

P1C

I. Cruise Narrative

Masao Fukasawa (Tokai University)

P1C cruise was a leg of MR99K05 on the board of Mirai of JAMSTEC, and was planned as part of the collaboration program between SAGE (Sub-Arctic Gyre Experiment: a Japanese ocean science program funded by the Science and Technology Agency) and IOS (Institute of Ocean Sciences, Canada) to re-visit WHP P1 which was previously occupied by United States in 1985. As it has been 15 years since P1 was observed last, any possible climatological change may occur in the water column structure. Thus, P1 revisit cruises were called for.

The original purpose of the cruise was to back-up WHP P1 revisit stations located between 166 deg. W and 143.5 deg. W. But Kaiyo-maru cruise (P1W), which has planned to occupy stations in the west of 160 deg. W, could not occupy planned stations in the south of Hokkaido because of the temporal activity of the salmon fisheries there. As the result, those stations not occupied by Kaiyo-maru were added to this cruise forming our duty to visit sixteen extra stations in the south of Hokkaido and twenty two stations between 166 deg. W and 143.5 deg. W.

We set sail on August 24, 1999 at Sekinehama, Japan. The first station of the cruise was located at 42.81 deg. N, 145.56 deg. E where the CTD+RMS observation began at 08:31 JST on August 25. At the fourth station of P1_#7, we lost whole CTD+RMS system and LADCP system with CTD cable of 4000m long. As the back up CTD+RMS system did not work properly, we made a port at Hachinohe on August 27 for another new ROSETTE system and started the cruise again. However, it was estimated that the preparation of new CTD+RMS system on the board would force us to spend more than 72 hours. Then we gave up our duty off Hokkaido for the most important objective of the cruise, i.e. to occupy stations between Japanese efforts and Canadian efforts. P1_#74 located 47 deg. N, 165.96 deg. W was set ahead.

On the course to P1_#74, 47 XBTS and 47 XCTDs were casted by Hydrographic department of Japan Maritime Safety Agency. We arrived at P1_#74 on September 3 1999 UTC. We occupied seventeen stations before we left the easternmost station of P1_#92 located at 46.99 deg N, 145.80 deg W on September 8. Four SVP drifters were deployed in the center of the Alaskan Gyre and in the Alaskan stream on the way to Dutch Harbor.

The cruise experienced very rare but fatal accidents. But 2/3 of planned stations were

occupied and 1/2 of planned water samplings were carried out.

We heartily hope that our data will be useful for studies on climate changes in the ocean. Raw data including underway observations e.g. the multi-narrow beam and meteorology are kept in DMO of JAMSTEC, however, the ship board ADCP did not work properly.

II. Cruise summary

1. Ship name

Mirai (Japan Marine Science and Technology Center)

2. Cruise period

From 24 August 1999 to 10 September 1999

3. Observation

4 stations of WHP P1 in the south of Hokkaido and 17 stations along WHP P1 from 172 deg. W to 145 deg W

4. Chief Scientist

Masao Fukasawa (Tokai University): fksw@jamstec.go.jp

5. Observation Item and PI

CTD/DO	Masao Fukasawa (Tokai University): fksw@jamstec.go.jp
Bottle Salinity	Hiroyuki Yoritaka (Hydrographic Department Japan Maritime Safety Agency): yoritaka@jodc.go.jp
Bottle Oxygen	Masao Fukasawa (Tokai University): fksw@jamstec.go.jp
Nutrients	Chizuru Saitoh (Japan Marine Science and Technology Center): saitoc@jamstec.go.jp
CFC11,12,133	Yutaka Watanabe (National Institute for Resource and Environment): yywata@ees.hokudai.ac.jp
SF6	Yutaka Watanabe (National Institute for Resource and Environment): yywata@ees.hokudai.ac.jp
DIC, pH, TAlk	Tsuneo Ono (National Research Institute of Fisheries Laboratory): onot@jamstec.go.jp
delta 14C	Robert Key (Princeton University): key@Princeton.EDU Masao Fukasawa (Tokai University): fksw@jamstec.go.jp

delta 13C	Yutaka Watanabe (National Institute for Resource and Environment): yywata@ees.hokudai.ac.jp
Barium,Calcium	Yoshihisa Kato (Tokai University): ykato@scc.u-tokai.ac.jp
Chlorophyll_a	Yoshimi Suzuki (Shizuoka University): ysuzu@shizuoka-u.ac.jp
Total Organic Carbon	Yoshimi Suzuki (Shizuoka University): ysuzu@shizuoka-u.ac.jp
Cu, Ni	Chizuru Saitoh (Japan Marine Science and Technology Center): saitoc@jamstec.go.jp

III. Sample water salinity measurements

(1) Personal

Hiroyuki Yoritaka (Hydrographic Department, Maritime Safety Agency)

Satoshi Ozawa (Marine Works Japan)

Toru Idai (Marine Works Japan)

Hitoshi Yamanobe (Marine Works Japan)

Hiroyuki Nakajima (Tokai University)

Satoko Katsuyama (Tokai University)

Fujio Kobayashi (Marine Works Japan)

(2) Objective

Calibration of salinity measured by CTD.

(3) Measured Parameter

Sample water salinity

(4) Instruments and Method

The salinity analysis was carried out by a Guildline Autosol salinometer model 8400B, which was modified by addition of an Ocean Science International peristaltic-type sample intake pump. Data of salinometer was collected simultaneously by a personal computer. A double conductivity ratio was defined as a median of 15 readings of the salinometer. Data collection was started after 5

seconds and it took about 5 seconds to collect 15 readings by a personal computer.

The salinometer was operated in the air-conditioned ship's laboratory at a bath temperature of 24 degree C. An ambient temperature varied from approximately 23 to 24 degree C.

i) Standard Sea Water

Autosal model 8400B was standardized only before sequence of measurements by use of IAPSO Standard Seawater batch P135 whose conductivity ratio was 0.99992. After the standardization, 8400B was monitored by SSW ampoule before and after the measurements for samples of one station. Total 23 ampoules of SSW were measured for monitoring, whose standard deviation was 0.0004 psu.

ii) Salinity Sample Collection

The bottles in which the salinity samples are collected and stored are 250ml clear glass bottles with inner caps and outer screw caps. Each bottle were rinsed twice and filled with sample water. Salinity samples were stored by the end of leg 1 in the same laboratory as the salinity measurement was made.

iii) Replicate Samples

Replicate samples were drawn from several Niskin bottles for each station. Standard deviation in the measurements of replicate samples was 0.0013 psu for 54 pairs.

iv) Quality Flag

Quality flag was made according to difference from corrected salinity measured with CTD. CTD salinity was corrected by linear fitting with bottle salinity for pressure in the upper layer (<1000db) and the deep layer (>1000db) at each station (see CTD). For the bottle salinity exceeded double standard deviation, bad (4) or doubt (3) flag was made. Rms of residual difference was 0.001 between CTD salinity and good bottle salinity for deeper layer.

IV. Sample water oxygen measurements

(1) Personal

Masao Fukasawa (Tokai University)

Fuyuku Shibata (Marine Works Japan)

Katsunori Sagishima (Marine Works Japan)

(3) Objective

To describe changes in DO transect between 1985 and 1999.

(3) Measured Parameter

Sample water dissolved oxygen

(4) Instruments and Method

(a) Instruments and Apparatus

Dispenser: Eppendorf Comforpette 480/ 1000 μ l.
OPTIFIX/ 2ml
Metrohm Model 725 Multi Dosimat/ 20ml

Titration: Metrohm Model 716 DMS Titrino / 10ml of titration vessel
Pt electrode/ 6.0403.100(NC)

Software: Data acquisition / Metrohm, METRODATA / 606013/000
Endpoint evaluation

(b) Methods

Samples were collected from 12L Niskin bottles and a bucket for the surface into the volumetrically calibrated dry glass bottles. At least two times of bottle volumes of sample water were overflowed before each sampling. Sampling water temperatures for 4 or 5 bottles were measured by a thermister-thermometer to calculate the change in the volume of sampled water at the time of the titration. For other samples of which temperature were not measured, potential temperatures derived from CTD data were used. The sampling bottles consist of ordinary BOD flask (ca. 180ml) and glass stopper with long nipple inside which is modified from the nipple in Green and Carritt (1966). Oxygen in the sample was fixed immediately after the collection. Bottles were kept in a wooden box in the temperature-controlled laboratory until the titration.

The analytical method and the preparation of reagents were carried out in the same way as described in WHP Operations and Methods (Culberson, 1991). A 0.05N thiosulfate of titrant was adopted during the cruise. Volumetric apparatus except titration were calibrated before the cruise. A titration was started about one hour after the fixation of dissolved oxygen. Two sets of Metrohm titrators with the automatic piston burette of

10ml and Pt electrode were used for the titration in the temperature-controlled laboratory. The temperature of samples which had been stored was 21 deg. C +/- 1 deg. C during the cruise. The end point was determined by the potentiometric method and evaluated by the second-derivative curve method. Concentration of dissolved oxygen was computed using the equation in WHP Operation and Methods (Culberson, 1991).

(5) Results

We carried out 366 analyses of DO. Results are shown in .sea file.

(a) Thiosulfate Standardization

Thiosulfate reagent was standardized when thiosulfate bottles of titration were empty. Two kinds of 0.0100N KIO₃ standard solutions were used for the standardization e.g. Lot 990420b(0.01003N) and Lot 990421(0.01002N). The averaged volumes of thiosulfate for the standardization were 1.969ml (titration #1) and 1.973ml (titration #2), with standard deviation of 0.007ml and 0.001ml, respectively.

(b) Pure water blank

The blank value comes from the presence of redox species apart from oxygen in the reagents, which behaves equivalently to oxygen to be analysed. The pure water blank or the titration blank was determined using deionized water (Milli-Q SP, Millipore) at each thiosulfate standardization. The average of pure water blanks was -0.015ml (#1) and -0.015ml (#2) with standard deviation of 0.003ml and 0.004ml, respectively.

(c) Reproducibility

In the cruise, replicate samples were drawn from some Niskin bottles at each station to estimate the precision of the analysis. 85 pair of replicate samples are analyzed to show the standard deviation (2 sigma) of 0.016ml/l or 0.2% of maximum value of DO concentration of 7.843ml/l in the cruise.

V. Carbonate species and Chemical transient tracers

(1) Personnel

Yutaka Watanabe (National Institute of Resource and Environment)
Tsuneo Ono (National Research Institute of Fishery Laboratory)
Yoshiyuki Nakano (Hokkaido University)

Masahide Wakita (Hokkaido University)

(2) Objectives

Total dissolved inorganic carbon (DIC), titration Alkalinity (TA) and pH are the main parameters of oceanic carbon cycle, which owes significant importance recently for understanding of the fate of human-released CO₂. On the other hand, CFC11, CFC12, CFC113 and SF₆ as chemical transient tracers are very useful to clarify the water movement and/or the fate of human-released CO₂. If we observed the above parameters simultaneously, it will allow us to get more information about oceanic carbon cycle.

Thus observing them together, and comparing the 1985 WOCE/WHP P01 data with our data, we tried to get the time change of carbonate species and water movement in the North Pacific subpolar region.

(3) Sampling and Methods

(a) DIC

Method: Extraction/Coulometry (Ono et al., 1998)

Analyzer: UIC CM5012 coulometer & KIMOTO EN-501 auto-coulometer

Standard: Primary standard grade Na₂CO₃ (Asahi grass Co.)

Precision: +/- 2.7 μmol/kg

Sub-samples were drawn into a 150 ml grass salinity bottle and closed after 5 seconds of overflow. Duplicate samples were taken on every station. All samples were stored under room temperature and analyzed within 12 hours after the sampling followed by a coulometric method (Ono et al., 1998). In some stations, measurement was also done by the automatic DIC measurement system by coulometry (KIMOTO EN-501, KIMOTO Electronic CO.).

Two solutions of standard grade sodium carbonate were used as the primary standard. Two concentrations of the seawater standards containing a constant amount of DIC were made in laboratory as working standard in the cruise. The DIC content of this working standard was determined on board using the primary standard sodium carbonate solutions. The Certified Reference materials distributed by Scripps Institution of Oceanography was measured together with the measurement at several stations.

(b) TA

Method: Modified one-point method (Culberson et al., 1970)

Analyzer: Manual measurement

Standard: Primary standard grade Na₂CO₃ (Asahi grass Co.)

Precision: +/- 3.5 μmol/kg

Sub-samples were drawn into a 120 ml vial grass bottle. Duplicate samples were taken on every station. All samples were stored under room temperature and analyzed within 12 hours after the sampling followed by the modified one-point titration method of Culberson et al. (1970).

2l of 0.6N HCl solution was prepared and normality was calibrated against the primary standard sodium carbonate solutions. Calibration of pH probe was made by Tris and 2-Aminopyridine Buffers (Dickson, 1993). To correct the drift of glass electrode during the measurement of pH after titration, we measure the pH of acidified seawater which pH was controlled at 3.38 by adding HCl at interval of every 10 samples.

(c) pH

Method: Continuous-flow Spectrophotometric pH measurements (Clayton et al., 1993)

(The pH indicator is m-cresol purple)

Analyzer: Spectrophotometer: Spectro multi channel photo detector MCPD-2000 (Otsuka ELECTRONICS CO., LTD)

Standard: 2-amino-2-hydroxymethyl-1, 3-propanediol (tris) buffer in synthetic seawater, 2-aminopyridine buffer in synthetic seawater (Dickson, Goyet, DOE, 1994)

Precision: +/- 0.002pH

Sub-samples were drawn into a 120 ml grass bottle. Duplicate samples were taken from surface water on every station. All samples were stored under room temperature and analyzed within 12 hours after the sampling followed by the modified Continuous-flow Spectrophotometric pH measurements (Clayton et al., 1993)

(d) CFC11, CFC12 & CFC113

Method: Purged and trapped ECD-GC method (Bullister and Weiss, 1988)

Analyzer: ECD-GC (Hitachi 263-30E)

Standard: Inter-calibrated gaseous bomb

Precision: +/- 0.01 pmole/kg

Sub-samples were drawn into a 120 ml glass syringe. Duplicate samples were taken on every station. We used 30 ml as a sample. All samples were stored within 12 hours after the sampling followed by the modified purged and trapped ECD-GC method (Bullister and Weiss, 1988). We measured water sample of 30 ml. All data were normalized to SIO '93 scale.

(e) SF₆

Method: Purged and trapped ECD-GC method (Law et al., 1994)

Analyzer: ECD-GC (Hitachi 5000A)

Standard: Inter-calibrated gaseous bomb

Precision: +/- 0.03 fmole/kg

Sub-samples were drawn into a 1200 ml glass bottle. We used 500 ml as a sample. All samples were stored within 12 hours after the sampling followed by the modified purged and trapped ECD-GC method (Law et al., 1994).

(4) Preliminary results

Measurements of DIC, TA, pH, CFC11, CFC12, CFC113 and SF₆ were made with the above precision. This was the first result of the east-west cross section where precise carbonate species and chemical transient tracers were simultaneously observed in the North Pacific subpolar region. We will try to get these detailed spatial distributions with the results of SAGE-P1 revisit first leg by R/V Kaiyo-maru of Japan Fisheries Agency during May-June 1999. We also will do the time change of carbonate species and water movement by comparing the 1985 WOCE/WHP P01 data with our data in the future.

VI. Carbon Isotope Ratios in dissolved inorganic carbon ($\Delta^{14}\text{C}$)

(1) Personnel

Masao Fukasawa (Tokai University): sample collection

Robert Key (Princeton University): sample analysis

(2) Sample collection

Sampling stations of ^{14}C are planned to be every five degrees except the western boundary area. Samples were collected from depth using 12 liter Niskin bottles. Sampling glass bottles of c.a. 500ml were baked at 450 degree C for two hours after dipped into 1 N of HCl solution. After

baking, each bottle was capped with an aluminum foil until the sampling on the ship board. The seawater sample was siphoned into the glass bottle with enough seawater to fill the glass.

Immediately after the collection, about 10 ml of seawater was removed from the bottle and poisoned by 1 ml of saturated HgCl₂ solution. The bottle was put a screwed plastic cap on and sealed with butyl tape. Then the bottle was put in a wooden container.

143 samples were collected from 7 stations.

(3) Sample measurement

All samples were sent to Dr. Robert Key of Princeton University to be analyzed.

VII. CTD measurement

(1) Personnel

Masao Fukasawa (Tokai University)

Satoshi Ozawa (Marine Works Japan)

(2) Apparatus

Body and Circuit: Sea-Bird CTD9 plus

Sensors

Temperature sensor (Primary): 2445

Conductivity sensor: 041723,041723

Pressure sensor: Digiquartz 410k-105 s/n 59985

(3) Sensor calibration

(3)-1 Temperature sensor

(3)-1-1 Primary sensor

Temperature sensor was calibrated before and after the cruise on 16 Apr. 99 and on 22 Sep. 99 at Sea-Bird Electronics and Marine Works Japan, respectively. Post-cruise residuals defined as differences between the bath temperature and the instrument temperature were checked at eleven temperature points of -1.4068, 1.0382, 4.5401, 8.1934, 11.6512, 15.1937, 18.6689, 22.1613, 25.6567, 29.1251 and 32.6239 ITS-90 degree C.

The largest sensor drift during the period from the pre-cruise calibration to the post-cruise calibration was found to be +0.00009 deg C at 8.1934 deg C. On the other hand, the absolute

temperature difference between the bath and the instrument temperature was found to be largest as 0.00035 deg C also at +8.1934 deg C using coefficients decided at the time of pre-cruise. As the result the drift of the temperature sensor was found to be +0.00021 of average with 0.00010 of standard deviation.

Consequently, if we define the accuracy of the sensor as the sum of the drift and the absolute temperature difference at eleven bath temperature, the result can be expressed as follows;

bath temp (degC)	ambiguity (degC)
-1.4068	0.0001
1.0382	0.0003
4.5401	0.0004
8.1934	0.0004
11.6512	0.0004
15.1937	0.0000
18.6689	0.0001
22.1613	0.0000
25.6567	0.0000
29.1251	0.0000
32.6239	0.0000

(3)-2 Conductivity sensors

Sensor 041723 was used during PIW five months ago. It was not calibrated specially for this cruise.

(3)-3 Pressure sensor

Pressure sensor was calibrated in Aug. 98, one year before the cruise and on Jun. 00, a half a year after the cruise at Marine Works Japan using the Bunden Burge weight tester. Calibration was carried out on six pressure values from 14 psia to 10000 psia for both case of the calibration. Any apparent hysteresis were found. Coefficients were decided by linearly for pre- and post calibrations. Using the same coefficients, the slope value and intersect value were found to be shifted to 1.00010 and +1.54 psi or +1.0646 db.

The linearity of calibration line was so good that the largest offset of -0.12 db was found at

around 2500 psi.

(3)-4 DO sensor

DO sensor was not used.

(4) Data calibration

(4)-1 Temperature

Residual which was detected at post-cruise sensor calibration at 14 temperature points were so large and it is impossible to know the history of the time drift. So, we gave up to add any artificial values to out put from CTD.

(4)-2 Salinity

Bottle salinity values of which flags were 2 were used for the salinity calibration. Differences between CTD salinity and bottle salinity were minimized using the least square method against the pressure. Linear calibration equations were estimated for depths shallower than 1000 db and deeper than 1000 db, respectively. The calibration equation for deeper data was estimated first. The calibration value at 1000 db was calculated and used as a fix point for the calibration for shallower data. As the result, two calibration equations which were connected to each other at 1000 db were decided for every station. CTD salinity was re-produced using these equations. Standard deviation from the bottle salinity at each station is as follows;

stn	PSS78	PSS78
	SD(0-1000)	SD(1000-bottom)
74	2.7458379e-003	8.6143565e-004
X15	3.1117788e-003	6.7851397e-004
77	2.4775832e-003	1.1432165e-003
78	1.3604482e-003	4.2864640e-004
79	1.0595436e-003	5.3101096e-004
80	1.2087674e-003	9.6035486e-004
81	6.4672157e-004	4.4532393e-004
82	2.0460944e-003	3.9105123e-004
83	1.2817455e-003	9.2143370e-004
84	8.6565011e-004	3.6727151e-004
85	1.8649106e-003	5.5852840e-004

X16	1.7737935e-003	5.6941223e-004
88	1.6532946e-003	4.8886168e-004
89	1.2022222e-003	4.1798853e-004
90	1.5892371e-003	7.6844965e-004
91	5.7392606e-003	1.2130803e-003
92	1.6755848e-003	8.5333845e-004

As for the traceability of SSW P-135 was -15/10000 psu to Mantyla's value. Aoyama et al. (2002) also reported -16/10000, -14/10000, -14/10000 for P135. It must be noted that data calibration did not include the traceability.

(4)-3 Pressure

CTD outputs were re-produced using coefficients noted above.