pressure adjusted from 5 to 10 psi						
I5W14	10	21.4506 *	0.0023	0.01	19.93	5W4 <sub>s,e</sub>
I7N	8	21.4506	0.0032	0.02	20.36	7N <sub>s,m,e</sub>
I1	5	21.4462	0.0074	0.03	20.12	7N <sub>e</sub> , 1 <sub>e</sub>
Pipette dismounted, cleaned, and recalibrated						
I10	5	21.4460	0.0110	0.05	20.08	10 <sub>e</sub>
I12	8	21.4482	0.0091	0.04	20.08	10 <sub>e</sub> , 2 <sub>s,e</sub>
<i>System II</i>						
I8S19S	18	21.6388	0.0068	0.03	20.24	8S9S <sub>s,e</sub>
I9N	9	21.6360	0.0163	0.08	20.49	8S9S <sub>e</sub> , 9N <sub>e</sub>
Gas generator introduced as CG source						
I8N15E	8	21.6239	0.0080	0.04	20.56	9N <sub>e</sub> , 3 <sub>m</sub>
I3	14	21.6243	0.0068	0.03	20.31	9N <sub>e</sub> , 3 <sub>m</sub> , 4 <sub>s</sub>
Gas generator output pressure adjusted from 5 to 10 psi						
I5W14	11	21.6293	0.0068	0.03	19.97	5W4 <sub>s,e</sub>
I7N	8	21.6194 *	0.0048	0.02	20.05	7N <sub>s,m,e</sub>
I1	4	21.6156	0.0035	0.02	20.00	7N <sub>e</sub> , 1 <sub>e</sub>
Pipette dismounted, cleaned, and recalibrated						
I10	4	21.6269 *	0.0017	0.01	19.95	10 <sub>e</sub>
I12	9	21.6270	0.0028	0.01	19.94	10 <sub>e</sub> , 2 <sub>s,e</sub>

The subscripts (s, m, or e) for the pipette volume determinations averaged to calculate  $V_{\text{cal}}$  signify determinations made at the start, middle, or end of a leg, respectively. Values of  $V_{\text{cal}}$  which are significantly different from the  $V_{\text{cal}}$  of the preceding leg are denoted by the asterisk.

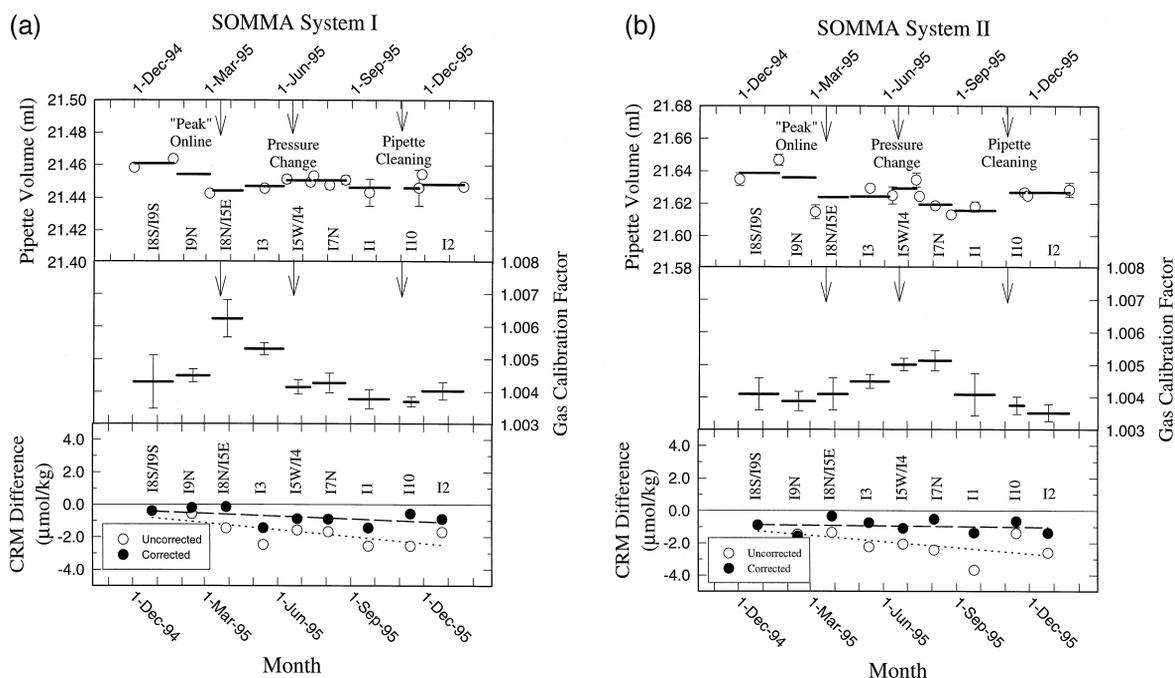


Fig. 4. The temporal record of the analytical performance of SOMMA-coulometer system I (Fig. 4a) and II (Fig. 4b) during the Indian Ocean Survey 1994–1996. The top section of the three-part graphs shows the leg-specific pipette volumes,  $V_{\text{cal}}$ , as horizontal lines corresponding to the duration of the individual legs, and the relative chronological order of the means of the individual pipette determinations from which  $V_{\text{cal}}$  was calculated as open circles placed before, in the middle of, or following the horizontal lines representing  $V_{\text{cal}}$  (see text and Table 2 for details). The middle section depicts the mean gas calibration factors for each leg (horizontal lines), and the bottom section shows the mean analytical differences for the CRM analyses assuming a constant pipette volume ( $V_{\text{cal}}$  for leg I8S) for the duration of the survey (open circles) vs. the leg-specific  $V_{\text{cal}}$  (closed circles). The error bars through the plot symbols represent the S.D. of the determinations. Procedural changes (introduction of the gas generator, pressure adjustments, and cleaning) which may have affected pipette volume are indicated by the arrows.

system II. This averaging increases the number of determinations used to calculate  $V_{\text{cal}}$ , and ensures that  $V_{\text{cal}}$  is based on at least two sets of determinations, separated in time, for all legs except the initial leg (I8SI9S) and leg I10 after the pipette was cleaned. Table 2 and Fig. 4a and b show the timing of events which could conceivably have affected pipette volume. For I8SI9S, the pipette volumes were determined in the laboratory prior to the cruise; however, the volume of system I had to be empirically redetermined at-sea because its pipette was broken during transit. This was done as follows: after replacing the pipette,  $V_{\text{cal}}$  was determined by simultaneously analyzing a replicate from a single seawater sample on systems I and II. Because  $V_{\text{cal}}$  was well known for system II, the  $\text{TCO}_2$  concentration determined on system II was used to calculate the pipette volume of

system I by rearranging Eq. (2) to solve for  $V_{\text{T}}$  and letting  $V_{\text{T}}$  be equal to  $V_{\text{cal}}$  for the subsequent analyses on system I during leg I8SI9S. As Table 2 shows, numerous volume determinations were made for both systems I and II on succeeding legs.

For I10, data from the prior leg could not be used to calculate  $V_{\text{cal}}$  because leg I10 took place after the pipettes had been dismantled for cleaning, which may have altered their volumes. On legs I5WI4 and I7N, replicate volume determinations were made at the beginning, middle, and end of the leg by the same measuring group so that  $V_{\text{cal}}$  for these legs do not include results from preceding or succeeding legs. The survey mean pipette volumes and their standard deviations for systems I and II are  $21.4502 \pm 0.0032 \text{ cm}^3$  at  $20.25^\circ\text{C}$  ( $n = 43$ ) and  $21.6261 \pm 0.0028 \text{ cm}^3$  at  $20.14^\circ\text{C}$  ( $n = 56$ ), respectively. The

pooled standard deviation ( $sp^2$ ) calculated according to Youden (1951) for the 28 sets of gravimetric determinations is  $\pm 0.0042 \text{ cm}^3$ . Individually,  $sp^2$  for system I is  $\pm 0.0049 \text{ cm}^3$ , and for system II  $sp^2$  is  $\pm 0.0036 \text{ cm}^3$ , suggesting a very slightly higher precision for system II.

Significant differences at the 95% confidence level in  $V_{\text{cal}}$  for comparisons between each leg with the succeeding leg were determined by two-tailed *t*-tests according to Taylor (1990), and are denoted by asterisks in Table 2. For the most part, leg to leg

differences in  $V_{\text{cal}}$  are not significant (significance in 2 of 9 comparisons for each instrument), but it should be noted that for both systems, the differences between the initial leg (I8SI9S) pipette volumes and all leg-specific volumes after leg I9N are significant. In both systems, the to-deliver pipette volume declines slightly with time. However, the decline is not consistent between instruments. In system I, significant decreases in volume appear earlier in the survey and may be correlated with the switch to the  $N_2$  generator and a documented generator outlet pres-

Table 3

A summary of the mean analytical parameters and mean analytical differences for the three batches of CRM analyzed on SOMMA-coulometer systems I and II during the Indian Ocean Survey 1994–1996

Leg	Slope <sub>ec</sub>	Int <sub>ec</sub>	Calfactor	CRM (batch)	Precision, <i>n</i> ( $\pm \mu\text{mol/kg}$ )	Analytical difference const-vp/corr-vp
<i>System I</i>						
I8SI9S	1.0002	0.0008	1.0043	23	1.15 (54)	−0.41/−0.41
I9N	1.0007	0.0013	1.0045	23	0.86 (71)	−0.83/−0.20
I8NI5E <sup>a</sup>	1.0007	0.0013	1.0062	23	1.36 (55)	−1.71/−0.15
I3	1.0007	0.0013	1.0053	23	0.98 (37)	−2.33/−1.31
I3	1.0007	0.0013	1.0053	26	0.98 (20)	−2.77/−1.72
I5WI4 <sup>b</sup>	0.9998	−0.0057	1.0041	26	1.31 (41)	−1.83/−0.88
I7N	0.9998	−0.0057	1.0043	23	1.71 (6)	−1.66/−0.69
I7N	0.9998	−0.0057	1.0043	26	1.88 (55)	−1.74/−0.78
I7N	0.9998	−0.0057	1.0043	27	0.88 (8)	−2.91/−1.95
I1	0.9998	−0.0057	1.0038	27	1.10 (64)	−2.82/−1.45
I10 <sup>c</sup>	0.9998	−0.0057	1.0037	27	0.72 (32)	−0.58/−0.58
I2	0.9998	−0.0057	1.0040	27	1.11 (27)	−0.57/−0.77
Mean			1.0045		1.17 (470)	−1.68/−0.91
S.D. ( $\pm$ )			0.0008		0.35	0.92/0.58
<i>System II</i>						
I18SI9S	0.9996	−0.0025	1.0041	23	1.18 (104)	−0.89/−0.89
I9N	0.9996	−0.0025	1.0039	23	0.90 (70)	−1.83/−1.57
I8NI5E <sup>a</sup>	0.9996	−0.0025	1.0041	23	1.14 (59)	−1.73/−0.35
I3	0.9996	−0.0025	1.0045	23	0.85 (35)	−2.14/−0.62
I3	0.9996	−0.0025	1.0045	26	0.69 (13)	−2.44/−1.11
I5WI4 <sup>b</sup>	0.9998	0.0045	1.0050	26	0.79 (41)	−2.14/−1.28
I7N	0.9998	0.0045	1.0051	23	0.88 (5)	−3.25/−1.47
I7N	0.9998	0.0045	1.0051	26	0.84 (54)	−2.09/−0.32
I7N	0.9998	0.0045	1.0051	27	0.77 (10)	−2.88/−1.10
I1	0.9998	0.0045	1.0041	27	1.11 (70)	−3.51/−1.38
I10 <sup>c</sup>	0.9998	0.0045	1.0038	27	0.65 (28)	−0.66/−0.66
I2	0.9998	0.0045	1.0035	27	1.11 (24)	−1.38/−1.39
Mean			1.0042		0.91 (513)	−2.08/−1.01
S.D. ( $\pm$ )			0.0005		0.18	0.87/0.44

For each CRM batch analyzed, precision is given as the standard deviation of the mean of (*n*) analyses. Abbreviations: ec, electronic calibration; calfactor, gas calibration factor; Int, intercept; const-vp, mean analytical difference calculated using a constant pipette volume; corr-vp, mean analytical difference calculated using the leg-specific  $V_{\text{cal}}$  (Table 2).

<sup>a</sup>Gas Generator introduced as CG source.

<sup>b</sup>Gas generator output pressure adjusted from 5 to 10 psi.

<sup>c</sup>Pipette dismantled, cleaned and recalibrated.

sure adjustment, but this is not the case with system II where dismantling and cleaning of the pipette late in the survey may have had the greatest effect.

### 3.2. CRM analyses and system accuracy

In addition to the leg-specific pipette volumes, Fig. 4a (system I) and Fig. 4b (system II) show the mean analytical differences (analyzed  $\text{TCO}_2$ -certified  $\text{TCO}_2$ ) and the mean gas calibration factors for each survey leg. The plots are scaled so that each Y-axis spans a similar range in order that the factors controlling system accuracy can be more readily identified. These data are also tabulated and summarized in Table 3. Table 3 shows that the gravimetric volume determinations (Table 2) have detected real changes in  $V_{\text{cal}}$  during the survey. The mean analytical differences calculated with the corrected pipette volumes (corr-vp, Table 3) are  $-0.91$  and  $-1.01$   $\mu\text{mol}/\text{kg}$  for systems I and II, respectively. If the pipette volumes determined at the beginning of the survey (const-vp) were used, the corresponding differences would be  $-1.61$  and  $-2.08$   $\mu\text{mol}/\text{kg}$ , showing that the routine determination of pipette volume increased accuracy by a factor of  $\sim 2$ .

Fig. 5 is a bar chart of the mean analytical difference (accuracy) for systems I and II as a function of cell carbon age. Both systems behave very

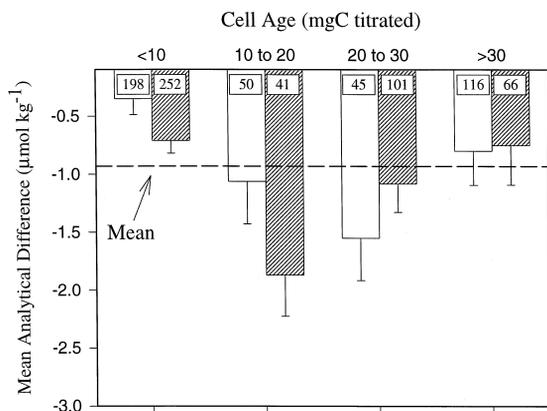


Fig. 5. A plot showing the distribution of mean analytical differences for CRM analyses vs. coulometer cell age for SOMMA-coulometer systems I (open bars) and II (filled bars) during the Indian Ocean Survey 1994–1996. The error bars represent the 95% confidence interval for the mean differences, and the numbers inside the columns are the number of measurements ( $n$ ) used to compute the means.

similarly with the best precision and accuracy early in the cell lifetime ( $< 10$  mg C), increasing differences for cells of intermediate ages ( $> 10$  to  $< 30$  mg C), and smaller differences for carbon ages exceeding 30 mg C which are not significantly different from those at ages  $< 10$  mg C. No corrections based on the analyzed-certified  $\text{TCO}_2$  differences or cell age have been applied to the CDIAC data set.

### 3.3. System repeatability and precision during the survey

For the survey as a whole, the operating conditions and analytical performance of the two SOMMA systems were virtually identical. Survey-wide the mean gas calibration factors of the two systems were nearly identical (1.0045 for system I compared to 1.0042 for II). While both systems yielded slightly negative ( $\sim 1.0$   $\mu\text{mol}/\text{kg}$ ) mean analytical differences (Table 3), the standard deviation of the analytical differences was slightly better on system II ( $\pm 0.91$   $\mu\text{mol}/\text{kg}$ ) than system I (1.17  $\mu\text{mol}/\text{kg}$ ). This is consistent with the gravimetric volume determinations where system II also exhibited a slightly higher precision ( $\text{sp}^2 = \pm 0.0036$   $\text{cm}^3$  vs.  $\pm 0.0049$   $\text{cm}^3$  for system I).

For the CRM analyses, the precision or pooled standard deviation ( $\text{sp}^2$ ) calculated according to Youden (1951) is 1.19  $\mu\text{mol}/\text{kg}$  ( $df = 977$ ). For this calculation, the three batches of CRM analyzed on the two systems are treated as six separate samples with multiple replicates. Because  $\text{sp}^2$  includes CRM data measured on both systems on all legs, it applies to both systems on all legs. For water samples,  $\text{sp}^2$  was calculated from duplicates analyzed on each system during leg I8SI9S at the start of the survey and leg I5WI4 about half way through the survey. The  $\text{sp}^2$  for leg I8SI9S is  $\pm 1.26$   $\mu\text{mol}/\text{kg}$  ( $df = 15$ ), and for leg I5WI4,  $\text{sp}^2$  is  $\pm 0.91$   $\mu\text{mol}/\text{kg}$  ( $df = 21$ ). These values are consistent with the precision of the CRM analyses given in Table 3. For the survey, the overall precision of the  $\text{TCO}_2$  determination is  $\pm 1.19$   $\mu\text{mol}/\text{kg}$ .

Fig. 6 is a plot of the analytical differences by system and CRM batch for the entire survey. The differences, calculated using the parameters in Table 3, reiterate the point that there are no significant

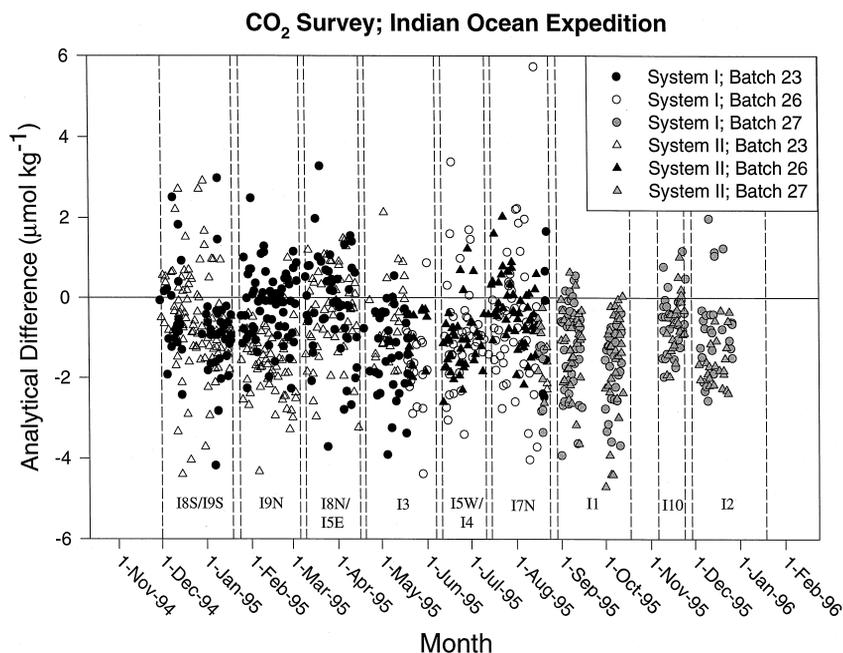


Fig. 6. The analytical differences for the CRM analyses made on SOMMA-coulometer systems I and II during the Indian Ocean Survey 1994–1996 with separate symbols for the results from the two systems and for the three batches of CRM analyzed. The beginning and end of each leg is marked by vertical dashed lines. The respective salinities and certified  $\text{TCO}_2$  ( $\mu\text{mol}/\text{kg}$ ) for batches 23, 26, and 27 are 33.483 and 1993.10, 33.258 and 1978.34, 33.209 and 1988.10  $\mu\text{mol}/\text{kg}$ .

analytical differences (bias) between systems or between CRM batches.

#### 4. Discussion

The Indian Ocean  $\text{CO}_2$  Survey differed from the previous DOE  $\text{CO}_2$  Survey efforts in that a single ship was used for all legs, and that the measurement groups shared the same analytical equipment. The latter included the use of a single cache of coulometric reagents (two different lot numbers both of which were tested pre-cruise with CRM), invariant sources of analytical gases, use of the same titration cell assemblies, standard sampling procedures, and standardized software. There was a pre-cruise training session, and all of the participants had prior experience with the sampling and measurement techniques (poisoning, reagent concentrations, standard calculations, glassware calibration, etc.) documented in the DOE Handbook of Methods (DOE, 1994). Thus, an extraordinary effort over several years to ensure

analytical quality and uniformity culminated in the procedures used during the Indian Ocean Survey.

An improvement in system accuracy (Table 3) of approximately 1 part in 2000 shows that the effort to gravimetrically determine the pipette volumes on each leg was worthwhile. The volumes of both systems did decrease slightly but significantly with time. Possible explanations include pressure changes in the carrier gas source (system I) or fouling of the glass pipette walls causing altered surface tension or displacement of small amounts of liquid (system II). Because the samples were poisoned with  $\text{HgCl}_2$ , it is unlikely that biological fouling was a problem, but the high quantity of grease used to seal the CRM bottles makes it possible that some of this grease found its way into the pipettes. After cleaning,  $V_{\text{cal}}$  for leg I10 remained unchanged compared to the preceding leg I1 on system I and increased slightly on system II, but for both systems it was significantly smaller than the  $V_{\text{cal}}$  determined for the initial leg (I8S19S). After cleaning, the mean analytical difference for leg I10 (system I and II,  $n = 2$ ) was  $-0.62 \mu\text{mol}/\text{kg}$  compared to  $-0.40 \mu\text{mol}/\text{kg}$  on

the initial leg I8S when the instruments were fresh from the laboratory indicating that pipettes were most accurate after cleaning. Whatever the cause of subsequent volume changes, the data confirm the importance of periodically redetermining the volume, and indicate that the procedure is mandatory for the highest accuracy over extended periods of analytical work and/or after major changes in system plumbing. In aggregate, both systems share a small negative analytical difference ( $-1.0 \mu\text{mol}/\text{kg}$ ) for the CRM analyses throughout the survey even after pipette volume corrections have been applied.

The cell accuracy vs. carbon age relationship shown in Fig. 5 is typical of data from previous cruises (K.M. Johnson, unpublished data). The best precision and accuracy is found at a carbon age of 5–10 mg C, a slightly reduced accuracy (usually as lower recoveries of CRM carbon) is observed between 10–30 mg C, gradually increasing recoveries and imprecision after 30 mg C until cell death where cell death is defined as a positive difference  $\geq 3.0 \mu\text{mol}/\text{kg}$ . This behavior underlies the recommendation that cell lifetimes be limited to a carbon age of  $\leq 35$  mg C, i.e., to limit imprecision and because cell death normally occurs at carbon ages  $\geq 35$  mg C. During the survey, neither CRM or samples were run until the carbon age exceeded 5 mg C. This was accomplished by configuring the software to automatically run a test sample and three consecutive gas calibrations before samples were analyzed. The reasons for the observed cell behavior are not understood, but limiting cell lifetimes from  $\geq 5$  to  $\leq 35$  mg C probably helps to limit system drift which might compromise the sample analyses. Although the imprecision associated with cell aging is small and cell failure is rare at carbon ages  $\leq 35$  mg C, good analytical practice requires that samples should be run in random order rather than systematically in order of depth to avoid systematic biases which might result from any drift associated with cell age.

Fig. 4a and b shows no correlation between the gas calibration factors and the analytical differences after the CRM analyses were corrected for pipette volume changes (Table 3). These data do show that the overall mean gas calibration factor for both systems is nearly the same (1.004), but that the temporal record with respect to gas calibration factor variation is not. Calibration factor variation

(R.S.D. = 0.06–0.08%) is greater than the variation in  $V_{\text{cal}}$  (R.S.D. = 0.03%), and is therefore a potentially more important control on system accuracy. For system I, the highest mean gas calibration factor (poorest recovery of  $\text{CO}_2$ ) was observed on leg I8N, while for system II, the corresponding result occurred months later, on leg I7N (same measurement group, see Table 1). Because the system calibration factors are not correlated with the analytical differences, the observed variations in calibration factors are real, i.e., they document a change in system response shared by the calibration and sample analyses rather than an isolated malfunction of the gas calibration hardware (see Fig. 2).

The reason for gas calibration factor variation is not known. It could conceivably be due to procedures unique to each measurement group, e.g., positioning of the cathode electrode and the gas inlet tube with respect to the coulometer light source and photodetector (Fig. 3), plumbing differences resulting in leaks and small losses of  $\text{CO}_2$ , or the amount of reagents used to dry the gas stream (Fig. 2). These procedural differences would affect sample determinations and gas calibration results similarly because, as Fig. 2 shows, the calibration gas follows the same route to the coulometer as the  $\text{CO}_2$  extracted from samples. Table 3 suggests at least one other possible cause of gas calibration factor variation. The coulometers were electronically calibrated by the BNL group at the start of the survey (I8SI9S) and about half way through the survey on leg I5WI4. Between legs I8SI9S and I5WI4 the coulometer calibration appears to have changed by 0.08% for system I, and by 0.02% for system II. These calibrations were separated by many weeks so the exact magnitude or timing of the shift is not known. Changes in the coulometer's circuitry affecting the electronic slope ( $\text{Slope}_{\text{ec}}$ ) and intercept ( $\text{Int}_{\text{ec}}$ ) would alter the gas calibration factor but would not affect system accuracy because, until recalibration, the previous electronic calibration coefficients represent constants in Eq. (1). In both systems, the sense of the apparent change in electronic calibration coefficients compared to the earlier coefficients is qualitatively consistent with the observed short-lived variation in gas calibration factors, and it is possible that this variation was due to unexplained changes in the coulometer response.

The important point is the efficacy of the gas calibration procedure: corrections to data based solely on the CRM analyses which would usually be applied on a cruise-average basis may mask short term variation or step changes in system response arising from stochastic or procedural changes. The gas calibration procedure, in which known masses of pure CO<sub>2</sub> are regularly analyzed, is an independent check of all system components except pipette volume, and it provides traceable documentation for the subsequent survey results.

The importance of cell assembly selection should be stressed. Investigators have found that the behavior of individual cell assemblies can vary significantly (e.g., D. Chipman, personal communication, July 1996). The factors affecting cell performance are still not yet completely understood. Hence, the use of empirical selection criteria such as those given in Section 2 is recommended. It is beyond the scope of the paper to go into detail, but point 'a' in Fig. 3 illustrates one of the locations for potential problems. A faulty seal where the platinum electrode emerges from the glass insulator could allow infiltration and trapping of the cell solution in the insulator where electrochemical or chemical reactions could take

place. Small quantities of this solution (at a pH different from the bulk cell solution) could randomly exchange with the bulk cell solution and cause titration errors. This would be difficult to detect. Assemblies which did not meet the empirical performance criteria in Section 2 were simply not used. The attention to cell assembly testing and selection is believed to a major reason for the success of the Indian Ocean TCO<sub>2</sub> Survey. The survey assemblies were also carefully washed and dried. Drying at  $55 \pm 5^\circ\text{C}$  removes traces of the volatile and reactive cell solution from the rubber caps.

### 5. Crossover analysis

The agreement between TCO<sub>2</sub> measurements made at similar locations, but on different legs of the survey, were used as a check on the internal consistency of the measurements. Deep measurements were used because of the lower variability in TCO<sub>2</sub> observed in the deep ocean. Because most motion in the ocean interior takes place along surfaces of constant density (isopycnals), comparisons were made along isopycnal surfaces rather than depth.

Table 4  
Results of the crossover analysis (see text for details)

Crossover no.	Expedition legs		Stations		TCO <sub>2</sub> difference $\pm$ S.D. ( $\mu\text{mol}/\text{kg}$ )
	Late	Early	Late	Early	
1	I1	I7N	927:931	780:784	$-2.5 \pm 0.5$
2	I1	I9N	987:990	266:270	$-2.7 \pm 6.3^a$
3	I1	I9N	996:998	233:235	$-0.9 \pm 1.7$
4	I2	I7N	1205	728:730	$-0.4 \pm 1.1$
5	I2	I8NI5E	1137:1139	320:324	$1.5 \pm 1.5$
6	I2	I9N	1094:1096	191:193	$-3.0 \pm 0.7$
7	I2	I10	1078	1075	$-1.5 \pm 1.5$
8	I5W14	I3	705	547:549	$1.6 \pm 0.5$
9	I3	I8NI5E	498:501	346:348	$-2.6 \pm 0.7$
10	I3	I9N	472	169	$1.1 \pm 1.2$
11	I10	I3	1039	452:454	$1.1 \pm 0.3$
12	I8NI5E	I8SI9S	404:408	9:13	$-1.1 \pm 1.0$
13	I1	I7N	861	808	$1.3 \pm 0.4^b$
Mean					$-0.78$

The TCO<sub>2</sub> difference between legs is calculated by subtracting data from the earlier sampling of a crossover location from that of the later sampling. The station numbers refer to the actual stations used for this analysis.

<sup>a</sup>The LOESS fit diverged significantly from the data.

<sup>b</sup>Not considered reliable due to insufficient data.

Our crossover analysis was performed as follows:

(1) Locations at which different cruise legs intersected were identified as ‘crossover points.’ These are identified in Table 4 and are plotted on Fig. 1.

(2) Stations located in the immediate proximity of these crossover points, for which  $\text{TCO}_2$  data existed, were selected for the comparison. In general, stations located within 100 km of the crossover location were selected.

(3) For water samples collected below 2500 m, smooth curves were fit through the  $\text{TCO}_2$  data as a function of the density anomaly referenced to 3000 dbar ( $\sigma_3$ ) using Cleveland’s LOESS smoother (Cleveland and Devlin, 1988). A separate fit was performed to the data collected from each of the two intersecting legs. The tension parameter for the smoother was adjusted subjectively to give a ‘reasonable’ fit to the data at the majority of the crossover locations, and the same value for the tension parameter was used for all of the crossovers. Hence, while

the fits to the data may not necessarily represent the best possible at each individual crossover point, the smoothing function has been consistently applied to all crossovers.

(4) For each crossover, the difference between the two smooth curves was evaluated at 50 evenly spaced intervals which covered the density range over which the two data sets overlapped. A mean and a standard deviation of the difference between the two curves was estimated based on these 50 values, and these values are reported in Table 4. An illustration of a typical analysis, the fitted data for crossover 4, is plotted on Fig. 7.

The results of the crossover analysis indicate that absolute leg-to-leg differences are always  $< 3.0 \mu\text{mol}/\text{kg}$  (Table 4). Note that the comparisons were evaluated consistently such that the fit to data from the earlier leg at each crossover was subtracted from the fit to the later leg’s data. Any uncorrected, long-term, monotonic drift in the calibration of the

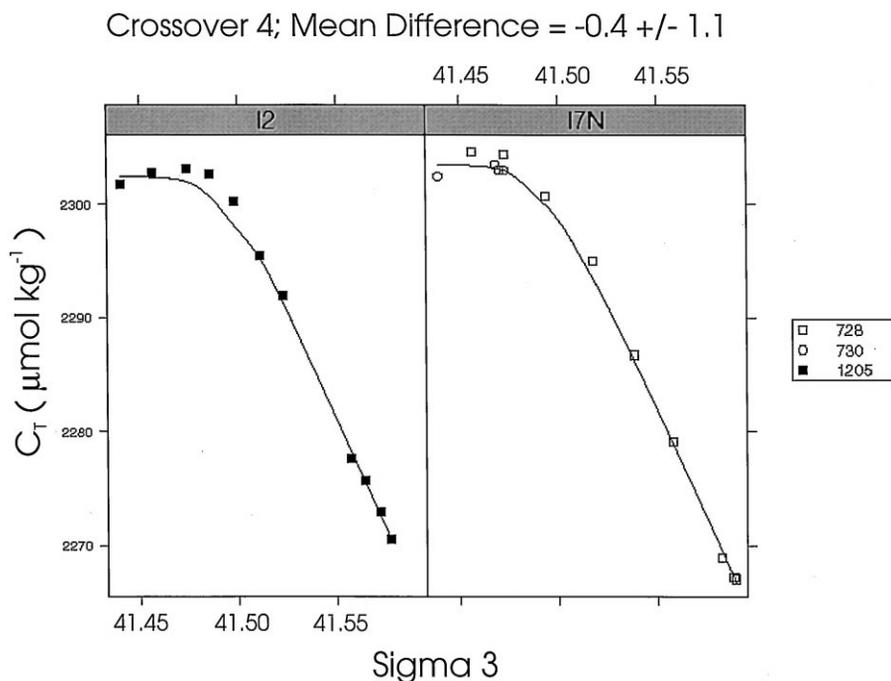


Fig. 7. An example of a crossover analysis using the  $\text{TCO}_2$  vs. density fits at crossover location #4. This location was first sampled on leg I7N in July 1995. It was resampled during January 1996 on leg I2. The  $\text{TCO}_2$  data from stations within 100 km of the crossover location and depths  $> 2500$  m have been plotted vs. the potential density anomaly referenced to 3000 dbar ( $\sigma_3$ ). The solid curves represent fits to the data using a LOESS smoother (see text). The difference between the fits for the two separate legs was evaluated at 50 density intervals spaced evenly within the overlapping density range of the two legs (see Table 4). The legend shows the station numbers used for the comparison.

SOMMA analyzers over the course of the Indian Ocean expedition would therefore result in a non-zero value for the overall mean of these differences. The overall mean and standard deviation of the differences at crossovers 1–12 is  $-0.78 (\pm 1.74)$   $\mu\text{mol}/\text{kg}$ , and there was also no significant correlation between the individual differences derived from each crossover and the number of days which separated the crossover samplings. In general, the results of the crossover analysis are quite consistent with the overall precision ( $\pm 1.2$   $\mu\text{mol}/\text{kg}$ ) of the CRM analyses (see Section 3.3), and confirms that this precision applies to both systems throughout the survey. There is no suggestion in the crossover results of any additional significant sources of error or uncertainty.

## 6. Conclusions

In summary, personnel aboard the R/V Knorr have been able to use the SOMMA-coulometer system to consistently replicate within analytical error the certified CRM  $\text{TCO}_2$  values. They have been able to use these systems to make, counting duplicates and CRM, over 20,000 determinations of  $\text{TCO}_2$  during the 14 months of the Indian Ocean Survey without significant instrument down time. The measurement groups have accomplished the following.

(1) They have charted the history of the to-deliver volume of the sample pipettes by gravimetric determinations, and corrected the water sample data for the documented changes in the pipette volumes. The change in system response due to the change in pipette volume corresponded to approximately 1 part in 2000 for  $\text{TCO}_2$  on both systems over the 10 months prior to recleaning of the pipettes.

(2) The groups have determined that the survey precision for the  $\text{TCO}_2$  analyses, irrespective of which leg or system the water samples were analyzed on, was  $\pm 1.2$   $\mu\text{mol}/\text{kg}$ . The precision of the two instruments was nearly identical and consistent throughout the 14 months of the survey.

(3) They have analyzed nearly 1000 CRM with an overall difference between the analyzed and certified  $\text{TCO}_2$  of  $-1.0$   $\mu\text{mol}/\text{kg}$  (0.05%) on both systems which demonstrates the equivalency of the two independent instruments, and meets the survey's goal for accuracy.

(4) The measurement groups have documented the influence of factors besides pipette volume which could have affected accuracy including electronic calibration, gas calibration, cell age, and cell assembly selection.

For precision, the pooled standard deviation ( $sp^2 = 1.2$   $\mu\text{mol}/\text{kg}$ ), calculated according to Youden (1951), is the most conservative estimate of precision because it includes all random analytical errors (sampling, instrumental, and method). The identical accuracy for the CRM analyses on both systems and the results of the crossover analysis (Table 4) indicate that the  $sp^2$  statistic can be used to evaluate survey data sets irrespective of the leg or system the data originated from.

The SOMMA-coulometry systems have allowed several scientific groups in a shared effort to examine carbon inventories and aquatic carbon cycling. For the Indian Ocean Survey, the sensitivity of the  $\text{TCO}_2$  determinations defined as the ratio of their precision (1.2  $\mu\text{mol}/\text{kg}$ ) over the  $\text{TCO}_2$  dynamic range (250  $\mu\text{mol}/\text{kg}$ ) was 0.4% which approaches the 0.1% sensitivity of the salinometers used, and these systems were as reliable as the salinometers. If their reliability is to be improved, the focus should be on understanding the basic behavior of the cell assemblies and the chemical behavior of the cell solutions as they age, so that procedural corrections can be made. The accuracy and precision of the Indian Ocean  $\text{TCO}_2$  analyses indicates that these data will be more than adequate for testing applicable oceanographic models, and allow the direct measurement of the  $\text{CO}_2$  uptake if and when these lines are resampled.

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## **APPENDIX C:**

### **REPRINT OF PERTINENT LITERATURE**

Millero F.J., A.G. Dickson, G. Eiseid, C. Goyet, P. Guenther, K.M. Johnson, R.M. Key, K. Lee, D. Purkerson, C.L. Sabine, R.G. Schottle, D.W. .R. Wallace, E. Lewis and C.D. Winn, Assessment of the quality of the shipboard measurements of total alkalinity on the WOCE Hydrographic Program Indian Ocean CO<sub>2</sub> survey cruises 1994-1996, *Marine Chemistry* 63:9-20.

# Assessment of the quality of the shipboard measurements of total alkalinity on the WOCE Hydrographic Program Indian Ocean CO<sub>2</sub> survey cruises 1994–1996

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## Abstract

In 1995, we participated in a number of WOCE Hydrographic Program cruises in the Indian Ocean as part of the Joint Global Ocean Flux Study (JGOFS) CO<sub>2</sub> Survey sponsored by the Department of Energy (DOE). Two titration systems were used throughout this study to determine the pH, total alkalinity (TA) and total inorganic carbon dioxide (TCO<sub>2</sub>) of the samples collected during these cruises. The performance of these systems was monitored by making closed cell titration measurements on Certified Reference Materials (CRMs). A total of 962 titrations were made on six batches of CRMs during the cruises. The reproducibility calculated from these titrations was  $\pm 0.007$  in pH,  $\pm 4.2 \mu\text{mol kg}^{-1}$  in TA, and  $\pm 4.1 \mu\text{mol kg}^{-1}$  in TCO<sub>2</sub>. The at-sea measurements on the CRMs were in reasonable agreement with laboratory measurements made on the same batches. These results demonstrate that the CRMs can be used as a reference standard for TA and to monitor the performance of titration systems at sea. Measurements made on the various legs of the cruise agreed to within  $6 \mu\text{mol kg}^{-1}$  at the 15 crossover points. The overall mean and standard deviation of the differences at all the crossovers are  $2.1 \pm 2.1 \mu\text{mol kg}^{-1}$ . These crossover results are quite consistent with the overall reproducibility of the CRM analyses for TA ( $\pm 4 \mu\text{mol kg}^{-1}$ ) over the duration of the entire survey. The TA results for the Indian Ocean cruises provide a reliable data set that when combined with TCO<sub>2</sub> data can completely characterize the carbonate system. © 1998 Elsevier Science B.V. All rights reserved.

*Keywords:* alkalinity; WOCE Hydrographic Program; CO<sub>2</sub>

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## 1. Introduction

From 1994 to 1996, a number of cruises were made in the Indian Ocean as part of the World Ocean Circulation Experiment (WOCE) Hydrographic Program to characterize the carbon dioxide system. This survey of CO<sub>2</sub> was an integral part of the Joint Global Ocean Flux Study (JGOFS). The goals of this survey were to: (1) Quantify the uptake of anthropogenic carbon dioxide by the oceans to better predict future atmospheric carbon dioxide levels; (2) Provide a global description of the carbon dioxide in the oceans to aid in the development of a 3-dimensional model of the oceanic carbon cycle; and (3) Characterize the transport of CO<sub>2</sub> across the air–sea interface and the large scale transports of carbon dioxide within the oceans.

To satisfy these goals, it was necessary to make very precise measurements of at least two of the carbonate system parameters (pH; total alkalinity, TA; total carbon dioxide, TCO<sub>2</sub>; and the fugacity of carbon dioxide, *f*CO<sub>2</sub>). Within the United States a large part of this survey was conducted by a team of investigators supported by the US Department of Energy. The team selected the measurement of TCO<sub>2</sub> (Johnson et al., 1998) and of TA as the parameters to be measured in the water column and *f*CO<sub>2</sub> in the atmosphere and surface waters. To insure that the measurements of TCO<sub>2</sub> and TA were as precise and accurate as possible Certified Reference Materials (CRMs) (Dickson, 1990a) were used throughout the studies. The team also developed a set of Standard Operating Procedures<sup>1</sup> (DOE, 1994) and, to a large extent, shared a common approach to the measurement program.

For the studies in the Indian Ocean, the team shared equipment throughout the study. This paper presents the results of this team effort to precisely and accurately determine the total alkalinity during these cruises and the intercomparison between cruises. A companion paper (Johnson et al., 1998) describes the total carbon dioxide measurements.

<sup>1</sup> DOE, 1991. Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water, In: Dickson, A.G., Goyet, C. (Eds.), Version 1.0, Unpublished manuscript

## 2. Methods

The total alkalinity was determined on the JGOFS Indian Ocean cruises by the DOE group using systems described in detail by Millero et al. (1993). The total alkalinity of seawater was evaluated from the proton balance at the alkalinity equivalence point, pH<sub>equiv</sub> ~ 4.5, according to the exact definition of total alkalinity (Dickson, 1981)

$$\begin{aligned} \text{TA} = & [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] \\ & + [\text{OH}^-] + [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] \\ & + [\text{SiO}(\text{OH})_3^-] + [\text{HS}^-] \\ & + [\text{NH}_3] - [\text{H}^+] - [\text{HSO}_4^-] \\ & - [\text{HF}] - [\text{H}_3\text{PO}_4] \end{aligned} \quad (1)$$

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

$$\begin{aligned} (W_0 \times \text{TA} - W \times C_{\text{HCl}}) / (W_0 + W) = & [\text{HCO}_3^-] \\ & + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] + [\text{HPO}_4^{2-}] \\ & + 2[\text{PO}_4^{3-}] + [\text{SiO}(\text{OH})_3^-] + [\text{HS}^-] + [\text{NH}_3] \\ & - [\text{H}^+] - [\text{HSO}_4^-] - [\text{HF}] - [\text{H}_3\text{PO}_4] \end{aligned} \quad (2)$$

where  $W_0$  is the mass of the sample to be titrated,  $C_{\text{HCl}}$  is the concentration of acid titrant, and  $W$  is the mass of acid added. In the calculations, volumes of the sample and of the acid were converted to mass using the density of seawater (Millero and Poisson, 1981) and the density of HCl in NaCl (Millero et al., 1977). Direct measurements made on the density of the acid used agreed to within 10 ppm with the equations used in the computer code. At the endpoint ( $W_2$ ) the total alkalinity is given by

$$\text{TA} = W_2 \times C_{\text{HCl}} / W_0 \quad (3)$$

The uncertainties in TA associated with acid concentration ( $\sim 0.25 \pm 0.0001$  M), mass of acid delivered ( $\sim 2.5 \pm 0.0005$  g), and mass of the sample

( $\sim 200 \pm 0.05$  g) are  $\pm 1$ ,  $\pm 0.5$ , and  $\pm 0.5$   $\mu\text{mol kg}^{-1}$ , respectively (which gives a probable error of about  $\pm 1$   $\mu\text{mol kg}^{-1}$ ). By using the same acid, titrators, and acid throughout a given cruise one can obtain a precision that is comparable with this probable error. Discussed below are more details on the components of the titration systems.

### 2.1. Titration system

The titration systems used to determine TA consist of a Metrohm 665 Dosimat titrator and an Orion 720A pH meter controlled by a personal computer (Millero et al., 1993). Both the acid titrant in a water-jacketed burette and the seawater sample in a water-jacketed cell were controlled to a constant temperature of  $25 \pm 0.1^\circ\text{C}$  with a Neslab constant temperature bath. The plexiglass water-jacketed cells used for our studies were similar to that used by Bradshaw and Brewer (1988) except a larger volume (about  $200\text{ cm}^3$ ) was used to improve the precision. These cells have fill and drain valves that increased the reproducibility of the cell volume.

A Lab Windows C program is used to run the titration and record the volume of the added acid and the emf of the electrodes using RS232 interfaces. The titration is made by adding HCl to seawater past the alkalinity end point. A typical titration records the average of ten emf readings after they become stable ( $\pm 0.09$  mV) and adds enough acid to change the voltage by a pre-assigned increment ( $\sim 13$  mV). In contrast to the delivery of a fixed volume of acid, this method gives more data points in the range of a rapid increase in the emf near the endpoint. A full titration (25 points) takes about 20 min.

#### 2.1.1. Electrodes

The electrodes used to measure the emf of the sample during a titration consist of a ROSS glass pH electrode and an Orion double junction Ag, AgCl reference electrode. A number of electrodes were screened to select those to be used in the titrators. Electrodes with non-Nernstian behavior (slopes more than  $1.0$  mV different from the theoretical value) were discarded. The reliability of the electrodes was evaluated by determining the TA,  $\text{TCO}_2$  and pH of

Gulf Stream seawater. The titration values of  $\text{TCO}_2$  are normally higher than the values measured by coulometry and the values of pH are typically lower than the values obtained by spectrophotometric methods. These differences in  $\text{TCO}_2$  and pH are caused by the non-Nernstian behavior of the electrodes (Millero et al., 1993). We selected electrodes which gave values of  $\text{TCO}_2$  and pH close to the values determined by coulometric and by spectrophotometric methods, respectively.

#### 2.1.2. Standard acids

The HCl used for this study and for all of our cruises was made in the laboratory, standardized, and stored in  $500\text{ cm}^3$  glass bottles. The  $\sim 0.25$  M HCl solutions were made from 1 M Mallinckrodt standard solutions in 0.45 M NaCl to yield an ionic strength equivalent to that of average seawater ( $\sim 0.7$  M). The concentration of HCl was measured using a constant current coulometric technique (Taylor and Smith, 1959; Marinenko and Taylor, 1968). Coulometric analysis of the acids used for these cruises agreed to  $\pm 0.0001$  M with the analyses performed independently on the same batches of acids in Dr. A. Dickson's laboratory at Scripps Institution of Oceanography (SIO). The mutual consistency of these acids was also confirmed by comparing the values of TA measured on Gulf Stream seawater using different batches of acids, but using the same titrator and electrodes. The uncertainties in TA associated with acid concentration ( $\pm 0.0001$  M) is  $\sim 1$   $\mu\text{mol kg}^{-1}$ .

#### 2.1.3. Volume of the cells

The volume of each of the titration cells used at sea was determined by comparing the values of TA obtained for Gulf Stream seawater with open and closed cells in the laboratory. All of the open cell laboratory TA measurements were made with weighed amounts of seawater in a cell with a small head-space. If the volume is correct, the TA from the open and closed cells should be the same, provided that the same acid, titrator, and electrodes are used. At least 10 measurements were made on each cell yielding an average TA that agreed with the assigned value to better than  $1$   $\mu\text{mol kg}^{-1}$ . If the volume of a

Table 1  
Comparison of the total alkalinity of Certified Reference Materials

Batch	SIO	Miami	$\Delta(S-M)$	Cruise
23	2212.7	2213.7	-1.0	I8S/I9S, I9N, I8N /I5E, I3, I7N
24	2215.5	2215.8	-0.3	I8R
26	2176.6	2175.1	1.5	I3, I5W/ I4, I-7N
27	2214.9	2214.3	0.6	I7N, I1, I10, I2
29	2184.8	2182.3	2.5	I8R
30	2201.9	2200.5	1.4	I2

titration cell needed to be adjusted during the cruise (because of broken electrodes, plungers etc.), the volumes were determined from the daily titrations on low-nutrient surface seawater (usually collected before the first station) and Certified Reference Materials (CRMs) provided by Dr. A. Dickson (SIO). Post-cruise calibrations of the cells were made by comparing the values of TA for the Gulf Stream seawater and CRM with open and closed cells. The nominal volumes of all the cells were about 200 cm<sup>3</sup>, and the values were determined to  $\pm 0.05$  cm<sup>3</sup>. The uncertainty in TA associated with this uncertainty in

the volume of the cells ( $\pm 0.05$  cm<sup>3</sup>) is  $0.5 \mu\text{mol kg}^{-1}$  obtained for the weighed samples.

#### 2.1.4. Volume of titrant

The volume of HCl delivered to the cell is traditionally assumed to have small uncertainty (Dickson, 1981) and equated to the digital output of the titrator. Calibrations of all the burettes of the Dosimats used were made with Milli-Q water at 25°C. Since the cell volumes are calibrated using standard solutions, errors in the accuracy of volume delivery will be partially canceled and included in the value of cell volumes assigned. The calibration of all the Dosimats used at sea and in the laboratory indicated that the amount of acid delivered (for a typical calculation) was uncertain to  $\pm 0.0005$  cm<sup>3</sup>. This uncertainty in the volume delivered leads to an error in the TA of  $\pm 0.5 \mu\text{mol kg}^{-1}$ . Nevertheless, corrections to the Dosimat reading were made in all of our laboratory TA measurements and calibrations to insure that the assigned value for a different batch of CRM and Gulf Stream water was not affected by the

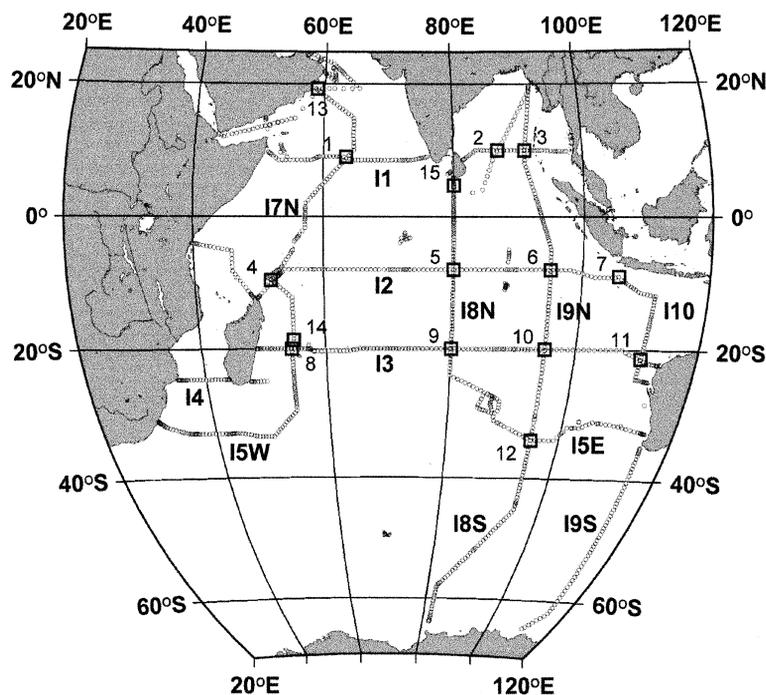


Fig. 1. Cruise tracts of the Indian Ocean Studies showing crossover points.

Table 2  
Measurements of pH, TA and TCO<sub>2</sub> of CRM at sea

Cruise	Start date	End date	Batch	Cell	N	TA average	S.D.	TCO <sub>2</sub> average	S.D.	pH average	S.D.
I8S/I9S	12/1/94	1/19/95	23	All	49	2221.5	5.1	2004.5	4.1		
				5	18	2223.3	4.8	2003.8	2.5		
				6	18	2220.8	4.0	2008.0	3.1		
				20	13	2220.0	6.4	2001.4	3.8		
I9N	1/24/95	3/6/95	23	All	138	2216.2	3.3	2000.1	3.5	7.891	0.005
				5	68	2215.0	3.3	1999.1	3.3	7.892	0.004
				6	65	2217.5	3.3	2001.3	3.3	7.891	0.005
				20	5	2214.2	3.1	1996.5	3.5	7.895	0.007
I8N/I5E	3/10/95	4/16/95	23	All	80	2211.6	4.9	1997.0	3.0	7.890	0.006
				5	36	2213.0	5.5	1998.6	3.8	7.890	0.005
				6	44	2210.1	3.6	1996.2	2.6	7.890	0.007
I3	4/20/95	6/7/95	23	All	65	2215.4	1.4	2002.1	1.4	7.894	0.005
				2	33	2215.7	1.3	2000.7	1.4	7.898	0.006
				13	35	2215.0	1.4	2003.6	1.3	7.890	0.004
			26	All	30	2178.0	1.2	1984.8	1.2	7.858	0.004
				2	14	2178.3	1.3	1983.3	1.2	7.862	0.003
				13	16	2177.7	1.2	1986.0	1.1	7.855	0.004
I5W/I4	6/11/95	7/11/95	26	All	79	2182.6	3.8	1990.2	3.4		
				2	41	2183.3	3.9	1988.0	2.4		
				13	38	2182.0	3.5	1992.9	2.3		
I7N	7/15/95	8/24/95	26	All	59	2184.0	5.7	1984.7	3.4	7.862	0.009
				2	33	2186.2	3.1	1984.3	2.6	7.862	0.009
				13	26	2181.5	7.4	1985.2	4.0	7.858	0.006
			27	All	8	2221.5	3.1	1995.5	1.4	7.916	0.005
				2	4	2221.4	2.4	1994.9	1.4	7.914	0.005
				13	4	2221.5	4.1	1996.0	1.5	7.918	0.006
			23	All	10	2222.4	7.4	2002.0	4.0	7.896	0.006
				2	5	2227.5	5.8	2003.2	4.1	7.897	0.005
				13	5	2216.2	6.4	1999.9	3.9	7.893	0.009
I1	8/29/95	10/18/95	27	All	244	2219.4	3.9	1998.8	5.4	7.906	0.013
				2	123	2220.1	3.2	1995.3	3.2	7.911	0.005
				7	54	2219.6	3.6	1999.7	4.1	7.908	0.013
				13	15	2216.2	4.7	1994.6	4.5	7.909	0.005
				14	52	2217.9	4.5	2006.5	3.6	7.885	0.009
I10	11/6/95	11/24/95	27	All	62	2212.9	4.0	1991.3	2.9	7.912	0.006
				11	30	2212.3	4.5	1989.6	2.4	7.914	0.005
				16	32	2213.5	3.5	1993.1	2.0	7.910	0.006
I8R	9/23/95	10/24/95	29	All	36	2184.2	1.8	1914.8	2.4	8.006	0.006
NOAA Cruise				4	9	2185.5	1.7	1914.5	1.9	8.006	0.005
				17	17	2183.9	1.6	1914.4	2.2	8.007	0.005
				18	10	2183.4	2.1	1915.7	3.1	8.004	0.009
			24	All	10	2216.6	2.3	1998.7	1.7	7.902	0.006
				4	2	2218.5	3.8	1998.6	3.9	7.907	0.004
				17	5	2215.1	0.6	1998.5	1.4	7.902	0.006
			18	3	2217.3	2.6	1998.6	1.7	7.899	0.006	
I2	11/28/95	1/19/96	27	All	67	2219.4	4.5	1994.0	2.8	7.916	0.005
				11	36	2219.9	5.7	1993.1	3.3	7.918	0.005

Table 2 (continued)

Cruise	Start date	End date	Batch	Cell	<i>N</i>	TA average	S.D.	TCO <sub>2</sub> average	S.D.	pH average	S.D.
				16	31	2218.9	3.2	1994.7	2.2	7.915	0.006
			30	All	9	2204.6	2.7	1996.8	2.1	7.879	0.004
				11	4	2205.3	2.3	1995.0	2.2	7.880	0.002
				16	5	2204.0	3.0	1998.4	0.8	7.879	0.006

use of different Dosimats. These corrections were also made when calculating the volume of each cell.

## 2.2. Evaluation of the carbonate parameters

A FORTRAN computer program has been developed to calculate the carbonate parameters (pH,  $E^*$ , TA, TCO<sub>2</sub>, and  $pK_1$ ) in the seawater solutions. The program is patterned after those developed by Dickson (1981), Johansson and Wedborg (1982) and Dickson (1984; DOE, 1994). The fitting is performed using the STEPIT routine (J.P. Chandler, Oklahoma State University, Stillwater, OK 74074). The STEPIT software package minimizes the sum of squares of residuals by adjusting the parameters  $E^*$ , TA, TCO<sub>2</sub> and  $pK_1$  of carbonic acid. The computer program is based on Eq. (2) and assumes that nutrients such as phosphate, silicate and ammonia are negligible. This assumption is strictly valid only for surface waters. Neglecting the concentration of nutrients in the seawater sample does not affect the accuracy of TA, but must be considered when calculating the carbonate alkalinity ( $CA = [HCO_3^-] + 2 [CO_3^{2-}]$ ) from TA.

The pH and  $pK$  of the acids used in the program are on the seawater scale,  $[H^+]_{sw} \sim [H^+] + [HSO_4^-] + [HF]$  (Dickson, 1984). The dissociation constants used in the program were taken from Dickson and Millero (1987) for carbonic acid, from Dickson (1990b) for boric acid, from Dickson and Riley (1979) for HF, from Dickson (1990c) for HSO<sub>4</sub><sup>-</sup> and from Millero (1995) for water. The program requires as inputs the concentration of acid, volume of the cell, salinity, temperature, measured emfs ( $E$ ) and volumes of HCl ( $V$ ). To obtain a reliable TA from a full titration, at least 25 data points should be collected (9 data points between pH 3.0 to 4.5). The precision of the fit is less than 0.4  $\mu\text{mol kg}^{-1}$  when  $pK_1$  is allowed to vary and 1.5  $\mu\text{mol kg}^{-1}$  when  $pK_1$  is fixed. Our titration program has been com-

pared to the titration programs used by others (Johansson and Wedborg, 1982; Bradshaw and Brewer, 1988) and the values of TA agree to within  $\pm 1 \mu\text{mol kg}^{-1}$ .

## 3. Results and discussion

### 3.1. Laboratory TA measurements of CRMs

The laboratory TA measurements made on the CRMs used throughout this study are summarized in Table 1. The results obtained by both laboratories demonstrate that no systematic differences in TA are found. With the exception of Batch 29, the differences in the measurements of the CRMs between the two laboratories are less than 2  $\mu\text{mol kg}^{-1}$ . Since the Miami measurements were made with the same acid as used at sea, one cannot attribute the differences in Batch 29 to differences in the concentration of the acids (calibrated at SIO). The Miami measurements were also made using the same acid for all the batches of CRM within a one-week period to ensure the internal consistency of its results. The measurements made on the acid concentration in Miami and SIO by a coulometric titration were in agreement to  $\pm 0.0001$  M, which is equivalent to an error of  $\pm 1 \mu\text{mol kg}^{-1}$  in TA.

### 3.2. At sea measurements of TA, TCO<sub>2</sub>, and pH on CRMs

#### 3.2.1. Accuracy of at sea measurements

The tracks of the cruise made during the Indian Ocean studies are shown in Fig. 1. A total of 962 titrations were made on six batches of the CRMs during the cruises (Table 2). A summary of the pH, TA and TCO<sub>2</sub> measurements made on CRMs

Table 3

The overall precision of at sea TA, TCO<sub>2</sub>, and pH measurements on the Certified Reference Material

Parameters	Precision (1 $\sigma$ ) ( $\mu\text{mol kg}^{-1}$ )	Number of measurements
TA	4.2	949
TCO <sub>2</sub>	4.1	947
pH	0.007	793 <sup>a</sup>

<sup>a</sup>The numbers of the pH measurements were less than for TA and TCO<sub>2</sub> because some values were not recorded.

(Table 3) throughout the cruise is shown in Figs. 2–4. The reproducibility on the six batches of the CRMs used was  $\pm 0.007$  in pH,  $\pm 4.2 \mu\text{mol kg}^{-1}$  in TA, and  $\pm 4.1 \mu\text{mol kg}^{-1}$  in TCO<sub>2</sub>. The at sea TA measurements on the CRMs were in good agreement ( $\sim 2\text{--}4 \mu\text{mol kg}^{-1}$ ) with laboratory measurements made on the same batches at MIAMI and SIO. These small differences ( $\sim 2\text{--}4 \mu\text{mol kg}^{-1}$ ) are well within the overall precision of our measurements and can be attributed to uncertainties in the volume of cells assigned in the laboratory before the cruises. However, the cells used on I7 gave significantly greater

errors than the values obtained in the laboratories on the same batch of CRM. These large discrepancies might be attributed to inaccurately assigned volumes of the cells after they were repaired for leakage due to repositioning of a reference electrode after changing the inner filling solution.

### 3.2.2. Long term stability of a cell performance

The at sea TA measurements on the CRMs can be used to examine the long-term stability of the cells used during the cruises. Overall, the TA results obtained using cells for a given cruise did not show any systematic trends. Differences in TA between laboratory and field measurements remained unchanged over the entire period of each cruise. However, inter-cruise variations in TA between laboratory and field results were observed when the same cells were used. For instance, cells 2 and 13 were used for four consecutive cruises over the period of six months. When these two cells were used on the first cruise (I3), the field measurements agreed to within  $\pm 2 \mu\text{mol kg}^{-1}$  with the values obtained in

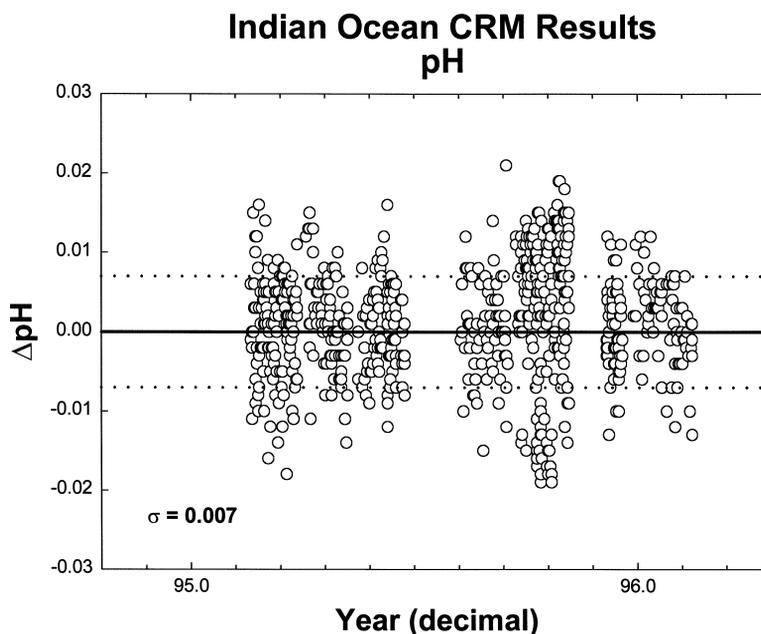


Fig. 2. The reproducibility of the titration pH measurements made on Certified Reference Material on the Indian Ocean Study.

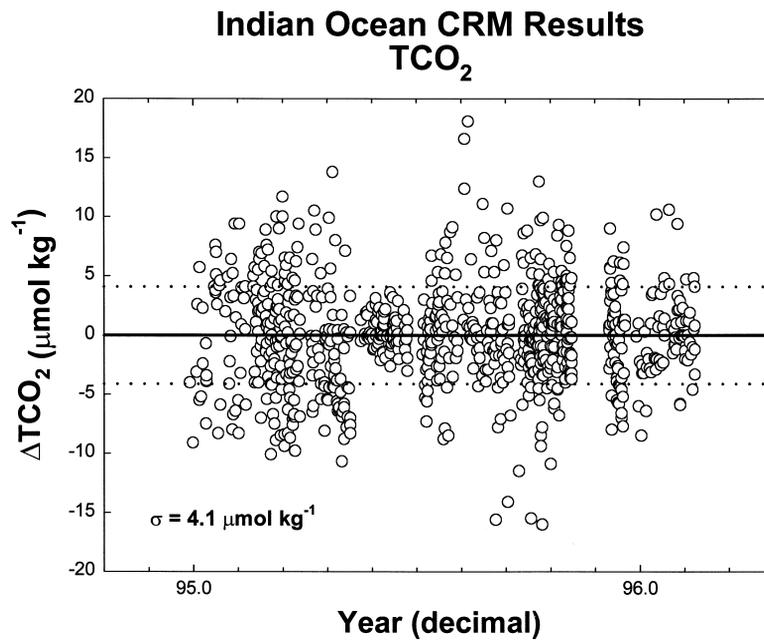


Fig. 3. The reproducibility of the titration TCO<sub>2</sub> measurements made on Certified Reference Material on the Indian Ocean Study.

the laboratory. These small discrepancies are within the precision of our measurements. When the same cells were used for the later cruises, the differences

in TA between laboratory and field measurements became significantly larger ( $9 \mu\text{mol kg}^{-1}$ ). As mentioned in Section 3.2.1, these larger differences can

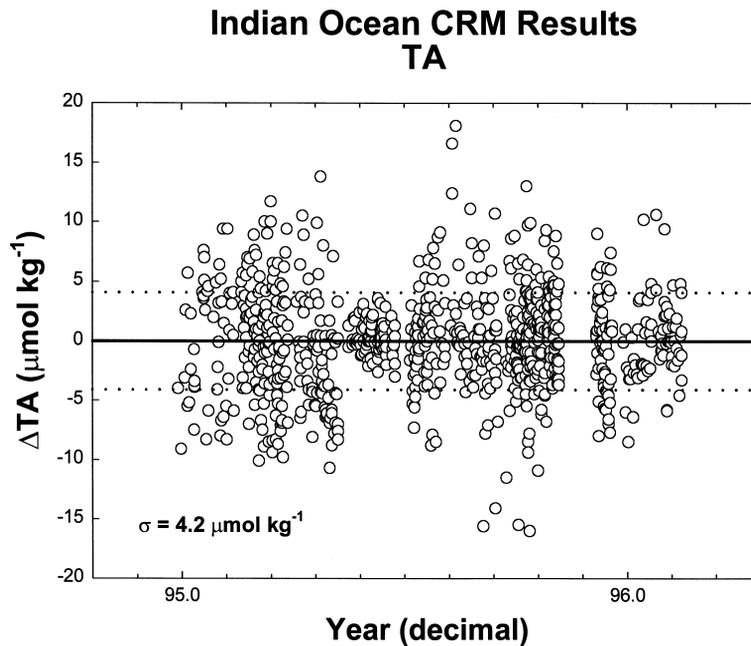


Fig. 4. The reproducibility of the titration TA measurements made on Certified Reference Material on the Indian Ocean Study.

Table 4

Differences between TA measurements made at sea and values measured in the laboratory (SIO)

Cell	I8S/I9S	I9N	I8N/I5E	I3	I5W/I4	I7N	I1	I8R	I10	I2
2				+2.6 <sup>a</sup>	+6.7	+9.9 <sup>a</sup>	+5.2			
4								0.7		
5	+10.6	+2.3	+0.3							
6	+8.1	+4.8	-2.6							
7							+4.7			
11									-2.6	+4.8 <sup>a</sup>
13				+2.1 <sup>a</sup>	+6.0	+4.9 <sup>a</sup>	+1.3			
14							+3.0			
16									-1.4	+3.7 <sup>a</sup>
17								-0.9		
18								-1.4		
20	+7.3	+1.5								

<sup>a</sup>Based on the weighted average on different CRM.

be attributed to changes in the assigned volume of the cells due to repositioning of a reference electrode. These inter-cruise variations in TA can be corrected by normalizing the measured values obtained during the cruises using the corrections required to reproduce the values assigned for the CRMs by SIO (Table 4). This correction was applied using

$$\Delta = \text{TA}(\text{meas}, \text{CRM}) - \text{CRM} \quad (4)$$

$$\text{TA}(\text{corr.}) = \text{TA}(\text{meas.}) \times [\text{CRM}/(\text{CRM} + \Delta)] \quad (5)$$

where CRM is the SIO-certified values.

### 3.3. Crossover analysis

In order to cross-check our estimates of accuracy of the TA data, which are derived from analyses of CRMs, we examined the agreement between TA measurements made at identical locations on different legs of the Indian Ocean expedition. All of these comparisons have been made after applying the corrections given in Table 4. The implicit assumption is that temporal and spatial gradients of TA concentrations in the deep ocean are small relative to measurement accuracy, so that water sampled at the same location in the deep ocean at two different times should have near-identical values of TA. In practice, vertical gradients of TA can be significant relative to measurement accuracy and there can also be significant vertical motions in the deep ocean. Hence,

measurements made at the same geographical location cannot be compared simply on the basis of their common depth. Because most motion in the ocean interior takes place along surfaces of constant den-

Table 5

Crossover results for the TA measurements made in the Indian Ocean

Number	Stations	Legs	$\Delta\text{TA}$
1	927,929,931, 780,782,784	I1-I7N	$1.7 \pm 1.0$
2	987,990,266, 268,270	I1-I9N	$-2.1 \pm 5.9$
3	996,998, 233,235	I1-I9Nb	$1.2 \pm 0.8$
4	1205,728, 730	I2-I7N	$5.6 \pm 2.4$
5	1137,1139, 320,324	I2-I9N/I5E	$3.4 \pm 2.2$
6	1094,1096, 191,193	I2-I9N	$-3.4 \pm 1.4$
7	1078,1075	I2-I10	$1.8 \pm 2.4$
8	705,547,549	I5W/I4-I3	$0.7 \pm 1.7$
9	498,499,501, 346,348	I3-I8N/I5E	$-0.8 \pm 2.3$
10	472,169	I3-I9N	$-0.8 \pm 0.6$
11	1039,452,454	I10-I3	$-1.0 \pm 0.7$
12	404,406,408, 9,11,13	I8N/I5E-I8S/I9S	$-2.7 \pm 3.8$
13	861,808	I1-I7N	$0.3 \pm 0.6$
14	709,707	I7N-I5W/I4	$2.4 \pm 1.7$
15	966,968,969, 283,287	I1-I8N/I5E	$-4.2 \pm 4.5$

## Alkalinity Comparison

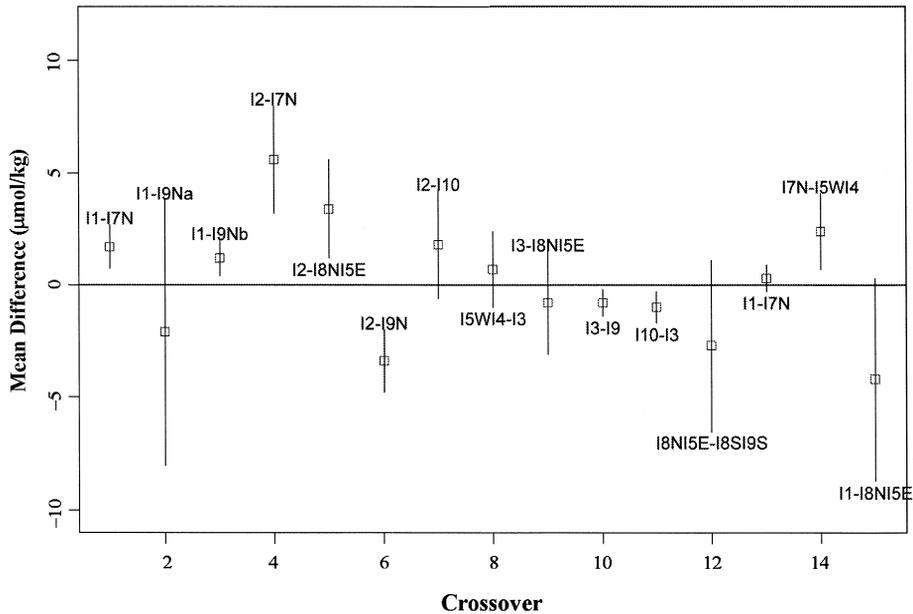


Fig. 5. Summary of the TA reproducibility for crossover points in the Indian Ocean.

sity (isopycnals), it is preferable to compare concentrations using density as the frame of reference rather than depth.

Our crossover analyses were performed as follows.

(1) Locations at which different cruise legs intersected were identified as crossover points. These are identified in Table 5 and Fig. 1.

(2) Stations located in the immediate proximity of these crossover points, for which TA data existed, were selected for the comparison. In general, stations located within 100 km of the crossover location were selected.

(3) For water samples collected below 2500 m, smooth curves were fit through the TA data as a function of the density anomaly referenced to 3000 db ( $\sigma\text{-3}$ ) using Cleveland's loess or smoother local regression (Cleveland and Devlin, 1988; Cleveland and Grosse, 1991; Chambers and Hastie, 1991). A separate fit was performed to the data collected from each of the two intersecting legs. The tension parameter for the smoother was adjusted subjectively to give a 'reasonable' fit to the data at the majority of the crossover locations, and the same value for the tension parameter was used for all of the crossovers.

Hence, while the fits to the data may not necessarily represent the best possible at each individual crossover point, the smoothing function has been

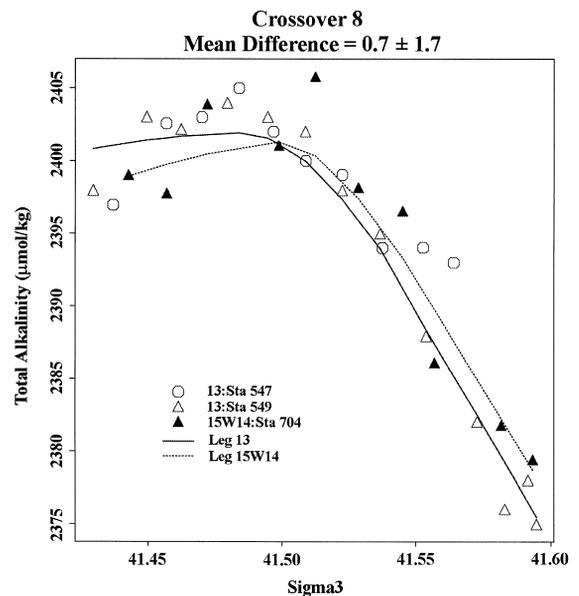


Fig. 6. Results for a typical crossover comparison (I3-I5W/14) in the Indian Ocean.

applied consistently. It is important to note that the comparison of the data at the crossover points does not depend on the fitting algorithm within the experimental error.

(4) For each crossover, the difference between the two smooth curves was evaluated at 50 evenly spaced intervals that covered the density range over which the two data sets overlapped. A mean and a standard deviation of the difference between the two curves was estimated based on these 50 values, and these values are reported in Table 5 and shown in Fig. 5. An example of the crossover for cruises I3-I5W/I4 is shown in Fig. 6.

The results of the crossover analysis indicate that absolute leg-to-leg differences are always  $< 6 \mu\text{mol kg}^{-1}$ . Note that the comparisons were evaluated consistently such that the fit to data from the earlier leg at each crossover was subtracted from the fit to the later leg's data. Any uncorrected, long-term, monotonic drift in the calibration of the titrators over the course of the Indian Ocean expedition would therefore tend to result in a non-zero value for the overall mean of these differences. The overall mean and standard deviation of the differences at all the crossovers are  $2.1 \pm 2.1 \mu\text{mol kg}^{-1}$ . In general, the results of the crossover analysis are quite consistent with the overall reproducibility of the CRM analyses ( $\pm 4 \mu\text{mol kg}^{-1}$ ) over the duration of the entire Survey.

#### 4. Conclusion

At-sea total alkalinity measurements on the several CRM batches demonstrated that the measurements made by various investigators were precise to about  $\pm 4 \mu\text{mol kg}^{-1}$ . This level of the precision of at sea measurements was approximately two times worse than that in the laboratory. Differences in the precision between different investigators suggest that the performance of TA measurements was dependent upon the operators. The inter-cruise variations in total alkalinity between laboratory and field results clearly demonstrate that CRMs are an essential component to monitor the performance of titration systems and increase the accuracy for total alkalinity measurements in the field.

#### Acknowledgements

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## **APPENDIX D:**

### **REPRINT OF PERTINENT LITERATURE**

Sabine, C. L., R. M. Key, K. M. Johnson, F. J. Millero, A. Poisson, J. L. Sarmiento, D. W. R. Wallace, and C. D. Winn (1999), Anthropogenic CO<sub>2</sub> Inventory of the Indian Ocean, *Global Biogeochem. Cycles*, 13(1), 179–198.

## Anthropogenic CO<sub>2</sub> inventory of the Indian Ocean

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**Abstract.** This study presents basin-wide anthropogenic CO<sub>2</sub> inventory estimates for the Indian Ocean based on measurements from the World Ocean Circulation Experiment/Joint Global Ocean Flux Study global survey. These estimates employed slightly modified  $\Delta C^*$  and time series techniques originally proposed by Gruber *et al.* [1996] and Wallace [1995], respectively. Together, the two methods yield the total oceanic anthropogenic CO<sub>2</sub> and the carbon increase over the past 2 decades. The highest concentrations and the deepest penetrations of anthropogenic carbon are associated with the Subtropical Convergence at around 30° to 40°S. With both techniques, the lowest anthropogenic CO<sub>2</sub> column inventories are observed south of 50°S. The total anthropogenic CO<sub>2</sub> inventory north of 35°S was 13.6±2 Pg C in 1995. The inventory increase since GEOSECS (Geochemical Ocean Sections Program) was 4.1±1 Pg C for the same area. Approximately 6.7±1 Pg C are stored in the Indian sector of the Southern Ocean, giving a total Indian Ocean inventory of 20.3 ±3 Pg C for 1995. These estimates are compared to anthropogenic CO<sub>2</sub> inventories estimated by the Princeton ocean biogeochemistry model. The model predicts an Indian Ocean sink north of 35°S that is only 0.61-0.68 times the results presented here; while the Southern Ocean sink is nearly 2.6 times higher than the measurement-based estimate. These results clearly identify areas in the models that need further examination and provide a good baseline for future studies of the anthropogenic inventory.

### 1. Introduction

The current Intergovernmental Panel on Climate Change (IPCC) estimate for the oceanic sink of anthropogenic CO<sub>2</sub> (2.0 ±0.8 Pg C yr<sup>-1</sup>) is based primarily on ocean models [e.g., Sarmiento *et al.*, 1992; Sarmiento and Sundquist, 1992; Siegenthaler and Sarmiento, 1993; Siegenthaler and Joos, 1992; Stocker *et al.*, 1994], atmospheric models [e.g., Keeling *et al.*, 1989; Keeling and Shertz, 1992] or on the oceanic distribution of related species such as  $\delta^{13}C$  [Quay *et al.*, 1992]. Although the basic assumptions used in these methods are reasonably well grounded, there will always be room for doubt with indirect approaches. Direct estimates of the oceanic CO<sub>2</sub> sink, however, have been primarily limited by a lack of high-quality data on a global scale.

Two general approaches can be used to estimate the uptake of anthropogenic CO<sub>2</sub> by the oceans. One approach, initially proposed by Tans *et al.* [1990], is to use direct measurements of the air-sea difference in CO<sub>2</sub> partial pressure together with global

winds and a gas exchange coefficient to estimate the net transfer of CO<sub>2</sub> into the oceans. These estimates, together with an atmospheric transport model, predicted that the oceanic sink was only 0.3 to 0.8 Pg C yr<sup>-1</sup>, much smaller than the model predictions. The difficulty with the  $\Delta pCO_2$  approach lies both in the large uncertainty in the wind speed dependence of the air-sea gas exchange velocity and in the ability to properly represent the large temporal and spatial variability of the surface ocean  $pCO_2$  because of a lack of seasonal, global data coverage. This estimate has recently been revised to 0.6 to 1.34 Pg C yr<sup>-1</sup> with the addition of more data and a lateral advection-diffusion transport equation to help with the necessary temporal and spatial interpolations [Takahashi *et al.*, 1997].

A second approach, which avoids many of the problems of temporal variability, is to estimate the inventory of anthropogenic CO<sub>2</sub> stored in the oceans interior based on inorganic carbon measurements. Again, the problem with this approach in the past has been a lack of high-quality global data coverage. As pointed out by Broecker *et al.* [1979] after completion of the last global oceanographic survey, GEOSECS (Geochemical Ocean Sections Program), the precision of ocean carbon measurements at that time was two orders of magnitude smaller than the predicted 0.035% annual increase in surface ocean dissolved inorganic carbon. Nearly 20 years have passed since GEOSECS, and the quality of today's carbon measurements has improved significantly.

This is the first of several papers aimed at estimating the anthropogenic CO<sub>2</sub> inventory of the oceans based on the recent global survey of CO<sub>2</sub> in the oceans. The survey was conducted as part of the JGOFS (Joint Global Ocean Flux Study) in close cooperation with the WOCE-HP (World Ocean Circulation Experiment - Hydrographic Programme). This program was a multiyear effort to collect high-precision inorganic carbon data with the highest possible spatial resolution on a global scale. This paper will focus on anthropogenic CO<sub>2</sub> estimates for the Indian Ocean. Papers will

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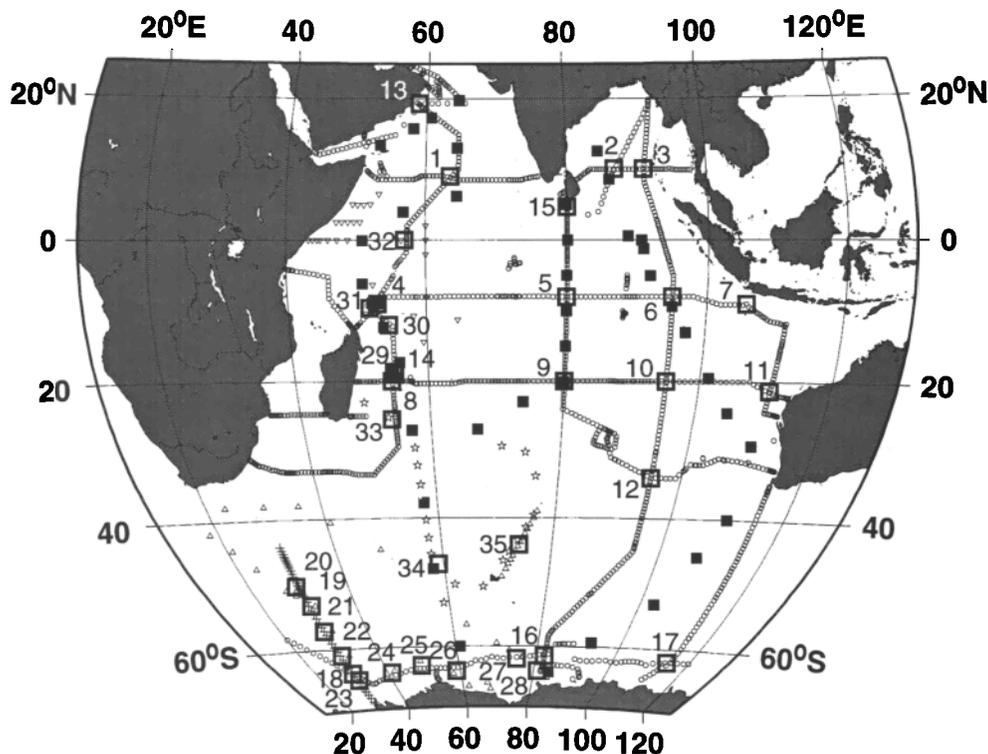
soon follow with estimates for the other major ocean basins, with the ultimate goal of generating an estimate of the global oceanic anthropogenic CO<sub>2</sub> sink based on direct carbon system measurements. The strength of these calculations lies not only in our ability to directly estimate the magnitude of the oceanic anthropogenic CO<sub>2</sub> sink but also in the fact that these estimates can be directly compared to anthropogenic CO<sub>2</sub> inventories estimated by carbon-cycle ocean general circulation models (GCMs). The two methods described here provide information over different timescales. The combined results place strong constraints on the uptake rate for anthropogenic CO<sub>2</sub> and are useful for identifying weaknesses in the models.

## 2. Methods

Estimates of the anthropogenic CO<sub>2</sub> inventory are determined from measured values using two different techniques. The first technique, referred to as the "time series" approach, is based on quantifying the increase in total carbon dioxide (TCO<sub>2</sub>) since GEOSECS. The second approach quantifies the total anthropogenic CO<sub>2</sub> inventory using a quasi-conservative tracer,  $\Delta C^*$ . Although the general idea for both techniques has been around for a long time, recent improvements in the estimation of the preserved end-member concentrations together with significant improvements in the accuracy and spatial coverage of global carbon data give us much more confidence in these results. Given the difficulty of isolating the anthropogenic signal from the large TCO<sub>2</sub> background, however, it is relevant to summarize the quality of the carbon data set and the techniques used to estimate the anthropogenic signal.

### 2.1. Data Quality

Over 20,000 water samples collected between December 1994 and July 1996 as part of the U.S. WOCE Indian Ocean survey were analyzed for both TCO<sub>2</sub> and total alkalinity (TA) using standard coulometric and potentiometric techniques, respectively. Figure 1 shows the locations of the 1352 stations occupied by U.S. WOCE as part of the Indian Ocean survey together with the station locations from the GEOSECS Indian Ocean Survey and the French INDIGO I, II, and III and CIVA1 (WOCE designation I6S) cruises. Details of the WOCE/JGOFS Indian Ocean CO<sub>2</sub> measurement program, including personnel, sampling procedures, measurement protocols and data quality assurance/quality control checks are described elsewhere [Johnson *et al.*, 1998; Millero *et al.*, 1998a]. Calibrations of both the TCO<sub>2</sub> and TA systems were checked approximately every 12 hours by analyzing Certified Reference Material (CRM) samples with known concentrations of TCO<sub>2</sub> and TA [Dickson, 1990] (A.G. Dickson, Oceanic carbon dioxide quality control at [http://www-mpl.ucsd.edu/people/adickson/CO2\\_QC/](http://www-mpl.ucsd.edu/people/adickson/CO2_QC/), 1998). On the basis of these CRM analyses the accuracy of the TCO<sub>2</sub> and TA measurements was estimated to be  $\pm 2$  and  $\pm 4$   $\mu\text{mol kg}^{-1}$ , respectively. Primary hydrographic data from the conductivity-temperature-depth/Rosette were collected and analyzed following standard procedures [Millard, 1982]. Samples were collected for salinity on every bottle and analyzed with an Autosol salinometer using standard techniques [UNESCO, 1981]. Oxygen samples were analyzed with an automated system using a modified Winkler technique [Culbertson *et al.*, 1991]. Nutrients were analyzed on a four-channel Technicon AutoAnalyzer II following the methods of Gordon *et al.* [1992]. Chlorofluorocarbon samples were analyzed



**Figure 1.** Station locations for WOCE Indian Ocean (circles), CIVA 1/I6S (crosses), INDIGO I (stars), INDIGO II (inverted triangles), INDIGO III (triangles), and GEOSECS (solid squares) Indian Ocean Surveys. Numbered boxes indicate location of crossovers discussed in the text. Map generated using Generic Mapping Tools version 3 [Wessel and Smith, 1995].

on a gas chromatograph using the techniques of *Bullister and Weiss* [1988]. Complete details of the analytical protocols and personnel can be obtained from the individual cruise reports available through the WOCE Office.

All of the data available at the time this manuscript was written have been included in the Indian Ocean analysis. For the primary hydrographic and nutrient data this means that the preliminary values available at the conclusion of the cruise were used. While we would prefer to use the final hydrographic data, typical postcruise corrections for the WOCE data sets are well below noise level for these calculations. Preliminary to semifinal chlorofluorocarbon (CFC) data were used to estimate the water age necessary for one of the correction terms in the  $\Delta C^*$  method. Although postcruise blank corrections can influence the final CFC concentrations, an examination of the existing data (except I8N15E because data were not available at time of writing) indicated that the CFC-11 and CFC-12 age comparisons as well as comparisons of the data from one leg to the next were reasonably consistent with each other. The calculations were limited to waters with CFC-12 ages of less than 40 years where potential blank corrections are a relatively small fraction of the signal and mixing effects are minimized. The carbon data, which primarily influence the quality of the calculations, have all been calibrated and finalized as discussed briefly below.

Examination of Figure 1 reveals that although the WOCE survey was extensive, a large data gap exists in the southwestern Indian Ocean. To fill in this gap, data from the three French survey legs INDIGO I (February-March 1985), II (April 1986) and III (January-February 1987) as well as the more recent French cruise CIVA1 (February-March 1993 (WOCE designation I6S)) were included in the analysis [*Poisson et al.*, 1988; 1989; 1990]. TCO<sub>2</sub> and TA were analyzed on the INDIGO cruises using standard potentiometric titration techniques developed by *Edmond* [1970]. Potentiometric titrations were also used to analyze the TA samples on CIVA1, but the TCO<sub>2</sub> samples were analyzed using the coulometric techniques of *Johnson et al.* [1985]. The internal consistency of these cruises was examined by comparing carbon values in the deep waters (pressure > 2500 dbars) at the intersections of different legs. The stations selected for each crossover were those with carbon values which were closest to the intersection point. Smooth curves were fit through the data from each cruise as a function of sigma-3 (density anomaly referenced to 3000 dbars) using Cleveland's loess function [*Cleveland and Devlin*, 1988; *Cleveland et al.*, 1992]. The difference between the curves was evaluated at 50 evenly spaced intervals that covered the density range over which the two data sets overlapped. The mean and standard deviation of the difference in TA and TCO<sub>2</sub> at the 35 intersections identified in Figure 1 are shown in Figure 2. The long-term stability of the WOCE/JGOFS measurements can be estimated from the first 17 crossover results. The mean of the absolute values for the leg-to-leg differences was less than the estimated accuracy for both TCO<sub>2</sub> ( $1.8 \pm 0.8 \mu\text{mol kg}^{-1}$ ) and TA ( $2.4 \pm 1.6 \mu\text{mol kg}^{-1}$ ). Although there is only one reliable crossover point between the WOCE/JGOFS cruises and the CIVA1 (I6S) cruise, the differences for both parameters are within the estimated accuracy of the measurements. Results from the analysis of CRM samples on the CIVA1 cruise also support the quality of the measurements. Some of the older INDIGO cruises, however, did appear to have offsets relative to the WOCE/JGOFS and CIVA1 data. INDIGO I and II alkalinity values averaged  $6.5 \mu\text{mol kg}^{-1}$  high and  $6.8 \mu\text{mol kg}^{-1}$  low, respectively, while the INDIGO III alkalinity values showed no clear offset. The INDIGO TCO<sub>2</sub> values were all consistently high relative

to WOCE/JGOFS and CIVA1, with differences of 10.7, 9.4, and  $6.4 \mu\text{mol kg}^{-1}$ , respectively. These offsets are consistent with differences observed between at-sea values and replicate samples run at C.D. Keeling's shore-based TCO<sub>2</sub> facility (P. Guenther, personal communication, 1998). Since the INDIGO cruises were run prior to the introduction of CRMs, these offsets were presumed to be calibration differences, and each leg was adjusted to bring the values in line with the remaining cruises. The dotted boxes in Figure 2 show the original offsets at the crossovers. The solid boxes show the final offsets used in the following calculations. The means of the absolute values for the leg-to-leg differences for all 35 crossover analyses suggest that the final data set is internally consistent to  $\pm 2.2$  and  $3.0 \mu\text{mol kg}^{-1}$  for TCO<sub>2</sub> and TA, respectively.

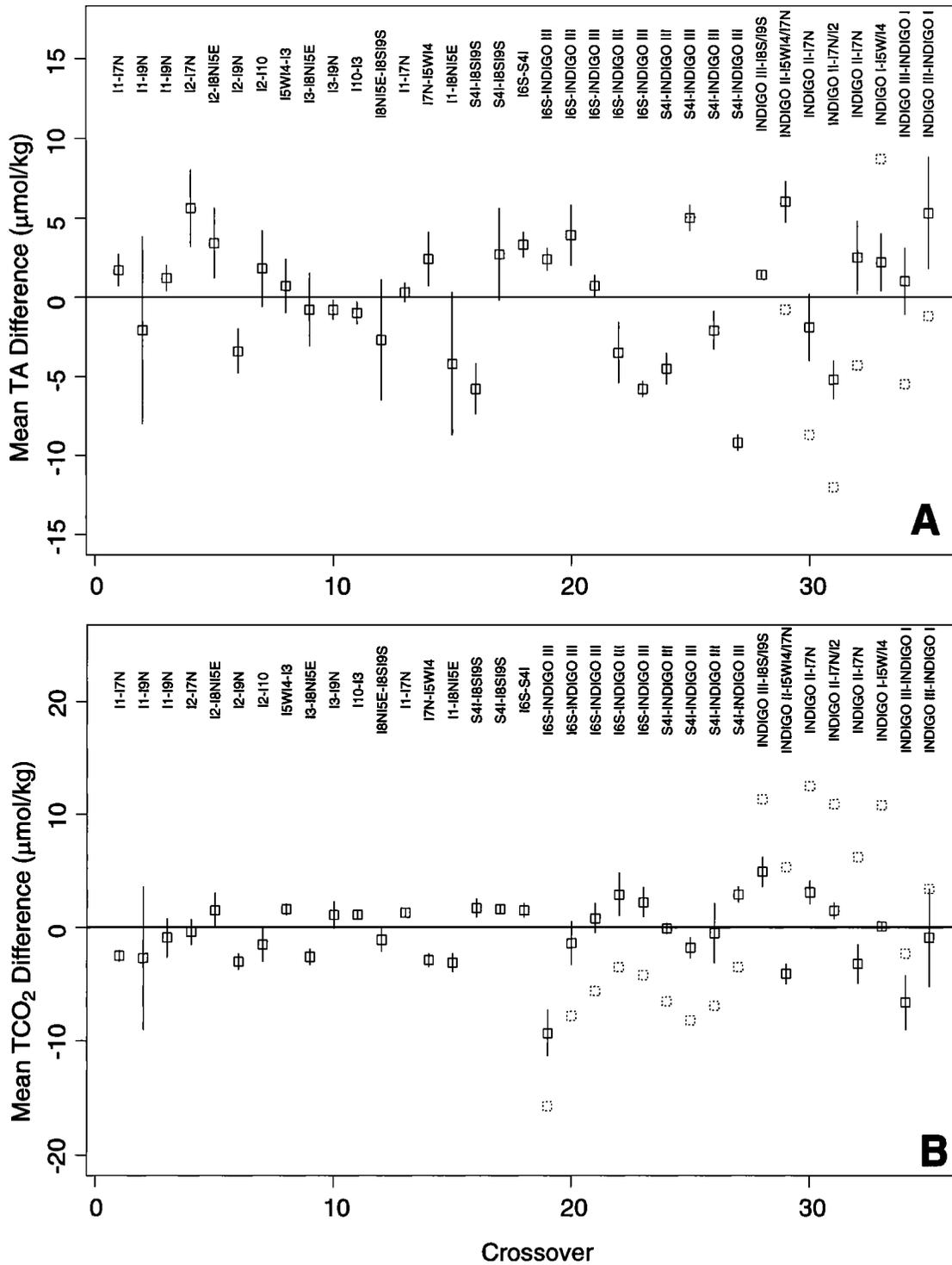
## 2.2. "Time Series" Calculations

The "time series" method for estimating the increase in the anthropogenic inventory uses measurements of TCO<sub>2</sub> made at a certain point in time to develop a predictive equation based on a multiple linear regression of the observed TCO<sub>2</sub> and simultaneously measured parameters such as temperature, salinity, oxygen, and TA (or silicate). These empirical multiparameter relationships have been shown to hold over large spatial scales, and their use drastically reduces the complicating effects of natural variability in determining temporal trends [*Brewer et al.*, 1995; *Wallace*, 1995; *Brewer et al.*, 1997]. The TCO<sub>2</sub> residuals from such predictive equations can be compared directly with patterns of residuals evaluated using the same predictive equation with TA, oxygen, and hydrographic data collected at different times (e.g., over decadal intervals). Since the uptake of anthropogenic CO<sub>2</sub> will increase the TCO<sub>2</sub> of the waters but will not directly affect the concentrations of the fit parameters, systematic changes in the magnitude and distribution of the TCO<sub>2</sub> residuals over time provide a direct estimate of the oceanic CO<sub>2</sub> inventory change due to the uptake of anthropogenic CO<sub>2</sub>. The most comprehensive historical carbon data set for the Indian Ocean is from the GEOSECS expedition. By examining the WOCE data relative to that collected during the 1977-1978 GEOSECS Indian Ocean Survey, the increase in anthropogenic inventory over the last 18 years can be estimated.

**2.2.1. GEOSECS fit.** All of the GEOSECS data from the Indian Ocean (excluding Gulf of Aden and Red Sea regions) were fit with a single predictive equation as a function of potential temperature ( $\theta$ ), salinity (S), apparent oxygen utilization (AOU), and TA. To minimize the influence of short-term temporal variability, only data from pressures greater than 200 dbars were included in the fit. Despite the large area covered, the GEOSECS TCO<sub>2</sub> values can be predicted from this equation to  $\pm 5.2 \mu\text{mol kg}^{-1}$  ( $R^2 = 0.992$  and  $N = 1120$ ). There is, however, a pattern in the residuals that correlates with observed hydrographic regions in the Indian Ocean (Figure 3).

In an attempt to improve the fit, a categorical variable based on region was added to the regression. The categorical variable differs from the other continuous variables by the fact that it is either applied or not applied depending on whether the sample is located within the region. The regions were defined as follows: 1, Arabian Sea (north of 10°N and west of 78°E); 2, North of 10°S (excluding Arabian Sea); 3, Chemical Front (21°S to 10°S); 4, Central Gyre (35°S to 21°S); and 5, Southern Ocean (south of 35°S)

The addition of the regional variable resulted in a marginal improvement in the fit ( $R^2 = 0.993$  and  $\sigma = 4.9 \mu\text{mol kg}^{-1}$ ) but

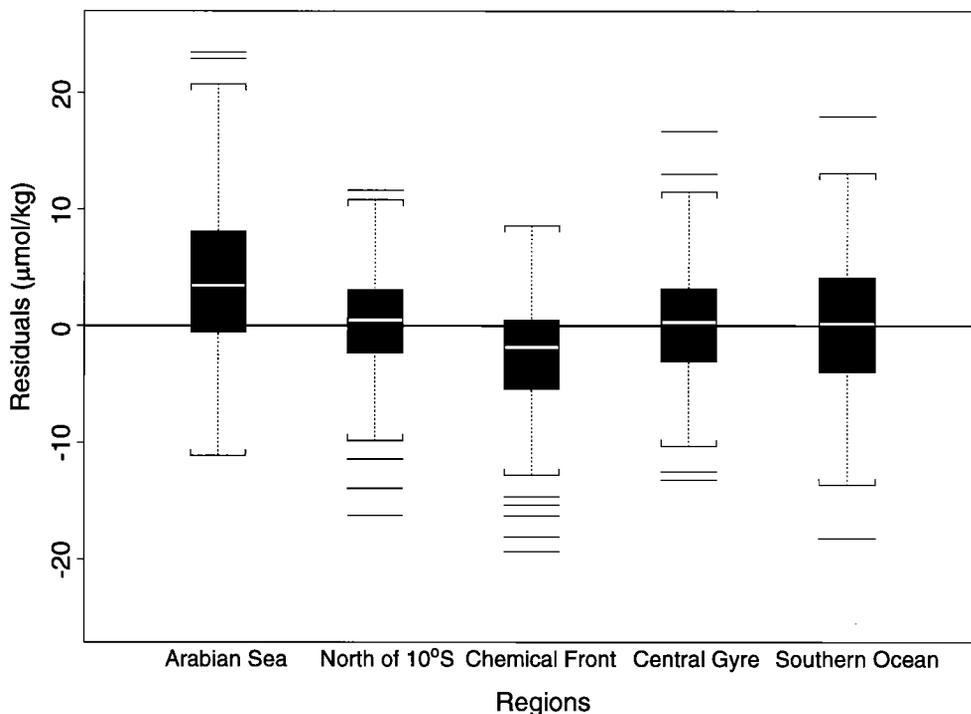


**Figure 2.** Mean difference between deep water values of (a) TA and (b) TCO<sub>2</sub> for cruise intersections identified in Figure 1. Bars indicate one standard deviation. Dotted boxes indicate difference before adjustment (see explanation in text).

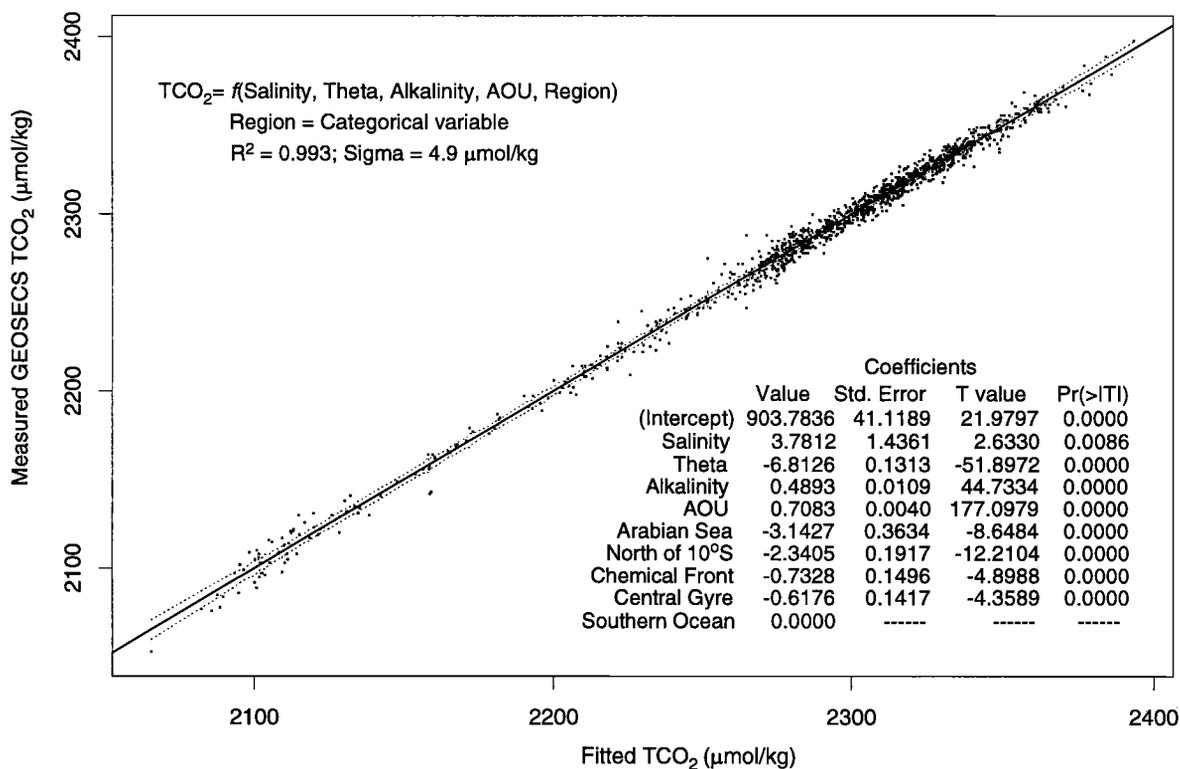
more importantly, removed the regional bias in the predictive equation. The coefficients of the final fit are shown in Figure 4 along with a plot of the measured versus calculated TCO<sub>2</sub> values for all of the points used in the fit. The resulting equation was then used to generate TCO<sub>2</sub> values for each of the WOCE sample locations based on the measured temperature, salinity, oxygen, and TA

values. The difference between the measured TCO<sub>2</sub> and the predicted TCO<sub>2</sub> reflects the CO<sub>2</sub> increase in the time between the two cruises. For this work the difference is referred to as “excess CO<sub>2</sub>.”

The residual method of estimating excess CO<sub>2</sub> was applied to the water column below 200 dbars. The surface waters, however, are dominated by seasonal variability which can bias the residual



**Figure 3.** Box and whiskers plot of residuals from a multiple linear regression of GEOSECS Indian Ocean data (pressure > 200 dbars) fit without the regional designator versus oceanographic region:  $TCO_2 = 706.5 + 7.7S - 6.68\theta + 0.513TA + 0.7257AOU$ . Solid boxes cover the range of  $\pm 1$  standard deviation about the mean. White lines within the boxes indicate median values. The whiskers indicate the range of data within the 99% confidence interval. The bars outside the whiskers give the values of outliers in the data set.



**Figure 4.** Plot of measured GEOSECS  $TCO_2$  versus the calculated values. Solid line shows 1:1 relationship. The dashed lines indicate the 99% confidence interval for the fit. Text gives coefficients and related statistics. The column labeled “Pr(>|T|)” gives the probability that the T value in the previous column is larger than the T table value in a student T test.

calculations. The excess CO<sub>2</sub> of the surface waters therefore was determined from the difference in the estimated annual mean TCO<sub>2</sub> concentrations between GEOSECS and WOCE. The annual mean TCO<sub>2</sub> concentration was calculated from TA and surface water *f*CO<sub>2</sub>. The surface alkalinity was estimated from the gridded annual mean salinity and temperature values of *Levitus et al.* [1994] and *Levitus and Boyer* [1994] using a multiple linear fit of the WOCE/JGOFS surface (pressure < 60 dbars) TA data to the measured surface temperature and salinity. The 1978 and 1995 surface water *f*CO<sub>2</sub> concentrations were estimated from the annual mean atmospheric concentration for the 2 years, and the annual mean Δ*p*CO<sub>2</sub> values estimated from the full correction scheme of *Takahashi et al.* [1997]. The excess TCO<sub>2</sub> values between the surface and 200 dbars were estimated with a linear approximation between the surface and 200 dbars values for each 1° grid box.

**2.2.2. Data consistency.** One of the major concerns with the time series technique is the necessity of having two data sets that are consistent with each other. This consistency can be well documented for both TCO<sub>2</sub> and TA today through the use of certified reference materials (CRMs) supplied by A. Dickson of Scripps Institute of Oceanography (SIO). Since CRMs were not available at the time of GEOSECS, the only way to infer consistency with the WOCE data set is to assume the deep water carbon distributions have not changed since GEOSECS. The most reliable way to compare the two data sets is to examine the difference between the predicted TCO<sub>2</sub> and the measured TCO<sub>2</sub> (excess CO<sub>2</sub>) in deep waters. The basic assumption with this technique is that the correlation between the different hydrographic parameters in the deep waters does not change with time. Given the long residence time of the deep and bottom waters in the ocean, this should be a reasonable assumption. This technique has the advantage that it implicitly accounts for the possibility of real variability in hydrographic properties between the two expeditions which would not be taken into account by simply comparing carbon profiles.

Examination of the excess CO<sub>2</sub> values in waters that should be free of anthropogenic CO<sub>2</sub> (pressures > 2000 dbars and containing no detectable chlorofluorocarbons) revealed that the GEOSECS values were 22.5 ± 3 μmol kg<sup>-1</sup> higher than the comparable WOCE measurements. This difference is comparable to the correction of -18 ± 7 μmol kg<sup>-1</sup> noted by *Weiss et al.* [1983] to make the TCO<sub>2</sub> measurements consistent with the TA and discrete CO<sub>2</sub> partial pressure measurements based on the *Merbach et al.* [1973] dissociation constants. Additional support for an adjustment of the original GEOSECS data comes from C. D. Keeling's shore-based analysis of TCO<sub>2</sub> samples collected on both the GEOSECS and the WOCE/JGOFS expeditions. *Weiss et al.* [1983] point out that the shore-based analyses of Keeling were systematically smaller than the at-sea measurements by 16.5 ± 5 μmol kg<sup>-1</sup> during GEOSECS. Similar comparisons between the WOCE/JGOFS at-sea measurements with Keeling's shore-based analyses indicate that the shore-based samples are approximately 5 μmol kg<sup>-1</sup> higher than the at-sea values (P. Guenther, personal communication, 1998). Together, the GEOSECS-Keeling-WOCE/JGOFS combination suggests an offset of 21.5 μmol kg<sup>-1</sup> between GEOSECS and WOCE/JGOFS at-sea measurements. It is also important to note that there is no indication of a depth or concentration dependent correction for the GEOSECS data. The shore-based comparison, based only on samples collected at the surface, is within 1 μmol kg<sup>-1</sup> of the deep comparison described above. On the basis of these results a constant correction of the -22.5 μmol kg<sup>-1</sup> was applied to the GEO-

SECS TCO<sub>2</sub> values to improve the consistency of the two data sets.

Ideally, the data used in the time series calculations would cover the same geographic region with as much of a time difference as possible. The trade-off, however, is that the quality and spatial coverage of the older data sets is generally very limited. Given the relatively small area of overlap between the WOCE/JGOFS and INDIGO data sets and the shorter time difference between cruises (9 years versus 18 years for WOCE - GEOSECS), the time series analysis was limited to a comparison between WOCE/JGOFS and GEOSECS in the main Indian Ocean basin.

**2.2.3. Evaluation of Errors.** An estimate of the random errors associated with the excess CO<sub>2</sub> calculation can be made with a simple propagation of errors based on the fit to the GEOSECS data and the estimated precision of the WOCE/JGOFS data. With a standard deviation of 4.9 μmol kg<sup>-1</sup> for the GEOSECS fit and an estimated long-term precision of ±2 μmol kg<sup>-1</sup> in the WOCE/JGOFS TCO<sub>2</sub> values the excess CO<sub>2</sub> error is estimated to be approximately ±5 μmol kg<sup>-1</sup>. This value compares well with the standard deviation of 3.5 μmol kg<sup>-1</sup> for the excess CO<sub>2</sub> below the maximum anthropogenic CO<sub>2</sub> penetration depth (pressure > 1500 dbars).

Systematic errors with this technique are very difficult to evaluate. The largest potential systematic error is probably associated with the surface water estimates. Because the same Δ*p*CO<sub>2</sub> value is used to estimate the TCO<sub>2</sub> for both years, the excess CO<sub>2</sub> (1995 TCO<sub>2</sub> - 1978 TCO<sub>2</sub>) is not very sensitive to potential errors associated with the actual Δ*p*CO<sub>2</sub> values used. The surface estimate is sensitive, however, to the assumption that the Δ*p*CO<sub>2</sub> has not changed over time (i.e., that the surface ocean increase has kept pace with the atmospheric increase). It is not likely that the surface ocean has increased at a faster rate than the atmosphere, but it is conceivable that the rate is slower. The current assumption results in a total inventory of 0.8 Pg C in the surface layer. If the surface ocean were increasing at half the rate of the atmosphere, the systematic bias in the final inventory would be around 0.4 Pg C. Below the surface layer the most likely systematic error would result from the uncertainty in fitting the GEOSECS data. Systematic errors associated with calibration differences between cruises are potentially quite large, but the analysis and subsequent correction given in section 2.2.2 should remove these biases. The estimated uncertainty for the GEOSECS adjustment was ±3 μmol kg<sup>-1</sup>. If this value is integrated for the area north of 35°S between 200 m and the average penetration depth of the excess CO<sub>2</sub> (~ 800 m), the potential error would be ±0.9 Pg C. Propagating the errors for the surface and deeper layers gives an estimated error of approximately ±1 Pg C in the total excess CO<sub>2</sub> inventory. Clearly, there are other ways of estimating the potential errors in these calculations, but we feel that this is a reasonable estimate based on the available data.

### 2.3. Δ*C*\* Calculations

*Gruber et al.* [1996] developed a method to estimate the total anthropogenic CO<sub>2</sub> inventory which has accumulated in the water column since preindustrial times. Although the details of the calculation are thoroughly discussed by *Gruber et al.*, the basic concept of the calculation can be expressed in terms of the following equation:

$$C_{\text{anth}} \left( \frac{\mu\text{mol}}{\text{kg}} \right) = C_{\text{m}} - \Delta C_{\text{bio}} - C_{280} - \Delta C_{\text{dis}} \quad (1)$$

where

$C_{\text{anth}}$	anthropogenic carbon concentration;
$C_m$	measured total carbon concentration;
$\Delta C_{\text{bio}}$	change in TCO <sub>2</sub> as a result of biological activity;
$C_{280}$	TCO <sub>2</sub> of waters in equilibrium with an atmospheric CO <sub>2</sub> concentration of 280 $\mu\text{atm}$ ;
$\Delta C_{\text{dis}}$	air-sea difference in CO <sub>2</sub> concentration expressed in $\mu\text{mol kg}^{-1}$ of TCO <sub>2</sub> .

The Gruber et al. technique employs a new quasi-conservative tracer  $\Delta C^*$ , which is defined as the difference between the measured TCO<sub>2</sub> concentration, corrected for biology, and the concentration these waters would have at the surface in equilibrium with a preindustrial atmosphere (i.e.,  $\Delta C^* = C_m - \Delta C_{\text{bio}} - C_{280}$ ). Rearranging (1) shows that  $\Delta C^*$  reflects both the anthropogenic signal and the air-sea CO<sub>2</sub> difference (i.e.,  $\Delta C^* = C_{\text{anth}} + \Delta C_{\text{dis}}$ ). The air-sea disequilibrium component can then be discriminated from the anthropogenic signal using either information about the water age (e.g., from transient tracers such as CFCs or <sup>3</sup>H-<sup>3</sup>He) or the distribution of  $\Delta C^*$  in regions not affected by the anthropogenic transient. The details of this technique will not be covered here except as necessary to explain small modifications that were necessary for use with the WOCE Indian Ocean data set.

**2.3.1. Preformed alkalinity equation.** The first modification to the Gruber et al. [1996] technique involved a recalculation of the preformed alkalinity equation. The preformed alkalinity ( $\text{Alk}^0$ ) of a subsurface water parcel is an estimate of the alkalinity that the water had when it was last at the surface. This value is necessary to determine the equilibrium concentration ( $C_{280}$ ) of the waters. Gruber et al. generated a single global equation for estimating  $\text{Alk}^0$  from salinity and the conservative tracer "PO" ( $\text{PO} = \text{O}_2 + 170 \cdot \text{P}$ ) [Broecker, 1974] based on the data collected during GEOSECS, South Atlantic Ventilation Experiment, Transient Tracers in the Ocean/North Atlantic Study and Transient Tracers in the Ocean/Tropical Atlantic Study. Given the limited representation of the Indian Ocean in these data and the improved quality of today's measurements, the Gruber et al. fit was examined for a possible bias with respect to the WOCE/JGOFS results.  $\text{Alk}^0$  values calculated from the Gruber et al. equation were found to be, on average,  $7 \pm 12 \mu\text{mol kg}^{-1}$  lower than the WOCE/JGOFS measured surface alkalinity values. Rather than making assumptions about which parameters would provide the best fit to the surface alkalinity data, several possible parameters were tested based on previously noted correlations. Although salinity has been shown to generally correlate very strongly with surface alkalinity [Brewer et al., 1986; Millero et al., 1998b], some areas, such as the high-latitude regions, require additional parameters to fit regional changes in alkalinity. Some investigators have used temperature as an additional variable [e.g., Chen and Pytkowicz, 1979; Chen, 1990; Millero et al., 1998b]. Others, such as Gruber et al. [1996], have used other conservative tracers to compensate for the regional differences. The best fit for the WOCE/JGOFS, INDIGO, and CIVA Indian Ocean data, with pressures less than 60 dbars, is given by (2):

$$\text{Alk}^0 = 378.1 + 55.22 \times S + 0.0716 \times \text{PO} - 1.236 \times \theta \quad (2)$$

$\text{Alk}^0$  has units of  $\mu\text{mol kg}^{-1}$  when salinity (S) is on the practical salinity scale, PO is in  $\mu\text{mol kg}^{-1}$ , and potential temperature ( $\theta$ ) is in degrees Celsius. The standard error in the new  $\text{Alk}^0$  estimate is  $\pm 8.0$

**Table 1.** Results From ANOVA Analysis of  $\text{Alk}^0$  Fit.

	Coefficient	Standard Error	T Value	Pr(> T )
Intercept	378.1	8.9	42.2715	0.0000
Salinity	55.22	0.23	235.0369	0.0000
PO	0.0716	0.0041	17.4693	0.0000
Theta	-1.236	0.061	-20.3697	0.0000

The column labeled "Pr(>|T|)" gives the probability that the T value in the previous column is larger than the T table value in a student T test.  $\text{Alk}^0$  is preformed alkalinity, an estimate of the alkalinity of a parcel of subsurface water when it was last at the surface.

$\mu\text{mol kg}^{-1}$  based on 2250 data points. A standard ANOVA analysis of the fit shows that all four terms are highly significant (Table 1). Reevaluating the  $\text{Alk}^0$  equation not only removed the  $7 \mu\text{mol kg}^{-1}$  offset of Gruber's equation but also resulted in a 35% reduction in the uncertainty.

**2.3.2. Denitrification Correction.** A second modification to the original  $\Delta C^*$  technique was necessary to properly account for the anoxic regions in the northern Indian Ocean. The  $C_{\text{bio}}$  term in (1) assumes that the remineralization of carbon in the interior of the ocean occurs in proportion to the oxygen uptake based on a standard Redfield type stoichiometry. The ratios used for these calculations were based on the global estimates of Anderson and Sarmiento [1994]. Gruber et al. [1996] demonstrated that the errors in the  $\Delta C^*$  calculation due to uncertainties in the C:O stoichiometric ratio only become significant for AOU values greater than  $80 \mu\text{mol kg}^{-1}$ . Given that most of the anthropogenic CO<sub>2</sub> is found in relatively shallow waters with low AOU, this error, on average, is small. For some regions of the Arabian Sea, however, oxygen depletion can be quite extensive at relatively shallow depths [Sen Gupta et al., 1976; Deuser et al., 1978; Naqvi and Sen Gupta, 1985]. In areas where the waters become anoxic, denitrification can significantly alter the dissolved carbon to oxygen ratio [Naqvi and Sen Gupta, 1985; Anderson and Dyrssen, 1994; Gruber and Sarmiento, 1997]. The dissolved carbon generated by denitrification shows up as high  $\Delta C^*$  values as demonstrated at the northern end of the section in Figure 5a. The distribution of  $\Delta C^*$  values along the density surface  $\sigma_\theta = 26.9\text{--}27.0$  shows maximum values at both the northern and southern ends of the section. One would expect the uptake of anthropogenic CO<sub>2</sub> to generate the highest values close to the outcrop region in the south, but this surface does not outcrop in the north. Following the methods of Gruber and Sarmiento [1997], the denitrification signal can be estimated using the  $N^*$  tracer.  $N^*$  is a quasi-conservative tracer which can be used to identify nitrogen (N) excess or deficits relative to phosphorus (P). Using the global equation of Gruber and Sarmiento [1997],  $N^*$  is defined as

$$N^* \left( \frac{\mu\text{mol}}{\text{kg}} \right) = 0.87(N - 16P + 2.90) \quad (3)$$

Figure 5b shows the magnitude of the denitrification signal along the  $\sigma_\theta = 26.9\text{--}27.0$  surface. The  $N^*$  values were converted from nitrogen units to  $\mu\text{mol C kg}^{-1}$  based on a denitrification carbon to nitrogen ratio of 106:104 [Gruber and Sarmiento, 1997]. Negative values reflect nitrogen fixation, while positive values indicate denitrification. As expected, the values of  $N^*$  are essentially zero in the main Indian Ocean basin but show a strong denitrification signal at

middepths in the Arabian Sea. The low N\* values at the north end of this surface (Figure 5b) are from the Bay of Bengal and show little or no denitrification in this region. Subtracting a denitrification correction term from the original  $\Delta C^*$  equation lowers the high  $\Delta C^*$  values at the northern end of the section leaving the expected maximum near the outcrop region (Figure 5c).

The final definition for  $\Delta C^*$  as used in this work is given by (4):

$$\begin{aligned} \Delta C^* = & \text{TCO}_2^{\text{(meas)}} - \text{TCO}_2^{\text{(S, T, Alk}^0, 280)} \\ & - \frac{117}{-170} (\text{O}_2 - \text{O}_2^{\text{(sat)}}) \\ & - \frac{1}{2} (\text{TA} - \text{Alk}^0 + \frac{16}{-170} (\text{O}_2 - \text{O}_2^{\text{(sat)}})) \\ & - \frac{106}{-104} \text{N}^* \end{aligned} \quad (4)$$

where  $\text{TCO}_2^{\text{(meas)}}$ , TA, and  $\text{O}_2$  are the measured concentrations for a given water sample in  $\mu\text{mol kg}^{-1}$ .  $\text{Alk}^0$  is the preformed alkalinity value as described in section 2.3.1.  $\text{O}_2^{\text{(sat)}}$  is the calculated oxygen saturation value that the waters would have if they were adiabatically raised to the surface.  $\text{TCO}_2^{\text{(S, T, Alk}^0, 280)}$  is the  $\text{TCO}_2$  value the waters would have at the surface with a TA value equal to  $\text{Alk}^0$  and an  $f\text{CO}_2$  value of 280  $\mu\text{atm}$ .

**2.3.3. Estimation of air-sea disequilibrium.** To isolate the anthropogenic  $\text{CO}_2$  component from  $\Delta C^*$ , the air-sea disequilibrium values ( $\Delta C_{\text{dis}}$ ) must be determined. *Gruber et al.* [1996] described two techniques for estimating these values on density surfaces. For deeper density surfaces one can assume that the waters far away from the outcrop region are free from anthropogenic  $\text{CO}_2$ . The mean  $\Delta C^*$  values in these regions therefore reflect only the disequilibrium value. For shallower surfaces the air-sea disequilibrium can be inferred from the  $\Delta C^*_t$  tracer.

$\Delta C^*_t$  is the difference between  $C^*$  and the concentration the waters would have in equilibrium with the atmosphere at the time they were last at the surface. The time since the waters were in contact with the surface is estimated from CFC-12 age ( $\tau$ ) and the atmospheric  $\text{CO}_2$  concentration history as a function of time ( $f\text{CO}_2\{t_{\text{sample}} - \tau\}$ ). The atmospheric  $\text{CO}_2$  time history from 1750 through 1996 was determined from a spline fit to ice core and measured atmospheric values [*Nefel et al.*, 1994; *Keeling and Whorf*, 1996]. The CFC-12-based ages were determined following the technique described by *Warner et al.* [1996]. The apparent age of the water is determined by matching the CFC-12 partial pressure ( $p\text{CFC-12}$ ) of the waters with the atmospheric CFC-12 concentration history (procedures and atmospheric time history provided by J. Bullister). Although CFCs do not give a perfect representation of the true calendar age of the waters, *Doney et al.* [1997] have shown that the CFC-12 and  $^3\text{H-}^3\text{He}$  ages in the North Atlantic agree within 1.7 years for ages less than 30 years. *Gruber* [1998] successfully used both CFC and  $^3\text{H-}^3\text{He}$  ages for his disequilibrium calculations in the Atlantic and has thoroughly discussed the assumptions and caveats associated with these techniques. The disequilibrium values on shallow density surfaces presented here were calculated using CFC-12 ages modified from the  $\Delta C^*_t$  equation of *Gruber* [1998] to include the denitrification correction:

$$\begin{aligned} \Delta C^*_t = & \text{TCO}_2^{\text{(meas)}} - \text{TCO}_2^{\text{(S, T, Alk}^0, f\text{CO}_2\{t_{\text{sample}} - \tau\})} \\ & - \frac{117}{-170} (\text{O}_2 - \text{O}_2^{\text{(sat)}}) \\ & - \frac{1}{2} (\text{TA} - \text{Alk}^0 + \frac{16}{-170} (\text{O}_2 - \text{O}_2^{\text{(sat)}})) \\ & - \frac{106}{-104} \text{N}^* \end{aligned} \quad (5)$$

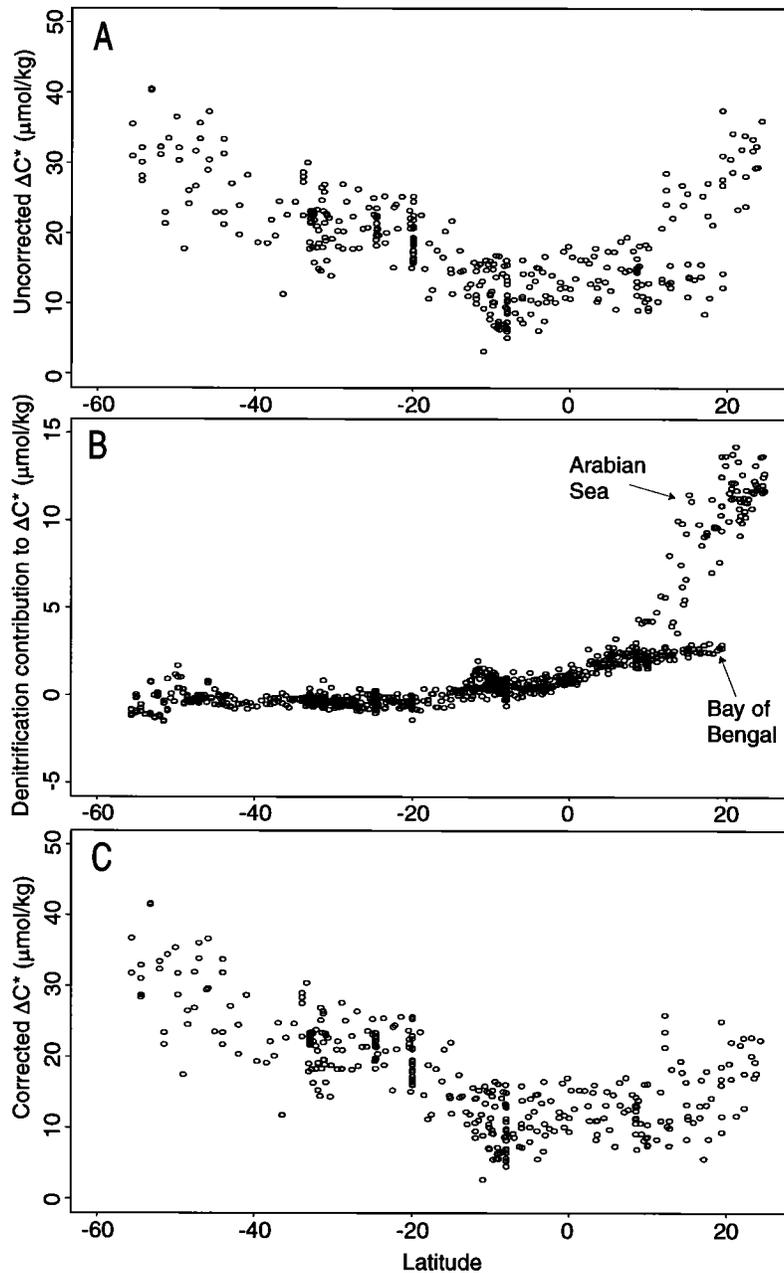
where  $\text{TCO}_2^{\text{(S, T, Alk}^0, f\text{CO}_2\{t_{\text{sample}} - \tau\})}$  is the  $\text{TCO}_2$  the waters would have at the surface with a TA value of  $\text{Alk}^0$  and an  $f\text{CO}_2$  value in equilibrium with the atmospheric  $\text{CO}_2$  concentration at the time the waters were last at the surface (date of sample collection minus CFC age).

The CFC age method was used for waters with densities less than  $\sigma_\theta = 27.25$  and CFC-12 ages less than 40 years. The anthropogenic  $\text{CO}_2$  of the waters with pressures less than 150 dbars or densities less than  $\sigma_\theta = 25.95$  was determined by subtracting the  $\Delta C^*_t$  value estimated at each sample location from the corresponding  $\Delta C^*$  value. Given that the Indian Ocean does not extend into the high northern latitudes, the major outcrop region for Indian Ocean waters below the mixed layer is toward the south. Although other tracers might be used to identify multiple end-members, the CFC-12 ages on each density surface get steadily older toward the north, and the  $\Delta C^*_t$  values are reasonably constant (see diamonds in Figure 6). This suggests that most of the water in the Indian Ocean is derived from the south or, at least in terms of the air-sea disequilibrium, cannot be distinguished from other sources. The  $\Delta C_{\text{dis}}$  term for the main Indian Ocean basin therefore was determined from a mean  $\Delta C^*_t$  value on each surface. The mean  $\Delta C_{\text{dis}}$  terms were then subtracted from the individual  $\Delta C^*$  values to determine the anthropogenic component. Table 2 summarizes the  $\Delta C_{\text{dis}}$  values for the density surfaces estimated exclusively from the  $\Delta C^*_t$  method.

One major exception to the southern source waters is observed in the Arabian Sea. Although none of the surfaces with  $\sigma_\theta$  values greater than 26.0 outcrop in the Arabian Sea, a number of higher-density surfaces do outcrop in the Red Sea and Persian Gulf. These outcrops could provide pathways for the introduction of CFCs and anthropogenic  $\text{CO}_2$  into the northern Arabian Sea and could reset the disequilibrium term. *Wyrki* [1973] noted that the Red Sea and Persian Gulf waters mix in the Arabian Sea to form the high-salinity North Indian Intermediate Water (NIIW). The  $\Delta C^*_t$  values in the Arabian Sea do vary significantly and generally have a strong correlation with salinity. The CFC-12 ages also begin to get younger toward the northern end of the Arabian Sea. These high-salinity waters appear to have a higher disequilibrium term than the lower-salinity waters that make up the majority of the Indian Ocean intermediate waters.

To account for this phenomenon, the Arabian Sea waters (north of 5°N and west of 78°E) were isolated, and the  $\Delta C^*_t$  values were fit against salinity with a linear regression. Thus this region was treated as a two-end-member mixing scenario between the high-salinity NIIW and the lower-salinity waters of the main Indian Ocean basin. The  $\Delta C_{\text{dis}}$  values in this region were determined based on the relative contributions of the two end-members using salinity as a conservative tracer. The coefficients for the Arabian Sea fits are given in Table 2. The difference between the high-salinity and lower-salinity disequilibria generally decreased as densities increased (note decreasing slope values in Table 2) to the point where the Arabian Sea disequilibrium values were no longer distinguishable from the main Indian Ocean basin values. The additional terms were dropped for surfaces where the two end-member mixing terms resulted in values within the error of the basin-wide mean (Table 2).

As stated previously, the disequilibrium term for the deeper, CFC free surfaces was determined directly from the mean  $\Delta C^*$  value of each density interval. Careful examination of the extent of CFC penetration along the density surface was used to limit data used in



**Figure 5.**  $\Delta C^*$  values for data on the 26.9 - 27.0  $\sigma_\theta$  surface: (a) calculated without denitrification, (b) denitrification signal put in terms of  $\Delta C^*$ , (c) with denitrification correction (i.e., data in Figure 5a minus the data in Figure 5b).

determining the  $\Delta C_{\text{dis}}$  term. Only regions where CFC concentrations were below a reasonable blank ( $0.005 \text{ pmol kg}^{-1}$ ) were considered. The  $\Delta C_{\text{dis}}$  values determined using this method are summarized in the lower half of Table 3 ( $\sigma_\theta > 27.5$ ).

Determination of the  $\Delta C_{\text{dis}}$  values for either shallow or deep surfaces is relatively straightforward using the techniques mentioned above. It is not straightforward, however, to estimate the  $\Delta C_{\text{dis}}$  values for intermediate levels where the CFC ages are relatively old and may be significantly influenced by mixing and yet the waters could have enough anthropogenic CO<sub>2</sub> to influence the

estimates based on  $\Delta C^*$ . The effect of using the  $\Delta C^*$  technique in waters that actually have anthropogenic CO<sub>2</sub> would be to overestimate the  $\Delta C_{\text{dis}}$  term and thus underestimate the anthropogenic CO<sub>2</sub>. The effect of mixing on the CFC ages, however, generally results in an underestimation of the CFC age which would lead to an underestimation of the  $\Delta C_{\text{dis}}$  term and an overestimation of the anthropogenic CO<sub>2</sub>. The CFC age technique has additional problems in waters with  $\sigma_\theta$  values greater than 27.25, because the waters with the younger ages are all found in the very high latitudes of the Southern Ocean and generally are not directly venti-

**Table 2.** Values of  $\Delta C_{\text{dis}}$  Determined on Potential Density ( $\sigma_\theta$ ) Intervals

Potential Density Range	Main Basin Mean (SDM)	Main Basin Number of Points	Arabian Intercept (SD)	Arabian Slope (SD)	Arabian Number of Points
25.95-26.05	-1.3 ( $\pm 0.88$ )	56	-740 ( $\pm 92$ )	21.3 ( $\pm 3$ )	12
26.05-26.15	-0.7 ( $\pm 1.21$ )	42	-745 ( $\pm 130$ )	21.4 ( $\pm 4$ )	12
26.15-26.25	-3.4 ( $\pm 0.65$ )	63	-699 ( $\pm 76$ )	20.0 ( $\pm 2$ )	11
26.25-26.35	-4.8 ( $\pm 0.62$ )	61	-516 ( $\pm 90$ )	14.8 ( $\pm 3$ )	12
26.35-26.45	-5.6 ( $\pm 0.48$ )	83	-316 ( $\pm 84$ )	9.1 ( $\pm 2$ )	20
26.45-26.55	-7.1 ( $\pm 0.34$ )	103	-558 ( $\pm 87$ )	15.9 ( $\pm 2$ )	21
26.55-26.65	-7.2 ( $\pm 0.32$ )	123	-512 ( $\pm 53$ )	14.5 ( $\pm 1$ )	28
26.65-26.75	-8.9 ( $\pm 0.27$ )	152	-397 ( $\pm 52$ )	11.2 ( $\pm 1$ )	34
26.75-26.85	-9.1 ( $\pm 0.23$ )	254	-428 ( $\pm 66$ )	12.0 ( $\pm 2$ )	28
26.85-26.95	-11.2 ( $\pm 0.31$ )	209	-285 ( $\pm 115$ )	7.9 ( $\pm 3$ )	6
26.95-27.00	-12.2 ( $\pm 0.35$ )	104	-	-	-
27.00-27.05	-13.8 ( $\pm 0.48$ )	92	-	-	-
27.05-27.10	-15.2 ( $\pm 0.40$ )	90	-	-	-
27.10-27.15	-16.3 ( $\pm 0.47$ )	84	-	-	-
27.15-27.20	-17.1 ( $\pm 0.51$ )	89	-	-	-
27.20-27.25	-19.5 ( $\pm 0.56$ )	74	-	-	-

Standard deviations (SD) are given for the slope and intercept terms for the Arabian Sea data. Standard deviation of the mean (SDM, i.e., standard deviation weighted by the number of individual determinations) is given for each main basin estimate. Values of  $\Delta C_{\text{dis}}$  are given in  $\mu\text{mol kg}^{-1}$ . Dashes indicate value not determined.

lated in these regions. Therefore the basic assumption that the  $\Delta C_{\text{dis}}$  term can be determined by following the density level to its outcrop and examining the younger waters there is not valid.

As a general rule, the errors associated with the CFC age technique increase at higher density levels, and the errors associated

with the  $\Delta C^*$  technique decrease at higher density levels. To minimize the errors in the final  $\Delta C_{\text{dis}}$  determination, waters with  $\sigma_\theta$  values between 27.25 and 27.5 were evaluated using a combination of the two methods mentioned above. The 27.25 cut in the CFC age technique was chosen because this density corresponds

**Table 3.** Values of  $\Delta C_{\text{dis}}$  Determined on Potential Density ( $\sigma_\theta$ ) Intervals

Potential Density Range	Mean $\Delta C^*$ (SDM)	Number of Points	Mean $\Delta C^*_t$ (SDM)	Number of Points	Final Mean $\Delta C_{\text{dis}}$ (SDM)
27.25-27.30	-2.3 ( $\pm 0.45$ )	42	-19.7 ( $\pm 0.98$ )	22	-8.3 ( $\pm 1.13$ )
27.30-27.35	-4.0 ( $\pm 0.49$ )	45	-21.0 ( $\pm 0.84$ )	19	-9.1 ( $\pm 1.06$ )
27.35-27.40	-5.3 ( $\pm 0.44$ )	72	-22.5 ( $\pm 1.25$ )	7	-6.8 ( $\pm 0.69$ )
27.40-27.45	-7.1 ( $\pm 0.26$ )	92	-23.5 ( $\pm 0.83$ )	10	-8.7 ( $\pm 0.54$ )
27.45-27.50	-7.9 ( $\pm 0.30$ )	98	-25.0 ( $\pm 1.65$ )	7	-9.0 ( $\pm 0.51$ )
27.50-27.55	-9.3 ( $\pm 0.28$ )	93	-	-	-9.3 ( $\pm 0.28$ )
27.55-27.60	-10.7 ( $\pm 0.28$ )	92	-	-	-10.7 ( $\pm 0.28$ )
27.60-27.65	-11.3 ( $\pm 0.34$ )	125	-	-	-11.3 ( $\pm 0.34$ )
27.65-27.70	-13.0 ( $\pm 0.36$ )	127	-	-	-13.0 ( $\pm 0.36$ )
27.70-27.75	-14.8 ( $\pm 0.30$ )	184	-	-	-14.8 ( $\pm 0.30$ )
27.75-27.80	-15.3 ( $\pm 0.24$ )	349	-	-	-15.3 ( $\pm 0.24$ )
>27.80	-18.6 ( $\pm 0.15$ )	629	-	-	-18.6 ( $\pm 0.15$ )

Standard deviation of the mean given in brackets (SDM, i.e., standard deviation weighted by the number of individual determinations). Values of  $\Delta C_{\text{dis}}$  are given in  $\mu\text{mol kg}^{-1}$ . Dashes indicate value not determined.

with the core of the Antarctic Intermediate water and also generally the highest-density water that outcrops in this region [Wyrki, 1973; Levitus and Boyer, 1994; Levitus et al., 1994]. To help ensure that the  $\Delta C_{\text{dis}}$  values were determined on waters moving into the main Indian Ocean basin, mean  $\Delta C^*_t$  values were only estimated from samples north of 35°S with CFC-12 ages less than 40 years. Mean  $\Delta C^*$  values were also determined on the same density surfaces for samples where CFCs were measured, but concentrations were below 0.005 pmol kg<sup>-1</sup>. The final mean value used for the  $\Delta C_{\text{dis}}$  correction on each surface was determined from the mean of the combined individual estimates from each method (Table 3).

Examination of the individual and combined means in Table 3 indicates that there is a sizeable spread in the estimates from the two techniques in the overlap region. This difference is maximized since these density levels are pushing the limits of both techniques, and the errors in both estimates serve to increase this difference. Since the number of points available from the CFC age technique generally decreased at greater density levels and the number of points from the  $\Delta C^*$  technique generally increased at greater density levels, the mean becomes progressively more heavily weighted toward the  $\Delta C^*$  technique as the density levels increased. Although this is not the ideal solution, we believe that this minimizes the potential errors as much as possible. The technique used to estimate final  $\Delta C_{\text{dis}}$  values in this region could systematically bias the anthropogenic CO<sub>2</sub> inventory estimates. The magnitude of this potential error on the final inventory was estimated to be approximately  $\pm 1.8$  Pg C by integrating the difference between the two methods over the affected water volume. This estimate represents a maximum potential error since the known limitations of each method work to increase the differences in  $\Delta C_{\text{dis}}$ .

**2.3.4. Time adjustment for INDIGO data.** One difficulty with combining data from different cruises for a time-dependent calculation like the anthropogenic CO<sub>2</sub> inventory is the issue of getting the data sets referenced to a common time. One of the advantages of the WOCE/JGOFS Indian Ocean survey data is the fact that all of the samples were collected in a little over a year's time. In terms of the CO<sub>2</sub> inventory this is essentially a synoptic data set. The couple of years between the CIVA1 cruise and the WOCE/JGOFS data are also not distinguishable in terms of the anthropogenic increase. The INDIGO data, however, were collected 8–10 years before the WOCE/JGOFS data set and must be adjusted to reflect the anthropogenic uptake during that time. Unfortunately, any correction of this sort can have large errors and potentially bias the results. This problem must be weighed against the errors of ignoring the time difference between cruises or omitting these data entirely. The decision to correct the INDIGO data was based on two factors. First, analysis of the change in anthropogenic inventory between GEOSECS and WOCE (discussed below) indicated that a significant fraction of the total anthropogenic uptake has occurred in the past 2 decades. Second, careful examination of objective maps of anthropogenic CO<sub>2</sub> made prior to the INDIGO correction showed obvious, anomalously low concentrations in the regions strongly dependent on the INDIGO data. Two different adjustment functions were made depending on whether the stations were located in the main Indian Ocean basin or in the Southern Ocean.

North of 30°S, where portions of the INDIGO data were located relatively near WOCE stations, a crossover comparison of the INDIGO anthropogenic CO<sub>2</sub> concentrations as a function of

density was made with the WOCE/JGOFS data in that region. The difference between the two data sets was evaluated at  $\sigma_\theta$  intervals of 0.05 from the surface to  $\sigma_\theta = 27.5$  and added to the INDIGO data. This correction ranged from approximately 12  $\mu\text{mol kg}^{-1}$  at the surface down to zero at 27.5.

South of 30°S, there were very few WOCE or CIVA1 stations close enough for a proper crossover comparison. It was clear from the northern data, however, that some correction was necessary. Given that the isolines for most properties in the Southern Ocean run east-west, we decided to correct the southern INDIGO data based on a crossover comparison with all results from CIVA1 and WOCE cruises in that region. The average adjustment for the southern stations was approximately 11  $\mu\text{mol kg}^{-1}$  over the same density range. The magnitude of the corrections in both regions is consistent with the expected increase over the time period between cruises.

**2.3.5. Evaluation of Errors.** Error evaluation is much more difficult for the  $\Delta C^*$  method than for the time series approach because of potential systematic errors associated with some of the parameters (i.e., the biological correction). The random errors associated with the anthropogenic CO<sub>2</sub> can be determined by propagating through the precision of the various measurements required for the calculation of (4).

$$\begin{aligned} \{\sigma_{C_{\text{anth}}}\}^2 &= \{\sigma_C\}^2 + \{-\sigma_{C_{\text{eq}}}\}^2 \\ &+ \{(-R_{\text{CO}} - 0.5R_{\text{NO}})\sigma_{\text{O}_2}\}^2 \\ &+ \{(R_{\text{CO}} + 0.5R_{\text{NO}})\sigma_{\text{O}_{2[\text{sat}]}}\}^2 \\ &+ \{-0.5\sigma_{\text{TA}}\}^2 + \left\{ \left( -\frac{\partial C_{\text{eq}}}{\partial \text{TA}} + 0.5 \right) \sigma_{\text{Alk}^0} \right\}^2 \\ &+ \{0.8667\sigma_{\text{N}}\}^2 + \{13.867\sigma_{\text{P}}\}^2 \\ &+ \left\{ 0.8667 \left( -P - \frac{N - 16P + 2.9}{120} \right) \sigma_{\text{R}_{\text{N:P}[\text{nit}]}} \right\}^2 \\ &+ \{-0.00111(N - 16P + 2.9)\sigma_{\text{R}_{\text{N:P}[\text{denitr}]}}\}^2 \\ &- \{\sigma_{\Delta C_{\text{dis}}}\}^2 \end{aligned} \quad (6)$$

where  $\sigma_C = 2 \mu\text{mol kg}^{-1}$ ;  $\sigma_{C_{\text{eq}}} = 4 \mu\text{mol kg}^{-1}$ ;  $\sigma_{\text{O}_2} = 1 \mu\text{mol kg}^{-1}$ ;  $\sigma_{\text{O}_{2[\text{sat}]}} = 4 \mu\text{mol kg}^{-1}$ ;  $\sigma_{\text{TA}} = 4 \mu\text{mol kg}^{-1}$ ;  $\frac{\partial C_{\text{eq}}}{\partial \text{TA}} = 0.842$ ;  $\sigma_{\text{Alk}^0} = 7.8 \mu\text{mol kg}^{-1}$ ;  $\sigma_{\text{N}} = 0.2 \mu\text{mol kg}^{-1}$ ;  $\sigma_{\text{P}} = 0.02 \mu\text{mol kg}^{-1}$ ;  $\sigma_{\text{R}_{\text{N:P}[\text{nit}]}} = 0.25$ ; and  $\sigma_{\text{R}_{\text{N:P}[\text{denitr}]}} = 15$ . The equation for the random error analysis is adapted from Gruber et al. [1996] (excluding those terms that involve the C:O Redfield error) with additional terms for the error propagation of the N\* correction [Gruber and Sarmiento, 1997]. The terms involving the C:O are evaluated separately below because the random errors cannot be isolated from potential systematic errors. The sigma values used in (6) were either taken from the appropriate WOCE cruise reports or from previously determined estimates of Gruber et al. [1996] and Gruber and

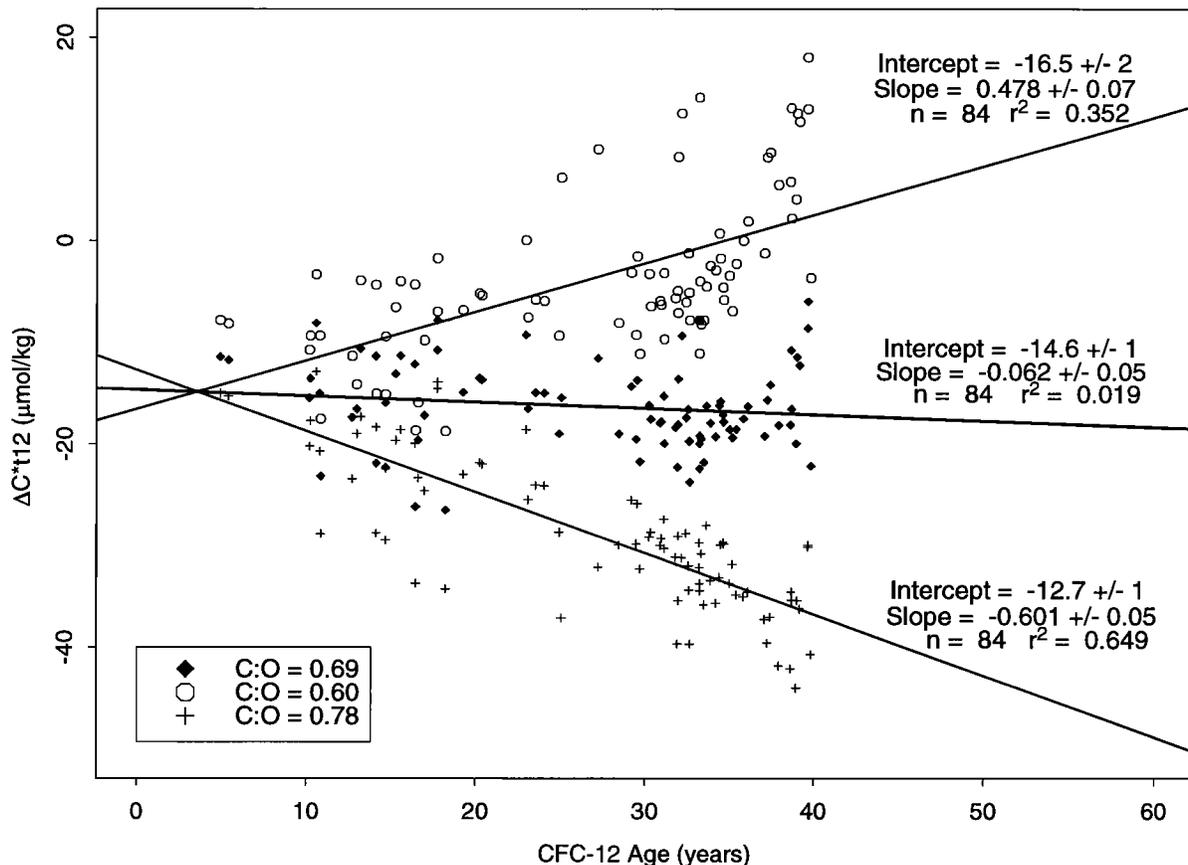
Sarmiento [1997]. The error in the  $\Delta C_{\text{dis}}$  term is taken from the average value for the standard deviation of the mean for the examined surfaces ( $\sigma_{\Delta C_{\text{dis}}} = 0.5 \mu\text{mol kg}^{-1}$ ). The formulation given in (6) results in an estimated error of  $6.1 \mu\text{mol kg}^{-1}$ . This estimate is larger than the standard deviation of the  $\Delta C^*$  values below the deepest anthropogenic CO<sub>2</sub> penetration depth ( $\pm 2.8 \mu\text{mol kg}^{-1}$  for pressure > 2000 dbars) suggesting that the propagated errors may be a maximum estimate of the random variability.

The potential systematic errors associated with the anthropogenic CO<sub>2</sub> calculation are much more difficult to evaluate. The random error estimate above includes all terms except those associated with the C:O biological correction. Although other terms involving N:O and N:P corrections potentially have systematic offsets associated with errors in the ratio estimates, the only potentially significant errors involve the C:O corrections [Gruber *et al.*, 1996; Gruber, 1998].

There is evidence, however, that the Anderson and Sarmiento [1994] stoichiometric ratios must be reasonably close to the actual remineralization ratios observed in the Indian Ocean. Figure 6 is a plot of  $\Delta C^*_{\text{t12}}$  based on CFC-12 ages for the density interval from  $\sigma_{\theta} = 27.1$  to  $\sigma_{\theta} = 27.15$ . The diamonds are the values calculated from (5). These values represent the preserved air-sea disequilibrium value for the past 40 years and should be constant if the air-sea dis-

equilibrium has not changed over time (i.e., that the surface ocean CO<sub>2</sub> is increasing at the same rate at the atmosphere). A linear regression of the diamonds in Figure 6 yields a slope that is not significantly different from zero. The circles and pluses are the  $\Delta C^*_{\text{t}}$  values one would get by using a C:O ratio of -0.60 and -0.78 in (5), respectively. These C:O values represent one standard deviation from the Anderson and Sarmiento [1994] mean value of -0.69. The -0.60 ratio results in values with a significant positive slope. This slope would imply that the surface ocean CO<sub>2</sub> is increasing much slower than the atmospheric increase. While this is possible, the -0.60 ratio is much larger than historical Redfield estimates and would be very difficult to justify. The -0.78 ratio is more typical of historical estimates but results in a significant negative slope in the  $\Delta C^*_{\text{t}}$  values with time. A negative slope would imply that carbon is accumulating in the ocean faster than the atmosphere. Neither of these scenarios seems very likely. The fact that none of the  $\Delta C^*_{\text{t}}$  values on the examined surfaces exhibit a statistically significant slope suggests that the C:O value of -0.69 does accurately represent the remineralization ratio for these waters and supports the methodology of taking a mean value of  $\Delta C^*_{\text{t}}$  on these density surfaces.

A sensitivity study was also used to evaluate the potential error associated with an incorrect C:O value. Two additional estimates of anthropogenic CO<sub>2</sub> were determined using the -0.60 and -0.78



**Figure 6.** Plot of  $\Delta C^*_{\text{t}}$  based on CFC-12 ages for the density interval from  $\sigma_{\theta} = 27.1$  to  $27.15$  versus CFC-12 age. The diamonds were calculated using the Anderson and Sarmiento [1994] C:O (-0.69). The circles and pluses were calculated from C:O of -0.60 and -0.78, respectively. Lines and text give results from a linear regression of the three sets of data.

C:O values. Since the C:O correction applies to both  $\Delta C^*$  and the  $\Delta C^*_t$  terms, the disequilibrium values were reevaluated in the same manner as described above. The range of anthropogenic values from these three estimates varied as a function of apparent oxygen utilization (AOU) from 0.0 to 22 with an average difference of only 4.2  $\mu\text{mol kg}^{-1}$ . Because the C:O correction affects both the  $\Delta C^*$  and  $\Delta C^*_t$  terms together, much of the systematic error in the final anthropogenic estimate ( $\Delta C^* - \Delta C^*_t$ ) cancels out.

#### 2.4. Inventory Estimates

Basin-wide anthropogenic and excess CO<sub>2</sub> concentrations (WOCE/JGOFS - GEOSECS) were evaluated on a 1° grid at 100 m intervals between the surface and 2600 m using the objective mapping techniques of *Sarmiento et al.* [1982]. Total anthropogenic CO<sub>2</sub> was mapped over an area from 20° to 120°E and 70°S to 30°N (excluding areas of land, the Red Sea, the Persian Gulf, and the South China Sea). Because the WOCE/JGOFS data set did not cover much of the Southern Ocean, the excess CO<sub>2</sub> maps were limited to the area north of 35°S. The values at each level were multiplied by the volume of water in the 100 m slab and summed to generate the total anthropogenic or excess CO<sub>2</sub> inventory. The method of integrating mapped surfaces compared very well with the technique of vertically integrating each station and mapping the station integrals.

It is extremely difficult to evaluate a reasonable estimate of the potential errors associated with the inventory estimates. A simple propagation of errors implies that the random errors associated with any individual anthropogenic estimate is approximately  $\pm 6.1 \mu\text{mol kg}^{-1}$ , but these errors should essentially cancel out for an integrated inventory based on nearly 25,000 individual estimates. Systematic errors have by far the largest impact on the inventory estimates. Potential errors as large as  $\pm 1.8 \text{ Pg C}$  have been estimated for the  $\Delta C_{\text{dis}}$  term. Sensitivity studies with the C:O variations give a range of total inventory estimates of  $\pm 2.5 \text{ Pg C}$ . Other systematic errors could also be generated from the denitrification term, the terms involving N:O, the time correction for the INDIGO data, and the mapping routines used in the inventory estimates. The magnitude of these errors is believed to be much smaller than the uncertainty in either the C:O correction or the  $\Delta C_{\text{dis}}$  determination. Propagation of the two estimated uncertainties gives an overall error of approximately  $\pm 3 \text{ Pg C}$  for the total inventory. An error of roughly 15% is comparable to previous error estimates using this technique [*Gruber et al.*, 1996; *Gruber*, 1998]. Errors for regional inventories are assumed to scale to the total.

### 3. Results and Discussion

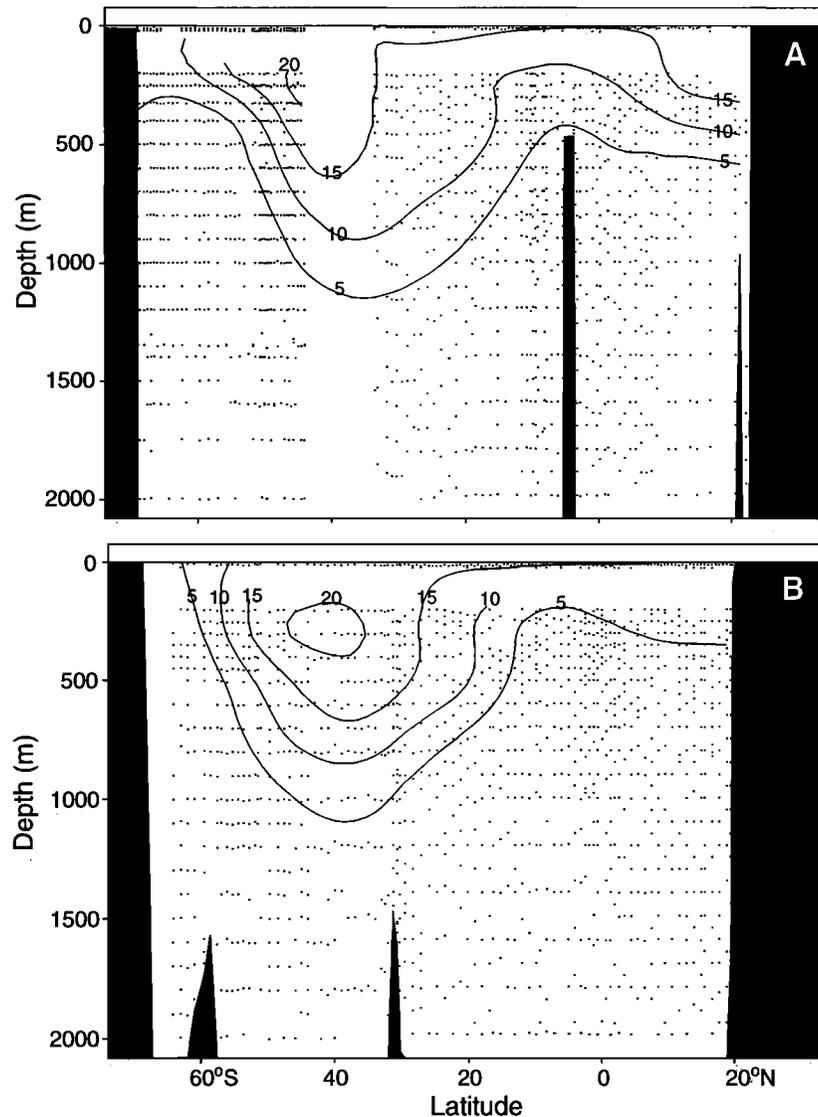
The excess CO<sub>2</sub> concentrations for the Indian Ocean range from 0 to 25  $\mu\text{mol kg}^{-1}$ . The most prominent feature in the excess CO<sub>2</sub> distribution, as shown with representative sections in the eastern and western Indian Ocean (Figure 7), is the maximum in concentrations at midlatitudes (~40°S). This maximum is coincident with the relatively strong gradient in surface density associated with the Subtropical Convergence and the transition from the high-salinity subtropical gyre waters to the low-salinity Antarctic waters. The outcropping of these density surfaces and subsequent sinking of surface waters provides a pathway for excess CO<sub>2</sub> to enter the interior of the ocean. Relatively high excess CO<sub>2</sub> concentrations can also be observed at the very northern end of the western section (Figure 7a). Although not readily evident from this

section, the distribution of concentration gradients indicates that excess CO<sub>2</sub> is entering the northern Indian Ocean from the Persian Gulf and Red Sea regions. This is likely to result from the outcropping of density surfaces in these areas which are not ventilated in the main Indian Ocean basin. The implied Red Sea and Persian Gulf sources of CO<sub>2</sub> are consistent with uptake estimates of anthropogenic CO<sub>2</sub> in these areas as observed by *Papaud and Poisson* [1986]. The third major feature observed in the excess CO<sub>2</sub> distribution is a dramatic shoaling of the excess CO<sub>2</sub> isolines south of approximately 40°S. *Poisson and Chen* [1987] attributed the low anthropogenic CO<sub>2</sub> concentrations in Antarctic Bottom Water to a combination of the pack sea ice blocking air-sea gas exchange and the upwelling of old Weddell Deep Water. This explanation is consistent with the observed excess CO<sub>2</sub> distributions in this study.

The general features observed with excess CO<sub>2</sub> are also observed in the anthropogenic CO<sub>2</sub> distribution (Figure 8). The range of values, however, extends up to 55  $\mu\text{mol kg}^{-1}$ . The maximum depth of the 5  $\mu\text{mol kg}^{-1}$  contour is approximately 1300 m at around 40°S, only 200 m deeper than the maximum depth of the 5  $\mu\text{mol kg}^{-1}$  contour of excess CO<sub>2</sub>. The similarity in maximum penetration depth between the 200 year and the 18 year anthropogenic CO<sub>2</sub> accumulation, together with the wide range of depths covered by the 5  $\mu\text{mol kg}^{-1}$  isoline, indicates that the primary pathway for CO<sub>2</sub> to enter the ocean's interior is from movement along isopycnals, not simple diffusion or cross isopycnal mixing from the surface. The 1300 m penetration results from the downwarping of the isopycnals in the region of the Subtropical Convergence. Likewise, the low anthropogenic CO<sub>2</sub> concentrations in the high-latitude Southern Ocean result from the compression and shoaling of isopycnal surfaces in that region. Although the complex oceanography of the Southern Ocean may call into question some of the assumptions regarding mixing and nutrient uptake ratios with these techniques, both the time series excess CO<sub>2</sub> and the  $\Delta C^*$  anthropogenic CO<sub>2</sub> calculations clearly indicate that the anthropogenic CO<sub>2</sub> concentrations south of approximately 50°S are relatively small.

The distribution of anthropogenic CO<sub>2</sub> determined in this study is similar to the distribution presented by *Chen and Chen* [1989] based on GEOSECS and INDIGO data. Although the penetration depth at 40°S was slightly deeper than observed with this study (1400-1600 m for the 5  $\mu\text{mol kg}^{-1}$  isoline), *Chen and Chen* also observed a significant shoaling of the anthropogenic CO<sub>2</sub> isolines toward the south. They suggest that anthropogenic CO<sub>2</sub> has only penetrated a few hundred meters into the high-latitude (>50°S) Southern Ocean.

There has been debate in the literature over recent years as to the importance of the Southern Ocean as a sink for anthropogenic CO<sub>2</sub> [e.g., *Sarmiento and Sundquist*, 1992; *Keeling et al.*, 1989; *Tans et al.*, 1990]. Most of the recent data-based estimates, however, indicate a relatively small Southern Ocean sink [*Poisson and Chen*, 1987; *Murphy et al.*, 1991; *Gruber*, 1998; this study]. The lack of observed anthropogenic CO<sub>2</sub> in the Southern Ocean is also qualitatively consistent with  $\Delta^{14}\text{C}$  estimates which show no measurable storage of bomb <sup>14</sup>C in the Southern Ocean since GEOSECS [*Leboucher et al.*, 1998; R. Key, unpublished data, 1998]. Recent studies by *Bullister et al.* [1998], which show evidence of deep CFC penetration in the Southern Ocean, may appear to contradict these low anthropogenic CO<sub>2</sub> estimates, but we believe it is further evidence that one must be careful when inferring anthropogenic carbon distributions from other tracers. One possible explanation of this apparent discrepancy may be the CFC equilibration



**Figure 7.** Sections of excess CO<sub>2</sub> along (a) ~57°E and (b) ~92°E. Dots indicate sample locations used in sections. Note that I6S data along 30°E were brought into the line of section for contours south of 40°S in Figure 7a.

rate of days which is significantly faster than the CO<sub>2</sub> equilibration time of months [e.g., England, 1995; Warner and Weiss, 1985; Tans et al., 1990]. This can become an issue in the Southern Ocean where upwelling and convection may allow the CFCs to equilibrate to a greater extent than the CO<sub>2</sub>. Again, we acknowledge the limitations of the methods used in the Southern Ocean, and it is possible that the apparent discrepancy in the CFC penetration versus the CO<sub>2</sub> penetration may also be an issue of detection limits. With a detection limit that is approximately 6 μmol kg<sup>-1</sup>, it is not possible to say with this technique that the concentration of anthropogenic CO<sub>2</sub> below 500 m at 60°S is zero. However, we can say with some confidence that the concentration is not 10 μmol kg<sup>-1</sup> or greater. Since there is no natural oceanic source of CFCs and these compounds are not biologically utilized, the ability to detect them is much greater. If mixing has diluted the anthropogenic signal to concentrations just below detection limits, it is possible that carbon measurement based techniques would underestimate the Southern Ocean sink.

The total anthropogenic CO<sub>2</sub> inventory for the main Indian Ocean basin (north of 35°S) was 13.6±2 Pg C in 1995. The increase in CO<sub>2</sub> inventory since GEOSECS was 4.1±1 Pg C for the same area. This represents a nearly 30% increase in the past 18 years relative to the total accumulation since preindustrial times. The relative oceanic increase is very similar to the 31% increase observed in atmospheric concentrations over the same time period [Keeling and Whorf, 1996]. This similarity suggests that the oceans, at least for now, are keeping pace with the rise in atmospheric CO<sub>2</sub>. Approximately 6.7±1 Pg C are stored in the Indian sector of the Southern Ocean giving a total Indian Ocean inventory (between 20° and 120°E) of 20.3±3 Pg C in 1995.

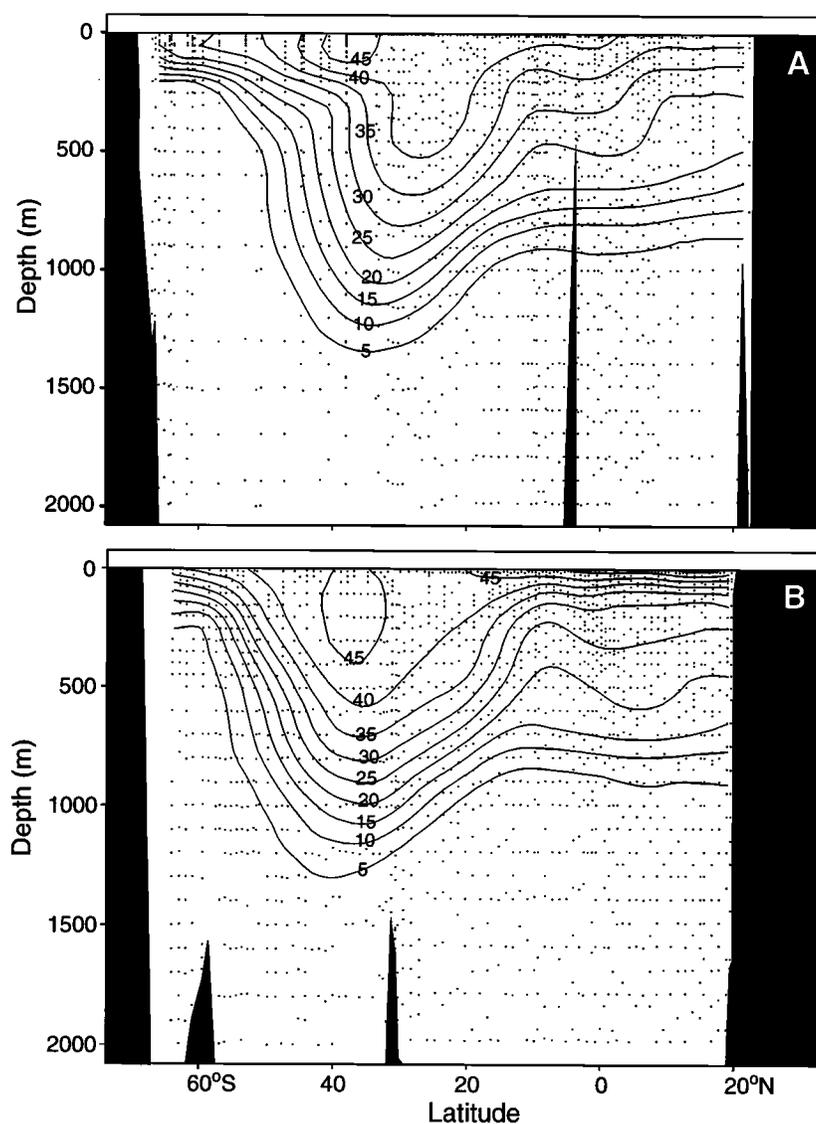
To put these results in a global perspective, the total inventory for the Indian Ocean is only half that of the Atlantic (40±6 Pg C [Gruber, 1998]), but it contains an ocean volume that is nearly 80% of the Atlantic. The main difference between the two oceans, of course, is that the Indian Ocean does not have the high northern latitude sink that the Atlantic has. The big unknown at this point is

the anthropogenic inventory of the Pacific. With nearly 50% of the total ocean volume the Pacific has the potential to be the largest oceanic reservoir for anthropogenic CO<sub>2</sub>.

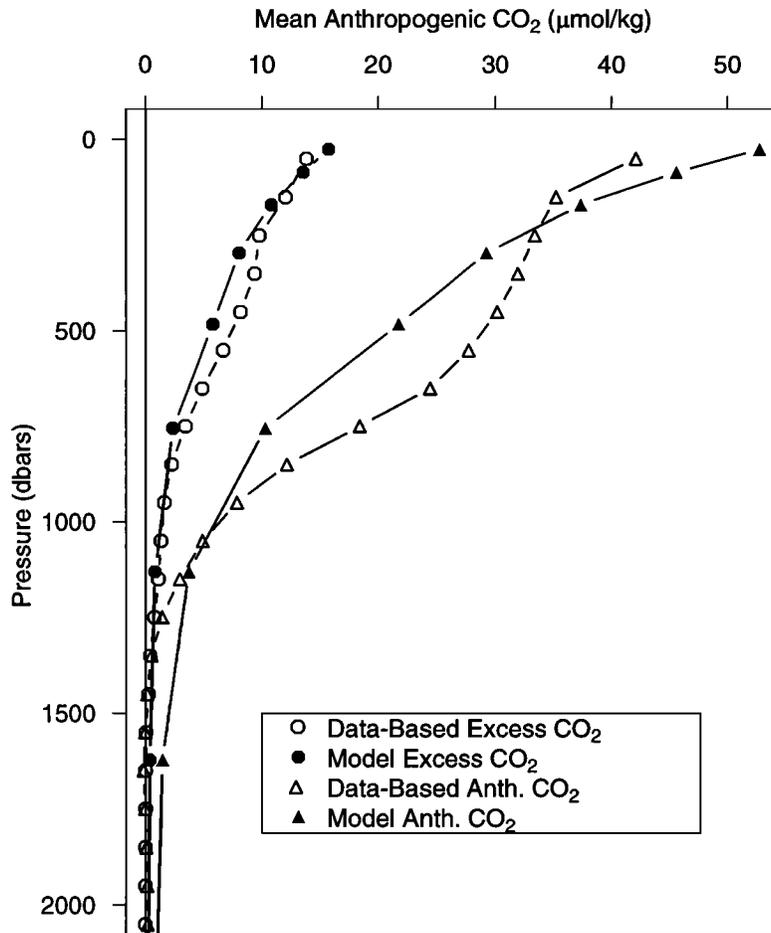
#### 4. Comparison With Princeton Ocean Biogeochemistry Model

Current IPCC anthropogenic estimates are primarily based on global carbon models. Ultimately, these models are necessary to predict the oceanic response to future climate scenarios. It is important, however, to validate these models. One way to compare results is to examine profiles of the average anthropogenic concentrations such as those shown in Figure 9. The model presented here is the Princeton Ocean Biogeochemistry Model (OBM). The Princeton OBM is based on the circulation of *Toggweiler et al.* [1989] with explicit parameterization for the biological and solubility carbon pumps [*Sarmiento et al.*, 1995; *Murnane et al.*, 1998]. On this scale the model-based concentrations for both the total anthropo-

genic CO<sub>2</sub> and the increase since GEOSECS appear to be reasonably consistent with the data. The primary difference is slightly higher values at middepths in the data-based estimates. A more detailed examination, however, indicates that the regional distribution of the model-based estimates is significantly different than the data-based distribution. Figure 10 presents maps of the vertically integrated excess CO<sub>2</sub> normalized to a unit area. The model shows a consistent decrease in column inventory toward the north. The lowest inventories in the data-based map are in a narrow band just south of the equator. The highest values are found in the southeastern Indian Ocean. Relatively high values are also observed in the Arabian Sea in the regions near the Red Sea and the Persian Gulf. The small patch of lower values immediately outside the Gulf of Aden does not result from low concentrations but rather results from the shallow water depth associated with the mid-ocean ridge in that area. The low values east of there, however, do result from lower concentrations near the southern tip of India. The total model-based inventory for the region north of 35°S is approximately 0.61 times the data-based inventory (Table 4).



**Figure 8.** Sections of anthropogenic CO<sub>2</sub> along (a) ~57°E and (b) ~92°E. Dots indicate sample locations used in sections.



**Figure 9.** Profile of area weighted mean anthropogenic CO<sub>2</sub> concentrations for model (solid symbols) and data-based (open symbols) estimates for main Indian Ocean basin (north of 35°S). Circles show increase since GEOSECS (1978-1995). Triangles show total increase since preindustrial times.

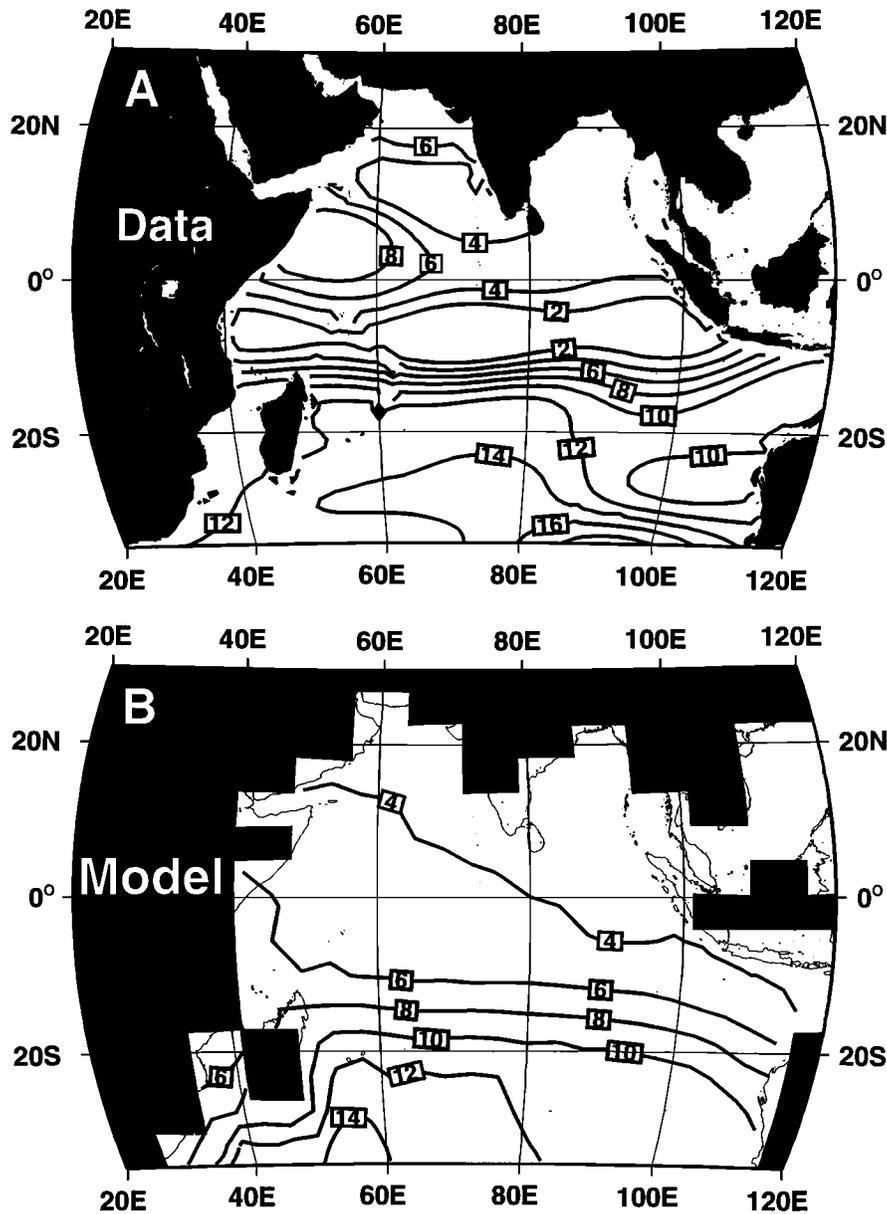
Figure 11 shows maps of total anthropogenic CO<sub>2</sub> column inventory. As with the excess CO<sub>2</sub>, the model predicts decreasing anthropogenic concentrations north of 35°S. The data-based distribution pattern is similar to the data-based excess CO<sub>2</sub> pattern with a minimum inventory band south of the equator and higher values toward the north and south. Similar to the findings with excess CO<sub>2</sub>, the model-based anthropogenic inventory north of 35°S is approximately 0.68 times the data-based inventory (Table 4). The largest difference between the data-based results and the model is evident, however, in the Southern Ocean (south of 35°S). In this region the model anthropogenic inventory is nearly 2.6 times the data-based inventory (Table 4). The primary reason for this difference is the presence of a large convective cell in the model at approximately 55°S and 90°E in the Southern Ocean. This is a region of intense, unrealistic convection which pumps relatively high concentrations of anthropogenic CO<sub>2</sub> down in excess of 4000 m. This problem is a known shortcoming with the mixing scheme used in several GCMs [e.g., England, 1995] but has never before been quantified in terms of its direct effect on anthropogenic CO<sub>2</sub> storage by the models. It is beyond the scope of this paper to examine the details of the model physics; however, this same general trend of getting too much anthropogenic CO<sub>2</sub> into the Southern Ocean has been observed in comparisons with three other global

carbon models with a range of mixing and advective schemes [C. Sabine, unpublished results, 1998]. This cursory comparison with the Princeton OBM clearly demonstrates the diagnostic usefulness of comparing the data distributions with models.

## 5. Conclusions

Although the general techniques proposed by Gruber *et al.* [1996] and Wallace [1995] can be important tools for estimating global anthropogenic CO<sub>2</sub>, careful consideration must be used when applying these techniques to new regions. Complicating factors such as those found in the Arabian Sea can influence the quality of the estimates if not properly addressed. An additional term had to be added to the basic  $\Delta C^*$  calculation to account for denitrification in the Arabian basin. For the excess CO<sub>2</sub> calculations a categorical variable was used to remove regional biases in the GEOSECS fit.

With the above mentioned modifications the anthropogenic inventory of the Indian Ocean was shown to be relatively small, approximately half of that found in the Atlantic. This study provides an important baseline for future studies of the Indian Ocean. The calculations presented here suggest that the oceanic increase in carbon storage (30%) has roughly kept pace with the atmo-



**Figure 10.** Maps of vertically integrated excess CO<sub>2</sub> based on (a) data and (b) model estimates. Contours are in mol m<sup>-2</sup>. Solid regions indicate land mask used for inventory estimates. Thin lines in Figure 10b indicate land regions used in Figure 10a.

**Table 4.** Summary of Data Based and Model Based Inventory Estimates

	Total Anthropogenic CO <sub>2</sub> , <sup>α</sup> Pg C	Southern Ocean Anthropogenic CO <sub>2</sub> , <sup>β</sup> Pg C	Main Basin Anthropogenic CO <sub>2</sub> , <sup>χ</sup> Pg C	Main Basin Excess CO <sub>2</sub> , <sup>χ</sup> Pg C	Increase since GEOSECS, %
Data based	20.3±3	6.7±1	13.6±2	4.1±1	29.9
Model based	26.7	17.4	9.3	2.5	26.7

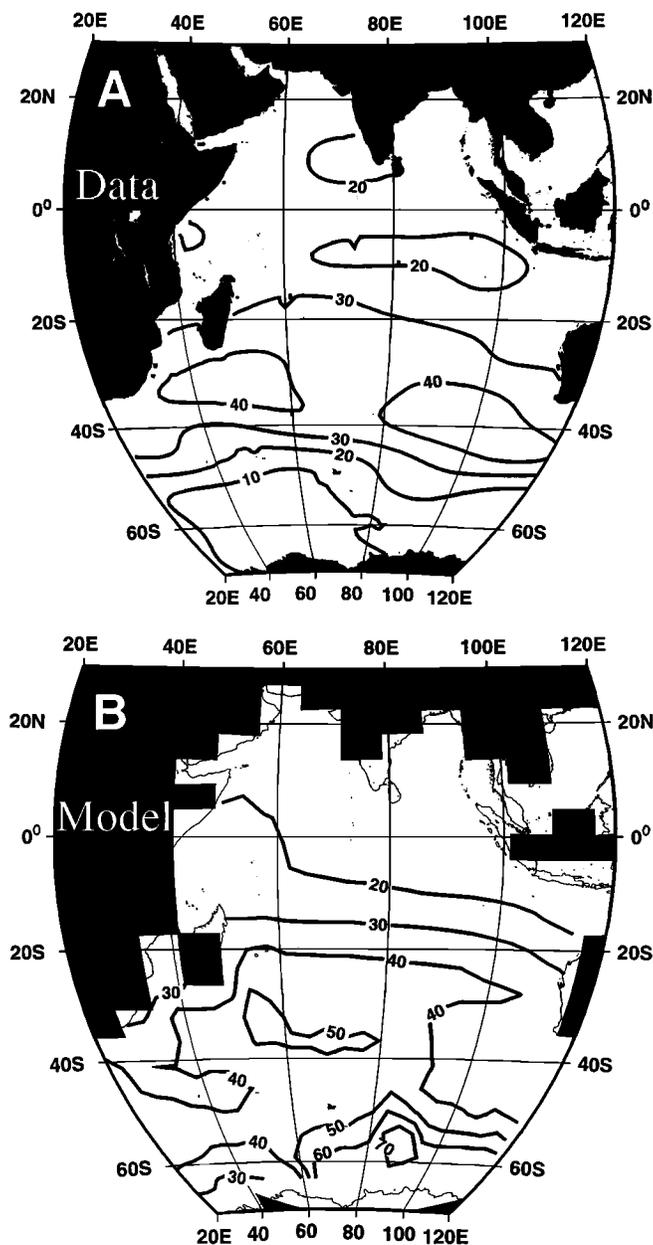
<sup>α</sup>Area between 20°-120°E.

<sup>β</sup>Latitude is < 35°S.

<sup>χ</sup>Latitude is > 35°S.

spheric increase (31%) over the past 18 years. Models predict that this trend is likely to change as atmospheric CO<sub>2</sub> concentrations continue to rise in the future [Sarmiento *et al.*, 1995]. As more CO<sub>2</sub> enters the ocean, the carbonate ion concentration will become depleted. This will decrease the buffering capacity of the ocean and its ability to continue carbon uptake at the current rate. Comparison of future survey cruises in the Indian Ocean with the anthropogenic and total carbon values from this study will allow us to document future changes in ocean chemistry and better understand the oceanic response to global change.

Finally, comparison of the spatial distribution of the anthropogenic carbon can be a powerful tool for understanding the carbon uptake of the models. The methods presented here provide a two-point calibration for examining the response of the models to



**Figure 11.** Maps of vertically integrated anthropogenic CO<sub>2</sub> based on (a) data and (b) model estimates. Contours are in mol m<sup>-2</sup>. Solid regions indicate land mask used for inventory estimates. Thin lines in Figure 11b indicate land regions used in Figure 11a.

observed atmospheric CO<sub>2</sub> increases. The anthropogenic CO<sub>2</sub> data can also be subtracted from the TCO<sub>2</sub> measurements to provide an estimate of the preindustrial TCO<sub>2</sub> distribution. Comparing these estimates with the steady state model distributions can provide insight into whether differences in the model and data-based anthropogenic inventories result from problems with the uptake parameterization or the basic physics and initialization parameters of the model. This paper is just the first step in the interpretation of the WOCE/JGOFS data set. Subsequent papers will analyze additional cruise data as they become available. Together, these analyses will significantly improve our understanding of the global carbon cycle.

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## **APPENDIX E:**

### **REPRINT OF PERTINENT LITERATURE**

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

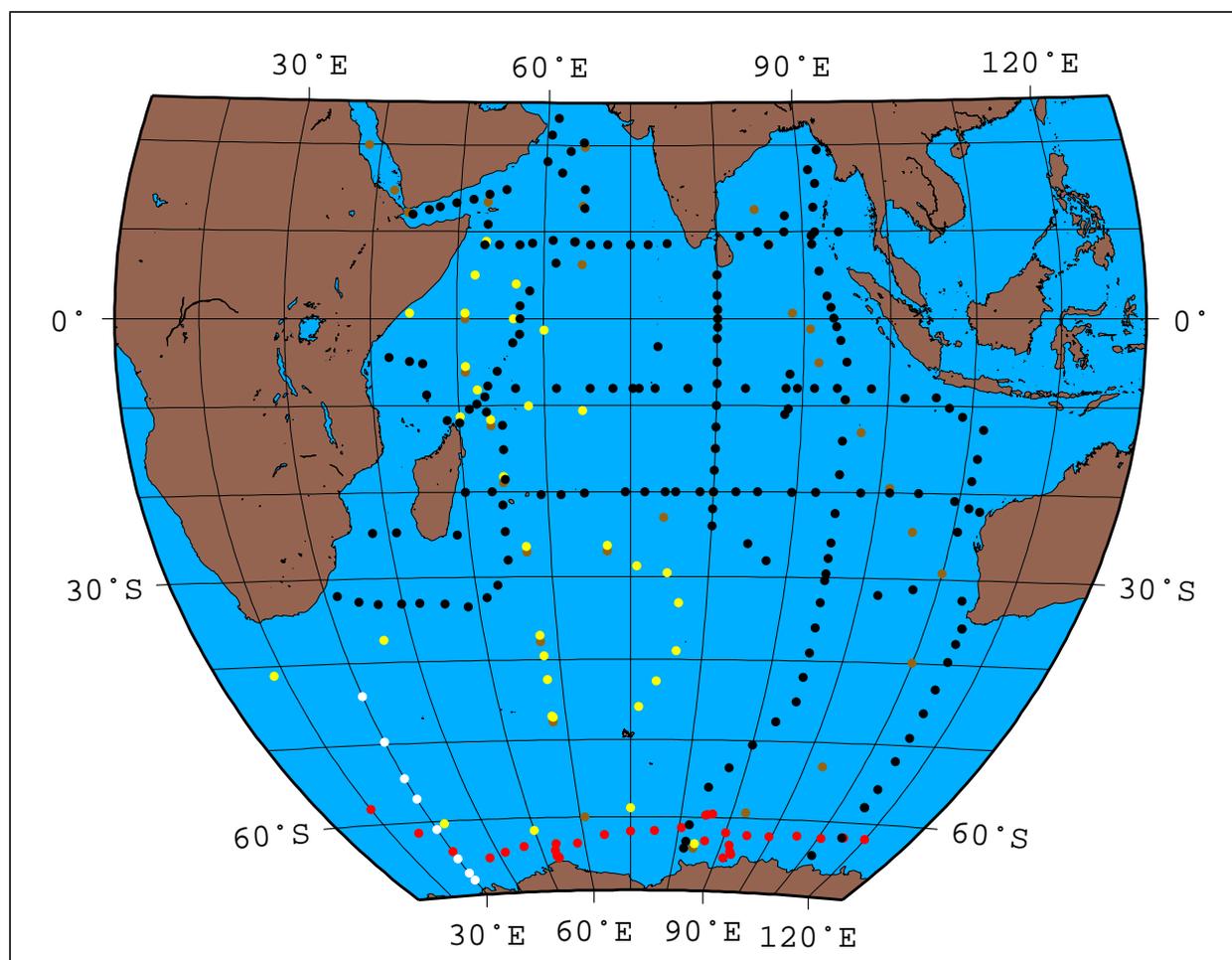
# U.S. Woce Indian Ocean Survey: Final Report for Radiocarbon

Robert M. Key and Paul D. Quay

July 12, 2002

## 1.0 General Information

The U.S. WOCE Indian Ocean Survey consisted of 9 cruises covering the period December 1, 1994 to January 22, 1996. All of the cruises used the R/V Knorr operated by the Woods Hole Oceanographic Institute. A total of 1244 hydrographic stations were occupied with radiocarbon sampling on 366 stations. The radiocarbon stations are shown as black dots in Figure 1. To give an indication of the total radiocarbon coverage for the Indian Ocean, the figure includes radiocarbon stations from WOCE sections S4I (Key, 1999; red dots) and I6S (Leboucher, *et al.*, 1999; white dots) and from the earlier GEOSECS (Stuiver and Ostlund, 1983; brown dots) and INDIGO (Bard, *et al.*, 1988; yellow dots) expeditions. Specific summary information on the 9



**Figure 1:** AMS <sup>14</sup>C station map for WOCE S4I.

WOCE survey cruises is given in Table 1.

**TABLE 1. Summary for Survey Sections**

Cruise	Chief Scientist	Start	End	$\Delta^{14}\text{C}$ Stations	$\Delta^{14}\text{C}$ Samples
I8SI9S	M. McCartney T. Whitworth	12/01/94 Fremantle Australia	01/19/95 Fremantle Australia	26	662
I9N	A. Gordon D. Olson	01/24/95 Fremantle Australia	03/05/95 Colombo Sri Lanka	22	364
I8NI5E	L. Talley M. Baringer	03/10/95 Colombo Sri Lanka	04/15/95 Fremantle Australia	20	414
I3	W. Nowlin B. Warren	04/20/95 Fremantle Australia	06/07/95 Port Louis Mauritius	20	462
I5WI4	J. Toole	06/11/95 Port Louis Mauritius	07/11/95 Port Louis Mauritius	15	361
I7N	D. Olson S. Doney D. Musgrave	07/15/95 Port Louis Mauritius	08/24/95 Muscat Oman	22	373
I1	J. Morrison H. Bryden	08/29/95 Muscat Oman	10/16/95 Singapore	24	426
I10	N. Bray J. Toole	11/11/95 Dampier Australia	11/28/95 Singapore	6	127
I2	G. Johnson B. Warren	12/02/95 Singapore China	01/22/96 Mombasa Kenya	28	651

## 2.0 Personnel

$\Delta^{14}\text{C}$  sampling for cruise I8SI9S was carried out by Melinda Brockington (University of Washington). Personnel for the remainder of the cruises came from the Ocean Tracer Lab (OTL Princeton University) and included G. McDonald, A. Doerty, R. Key, T. Key, and R. Rotter.  $\Delta^{14}\text{C}$  (and accompanying  $\delta^{13}\text{C}$ ) analyses were performed at the National Ocean Sciences AMS Facility (NOSAMS) at Woods Hole Oceanographic Institution. R. Key collected the data from NOSAMS, merged the files with hydrographic data, assigned quality control flags to the  $\Delta^{14}\text{C}$  and submitted the results to the WOCE office (4/02). R. Key is P.I. for the  $^{14}\text{C}$  data. P. Quay (U.W.) and A. McNichol (WHOI/NOSAMS) are P.I.s for the  $^{13}\text{C}$  data. In addition to collecting samples the ship-board  $^{14}\text{C}$  person was also responsible for operation of the underway  $\text{pCO}_2$  system provided by the OTL (Sabine and Key, 1997; Sabine, *et al.*, 2000).

### 3.0 Results

This  $\Delta^{14}\text{C}$  data set and any changes or additions supersedes any prior release.

#### 3.1 Hydrography

Hydrographic data from these cruises were submitted to the WOCE office by the chief scientists and are described in various reports which are available from the web site ([http://whpo.ucsd.edu/data/tables/onetime/1tim\\_ind.htm](http://whpo.ucsd.edu/data/tables/onetime/1tim_ind.htm)).

#### 3.2 $\Delta^{14}\text{C}$

The  $\Delta^{14}\text{C}$  values described here were originally distributed in the NOSAMS data reports listed in Table 2 and given in full in the References . Those reports included results which had not been through the WOCE quality control procedures. For WOCE applications, this report supersedes the NOSAMS reports.

**TABLE 2. NOSAMS Data Report Summary**

Cruise	Report
I8SI9S	99-089
I7N I9N	99-144
I1	99-199
I8N	00-218
I3 I5W14	01-013
I2	02-001

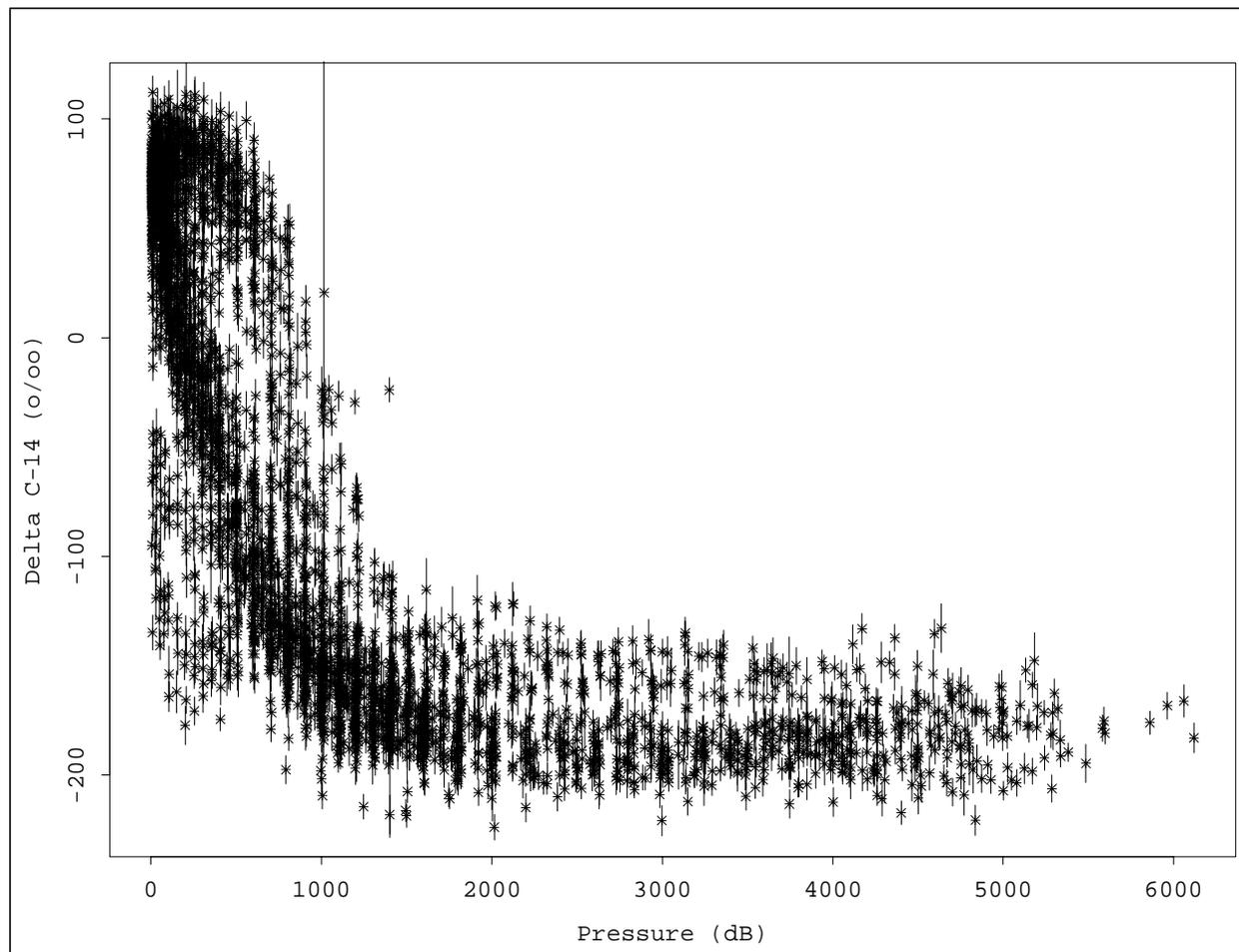
All of the AMS samples from these cruise have been measured using the AMS methods outlined in Key *et al.*, 1996 and citations therein (especially McNichol *et al.*, 1994; Osborne *et al.* 1994; and Scheideret *al.* 1995). Table 3 summarizes the number of samples analyzed and the quality control flags assigned for each cruise. Approximately 98% of the samples collected were deemed to be “good” (flagged 2 or 6). Quality flag values were assigned to all  $\Delta^{14}\text{C}$  measurements using the code defined in Table 0.2 of WHP Office Report WHPO 91-1 Rev. 2 section 4.5.2. (Joyce, *et al.*, 1994). No measured values have been removed from this data set.

**TABLE 3. Sample Analysis and QC Summary**

Cruise	Samples Analyzed	QC Flag Totals				
		2	3	4	5	6
I8SI9S	662	636	6	8	0	12
I9N	368	354	4	3	4	3
I8NI5E	416	401	6	0	2	7
I3	463	448	5	0	1	9
I5W14	366	342	3	1	5	15
I7N	383	370	3	0	10	0
I1	430	421	2	2	4	1
I10	127	127	0	0	0	0
I2	655	636	13	2	4	0
Total	3870	3735	42	16	30	47

## 4.0 Data Summary

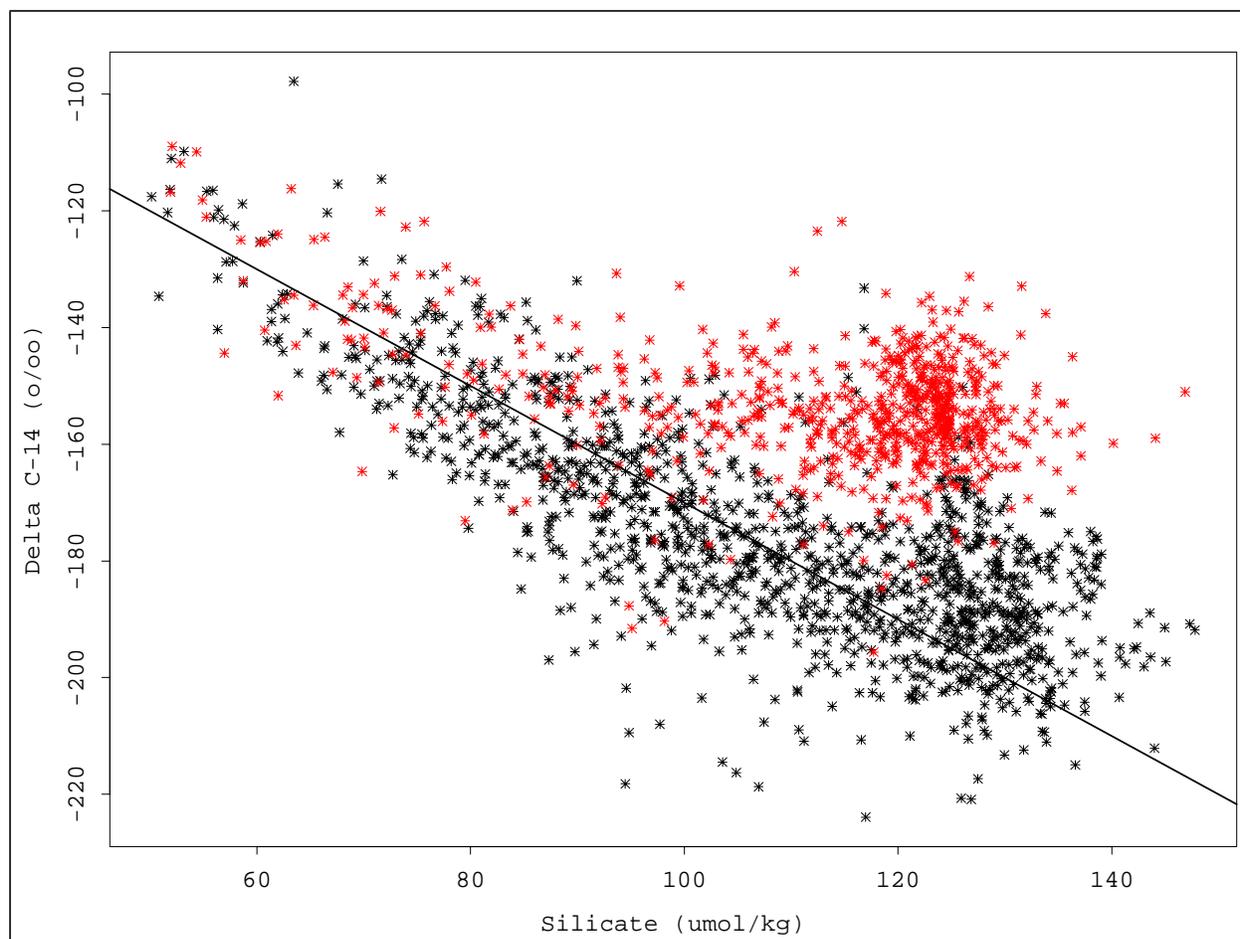
Figures 2-6 summarize the  $\Delta^{14}\text{C}$  data collected during the Indian Ocean survey. Only  $\Delta^{14}\text{C}$  measurements with a quality flag value of 2 (“good”) or 6 (“replicate”) are included in the figures. Figure 2 shows the  $\Delta^{14}\text{C}$  values with  $2\sigma$  error bars plotted as a function of pressure. The



**Figure 2:**  $\Delta^{14}\text{C}$  results shown with  $2\sigma$  error bars.

mid depth  $\Delta^{14}\text{C}$  minimum which occurs around 2500 meters in the Pacific is not apparent in these data. In fact, there is very little variation in the deep and bottom water other than the previously reported decrease in  $\Delta^{14}\text{C}$  from south to north. All of the samples collected at a depth greater than 1000 meters have a mean  $\Delta^{14}\text{C} = -165 \pm 25\text{‰}$  (standard error =  $0.5\text{‰}$  with  $n=2086$ ). A substantial fraction of this variability is due to the difference between the Southern Ocean and main basin deep waters.

Figure 3 shows the deep ( $>1000\text{m}$ )  $\Delta^{14}\text{C}$  values plotted against silicate. The black and red points are from north and south of  $35^\circ\text{S}$ , respectively. The straight line shown in the figure is the least squares regression relationship derived by Broecker *et al.* (1995) based on the GEOSECS global data set. According to their analysis, this line ( $\Delta^{14}\text{C} = -70 - \text{Si}$ ) represents the relationship between naturally occurring radiocarbon and silicate for most of the ocean. They noted that the technique could not be simply applied at high latitudes as confirmed by this data set.

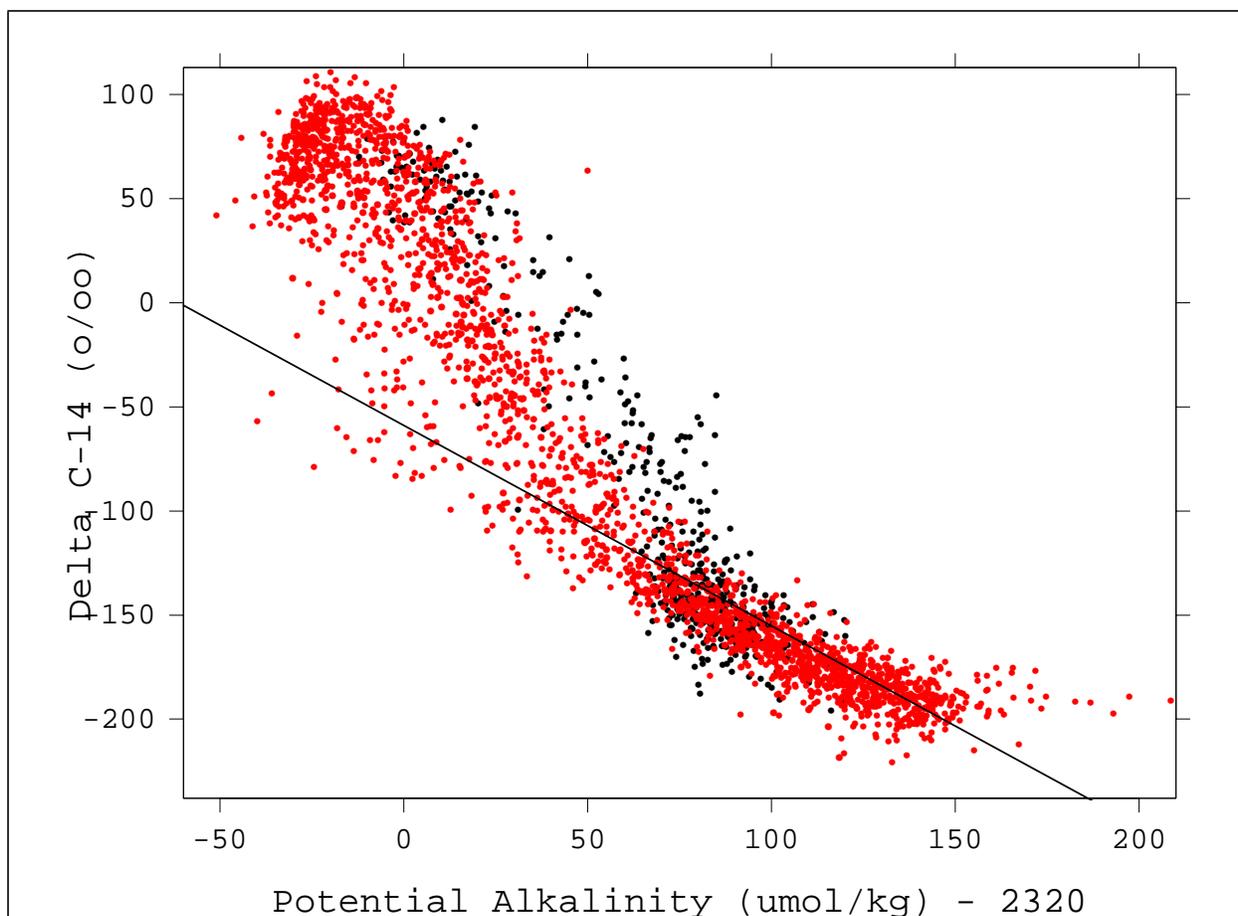


**Figure 3:**  $\Delta^{14}\text{C}$  as a function of silicate for samples collected deeper than 1000m. The black points are from north of  $35^\circ\text{S}$  and the red points south of  $35^\circ$ . The straight line shows the relationship proposed by Broecker, *et al.*, 1995 ( $\Delta^{14}\text{C} = -70 - \text{Si}$  with radiocarbon in ‰ and silicate in  $\mu\text{mol/kg}$ ).

Figure 4 shows all of the radiocarbon values plotted against potential alkalinity (defined as  $[\text{alkalinity} + \text{nitrate}] * 35 / \text{salinity}$ ). The straight line is the regression fit ( $^{14}\text{C} = -59 - 0.962(\text{PALK} - 2320)$ ) derived by Rubin and Key (2002) using GEOSECS measurements assumed to have no bomb-produced  $\Delta^{14}\text{C}$ . The value 2320 is the estimated surface ocean mean potential alkalinity. As with Figure 3 the black and red points in Figure 4 indicate measurements taken north and south of  $35^\circ\text{S}$ , respectively. Unlike the silicate plot (Figure 3), there is no apparent difference in the relationship for Southern Ocean vs Indian Ocean deep waters. The distance a point falls above the regression line is an estimate of the bomb radiocarbon contamination for the sample.

Figures 5-9 show gridded sections of the  $\Delta^{14}\text{C}$  data. In each figure the water column is divided into upper (0-1000m) and lower (1000-bottom) portions. The data were gridded using the loess method (Chambers *et al.*, 1983; Chambers and Hastie, 1991; Cleveland, 1979; Cleveland and Devlin, 1988). The span for the fits was adjusted to be minimum and yet capture the large scale features. The contour interval is 10‰ for the upper water column and 20‰ for intermediate and deep water.

Figure 5 and Figure 6 show the meridional  $\Delta^{14}\text{C}$  distribution in the eastern and western Indian Ocean. In both figures the distribution pattern is very similar to that seen in the Pacific

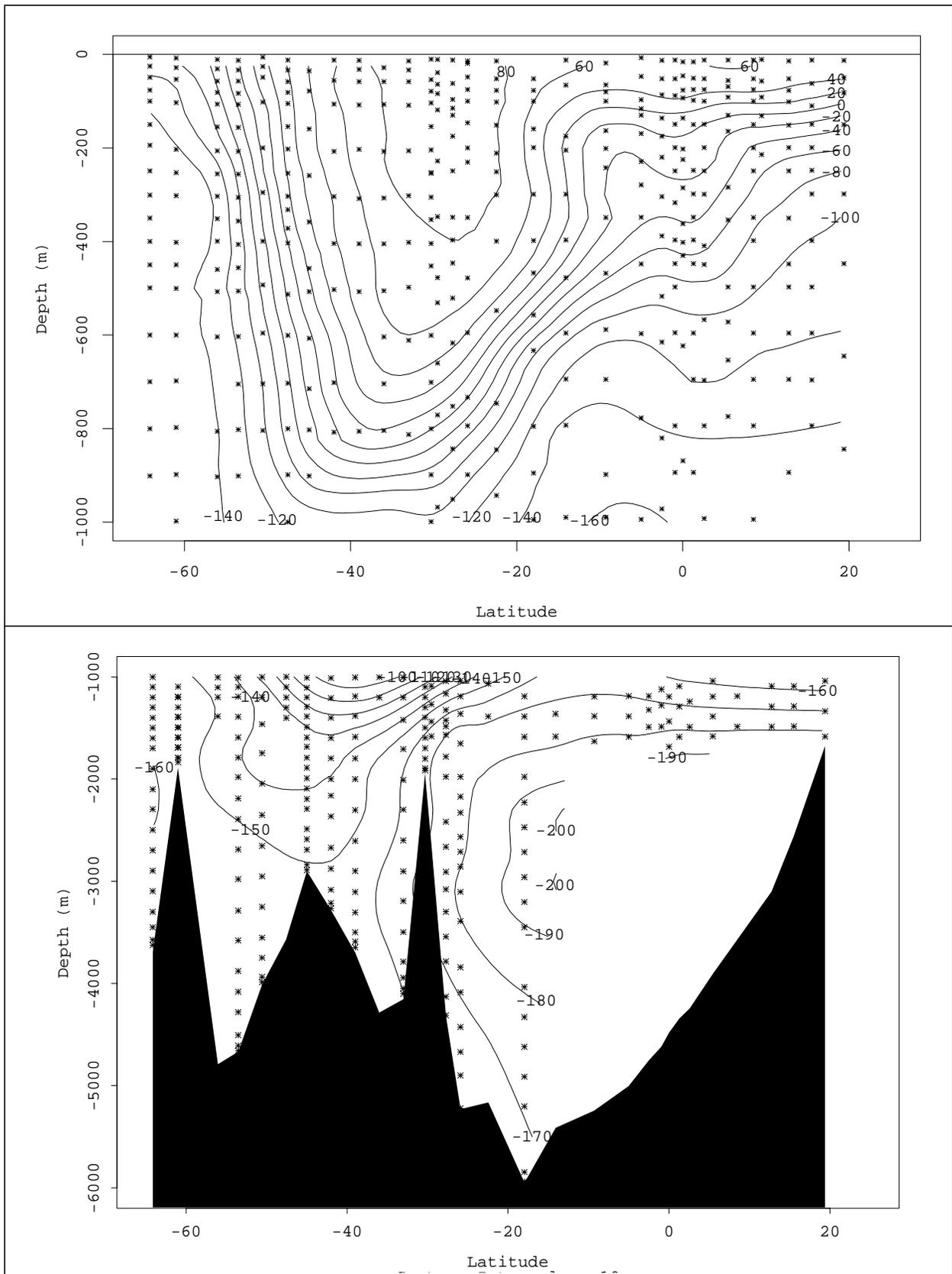


**Figure 4:** Based on the potential alkalinity method (Rubin and Key, 2002), the samples which plot above the line and have potential alkalinity values less than about 2400  $\mu\text{mole/kg}$  are contaminated with bomb-produced  $^{14}\text{C}$ .

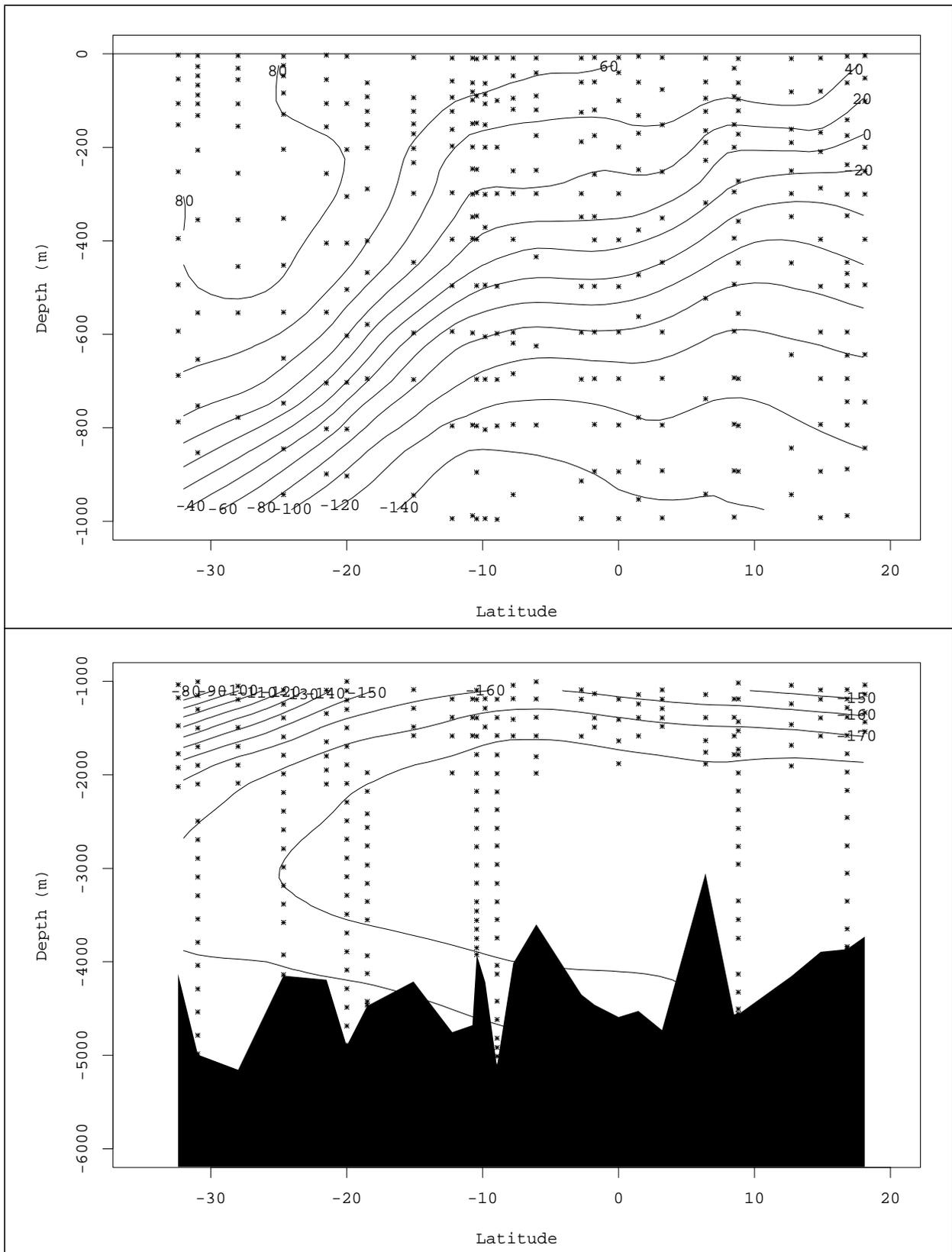
Ocean WOCE samples. In the Pacific the maximum  $\Delta^{14}\text{C}$  values were frequently found in shallow water, but beneath the surface. In the Indian Ocean data a subsurface maximum is not so common. Both sections show intrusion of Circumpolar Deep Water from the south along the bottom and return flow of deep water at 2000-3000m. As with the Pacific the middepth waters have the lowest  $\Delta^{14}\text{C}$  values, however the middepth Indian Ocean waters have significantly higher values than corresponding Pacific waters. This pattern is consistent with a mean ageing of waters from the Atlantic to Indian to Pacific.

Figure 7, Figure 8 and Figure 9 show zonal  $\Delta^{14}\text{C}$  sections along the WOCE lines I1 ( $\sim 10^\circ\text{N}$ ), I2 ( $\sim 8^\circ\text{S}$ ) and I3 ( $\sim 20^\circ\text{S}$ ). Except for the western ends, the  $\Delta^{14}\text{C}$  contours in the upper kilometer are relatively flat. In each section the deep waters of the western basins have somewhat higher  $\Delta^{14}\text{C}$  than at the same depth in the eastern basins. The strength of this signal decreases from south to north and is almost certainly due to the western basins having a higher fraction of North Atlantic Deep Water.

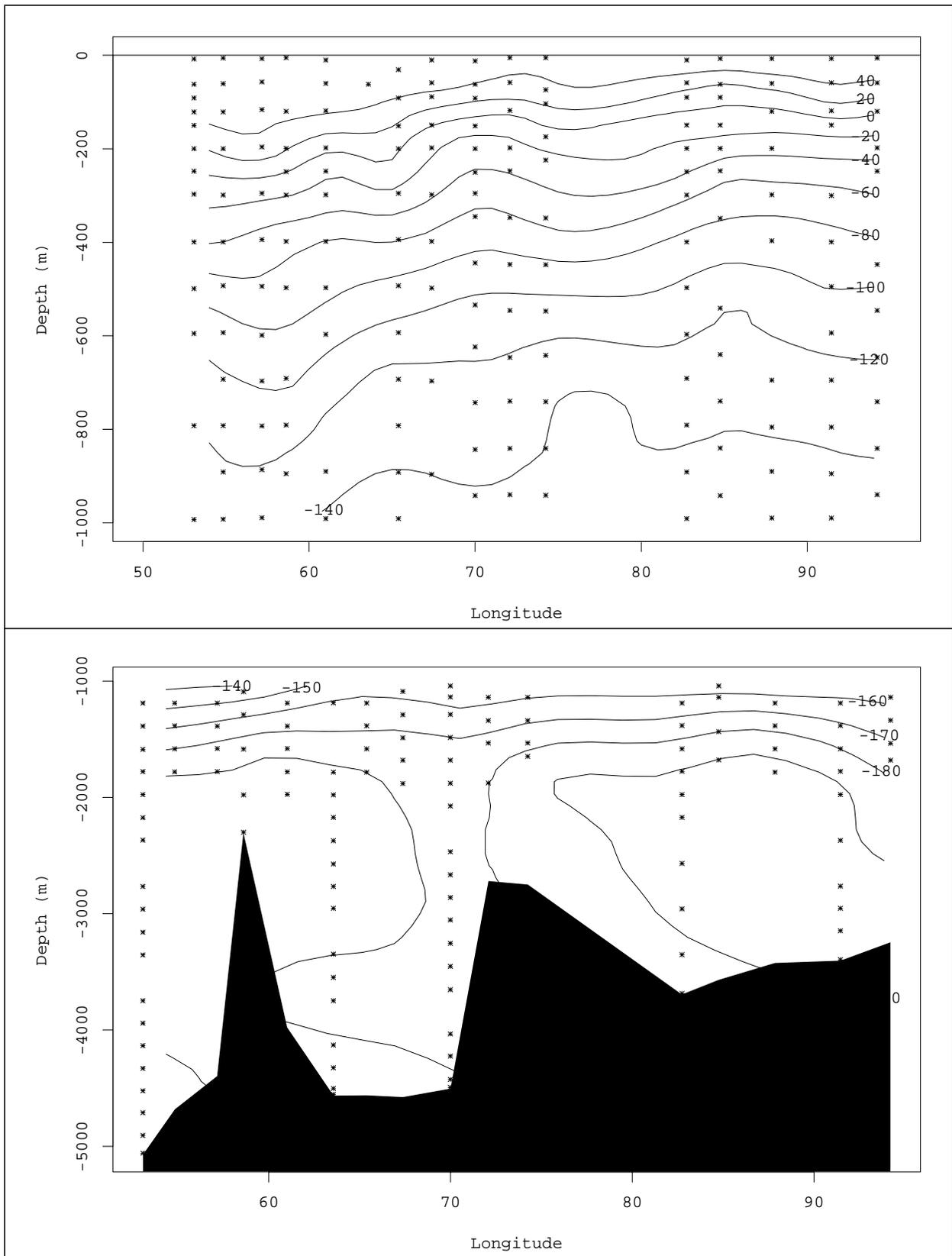
Figure 10 shows the meridional distribution of bomb produced  $\Delta^{14}\text{C}$  (via Rubin and Key, 2002) in the eastern and western Indian Ocean. The eastern section used all WOCE samples collected at depths less than 1000m and east of  $85^\circ\text{E}$ . The western section uses the same depth range, but samples from west of  $75^\circ\text{E}$ . Both sections are contoured and colored in potential density space rather against depth. One might expect *a priori* that the distributions would differ north of the



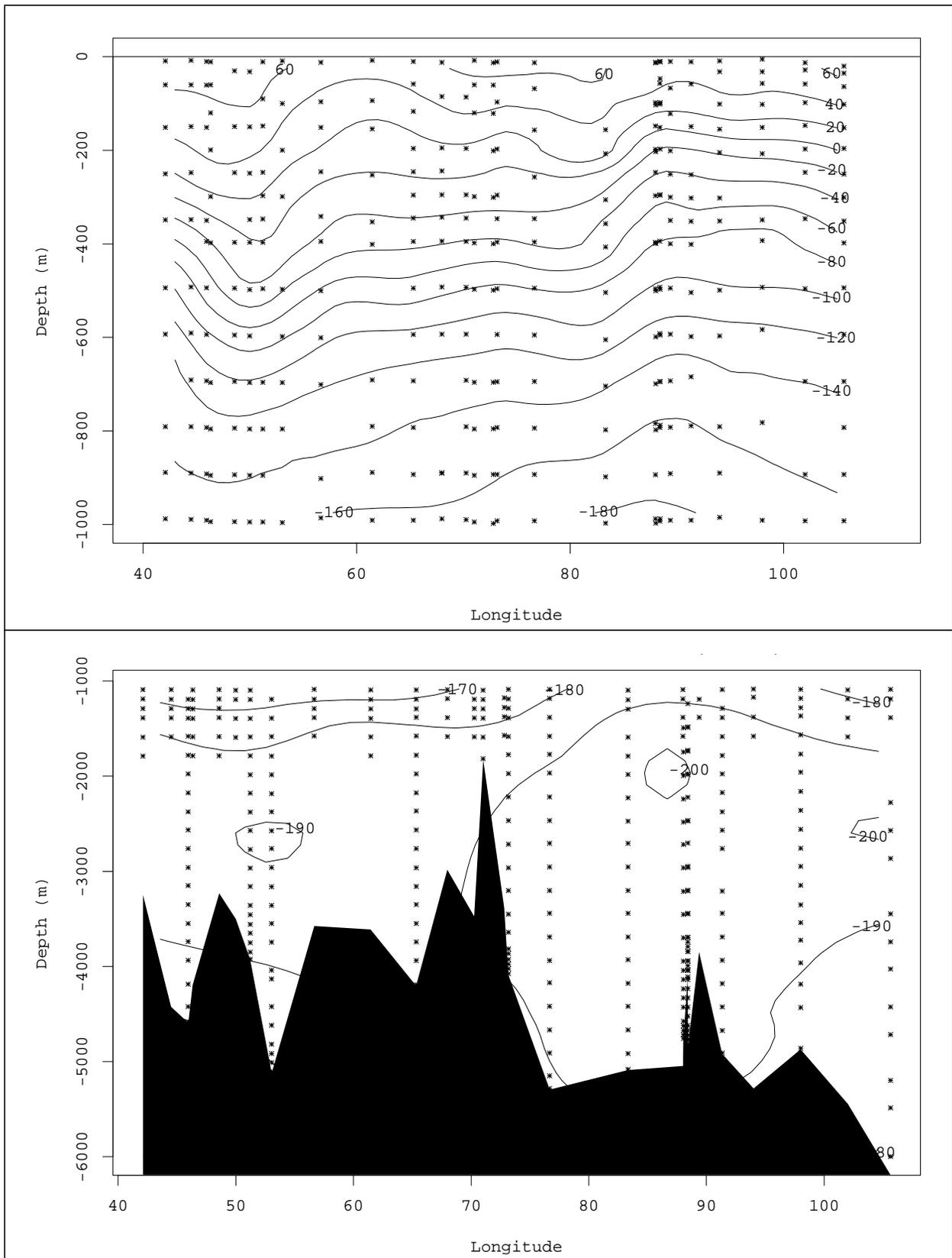
**Figure 5:**  $\Delta^{14}\text{C}$ , along I8S and I9N in the eastern Indian Ocean.



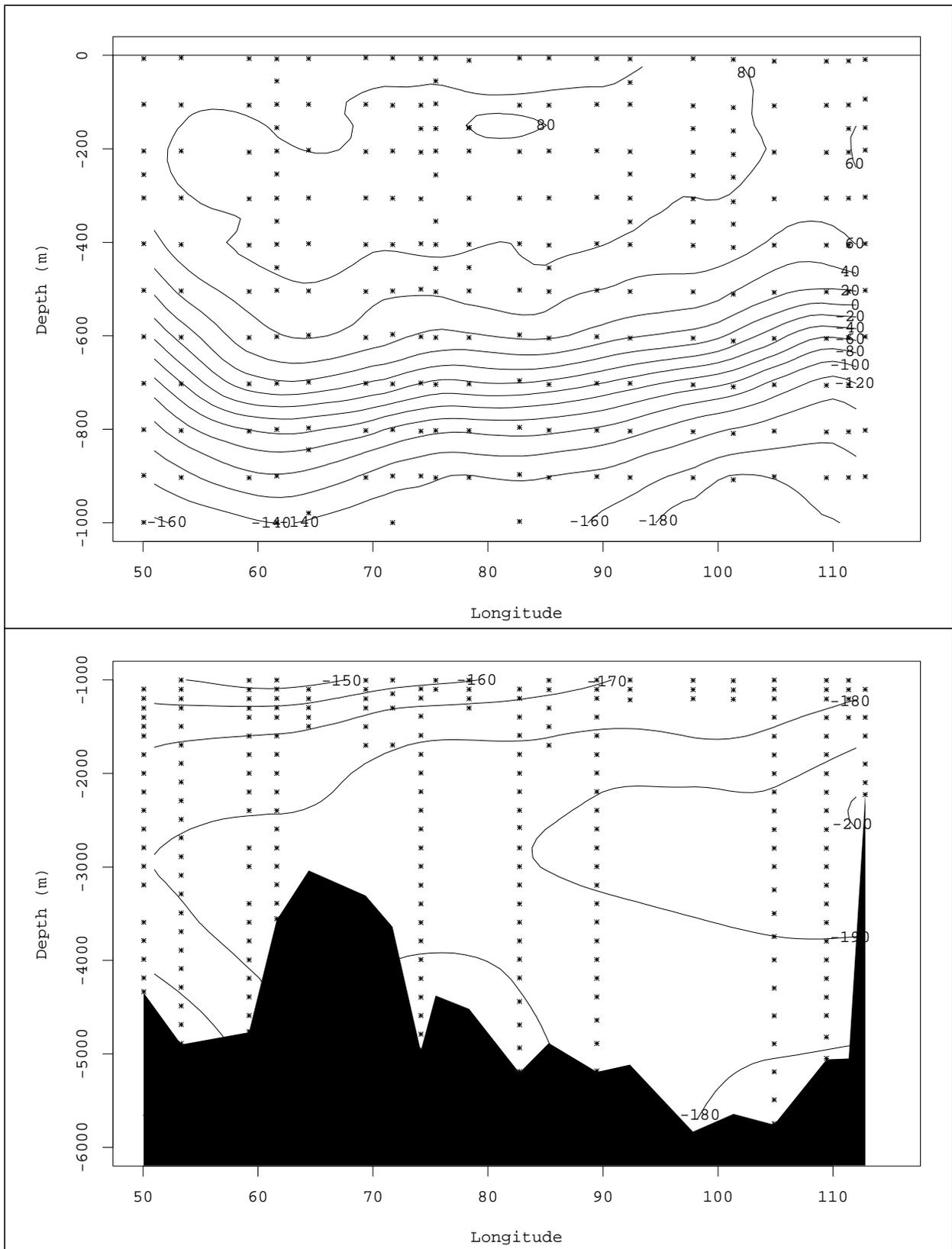
**Figure 6:**  $\Delta^{14}\text{C}$  along I7 in the western Indian Ocean.



**Figure 7:**  $\Delta^{14}\text{C}$  along I1 in the northern Indian Ocean.

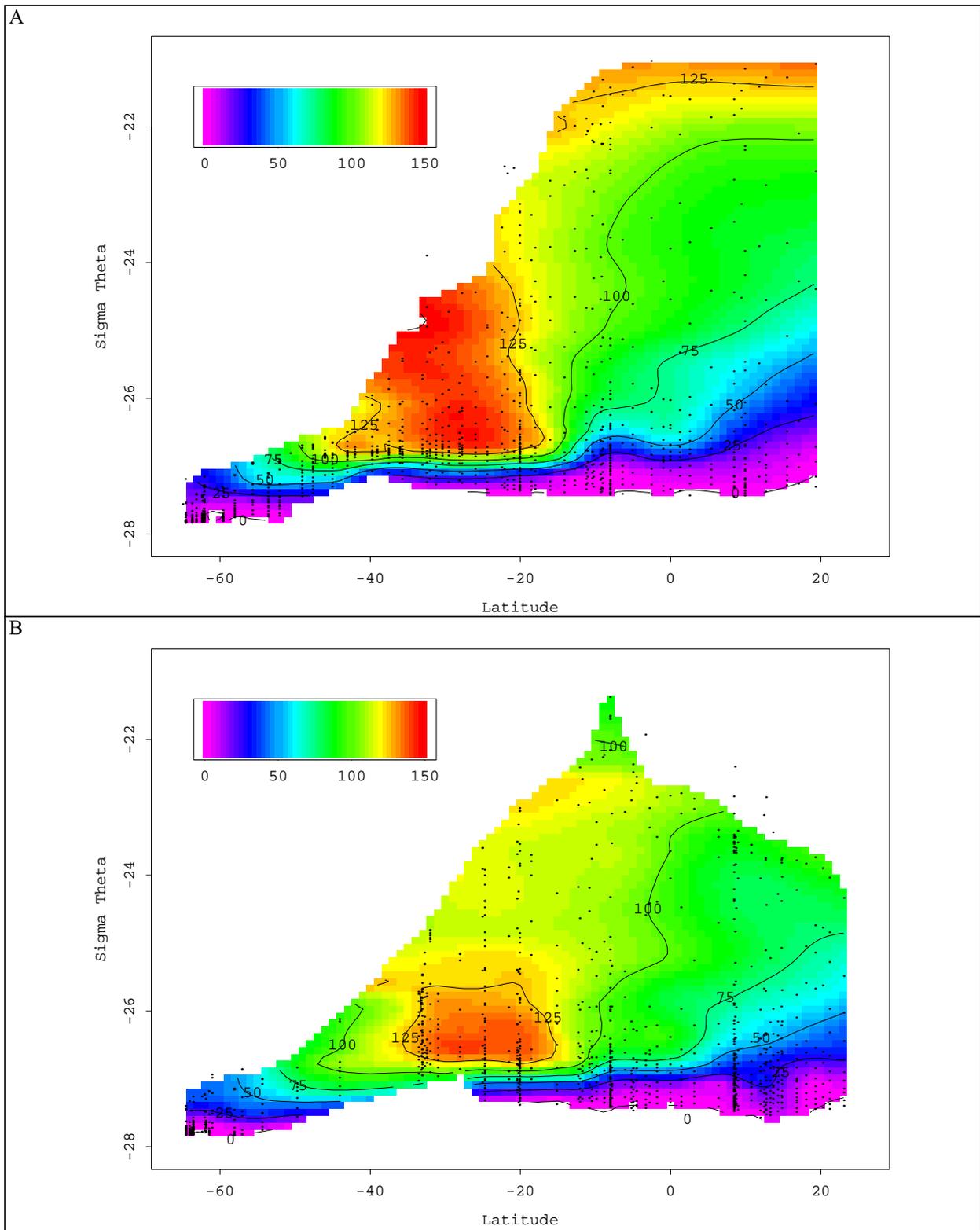


**Figure 8:**  $\Delta^{14}\text{C}$  along I2 in the southern tropical Indian Ocean.

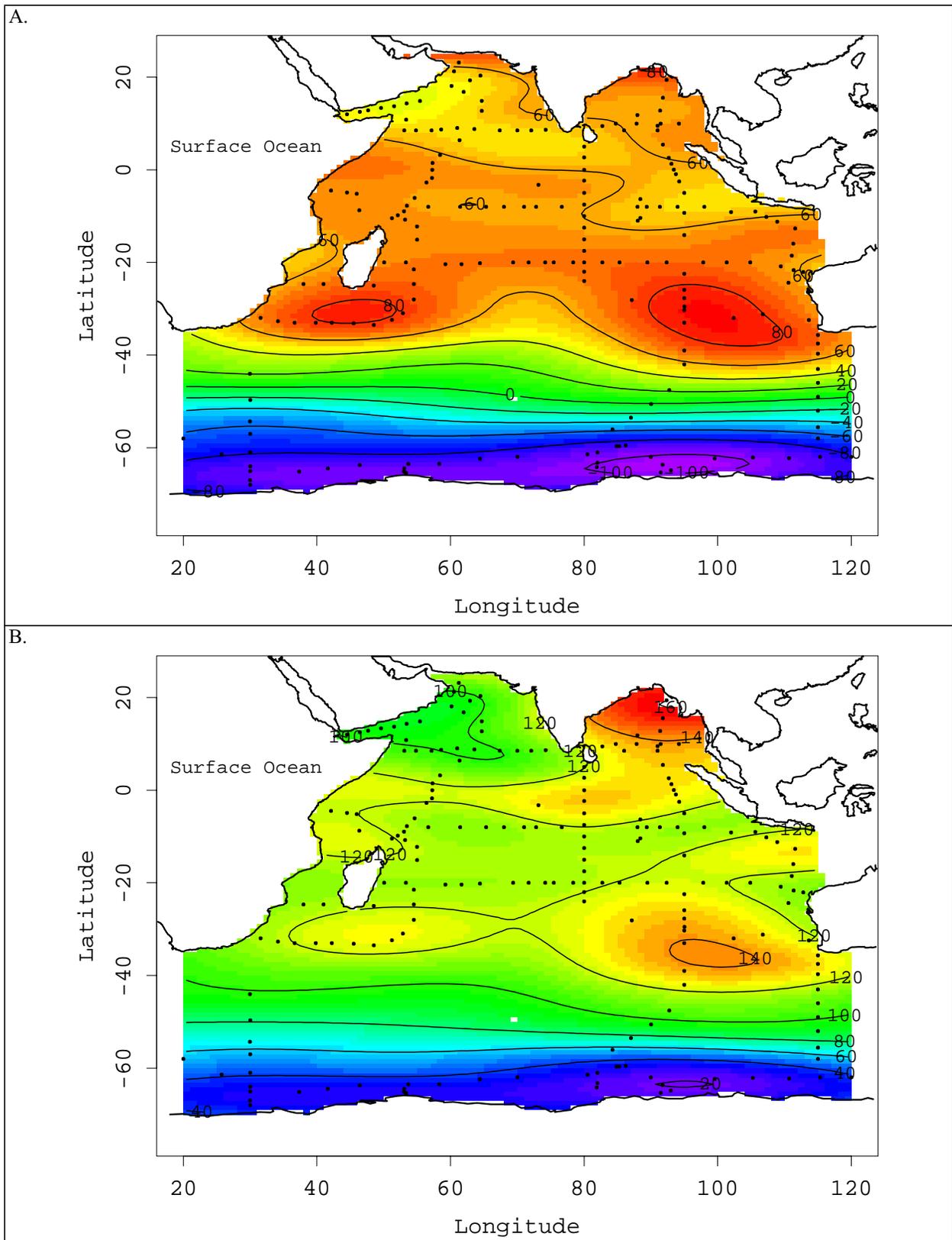


**Figure 9:**  $\Delta^{14}\text{C}$  along I3 in the southern subtropical Indian Ocean at approximately  $20^\circ\text{S}$ .

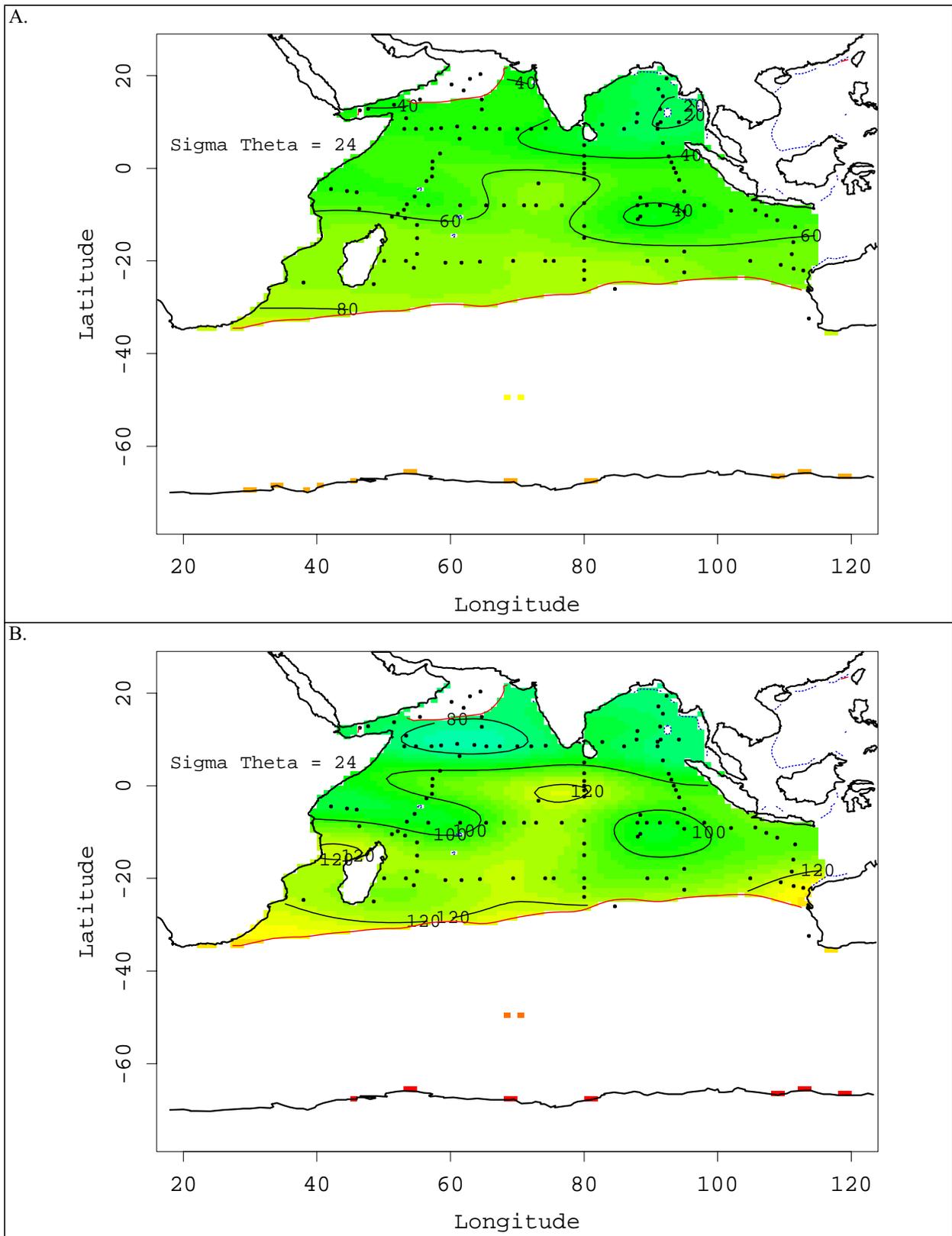
equator due to the geography and difference in chemistry between the Bay of Bengal and Arabian Sea. Perhaps unexpected is the fact that the distributions differ significantly as far as 40°S. In the eastern section the maximum bomb  $\Delta^{14}\text{C}$  values are found between 40°S and 20°S and more or less uniformly from the surface down to the level where  $\sigma_\theta \sim 26.5$ . The western section has a maximum in the same latitude range but in this case the maximum occurs as a subsurface lens.



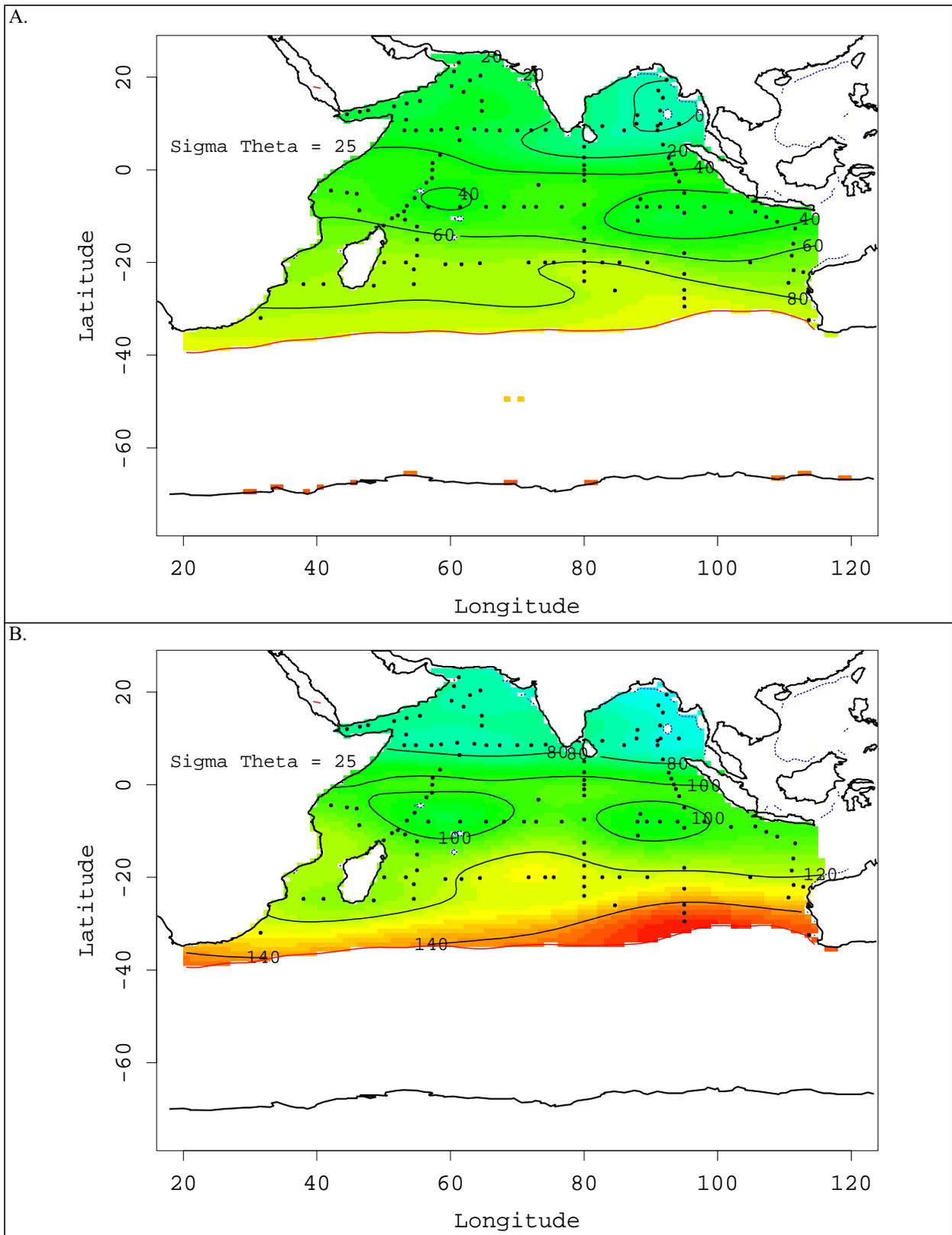
**Figure 10:** Mean bomb-produced  $\Delta^{14}\text{C}$  sections in the eastern (A) and western (B) Indian Ocean, shown in potential density space for samples from the upper 1000m.



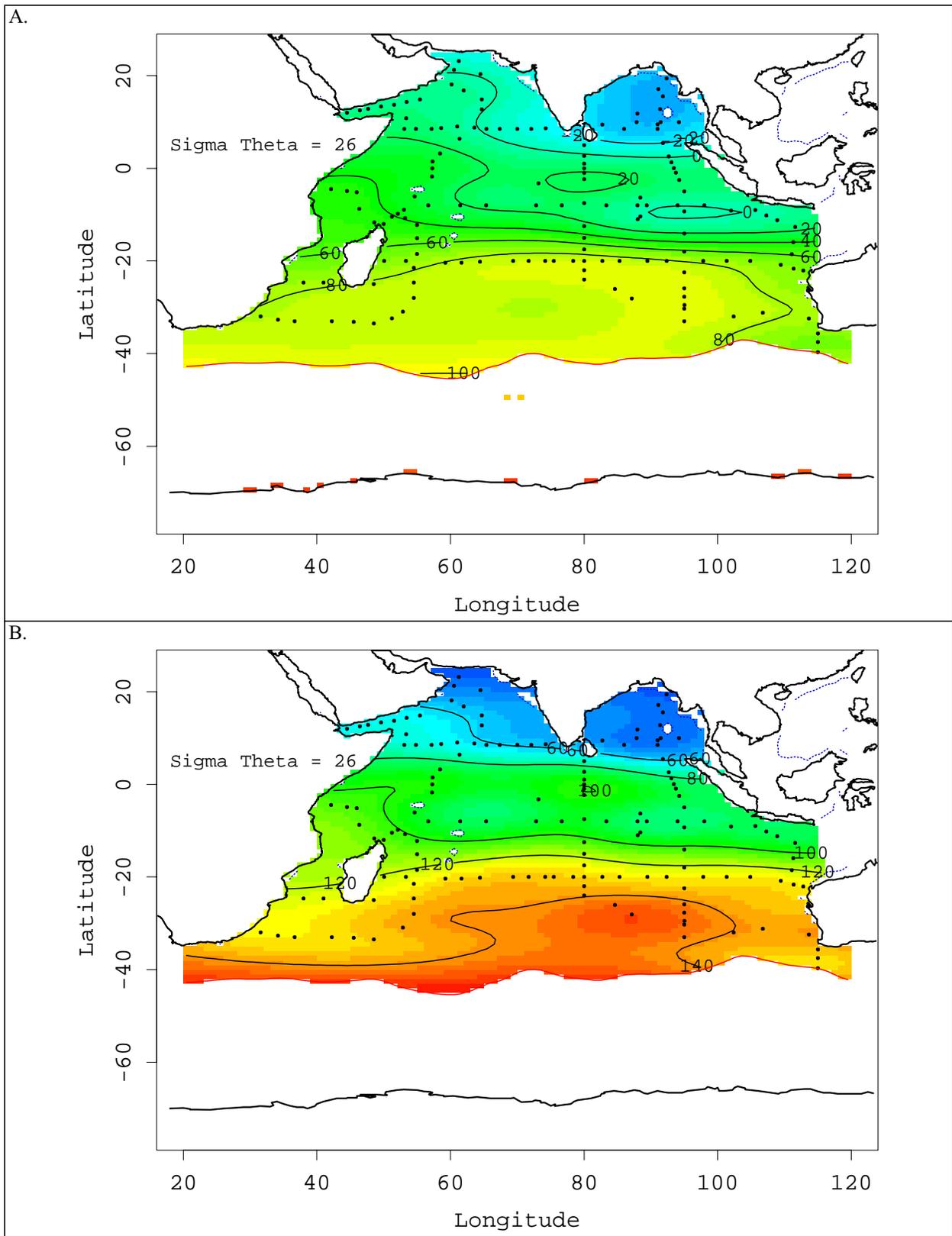
**Figure 11:** (A)  $\Delta^{14}\text{C}$  and (B) bomb-produced  $\Delta^{14}\text{C}$  for the surface Indian Ocean from WOCE measurements.



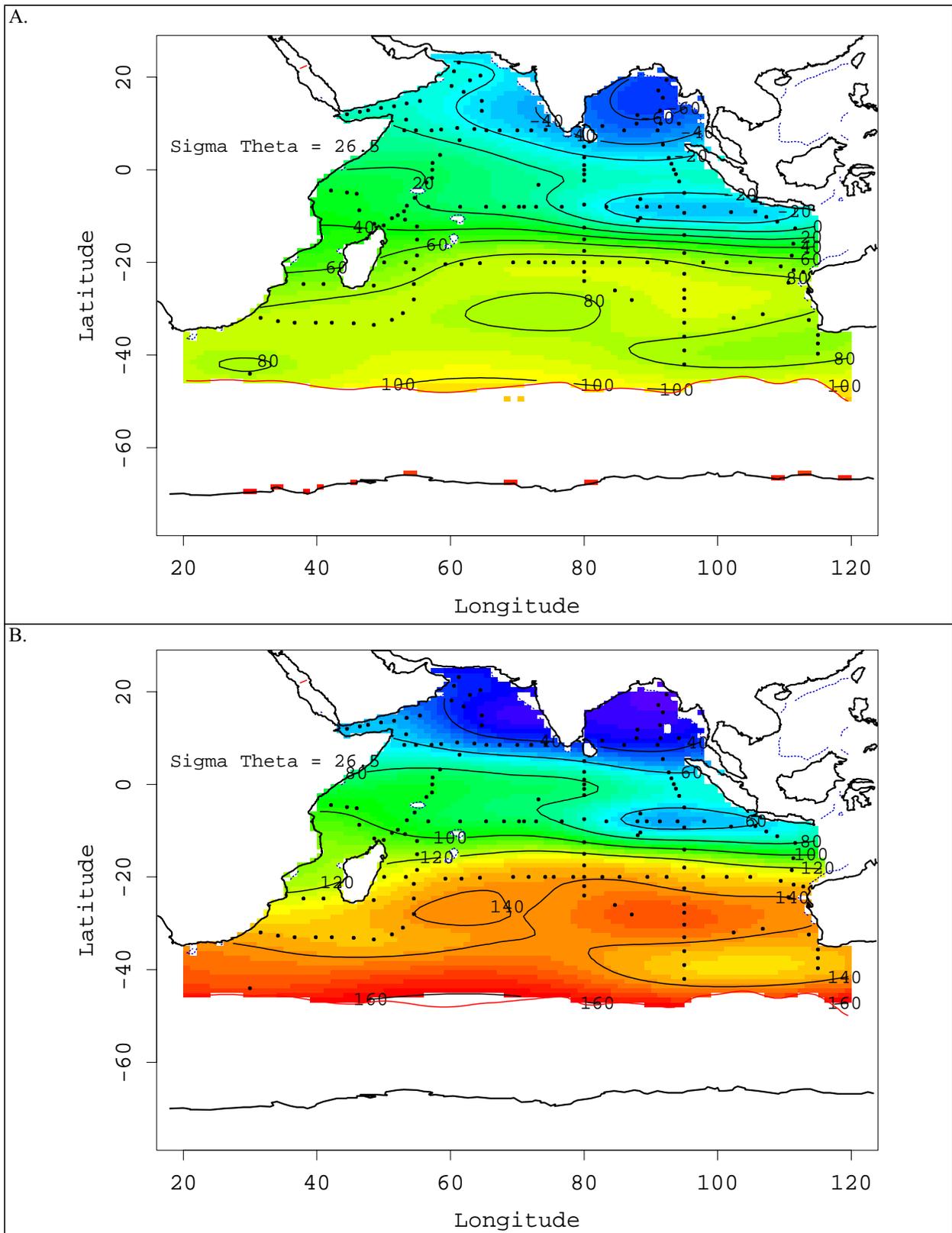
**Figure 12:** (A)  $\Delta^{14}\text{C}$  and (B) bomb-produced  $\Delta^{14}\text{C}$  on  $\sigma_\theta=24.0$ .



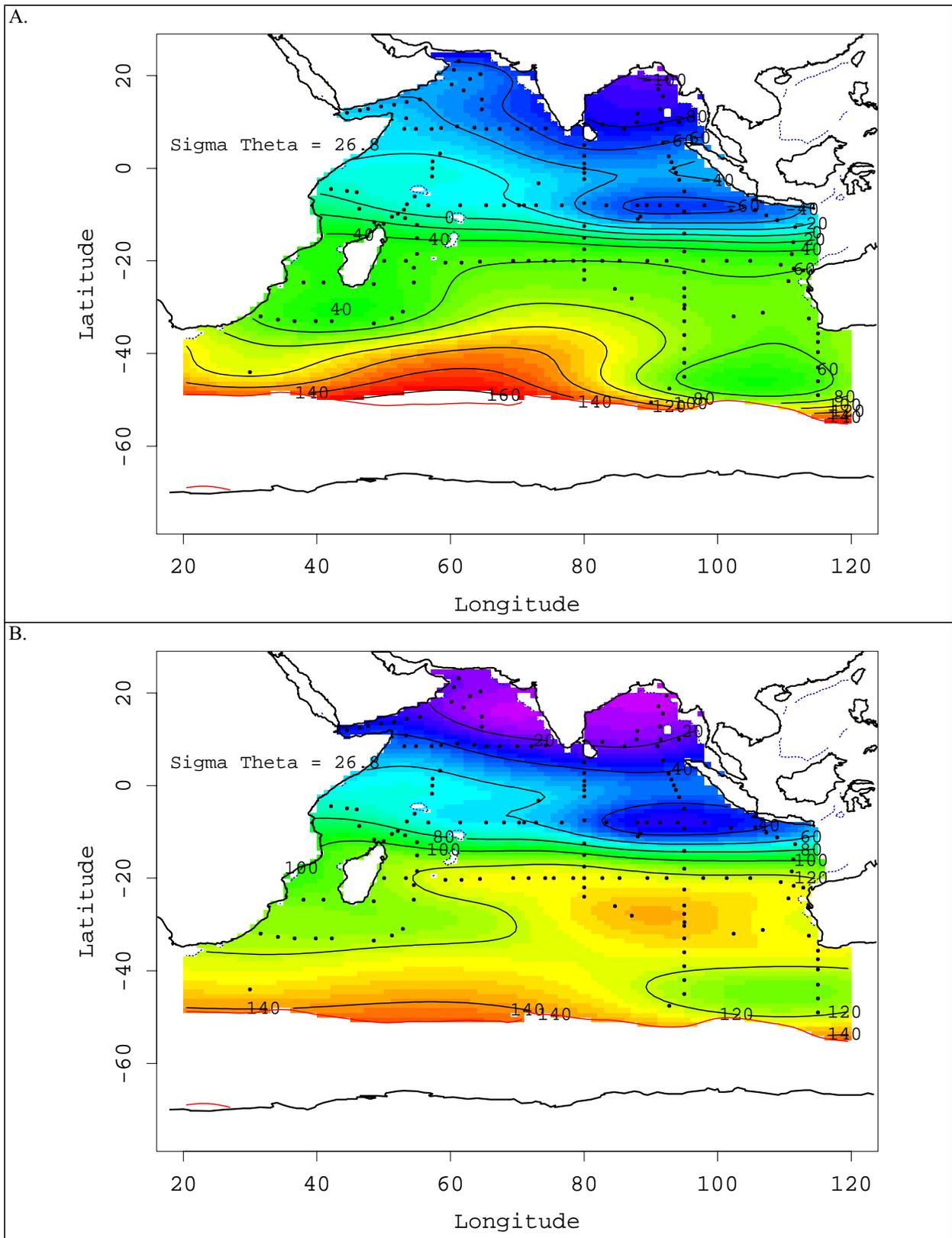
**Figure 13:** (A)  $\Delta^{14}\text{C}$  and (B) bomb-produced  $\Delta^{14}\text{C}$  on  $\sigma_{\theta}=25.0$



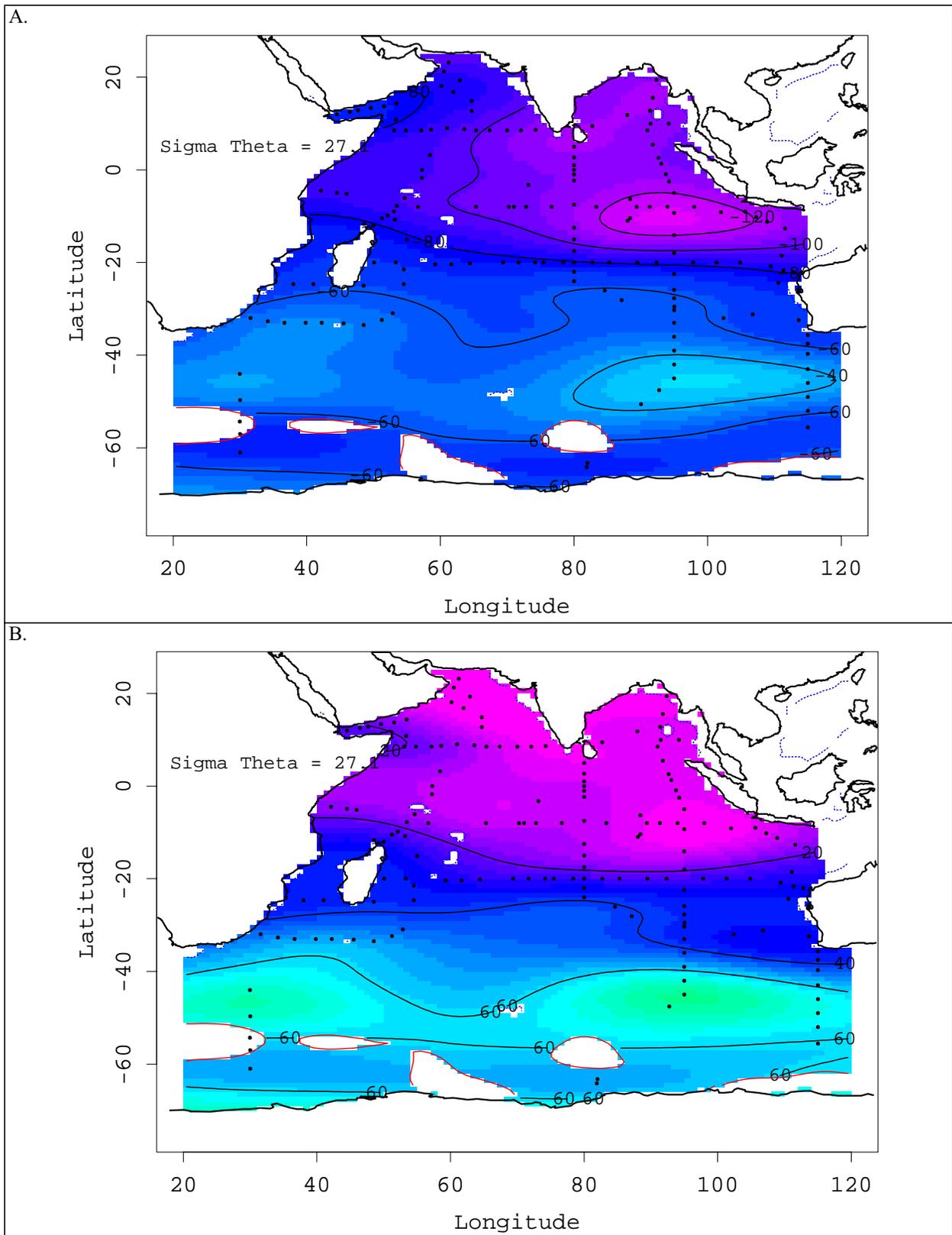
**Figure 14:** (A)  $\Delta^{14}\text{C}$  and (B) bomb-produced  $\Delta^{14}\text{C}$  on  $\sigma_{\theta}=26.0$



**Figure 15:** (A)  $\Delta^{14}\text{C}$  and (B) bomb-produced  $\Delta^{14}\text{C}$  on  $\sigma_{\theta}=26.5$



**Figure 16:** (A)  $\Delta^{14}\text{C}$  and (B) bomb-produced  $\Delta^{14}\text{C}$  on  $\sigma_{\theta}=26.8$



**Figure 17:** (A)  $\Delta^{14}\text{C}$  and bomb-produced (B)  $\Delta^{14}\text{C}$  on  $\sigma_{\theta}=27.1$

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## Data Processing Notes

Date	Contact	Data Type	Action Summary																				
1998-02-04	Anderson	BTL/SUM	Fixed line & expocode #s, & sta. dates																				
			<p>i01esu.txt</p> <p>Changed first header from R/V KNORR, I1,KN145, 11 to R/V KNORR CR. KN145, LEG 12 WHP-ID I01E</p> <p>Added time stamp</p> <p>changed EXPOCODE from 316N145/11b to 316N145_12</p> <p>changed WOCE SECT from I1 to I01E</p> <p>latitude was not left justified, corrected this</p> <p>deleted last record in file, it only had □</p> <p>The following stations had the wrong date. The cast started before midnight and ended after midnight according to the time but the date used was the same for the BE, BO, and EN event codes.</p> <table border="1"> <thead> <tr> <th>Sta. #</th> <th>Event Code</th> <th>Original Date</th> <th>Changed to Date</th> </tr> </thead> <tbody> <tr> <td>966</td> <td>EN</td> <td>093095</td> <td>100195</td> </tr> <tr> <td>987</td> <td>EN</td> <td>100795</td> <td>100895</td> </tr> <tr> <td>996</td> <td>EN</td> <td>100995</td> <td>101095</td> </tr> <tr> <td>1002</td> <td>EN</td> <td>101095</td> <td>101195</td> </tr> </tbody> </table> <p>i1b.sea</p> <p>Changed first header EXPOCODE and WHP-ID to conform with .sum file. EXPOCODE 31ka45 to 316N145_12, and WHP-ID WOCE to I01E.</p> <p>Changed CRUISE DATES 082995-101695 to 093095-101695</p> <p>Added time stamp</p> <p>Deleted last record in file, in only had □</p> <p>CHANGED FILE NAME TO i01ehy.txt</p>	Sta. #	Event Code	Original Date	Changed to Date	966	EN	093095	100195	987	EN	100795	100895	996	EN	100995	101095	1002	EN	101095	101195
Sta. #	Event Code	Original Date	Changed to Date																				
966	EN	093095	100195																				
987	EN	100795	100895																				
996	EN	100995	101095																				
1002	EN	101095	101195																				
1999-08-02	Schwartz	CTD	Submitted for DQE																				
1999-08-02	Schwartz	Cruise Report	Submitted																				
2002-01-08	Mantyla	BTL DQE	Submitted																				
2000-06-19	Kozyr	CO2	Final Data Submitted																				
			I have put the final/public CO2-related data files for the Indian Ocean WOCE Section I1W and I1E to the WHPO ftp INCOMING area. There are two CO2 parameters in the files: Total CO2 and Total Alkalinity with quality flags.																				
2000-08-03	Bartolacci	CTD	ctd files for i01e and i01w split																				
			Since the splitting of I01 into east and west lines, the ctd files for this cruise have remained as one zip file containing all stations for both east and west lines. As per Lynne Talley, I have split the east stations from the total zip file (stations 962-1014 according to the sumfile) and reziped them. They have replaced the original file which was renamed to indicate it contains all stations and moved to the original directory.																				
2000-09-14	Kappa	Cruise Report	cfc doc added to pdf file																				
2000-10-17	Jenkins	He/Tr	Submitted																				
			Reformatting needed																				
2000-11-15	Anderson	HELIUM/NEON	Converted to WOCE format																				
			I have put the Jenkins helium and neon in WOCE format. There were no quality codes so I set the HELIUM, DELHE3, and NEON to 2.																				
2001-01-04	Anderson	CTDTMP/OXY/CTDOXY	Update Needed																				
			<p>Working on an updated copy of i01ehy.txt (ANDY_ROSS.i01ehy.nut) from Andy Ross at OSU. This is the same data as was previously on-line, but the nutrient data has been corrected for units (previously uM/L, now uM/kg).</p> <p>Before putting this file back on-line, need to fix a few other problems:</p> <p>a) CTDTMP units are in ITS-68, should be ITS-90. All data need to be multiplied by 0.99976 to convert to ITS-90.</p>																				

## Data Processing Notes

			<p>Need to update header.</p> <p>b) OXYGEN and CTDOXY are in wrong units. Need to be converted from ml/l to uM/kg. Need to update headers. THIS NEEDS TO BE DONE FIRST, before converting CTDTMP to ITS-90.</p> <p>c) Formatting is incorrect for PO4, CFC11+12, OXYGEN and CTDOXY.</p>
2001-01-22	Anderson	TCARBN/ALKALI	Data reformatted
			<p>Converted CTDTMP from -68 to -90, changed header. Reformatted data columns in hyd file to comply with WOCE specs. Removed FCO2 column and associated Quality code (was '1').</p> <p>ALSO, changed the quality codes for previously merged ALKALI and TCARBN data from '1' to '2' where data is present.</p> <p>Realized after making other conversions, also needed to convert Theta from ITPS-68 to ITS-90. Used most up-to-date hyd file to make this conversion (multiplied all values by 0.99976).</p>
2001-02-01	Anderson	HELIUM, DELHE3, NEON	Data merged into BTL file
			<p>Merged TRITUM, TRITIER, HELIUM, HELIER, DELHE3, DELHER, NEON, NEONER from Sarilee's reformatted data files into hyd file.</p> <p>Data merged ok.</p> <p>NOTE: There were two values submitted for 979/1/25 (sta/cst/samp) TRITUM and TRITIER. Only merged first value into hyd file.</p>
2001-02-01	Anderson	TRITUM/TRITIER	Data merged into BTL file
			<p>Merged TRITUM, TRITIER, HELIUM, HELIER, DELHE3, DELHER, NEON, NEONER from Sarilee's reformatted data files into hyd file.</p> <p>Data merged ok.</p> <p>NOTE: There were two values submitted for 979/1/25 (sta/cst/samp) TRITUM and TRITIER. Only merged first value into hyd file.</p>
2001-06-21	Uribe	BTL	Exchange file online
			Bottle exchange files was put online.
2001-06-27	Uribe	CTD	Exchange file online
			CTD exchange files were put online.
2001-09-18	Wisegarver	CFCs	Submitted, update needed
			<p>This is information regarding line: I01E ExpoCode: 316N145_12 Cruise Date: 1995/08/29 - 1995/09/28 From: WISEGARVER, DAVID Email address: wise@pmel.noaa.gov Institution: NOAA Country: USA</p> <p>The directory this information has been stored in is: 20010918.165552_WISEGARVER_I01E The format type is: ASCII The data type is: BottleFile The Bottle File has the following parameters: CFC-11,CFC-12</p> <p>The Bottle File contains: CastNumber StationNumber BottleNumber SampleNumber WISEGARVER, DAVID would like the data PUBLIC. And would like the following done to the data: merge final dqe cfc's</p> <p>Any additional notes are: Submitted for D. Wyllie. CFC's on SIO98 Scale</p>
2001-09-27	Mantyla	NUTs/S/O	DQE Report Submitted
2001-12-26	Uribe	CTD	Exchange file online
			CTD has been converted to exchange using the new code and put online.

## Data Processing Notes

2002-01-08	Hajrasuliha	CTD	Internal DQE completed created *check.txt file for the cruise created *.ps files for this cruise.
2002-01-08	Anderson	BTL	Exchange file online Made new exchange file and put online.
2002-01-08	Anderson	BTL/SUM	DQ report online, The .sea file with the results of Arnold Mantyla's data quality evaluation and QUALT2 flags has been put online. Corrected a couple of error in the .sum file and put new file online. Jerry Kappa has been sent the DQ report.
2002-02-28	Bartolacci	CFCs	DQE'd data submitted I have placed the updated dqe'd CFC data sent by Wisegarver in the following directory .../onetime/indian/i01/i01e/original/2001.09.18_I01E_CFC_DQE_WISEGARVER included are data file and submission form README file. Data are in need of merging at this time.
2002-04-01	Anderson	DELC13	Submitted Date: Mon, 1 Apr 2002 09:49:35 -0800 (PST) From: WHPO Website <http@odf.ucsd.edu> To: dgerlach@whoi.edu, jrweir@whpo.ucsd.edu, whpo@ucsd.edu Subject: WHPO DATA I01E: OTHER from GERLACH This is information regarding line: I01E ExpoCode: Cruise Date: 1995/09/30 - 1995/10/16 From: GERLACH, DANA Email address: dgerlach@whoi.edu Institution: WHOI Country: USA  The file: C:\My Documents\C13-project\whpo_indian_march02\whpo_i01e.txt - 2667 bytes has been saved as: 20020401.094935_GERLACH_I01E_whpo_i01e.txt in the directory: 20020401.094935_GERLACH_I01E The data disposition is: • Public The file format is: • Plain Text (ASCII) The archive type is: • NONE - Individual File The data type(s) is: • Other: flagged 13C data The file contains these water sample identifiers: • Cast Number (CASTNO) • Station Number (STATNO) • Bottle Number (BTLNBR) GERLACH, DANA would like the following action(s) taken on the data: • Merge Data • Place Data Online Any additional notes are: • NOSAMS expocode affiliated with this line is: 316N145/11. Any questions or concerns, please contact • Dana Gerlach (dgerlach@whoi.edu) or • Ann McNichol (amcnichol@whoi.edu).
2002-04-12	Buck	C14	Submitted Moved data from /usr/export/ftp-incoming to i01/i01e/original/20020410_KEY_I1_C14. It is a CSV file and I added the following heading to it: #I01E/W,316N145_11-12,Key Data belongs to both I01E and I01W.

## Data Processing Notes

2002-08-13	Anderson	C13/C14/CO2/ALK/CFCs	Data Online
<p>Merged the DELC14 and C14ERR from Key, the DELC13 from Gerlach, the TCARB and ALKAL from Kozyr, and the CFCs from Wisegarver. Made new exchange file.</p> <p>Merge notes for i01e:</p> <p>Merged the DELC14 and C14ERR from file I1.C14 found in /usr/export/html-public/data/onetime/indian/i01/i01e/original/20020410_KEY_I1_C14 into the online file 20010927WHPOSIOSA.</p> <p>Merged the DELC13 from file 20020401.094935_GERLACH_I01E_whpo_i01e.txt found in /usr/export/html-public/data/onetime/indian/i01/i01e/original/20020401.094935_GERLACH_I01E into the online file.</p> <p>Merged the new TCARB and ALKAKI from file ilecarb.dat found in /usr/export/html-public/data/onetime/indian/i01/i01e/original/2000.06.19_I1_CARB_KOZYR into online file.</p> <p>Merged the new CFC's from file:</p> <p style="text-align: center;">20010918.165552_WISEGARVER_I01E_i01e_CFC_DQE.dat</p> <p>found in /usr/export/html-public/data/onetime/indian/i01/i01e/original/2001.09.18_I01E_CFC_DQE_WISEGARVER into the online file.</p>			
2002-08-15	Anderson	He/Tr/Helium/Neon	Data Online
<p>Merged the DELHE3, DELHER, HELIUM, HELIER, NEON, NEONER, TRITIUM, and TRITER from Jenkins. Made new exchange file.</p> <p>Merge notes for i01e:</p> <p>HE3, DELHER, HELIUM, HELIER, NEON, NEONER from file wihe.dat found in /usr/export/html-public/data/onetime/indian/i01/i01e/original/2000.10.17_I01E_TRITIUM_HELIUM_JENKINS into online file 20020813WHOPSIOSA.</p> <p>Merged the TRITIUM and TRITER from file witrit.dat found in above directory into online file.</p> <p>This merging had been done earlier by Stacey Anfuso but there is no rcs (at least I can't find it) and the file she merged appears not to have been put online or somehow was replaced with a file that did not have these parameters.</p>			
2002-10-05	Diggs	BTL	Units corrected
<p>Fixed original WOCE formatted bottle file per Tim Boyer's (NODC/OCL) suggestions to me.</p> <p>Units line: This is the units line from i01e_hy1.csv:</p> <p>DBAR,ITS-90,PSS-78,,PSS-78,,UMOL/KG,,UMOL/KG,,UMOL/KG,,UMOL/KG,,UMOL/KG,,UMOL/KG,,PM/K,,G</p> <p>PM/K,,G T,,U UMOL/K,,PERCNT,,G /MILL,,/MILLE,,NMOL/KG,,E UMOL/K,,G UMOL/K,,/MILLE,NMOL/KG,PERCNT,NMOL/KG,ITS-90,TU&amp;#034;</p> <p>Fixed units line, re-made HYD Exchange, NetCDF and inventories. Re-zipped all relevant files, checked in JOA3.1 (OSX), copied files to DVD 3.0 online site as well. Tarballed inventory, exchange, and NetCDF and sent to Shannon Niou of NODC for inclusion on the WOCE Version 3 DVD.</p>			

## Data Processing Notes

2003-04-16	Muus	CTDs/OXY/DELC13	Data Online
<p>Merged DELC13 decimal-2-data into bottle file. Merged new CTDPRS, CTDTMP, CTDSAL, CTDOXY, THETA, SALNTY &amp; OXYGEN from WHOI into bottle file.</p> <p>Notes on I01E merging    Apr 16, 2003    D. Muus</p> <p>1. Changed all Helium and Tritium quality flag 1s associated with missing data to 9s.  2. Merged DELC13 from:        /usr/export/html-public/data/onetime/indian/i01/i01e/original/        20020401.094935_GERLACH_I01E/20020401.094935_GERLACH_I01E_whpo_i01e.txt</p> <p>into current web bottle file (20021005WHPOSIOSCD) to replace 1 decimal place data with 2 decimal place DELC13 data.</p> <p>3. Merged CTDPRS, CTDTMP, CTDSAL, CTDOXY, THETA, SALNTY, &amp; OXYGEN from:        Jane Dunworth, WHOI, email of March 24, 2004.        email data can be found in:        /usr/export/html-public/data/onetime/indian/i01/i01e/original/        2003.04.16.I01E_C13_CTDPTSO_SAL_OXY_MERGE_MUUS/        dunworth.email030324.i01e.btldata</p> <p>Prior to merging, ITS-68 CTDTMP and THETA were changed to ITS-90 using ITS-90 = 0.99976(ITS-68) and CTDOXY and OXYGEN changed from ml/l to UMOL/KG using cvuwoce on minerva.ucsd.edu.</p> <p>4. 2001/01/23 ANFUSO, S. note in Data History. NUTRIENTS: Data was originally submitted in uM/L units, PI recalculated and resubmitted in uM/kg units. Also, original submission of nitrate data was actually nitrate nitrite. This error has been corrected in current data submission.</p> <p>Nutrients unchanged this version since only small changes in CTD pressure, salinity and temperature for samples with nutrient values.</p> <p>5. Made new exchange file for Bottle data.  6. Checked new bottle file with Java Ocean Atlas.</p>			
2005-02-28	Anderson	HELIUM/NEON	Data Online
<p>i01e and i01w</p> <p>Found file i1he.txt in ../indian/i01/i01/original/2000.10.04_I1_BOTTLE. This file contains the deep DELHE3, HELIUM, NEON, DELHER, HELIER, and NEONER for i01e and i01w.</p> <p>I merged these parameters into the online files, and made new exchangeand netcdf files. There were no Q1 or Q2 flags so I set them to 2.</p>			
2008-06-17	Kappa	Cruise Report	Added C14 & CO2 reports & Data Processing Notes
<p>Added 4 reports to pdf and text versions of cruise report:</p> <ol style="list-style-type: none"> <li>1) Assessment of the quality of total inorganic carbon measurements</li> <li>2) Assessment of the quality of the shipboard measurements of total alkalinity</li> <li>3) Anthropogenic CO2 Inventory of the Indian Ocean</li> <li>4) U.S. Woce Indian Ocean Survey: Final Report for Radiocarbon</li> </ol>			

## Data Processing Notes

1998-02-04	Anderson	BTL/SUM	Fixed line & expocode #s, & sta. dates																																																																																
	<p>i01wsu.txt -  Changed first header from R/V KNORR, I1,KN145, 11 to:  R/V KNORR CR. KN145, LEG 11 WHP-ID I01W  Added time stamp  changed EXPOCODE from 316N145/11a to 316N145_11  changed WOCE SECT from I1 to I01W  latitude was not left justified, corrected this</p> <p>The following records had the wrong date. The cast started before midnight and ended after midnight according to the time but the date used was the same for the BE, BO, and EN event codes.</p> <table border="1"> <thead> <tr> <th>Sta. #</th> <th>Event Code</th> <th>Original Date</th> <th>Changed to Date</th> </tr> </thead> <tbody> <tr><td>857</td><td>BO</td><td>082995</td><td>083095</td></tr> <tr><td>862</td><td>EN</td><td>083195</td><td>090195</td></tr> <tr><td>880</td><td>EN</td><td>090695</td><td>090795</td></tr> <tr><td>885</td><td>BO</td><td>090795</td><td>090895</td></tr> <tr><td>885</td><td>EN</td><td>090795</td><td>090895</td></tr> <tr><td>891</td><td>EN</td><td>090895</td><td>090995</td></tr> <tr><td>897</td><td>EN</td><td>091095</td><td>091195</td></tr> <tr><td>904</td><td>EN</td><td>091295</td><td>091395</td></tr> <tr><td>911</td><td>BO</td><td>091495</td><td>091595</td></tr> <tr><td>911</td><td>EN</td><td>091495</td><td>091595</td></tr> <tr><td>915</td><td>BO</td><td>091595</td><td>091695</td></tr> <tr><td>915</td><td>EN</td><td>091595</td><td>091695</td></tr> <tr><td>927</td><td>EN</td><td>091895</td><td>091995</td></tr> <tr><td>934</td><td>BO</td><td>092095</td><td>092195</td></tr> <tr><td>934</td><td>EN</td><td>092095</td><td>092195</td></tr> <tr><td>937</td><td>EN</td><td>092195</td><td>092295</td></tr> <tr><td>944</td><td>EN</td><td>092395</td><td>092495</td></tr> <tr><td>954</td><td>BO</td><td>092595</td><td>092695</td></tr> <tr><td>954</td><td>EN</td><td>092595</td><td>902695</td></tr> </tbody> </table> <p>i1a.sea  Changed first header EXPOCODE and WHP-ID to conform with .sum file.  EXPOCODE 31ka45 to 316N145_11, and WHP-ID WOCE to I01W.  Changed CRUISE DATES 082995-101695 to 082995-092895  Added time stamp  Deleted last record in file, it only had □  CHANGED FILE NAME TO i01why.txt</p>			Sta. #	Event Code	Original Date	Changed to Date	857	BO	082995	083095	862	EN	083195	090195	880	EN	090695	090795	885	BO	090795	090895	885	EN	090795	090895	891	EN	090895	090995	897	EN	091095	091195	904	EN	091295	091395	911	BO	091495	091595	911	EN	091495	091595	915	BO	091595	091695	915	EN	091595	091695	927	EN	091895	091995	934	BO	092095	092195	934	EN	092095	092195	937	EN	092195	092295	944	EN	092395	092495	954	BO	092595	092695	954	EN	092595	902695
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954	EN	092595	902695																																																																																
1998-09-16	Morrison	CTD	Submitted																																																																																
	Plots, unencrypt data for workshop, NO public distrib after workshop																																																																																		
1998-09-29	Morrison	CTDOXY	not yet submitted,																																																																																
	50 stas have bad ctd 02. Bob Millard will take another look at them																																																																																		
1998-09-29	Talley	BTL	Data Update:																																																																																
	<p>Following changes ftp'd to WHPO. Replace older HYD file with this one (OK'd by PI):</p> <ol style="list-style-type: none"> <li>1. Combine i01e and i01w into one line: i01</li> <li>2. Change expocode from 31ka45 to 316N145</li> <li>3. Bottle flag for station 1005, 1, 23 at 349.7 dbar is 3 and salinity is 4.</li> </ol> <p>It looks like all nutrients are bad here as well. I suggest that they all be flagged 4. Oxygen doesn't look out of place, but maybe for consistency, it should be flagged 3.</p>																																																																																		

## Data Processing Notes

1998-12-22	Srinivasan	He/Tr Deep	Submitted	Preliminary, not for DQE
	<p>This is Ashwanth Srinivasan from Noble Gas Isotope Lab , RSMAS, Univ of Miami. We have submitted four files, i7he.txt, i9he.txt and i1he.txt and readme.he to the incoming directory at your ftp site. These files contain tritium, helium and neon data from WOCE I7N, I9N and I1 cruises. These data are preliminary and proprietary and the format is explained in the readme.he file. In case of problems or questions please email to one of the following addresses:            Zafer Top: ztop@rsmas.miami.edu            Ashwanth Srinivasan: asrinivasan@rsmas.miami.edu</p>			
1999-04-06	Bartolacci	SUM	S.Anderson's (1998-02-04) updated files online	
1999-05-25	Top	He/Tr Deep	Data are Public	
	<p>My helium-tritium data from IO legs I1-I7N and I9N may now be made public . It should be kept in mind though that we are working on the synthesis ; some modifications may occur. Also there are some papers are in progress; interested parties should check with the tracer group (Schlosser, Jenkins, Lupton, Top)</p>			
1999-06-30	Morrison	CTD/BTL/SUM	Submitted	
	<p>6/27/99</p> <p>The WHOI processing programs could not handle 4 digit station numbers, therefore the processed data as passed to me for final approval had files with station numbers 857 - 999 and 00 - 14. I changed the names of the CTD files and the stations numbers in the CTD, SEA and SUM files to reflect the actual WOCE stations numbers: 857 - 1014.</p> <p>John M. Morrison, Chief Scientist, WOCE I1</p> <p>6/29/99</p> <p>I have just placed the final, corrected data for WOCE Indian Ocean Leg I1 on your server. All of the calibration documentation is in the directory DOC. Sorry that this was not submitted sooner, but I did not receive the data until last fall and was busy cleaning up JGOFS Indian Ocean and Southern Ocean data for submission to the JGOFS database. As you can see, the WOCE I1 dataset has some problems with the CTD data in that it was necessary to use Falmouth Scientific CTD's for the cruise (all of the WOCE Neil Brown WHOI CTD's were not working when the ship left of the WOCE Neil Brown WHOI CTD's were not working when the ship left Muscat, Oman.</p> <p>Let me know if you have received this dataset.</p>			
1999-06-30	Morrison	CTD	Data are Final	
	<p>I have just placed the final, corrected data for WOCE Indian Ocean Leg I1 on your server. All of the calibration documentation is in the directory DOC.</p> <p>As you can see, the WOCE I1 dataset has some problems with the CTD data in that it was necessary to use Falmouth Scientific CTD's for the cruise (all of the WOCE Neil Brown WHOI CTD's were not working when the ship left Muscat, Oman.</p>			
1999-07-26	Swartz	CTD/DOC	Data Update:	
1999-09-29	Falkner	BA	Data Update:	
	<p>The quality of the Ba data from most WOCE legs in the Indian Ocean turned out to be quite poor; far worse than attainable analytical precision (+/-20% as opposed to 2%). We recorded many vials which came back with loose caps and evaporation associated with that seems to be the primary problem. The only hope I have of producing a decent data set is to run both Ba and a conservative element simultaneously and then relating that to the original salinity of the sample. We will be taking delivery on a high resolution ICPMS here at OSU sometime this winter which would make the project analytically feasible and economical. I do not presently have the funds in hand to do this and so have archived the samples for the time being. I don't think the WHPO would derive any benefit from the present data set.</p> <p>KKF</p>			
1999-12-22	Elder	DEL14	Radiocarbon Data Report Submitted	
2002-01-08	Mantyla	BTL DQE	Submitted	emailed by S. Anderson

## Data Processing Notes

2000-03-27	Morrison	CTD/BTL	Website Updated:	Status changed to Public
	not hearing any decenting comments from my fellow PI's, I release the WOCE I1 data set to the general public.			
2000-05-01	Warner	CFCs	Revised data to be merged, made public	
	I just uploaded the revised CFC data for WOCE I1. It should be made public once it is merged. I have also included a report to be merged (eventually) into the metadata files.			
2000-06-19	Diggs	ALKALI/TCARBN	Submitted	
	Bottle: (tcarbn, alkali) data file received in INCOMING. In perfect WHP format. Will be merged asap. From Alex Kozyr I have put the final/public CO2-related data files for the Indian Ocean WOCE Section I1W and I1E to the WHPO ftp INCOMING area. There are two CO2 parameters in the files: Total CO2 and Total Alkalinity with quality flags. Please confirm the data submission.			
2000-08-02	Kappa	Cruise Report	pdf, txt docs online; need cfc report	
2000-08-03	Bartolacci	CTD	ctd files for i01e and i01w split	
	Since the splitting of I01 into east and west lines, the ctd files for this cruise have remained as one zip file containing all stations for both east and west lines. As per Lynne Talley, I have split the east stations from the total zip file (stations 962-1014 according to the sumfile) and rezzipped them. They have replaced the original file which was renamed to indicate it contains all stations and moved to the original directory.			
2000-08-12	Ross	SAL/NUTs/NITRAT	Data Update:	
	<p>Per your request - I've attached i0why.nut and i01ehy.nut files containing nutrient data in the units of umol/kg. The original I01WHY.txt and I01EHY.txt files that contained nutrient data in umol/liter units were downloaded from the WOCE program office sites:  <a href="http://whpo.ucsd.edu/data/onetime/indian/i01/i01e/index.htm">http://whpo.ucsd.edu/data/onetime/indian/i01/i01e/index.htm</a> and  <a href="http://whpo.ucsd.edu/data/onetime/indian/i01/i01w/index.htm">http://whpo.ucsd.edu/data/onetime/indian/i01/i01w/index.htm</a> and were used as the data sources. The attached files are in text format.</p> <p>For your records, in the conversion process the bottle salinity values were used to determine sample density along with the mean laboratory temperature for each leg as determined from our nutrient analysis notes. When a bottle salinity value was unavailable, the corresponding CTD salinity value was used. The mean lab temperature for I01W was 25°C and 26°C for I01E.</p> <p>An important note:  We also realized that the nitrate in the original files was in fact nitrate+nitrite. This has also been corrected in the new file versions that are attached.</p>			
2000-09-07	Huynh	Cruise Report	cfc report added to txt version; pdf pending	
2000-09-14	Kappa	Cruise Report	cfc doc added to pdf file	
2000-10-04	Uribe	BTL	Found data newer than file online	
	Bottle Moved file i01hy.txt from incoming file in /usr/export/. Website indicated i01e was equivalent to i01w. File stamp is WHPOSIO19980928LDT. Online stamp is WHPOSIO19980204SA. This indicates file data to be more recent than online version. Path is i01/i01e/original/1998.09.28_HY_LDT.			
2000-10-17	Jenkins	TRITUM	Preliminary Data Submitted	
	<p>*Files for Tritium Data:  WOCE Indian Ocean = WITrit.dat Contains all legs  WOCE Pacific P10 = WP10Trit.dat  WOCE Pacific P13 = WP13Trit.dat  WOCE Pacific P14c = WP14cTrit.dat  WOCE Pacific P18 = WP18Trit.dat  WOCE Pacific P19 = WP19Trit.dat  WOCE Pacific P21 = WP21Trit.dat  SAVE South Atlnt = SAVETrit.dat</p> <p>*Column Layout as follows: Station, Cast, Bottle, Pressure, Tritium, ErrTritium  *Units as follows: Tritium and ErrTritium in T.U.  *All data are unfortunately still preliminary until we have completed the laboratory intercomparision and intercalibration that is still underway.</p>			

## Data Processing Notes

2000-10-17	Jenkins	HELIUM/DELHE3	Preliminary Helium, DelHe3, Neon Submitted
	<p>*Files for Helium and Neon Data:</p> <p>WOCE Indian Ocean = WIHe.dat Contains all legs  WOCE Pacific P10 = WP10He.dat  WOCE Pacific P18 = WP18He.dat  WOCE Pacific P19 = WP19He.dat  WOCE Pacific P21 = WP21He.dat</p> <p>* Column Layout as follows:  Station, Cast, Bottle, Pressure, Delta3He, ErrDelta3He, ConcHelium, ErrConcHelium, ConcNeon, ErrConcNeon</p> <p>* Units as follows:  Delta3He and ErrDelta3He in %  ConcHelium, ErrConcHelium, ConcNeon, and ErrConcNeon in nmol/kg</p> <p>* Null values (for ConcNeon and ErrConcNeon only ) = -9.000</p> <p>* All data are unfortunately still preliminary until we have completed the laboratory intercomparison and intercalibration that is still underway.</p> <p>*Files for Helium and Neon Data:</p> <p>WOCE Indian Ocean = WIHe.dat Contains all legs  WOCE Pacific P10 = WP10He.dat  WOCE Pacific P18 = WP18He.dat  WOCE Pacific P19 = WP19He.dat  WOCE Pacific P21 = WP21He.dat</p> <p>* Column Layout as follows:  Station, Cast, Bottle, Pressure, Delta3He, ErrDelta3He, ConcHelium, ErrConcHelium, ConcNeon, ErrConcNeon</p> <p>* Units as follows:  Delta3He and ErrDelta3He in %  ConcHelium, ErrConcHelium, ConcNeon, and ErrConcNeon in nmol/kg</p> <p>* Null values (for ConcNeon and ErrConcNeon only ) = -9.000</p> <p>* All data are unfortunately still preliminary until we have completed the laboratory intercomparison and intercalibration that is still underway.</p>		
2000-11-08	Anderson	HELIUM/NEON	Reformatted by WHPO
	I have put the Jenkins helium and neon in WOCE format. There were no quality codes so I set the HELIUM, DELHE3, and NEON to 2.		
2000-11-13	Anderson	TRITUM	Reformatted by WHPO
	I have put the Jenkins tritium data into WOCE format. There were no quality codes so I set the TRITUM to 2.		
2000-11-21	Anfuso	NUTs	Update Requested
	Dear Dr. Gordon, We are reviewing all data submitted to WHPO for the Indian Ocean WOCE cruise lines and would like to request that you resubmit the nutrient data for I01E/I01W in uM/Kg units. The current data submission indicates the nutrient values are in uM/L units. All other nutrient data submissions from you research group for the Indian Ocean WOCE lines indicate the data have been submitted in uM/Kg units.		
2000-11-27	Uribe	He/Tr Shallow	Data Update:
	Files tritfrm.txt, savetrit.dat, witrtr.dat, heformat.txt and wihe.dat were moved from Jenkins' original data directory. witrtr.dat contains tritium data for the indian cruises. wihe.dat contains helium data for indian cruises. These files contain original data that was later re-formatted by S. Anderson. Files received by Jenkins on October 17th, 2000.		

## Data Processing Notes

2001-01-23	Anfuso	BTL	Website Updated:	BTL file reformatted
	Bottle: (ctdtmp, ctdoxy, theta, oxygen, silcat, nitrat, nitrit, phspht, tcarbn, alkali)			
	NUTRIENTS: Data was originally submitted in uM/L units, PI recalculated and resubmitted in uM/kg units. Also, original submission of nitrate data was actually nitrate nitrite. This error has been corrected in current data submission.			
	CTDOXY & OXYGEN: Data was originally in ml/l, Sarilee converted to uM/kg.			
	FCO2: Removed this data column and associated quality flag. All data values were -9.0.			
	CTDTMP & Theta: Converted data from ITPS-68 to ITS-90.			
	TCARBON & ALKALI: Changed quality flag from 1 to 2 where data exists.			
2001-02-01	Anfuso	He/Tr/Shallow	Website Updated:	Data Online
	Bottle: (tritium, helium, delhe3, neon, triter, helier, delher, neoner)			
	Merged TRITUM, TRITER, HELIUM, HELIER, DELHE3, DELHER, NEON, NEONER data into hyd file. Updated hyd file is on-line.			
	NOTE: The following NEON data (sta/cst/samp) had a -9.000 data value, with a -0.045NMOL/KG NEONER value. This doesn't make sense. Assumed samples were never drawn, NEONER value changed to -9.000.			
	866/1/28, 26, 24, 22, 21; 873/1/9; 874/1/2			
	Also, the following TRITUM and TRITIER had duplicate data values submitted, only merged first value into hyd file: 880/1/9;885/1/1;945/1/1;951/1/21			
2001-02-05	Anfuso	HE/TR/NEON	Website Updated:	Data merged into BTL file
	Merged TRITUM, TRITIER, HELIUM, HELIER, DELHE3, DELHER, NEON, NEONER from Sarilee's reformatted data files into hyd file.			
	Data merged ok.			
	NOTE: The following NEON data (sta/cst/samp) had a -9.000 data value, with a -0.045NMOL/KG NEONER value. This doesn't make sense. Assumed samples were never drawn, NEONER value changed to -9.000.			
	866/1/28, 26, 24, 22, 21; 873/1/9; 874/1/2			
	Also, the following TRITUM and TRITIER had duplicate data values submitted, only merged first value into hyd file: 880/1/9;885/1/1;945/1/1;951/1/21			
2001-02-06	Anfuso	ALKALI/TCARBON	Website Updated:	Data Online
	Merged updated TCARBON and ALKALI data and quality codes into hyd file. Merged over preliminary version of data. Updated hyd file is on-line. Merging notes are in original subdir 2000.06.19 I01W_CARB_KOZYR/00_Readme.			
2001-02-07	Mantyla	NUTs/S/O	DQE Begun	
	Sure, I would be glad to look over the Indian Ocean data for you. Sarilee has started plotting up I01 for me to start on.			
2001-06-21	Uribe	BTL	Website Updated:	Exchange file online
	Bottle exchange file was put online.			
2001-06-22	Muus	He/Tr Deep	Submitted/not on web	
	I01E,I01W Z. Top deep helium/tritium received May 25, 1999 not on web.			

## Data Processing Notes

2001-08-23	Mantyla	OXYGEN	Decimal correction needed	
	<p>I took another look at the exchange format for I 01E. The nutrient conversion back to UM/L appear to be OK, I had misread one station. However, the O2 data, listed as ML/L, should carry two more decimal places. The conversion is going from a 4 significant figure to only 2.</p> <p>What is supposed to be listed under the depth column? Since it appears with each sample and is next to the CTD pressure, I would assume that the sample depth would be listed there. However, what is showing up is the bottom sounding for every sample.</p> <p>At 08:55 AM 8/23/01 -0700, James H. Swift wrote: WHPO - Would someone kindly create a new bottle exchange file for I01E (316N145_12). There is a clear problem with the oxygens and nutrients in the present exchange file on line for this cruise (i01e_hy1.csv) and I want to see if it goes away when we create a new file.</p>			
2001-08-29	Top	NEON	Website Updated:	Status Changed to Public
	Zafer - Is it safe to assume that all WOCE One-Time Survey neon data from you are now public? Jim Yes they are. Zafer			
2001-11-01	Mantyla	NUTs/S/O	DQE Report Submitted	
2001-12-17	Hajrasuliha	CTD/BTL	Internal DQE completed	
	<p>The following are results from the examiner.pl and plotter.pl code that were run on this cruise. Not all of the errors are reported but rather a summary of what was found. For more information you can go to the cruise directory, and look at the NEW file called CruiseLine_check.txt. Two plot files are also present. _oxy.ps and _sal.ps _oxy.ps and _sal.ps files created. Exchange CTD file not created for this cruise.</p>			
2001-12-26	Uribe	CTD	Website Updated:	Exchange file online
	CTD has been converted to exchange using the new code and put online.			
2002-01-08	Anderson	BTL	Website Updated:	Exchange file online
	Made new exchange file and put online.			
2002-01-08	Anderson	BTL/SUM	Website Updated:	DQ report online,
	<p>The .sea file with the results of Arnold Mantyla's data quality evaluation and QUALT2 flags has been put online.</p> <p>Corrected a couple of error in the .sum file and put new file online.</p> <p>Jerry Kappa has been sent the DQ report.</p>			
2002-02-28	Bartolacci	CFC's	DQE'd data submitted	Data ready to be merged
	<p>I have placed the updated dqed CFC data sent by Wisegarver in the following directory .../onetime/indian/i01/i01w/original/ 2001.09.18_I01W_CFC_DQE_WISEGARVER included are data file and submission form README file. Data are in need of merging at this time.</p>			
2002-04-01	Gerlach	DEL13	Submitted	
	<p>Date: Mon, 1 Apr 2002 09:51:17 -0800 (PST)  From: WHPO Website &lt;http@odf.ucsd.edu&gt;  To: dgerlach@whoi.edu, jrweir@whpo.ucsd.edu, whpo@ucsd.edu  Subject: WHPO DATA I01W: OTHER from GERLACH  This is information regarding line: I01W  ExpoCode: 316N145/11  Cruise Date: 1995/08/29 - 1995/10/16  From: GERLACH, DANA  Email address: dgerlach@whoi.edu  Institution: WHOI  Country: USA</p> <p>The file: C:\My Documents\C13-project\whpo_indian_march02\whpo_i01w.txt - 8503 bytes has been saved as: 20020401.095117_GERLACH_I01W_whpo_i01w.txt in the directory: 20020401.095117_GERLACH_I01W  The data disposition is: Public  The file format is: Plain Text (ASCII)</p>			

Data Processing Notes

	<p>The archive type is: NONE - Individual File                  The data type(s) is: Other: flagged 13C data                  The file contains these water sample identifiers:                      Cast Number (CASTNO)                      Station Number (STATNO)                      Bottle Number (BTLNBR)</p> <p>GERLACH, DANA would like the following action(s) taken on the data:                      Merge Data                      Place Data Online</p> <p>Any additional notes are:                      Questions or concerns, please contact:                          Dana Gerlach (dgerlach@whoi.edu) or                          Ann McNichol (amcnichol@whoi.edu)</p> <p>Date: Mon, 1 Apr 2002 10:36:36 -0800 (PST)                  From: WHPO Website &lt;http@odf.ucsd.edu&gt;                  To: dgerlach@whoi.edu, jrweir@whpo.ucsd.edu, whpo@ucsd.edu                  Subject: WHPO DATA I01W: DOC/OTHER from GERLACH                  This is information regarding line: I01W                  ExpoCode: 316N145/11                  Cruise Date: 1995/08/29 - 1995/10/16                  From: GERLACH, DANA                  Email address: dgerlach@whoi.edu                  Institution: WHOI                  Country: USA</p> <p>The file: C:\My Documents\C13-project\whpo_indian_march02\i01w_desc.txt - 259 bytes                  has been saved as: 20020401.103636_GERLACH_I01W_i01w_desc.txt                  in the directory: 20020401.103636_GERLACH_I01W                  The data disposition is: Public                  The file format is: Plain Text (ASCII)                  The archive type is: NONE - Individual File                  The data type(s) is: Documentation\n                  flagged 13C replicate data                  The file contains these water sample identifiers:                      Cast Number (CASTNO)                      Station Number (STATNO)                      Bottle Number (BTLNBR)</p> <p>GERLACH, DANA would like the following action(s) taken on the data:                      Other: use as reference</p> <p>Any additional notes are:                      This description file lists the individual flags for the                  replicate values. \n                      It is a detailed listing of those                  stations which have c13f = 6.</p>			
2002-04-10	<table border="1" data-bbox="342 1560 1429 1596"> <tr> <td data-bbox="342 1560 505 1596">Key</td> <td data-bbox="505 1560 773 1596">C14</td> <td data-bbox="773 1560 1429 1596">Submitted</td> </tr> </table> <p>The file: I1.C14 - 87908 bytes has been saved as:                  20020410.072032_KEY_ALL&amp;#x2020;INDIAN&amp;#x2020;OCEAN_I1.C14                  in the directory: 20020410.072032_KEY_ALL&amp;#x2020;INDIAN&amp;#x2020;OCEAN</p> <p>The data disposition is: Public                  The bottle file has the following parameters: STATION, CAST, BOTTLE, DELC14, C14ERR, C14F                  The file format is: Plain Text (ASCII)                  The archive type is: NONE - Individual File                  The data type(s) is: Bottle Data (hyd)</p>	Key	C14	Submitted
Key	C14	Submitted		

## Data Processing Notes

	<p>The file contains these water sample identifiers: Cast Number (CASTNO), Station Number (STATNO), Bottle Number (BTLNBR)</p> <p>KEY, ROBERT would like the following action(s) taken on the data: Merge Data, Place Data Online, Update Parameters</p> <p>Any additional notes are: I've included the C14 from the French occupation of I6S. All files are same format. Tool does not accept mput syntax</p>		
2002-08-14	Anderson	BTL	C13/C14/Data Online
	<p>Merged DELC14 and C14ERR from Key, DELC13 from Gerlach, TCARBN and ALKALI from Kozyr, and CFCs from Wisegarver. Made new exchange file.</p> <p>Merge notes for i01w:</p> <p>Merged the DELC14 and C14ERR from file I1.C14 found in /usr/export/html-public/data/onetime/indian/i01/i01w/original/20020410_KEY_I1_C14 into the online file 20011026WHPOSIOSA.</p> <p>Merged the DELC13 from file 20020401.095117_GERLACH_I01W_whpo_i01w.txt found in /usr/export/html-public/data/onetime/indian/i01/i01w/original/20020401.095117_GERLACH_I01W into the online file.</p> <p>Merged the new TCARBN and ALKAKI from file i1wcarb.dat found in /usr/export/html-public/data/onetime/indian/i01/i01w/original/2000.06.19_I01W_CARB_KOZYR into online file.</p> <p>Merged the new CFC's from file 20010918.165933_WISEGARVER_I01W_i01w_CFC_DQE.dat found in /usr/export/html-public/data/onetime/indian/i01/i01w/original/2001.09.18_I01W_CFC_DQE_WISEGARVER into the online file.</p>		
2002-08-15	Anderson	He/Tr/Neon	Website Updated: Data Online
	<p>Merged the DELHE3, DELHER, HELIUM, HELIER, NEON, NEONER, TRITIUM, and TRITER from Jenkins. Made new exchange file.</p> <p>Merge notes for i01w:</p> <p>Merged the DELHE3, DELHER, HELIUM, HELIER, NEON, NEONER from file wihe.dat found in /usr/export/html-public/data/onetime/indian/i01/i01w/original/2000.10.17_I01w_TRITIUM_HELIUM_JENKINS into online file 20020814WHOPSIOSA.</p> <p>Merged the TRITIUM and TRITER from file witrit.dat found in above directory into online file.</p> <p>This merging had been done earlier by Stacey Anfuso (2001/02/01) according to the res, but the file she merged appears not to have been put online or somehow was replaced with a file that did not have these parameters.</p>		

## Data Processing Notes

2003-04-11	Muus	CTD/C13	Website Updated:	Data merged into BTL file
<p>Merged DELC13 decimal-2-data into bottle file. Merged new CTDPRS, CTDTMP, CTDSAL, CTDOXY, THETA, SALNTY &amp; OXYGEN from WHOI into bottle file. Changed some quality flags per WHOI notes and results of Java Ocean Atlas check. Notes file sent to Jerry with details.</p>				
<p>Notes on I01W merging Apr 11, 2003 D. Muus</p>				
<p>1. Merged DELC13 from:          /usr/export/html-public/data/onetime/indian/i01/i01w/original/          20020401.095117_GERLACH_I01W/20020401.095117_GERLACH_I01W_          whpo_i01w.txt          into current web bottle file (20020815WHPOSIOSA)          to replace 1 decimal place data with 2 decimal place DELC13 data.</p> <p>2. Changed all Helium and Tritium quality flag 1s associated with missing data to 1s.</p> <p>3. Replaced all BTNNBR, CTDSAL &amp; CTDOXY quality flags with new flags received March 24, 2003, from Jane Dunworth, WHOI</p> <p>4. Changed flag 1s for Station 863 to 4s per WHOI message:          From jdunworth@whoi.edu Tue Mar 25 06:21:13 2003 found this is in the cruise summary info. it seems like this cruise had serious problems with calibration and instrumentation issues. you might want to change the ctdsal &amp; ctdoxy flags to 3 (questionable) or 4 (bad) for sta 863.</p>				
<p>STATION 863 Made the internally recording (IR) backup CTD, CTD 1338, the primary data for the station instead of CTD 9. CTD9's oxygen and salinity in the down profile were bad due to noisy pressure requiring heavy interpolation. ICTD 1338 data was used to make the down 2-db file. CTD 9's info was left with the bottle file. There were problems making the bottle file from the IR CTD. Note, there are different up and down calcs!, one for CTD1338, the other for CTD9.</p>				
<p>Following note also found in Documentation: Station 863: CTD9 with ICTD1338 in Memory mode. After Test station for CTD9, CTD 9 opened and found dessicant packs to be caught btw boards, causing components on board to short out. Thought was fixed, but everything dropped out twice during this station. -USE ICTD1338 DATA FOR THIS STATION</p>				
<p>5. Merged CTDPRS, CTDTMP, CTDSAL, CTDOXY, THETA, SALNTY, &amp; OXYGEN from: Jane Dunworth, WHOI, email of March 24, 2004.          email data can be found in:          /usr/export/html-public/data/onetime/indian/i01/i01w/original/          2003.04.08.I01W_C13_CTDPTS_SAL_OXY_MERGE_MUUS/          dunworth.email030324.i01w.btldata</p>				
<p>Prior to merging, ITS-68 CTDTMP and THETA were changed to ITS-90 using ITS-90 = 0.99976(ITS-68) and CTDOXY and OXYGEN changed from ml/l to UMOL/KG using cvuwoce on minerva.ucsd.edu.</p>				
<p>6. Station 863 Sample 36 was deleted because CTDTMP &amp; CTDSAL = 0 at 16 N Latitude surface.          STNNBR 863 CTDPRS 2.4 SALNTY 35.6305 NITRIT 0.63          Remaining parameters -9          CASTNO 1 CTDTMP 0.0029 OXYGEN 201.3 PHSPHT 1.24          SAMPNO 36 CTDSAL 0.0000 SILCAT 7.81 CFC-11 1.864          BTLNBR SIH024 CTDOXY 358.4 NITRAT 14.10 CFC-12 1.055</p>				
<p>7. 2001/01/23 ANFUSO, S. note in Data History.          NUTRIENTS: Data was originally submitted in uM/L units, PI recalculated and resubmitted in uM/kg units. Also, original submission of nitrate data was actually nitrate nitrite. This error has been corrected in current data submission.          Nutrients unchanged this version since only small changes in CTD pressure, salinity</p>				

Data Processing Notes

and temperature for samples with nutrient values.

8. Following CTDSAL and CTDOXY values differ from bottle values. QUALT1 was 2.

Sta/Ca/Smp	CTDPRS	Bottle -	CTD	Changed QUALT2 to:
		Salt	Oxygen	
890/1/1	2195.7db	No Btl S,	No Btl o2	CTDOXY 4
/2	2195.2	No CTD S,	No CTD o2	
	Smp1 - Smp2	ok	51.8 UMOL/KG	
900/1/10	298.9	2.93 PSU	ok	CTDSAL 4
/11	273.4	0.36	ok	CTDSAL 4
/12	248.6	0.24	ok	CTDSAL 4
/13	224.1	0.24	ok	CTDSAL 4
901/1/6	1002.3	1.02	ok	CTDSAL 4
/7	903.2	0.26	ok	CTDSAL 4
/8	808.0	1.08	ok	CTDSAL 4
/11	498.1	1.04	ok	CTDSAL 4
/12	403.9	1.02	ok	CTDSAL 4
/14	253.4	1.48	ok	CTDSAL 4
902/1/4	1799.4	1.25	ok	CTDSAL 4

No changes were made to quality flags of other parameters for these samples but conversions from /liter to /kg are suspect.

9. Made new exchange file for Bottle data.

10. Checked new bottle file with Java Ocean Atlas.

2004-02-13	Anderson	CTD	CTD files updated/WOCE formatted/Online
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Sharon Escher noted that the value in the RECORDS= field was sometimes incorrect. In checking this I discovered that almost every station had ^Z as the last record. A few stations also had a record at the end that just had zeros except for the QUALT1 field, which had values. I deleted these records and corrected the value in the RECORDS= field when necessary.

Station 899 data between 4583.0 and 4653.0db was repeated at the end. I deleted the duplicate levels.

Station 941 had a date of 092295 in the ctd file, and 092395 in the.sum file. I changed the ctd file to agree with the sum file.

Oxygen was in ml/l. I converted to umol/kg.

Station 870 and 871 had negative oxygens that I changed to 0.00 re J. Swift.

	PRESS	OXYGEN
Sta. 870	25.0	-0.407
	27.0	-0.439
	29.0	-0.236
Sta. 871	33.0	-0.260

Changed file names from xxx.CTD to i01wxxxx.wct.

Had to remove COR DEPTH from .sum header in order to get the exchange program to work.

2005-01-10	Key	DELC14	Report Submitted covers 9 Indian Ocean cruises
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The U.S. WOCE Indian Ocean Survey consisted of 9 cruises covering the period December 1,1994 to January 22,1996.All of the cruises used the R/V Knorr operated by the Woods Hole Oceanographic Institute. A total of 1244 hydrographic stations were occupied with radiocarbon sampling on 366 stations.

## Data Processing Notes

2005-02-18	Anderson	HELIUM/NEON	Website Updated:	Data online
	<p>i01e and i01w</p> <p>Found file i1he.txt in ../indian/i01/i01/original/2000.10.04_I1_BOTTLE. This file contains the deep DELHE3, HELIUM, NEON, DELHER, HELIER, and NEONER for i01e and i01w.</p> <p>I merged these parameters into the online files, and made new exchange and netcdf files. There were no Q1 or Q2 flags so I set them to 2.</p>			
2005-05-06	Anderson	CTD	sta 882 O2 changed to $\mu\text{mol/kg}$	
	<p>As noted by Sharon Escher, sta. 882 was missing from the ctd stations. I converted the oxygen to <math>\mu\text{mol/kg}</math> on sta 882, added it to the ctd .zip file, made new exchange and netcdf files and put all files online.</p>			
2005-05-11	Reid	NUTs	Update Needed	various anomalies
	<p>I've finally had a chance to look at the Indian Ocean (I1W) data.</p> <p>We noted in our cruise report that Niskin 7 at Stn 910 was an obvious leaker and that the nutrients were flagged as 4. I'm pretty sure that's the 3793 dbar bottle.</p> <p>I don't know why the nutrients aren't flagged, as my notes say they were.</p> <p>Re the odd deep nutrients at Stn 859: The original at-sea calculation of those nutrients was made incorrectly, using the wrong values for the standard concentrations. They were recalculated post-cruise and look as though they will fit within the envelopes of the property plots from the other Red Sea stations. Again, I don't know why the corrected version wasn't part of the final data set.</p> <p>I will dig out or create a digital version of stn 859 and send it to you, hopefully before the end of the week.</p>			
2005-05-11	Reid	NUTs	Follow-up on previous note	
	<p>I found our Zipped data files and will attach a text file with the data from I1W Stn 859. The nutrient data matches the paper listing of the recalculated version that I found yesterday.</p> <p>Could you let us know if this version agrees with the other Red Sea data? (It looks like it will.) Once I hear from you, I'll send the correct data to the WHPO and others.</p>			
2005-06-13	Anderson	NUTs	WOCE/Exchange/NetCDF files online	
	<p>i01w 316N145_11 Made changes to SILCAT, NITRAT, NITRIT, and PHSPHT on sta. 859 re Joe Jennings. Put corrected file online, made new exchange and netcdf files.</p>			
2008-06-17	Kappa	Cruise Report	Added C14 & CO2 reports & Data Processing Notes	
	<p>Added these WOCE/CCHDO Data Processing Notes</p> <p>Added 4 reports to pdf and text versions of cruise report:</p> <ol style="list-style-type: none"> <li>1) Assessment of the quality of total inorganic carbon measurements</li> <li>2) Assessment of the quality of the shipboard measurements of total alkalinity</li> <li>3) Anthropogenic CO2 Inventory of the Indian Ocean</li> <li>4) U.S. Woce Indian Ocean Survey: Final Report for Radiocarbon</li> </ol>			