3 HYDROGRAPHIC MEASUREMENT TECHNIQUES AND CALIBRATIONS

3.1 Salinity

Personnel

Hiroshi Uchida (JAMSTEC): Principal Investigator
Naoko Takahashi (MWJ): Operation Reader

Objectives

Salinity Measurement of Sampled Water

Measured Parameters

Sample water salinity

Instrument and Method

The salinity analysis was carried out on R/V Mirai during the cruise of MR03-K02 by the Guildline Autosal Salinometer model 8400B (Guildline Instruments Ltd., CANADA), S/N 62827, modified with addition of a peristaltic-type intake pump (Ocean Scientific International Inc., UK). The Autosal was operated in the air-conditioned Autosal room and its bath temperature was held at 24 degrees C. An ambient temperature varied from approximately 21 to 26 degrees C. An AC power supply, PCR-1000L (Kikusui Electronics Co., JAPAN), was used for the Autosal in order to remove voltage fluctuations and irregularities in power lines.

The Autosal was standardized with the use of IAPSO Standard Seawater (Ocean Scientific International Inc., UK) before a series of measurements. The Standard Seawater was provided by 200 ml sealed glass bottles. The batch number, conductivity ratio and salinity of the Standard Seawater used in this cruise were P141, 0.99993 and 34.997, respectively. In this cruise, totally 440 samples (see Table 3.1.1) were divided to fore series of measurements. The measurement of the Standard Seawater was carried out approximately every 20 samples in order to check stability of the Autosal. Totally 36 shot bottles of the Standard Seawater were measured. The standard deviation of the salinity was 0.0002 except for two bad measurements. Drift of the Autosal was not corrected because the drift in each series of measurements was sufficiently small from 0 to 0.00001 in double conductivity ratio (2K). Sub-standard seawater was also measured every 10 samples in order to monitor the drift of the Autosal. The sub-standard seawater was deep-sea water filtered by Millipore filter (pore size of 0.45 micro m) and stored in a 20 liters container made from polyethylene.

Seawater samples were collected using 12 liter Niskin-X bottles (no Teflon coating) with O-rings. Salinity sample bottle was a 250 ml brown grass bottle with screw cap. Each salinity sample bottle was rinsed three times with the sample water, and was filled with it to the shoulder of the salinity sample bottle. Its cap was also thoroughly rinsed. The salinity sample bottles were stored longer than 24 hours in the Autosal room before the salinity measurements.

A double conductivity ratio (2K) of the salinity sample was determined as follows. Conductivity cell of the Autosal was flushed 5 times with the sampled water before the double conductivity ratio measurements. The double conductivity ratio was collected after 5 seconds from reading and stored 31 times reading during about 10 seconds automatically by a personal computer. The double conductivity ratio for the measurement was defined as median of 31 times reading. When the standard deviation of the 31 reading was greater than 0.00015, the measurement was ignored and performed again. The measurement of the double conductivity ratio was performed repeatedly at the maximum 5 times. When two measurements among the repeated measurements
agreed within ±0.00001, the measurements for the salinity sample was finished and the double conductivity ratio of the salinity sample was determined as average of the two repeated measurements. When two measurements did not agreed within the criterion among the repeated 5 measurements, maximum and minimum values were ignored and the double conductivity ratio of the salinity sample was determined as average of the rest of the 3 measurements with quality “bad” flag.

TABLE 3.1.1: NUMBER OF SAMPLES.

<table>
<thead>
<tr>
<th>Variety of Samples</th>
<th>Number of Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Samples for CTD</td>
<td>427</td>
</tr>
<tr>
<td>Samples for EPCS</td>
<td>9</td>
</tr>
<tr>
<td>Reference Material for DIC</td>
<td>4</td>
</tr>
<tr>
<td>Total</td>
<td>440</td>
</tr>
</tbody>
</table>

Result

Figure 3.1.1 shows the history of the measured double conductivity of SSW. During the measurement from the station TR1 to WC2, we measured 12 bottles of P141 and the average of the double conductivity ratio was 1.99986 and the root-mean-square was 0.000010, which is equivalent to 0.0002 in salinity. During the measurement from the station WC1 to TC2, we measured 3 bottles of P141 after standardization of the Autosal and the average of the double conductivity ratio was 1.999986.

FIGURE 3.1.1: HISTORY OF THE MEASURED DOUBLE CONDUCTIVITY RATIO OF SSW.
48 pairs of replicate were collected except for bad and questionable measurements. 2 pairs were collected at 2000 m, 1 pair was collected at 1000 m, and other pairs were collected at deeper than 3500 m. Figure 3.1.2 shows the histogram of all the absolute difference between replicate samples. The average and the standard deviation of the absolute differences are 0.0003 and 0.0003, respectively in Practical Salinity Unit. Note that the standard deviation of the absolute difference between replicate samples is calculated as follows.

\[
\text{Standard deviation} = \sqrt{\frac{\text{SUM} \ (\text{difference between replicates})^2}{2N}}
\]

where N is number of replicates.

FIGURE 3.1.2: HISTOGRAM OF THE DIFFERENCE BETWEEN REPLICATE SAMPLES.

Data Archive
All data will be submitted to JAMSTEC Data Management Office (DMO) and will be under its control.
3.2 Oxygen

Personnel
Takayoshi SEIKE (Marine Works Japan Ltd.: MWJ)
Tomoko MIYASHITA (MWJ)
Hiroshi UCHIDA (JAMSTEC): Principal Investigator

Objectives
Determination of dissolved oxygen in seawater by Winkler titration.

Instruments
Burette: APB-510 manufactured by Kyoto Electronic Co. Ltd. / 10 ml of titration vessel
Detector and Software: Automatic photometric titrator manufactured by Kimoto Electronic Co. Ltd.

Methods
This procedure is based on the WHP Operations and Methods (Dickson, 1996).

36 seawater samplers were collected with Niskin bottle attached CTD-system. Seawater was transferred from
Niskin sampler bottle to a calibrated clear glass bottles (ca. 100 ml) before much other water has been removed
from it. Glass bottle was rinsed with three times seawater of bottle volume. Temperature was measured by
digital thermometer during overflowing the sample bottle. Two reagent solutions (Reagent I, II) were added
immediately each 0.5 ml after the sample is drawn. The stopper was then inserted carefully into the sample
bottle. The sample bottle was then shaken vigorously to mix the contents thoroughly and to disperse the
precipitate finely throughout. After the precipitate has settled at least half-way down the bottle (about 30 min),
shake the bottle vigorously to disperse the precipitate. Sample bottles containing pickled samples should be
stored in a cool, dark, location until they were titrated.

After precipitation remove the sample bottle stopper. Sulfuric acid solution was added 1 ml. A magnetic
stirrer bar was added to the solution and began stirring. Samples were titrated by sodium thiosulfate. This
normality was determined by potassium iodate solution on new reagents were made up. Temperature of sodium
thiosulfate during titration was recorded by digital thermometer.

Reagents:
Reagent I: Manganous chloride solution (3M)
Reagent II: Sodium hydroxide (8M) / sodium iodide solution (4M)
Sulfuric acid solution (5M)
Sodium thiosulfate (0.025M)
Potassium iodate (0.001667M)

Results
1) Reproducibility of Winkler Titration Data
Replicate samples were taken on every cast; usually these were more than 10% of samples in each cast during
this cruise. 63 pairs of replicate were collected except for bad and questionable measurements. Figure 3.2.1
shows the histogram of all the absolute difference between replicate samples. The average and the standard
deviation of the absolute differences are 0.13 and 0.13 μmol/kg, respectively. Note that the standard deviation
of the absolute difference between replicate samples is calculated the same as Section 3.1.
FIGURE 3.2.1: HISTOGRAM OF THE DIFFERENCE BETWEEN REPLICATE SAMPLES.

2) Vertical Section
Vertical section (16.5N to 12.75N) of dissolved oxygen in μmol/kg is shown in Fig. 3.2.1.

FIGURE 3.2.1: VERTICAL SECTION OF DISSOLVED OXYGEN.

Data Archive
All data will be submitted to JAMSTEC Data Management Office (DMO) and will be under its control.

References
### 3.3 Nutrients

Kenichiro SATO (Marine Works Japan Ltd.: MWJ)
Shinichiro YOKOGAWA (MWJ)
Yuki OTSUBO (MWJ)
Akihiko MURATA (JAMSTEC): Principal Investigator

#### Objectives

The vertical and horizontal distributions of the nutrients are one of the most important factors on the primary production. During this cruise nutrient measurements will give us the important information on the mechanism of the primary production or seawater circulation.

#### Instruments and Methods

Nutrient analysis was performed on two BRAN+LUEBBE TRAACS 800 systems that have 4-channel analyzing systems for nitrate, nitrite, silicate and phosphate. The systems of analysis were improved which proposed for nutrients of seawater by BRAN+LUEBBE. The new systems are shown from Fig. 3.3.1 to Fig. 3.3.4.

The laboratory temperature was maintained between 19 - 24 deg C.

#### a) Measured Parameters

Nitrite:

Nitrite was determined by diazotizing with sulfanilamide and coupling with N-1-naphthyl-ethylenediamine (NED) to form a colored azo dye that was measured absorbance of 550 nm using 5 cm length cell.

Nitrate:

Nitrate in seawater is reduced to nitrite by reduction tube (Cd - Cu tube), and the nitrite determined by the method described above, but the flow cell used in nitrate analysis was 3 cm length cell. Nitrite initially present in the sample is corrected.

Silicate:

The standard AAII molybdate-ascorbic acid method was used. The silicomolybdate produced is measured absorbance of 630 nm using a 3 cm length cell.

Phosphate:

The method by Murphy and Riley (1962) was used with separate additions of ascorbic acid and mixed molybdate-sulfuric acid-tartrate. The phospho-molybdate produced is measured absorbance of 880 nm using a 5 cm length cell.

Nutrients reported in micromoles per kilogram were converted from micromoles per liter by dividing by density calculated at sample temperature.

#### b) Nutrients Standard

Silicate standard solution, the silicate primary standard, is obtained from Kanto Chemical CO., Inc. This standard solution is 1000 mg per litter with 0.5 M KOH and prepared for ICP analysis. Primary standard for nitrate (KNO₃), nitrite (NaNO₂) and phosphate (KH₂PO₄) obtained from Wako Pure Chemical Industries, Ltd.

#### c) Sampling Procedures

Samples were drawn into 10 ml acrylic screw-capped tubes that were rinsed three times before filling. Each sample was analyzed two times as soon as possible. Sets of 5 different concentrations of shipboard standards were analyzed at beginning, halfway and end of each group of analysis.
d) Low Nutrients Sea Water (LNSW)
Twelve containers (20 L) of low nutrients seawater were collected in February 2003 at equatorial Pacific and filtered with 0.45 μm pore size membrane filter (Millipore HA). They are used as preparing the working standard solution.

Results
Nutrient analysis of the 9 stations from the carousel was performed. Duplicate samples were collected from all bottles of each casting. Coefficient of variation (CV) of nitrate, nitrite, silicic acid, and phosphate analysis at each station were less than 0.39 % (33.16 μmol/kg), 4.53 % (0.91 μmol/kg), 0.23 % (126.27 μmol/kg) and 0.36 % (2.27 μmol/kg), respectively.

The vertical sections of nutrients along with CTD observations line are shown in Fig. 3.3.5.

Nutrient comparability
To establish comparability of nutrient analyses between other cruises, the RMNS [Aoyama et al., submitted] were measured during cruises MR03-K02, KH04-4 leg 2, and MR05-05. The RMNS lots T, AN, AK, AM, O, and AH were measured during the cruise in MR03-K02 and lots AS, AT, and AU were measured during the cruise in KH04-4 leg 2. All of these lots were measured immediately before the cruise in MR05-05. Averages of nutrient (nitrate, nitrite, silicate, and phosphate) measurements for each lot from MR03-K02 and KH04-4 leg 2 agree well with those from MR05-05 except for silicate measurements in this cruise (MR03-K02). A correction factor for silicate measurements from MR03-K02 was estimated to be 1.0121 based on a linear regression of the data (Fig. 3.3.6). This systematic difference between silicate measurements in MR03-K02 and MR05-05 was probably due to a lack of accuracy in the atomic absorption spectrometry silicon standard solution (1000 mg l⁻¹, lot 402F9041; Kanto Chemical Co., Tokyo, Japan) used for the silicate standards in MR03-K02.

Data Archive
All data will be submitted to JAMSTEC Data Management Office (DMO) and will be under its control.
FIGURE 3.3.1: 1CH. (NO$_3$+NO$_2$) FLOW DIAGRAM.

FIGURE 3.3.2: 2CH. (NO$_2$) FLOW DIAGRAM.
FIGURE 3.3.3: 3CH. (SiO₂) FLOW DIAGRAM.

FIGURE 3.3.4: 4CH. (PO₄) FLOW DIAGRAM.
FIGURE 3.3.5: VERTICAL SECTIONS OF NUTRIENTS ALONG WITH CTD OBSERVATIONS LINE.

3.4 Total CO$_2$ (TCO$_2$)

Personnel

Akihiko MURATA (JAMSTEC): Principal Investigator
Minoru KAMATA (MWJ)
Taeko OHAMA (MWJ)

Objective

Global warming due to an increase of CO$_2$ in the atmosphere is now regarded as a social problem. Therefore understanding of CO$_2$ cycling is an urgent task. Because the ocean plays a major role in absorbing atmospheric CO$_2$, accurate estimation of CO$_2$ absorption by the ocean is highly important. Total CO$_2$ (TCO$_2$) indicates sum of inorganic carbon species dissolved in seawater. Therefore we can understand how much CO$_2$ has been absorbed and accumulated in the ocean’s interior by measuring TCO$_2$ in the ocean.

The present investigation was carried out to estimate accumulation of CO$_2$ in the ocean’s interior of the western North Pacific subtropical gyre.

Measured Parameters

Total CO$_2$ (TCO$_2$)

Method

Seawater samples were collected by 12L Niskin bottles at 9 stations. Seawater was sampled in a 300 ml glass bottle, which was previously soaked in 5% non-phosphoric acid detergent (pH = 13) solution for 3 hours at least and was cleaned by fresh water and Milli-Q deionized water 3 times each. The glass bottle was filled smoothly from the bottom with a drawing tube connected to the Niskin drain. Seawater was overflowed for 20 seconds with care so as not to leave any bubbles in the bottle. Prior to the analysis, 3ml of the sample (1 % of the bottle volume) was removed from the glass bottle in order to make a headspace. The samples were then poisoned with 100 μl of saturated solution of mercury chloride within 1 hour from sampling time. After poisoning, the samples were sealed using grease (Apiezon M grease) and a stopper-clip. The samples were stored in a refrigerator at approximately 5 °C until analysis.

Table 3.4.1 illustrates station name and the position where discrete samples were collected.

Two analyzers systems for TCO$_2$ measurement were mounted on board the ship. Both the systems have a PC control sampling system and a Model 5012 coulometer (Carbon Dioxide Coulometer, UIC Inc.). Concentrations of TCO$_2$ were measured as follows.

CO$_2$ standard gas (1.8 % CO$_2$ in N$_2$), 10 % phosphoric acid solution and 6 seawater samples were sequentially measured. The CO$_2$ standard gas was measured to confirm the constancy of the calibration factor during a run, and the phosphoric acid was measured for acid blank correction. From a sampling bottle, approximately 27 ml of seawater was taken in a pipette and was mixed with 2 ml of 10% phosphoric acid in a chamber. The mixing solution was stripped of CO$_2$ by bubbling N$_2$ gas for 10 minutes at a flow rate of 140 ml / min. The stripped CO$_2$ was absorbed into Cathode solution (UIC, Inc). The amount of CO$_2$ was determined by titrating coulometrically the hydroxyethelcarbamic acid that is formed in the mixing solution.
Calibrations of the two systems were made by Certified Reference Material (CRM batch #60; provided by Dr. A.G. Dickson, Scripps Institution of Oceanography), which were conducted at times of renewal of coulometer solutions. We also measured reference materials (RM), which were prepared by JAMSTEC (batch Q09 and BGL2) and by KANSO (batch G) to monitor response of coulometer solutions.

**Preliminary Results**
During the cruise, 6 CRMs and 22 RMs were analyzed. The standard deviations of absolute differences of duplicate measurements of CRMs and RMs were 0.5 and 1.0 μmol/kg, respectively.

A duplicate seawater analysis was made on every 9th seawater sample. The average of the differences was 1.5 μmol/kg (n=37). The standard deviation was 1.4 μmol/kg.

**Data Archive**
All data will be submitted to JAMSTEC Data Management Office (DMO) and will be under its control.

**TABLE 3.4.1: INVENTORY OF THE WATER COLUMN SAMPLES.**

<table>
<thead>
<tr>
<th>Station</th>
<th>Lat.</th>
<th>Lon.</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC9</td>
<td>16-25.0’N</td>
<td>171-35.0’E</td>
</tr>
<tr>
<td>WC8</td>
<td>15-57.5’N</td>
<td>171-25.0’E</td>
</tr>
<tr>
<td>WC7</td>
<td>15-30.0’N</td>
<td>171-15.0’E</td>
</tr>
<tr>
<td>WC6</td>
<td>15-02.5’N</td>
<td>171-05.0’E</td>
</tr>
<tr>
<td>WC5</td>
<td>14-35.0’N</td>
<td>170-55.0’E</td>
</tr>
<tr>
<td>WC4</td>
<td>14-07.5’N</td>
<td>170-45.0’E</td>
</tr>
<tr>
<td>WC3</td>
<td>13-40.0’N</td>
<td>170-35.0’E</td>
</tr>
<tr>
<td>WC2</td>
<td>13.12.5’N</td>
<td>170-25.0’E</td>
</tr>
<tr>
<td>WC1</td>
<td>12-46.0’N</td>
<td>159-15.0’E</td>
</tr>
</tbody>
</table>
3.5 pH (potentiometric)

Personnel
Akihiko Murata (JAMSTEC): Principal Investigator
Taeko Ohama (MWJ)
Fuyuki Shibata (MWJ)
Minoru Kamata (MWJ)

Objective
Global warming due to an increase of CO₂ in the atmosphere is now regarded as a social problem. Therefore understanding of CO₂ cycling is an urgent task. Because the ocean plays a major role in buffering the increase of atmospheric CO₂, studies of air-sea exchanges of CO₂ are highly important.

Measured Parameters
pH (total scale)

Methods
pH (-log[H⁺]) of seawater was measured potentiometrically in a bottle made of glass.

The e.m.f. of a glass / reference electrode was measured with a pH / Ion meter (Radiometer PHM95). Separate glass (Radiometer PHG201) and reference (Radiometer REF201) electrodes were used. To prevent seawater sample from exchanging CO₂ with atmosphere during pH measurement, the electrodes were inserted to a rubber stopper, which was fit to the mouse of a sample bottle. The sample bottle was kept at 25°C within ±0.1°C in a water bath during the measurement. The temperature during pH measurement was monitored with a temperature sensor (Radiometer T901).

To calibrate the electrodes, the TRIS (pH=8.0893 pH unit at 25°C, Delvalls and Dickson, 1998) and AMP (pH=6.7866 pH unit at 25°C, Dickson and Goyet, 1996) in synthetic seawater (S = 35) were used (pH_T; total scale).

pH_T of seawater sample (pHsamp) is calculated from the expression:

\[ \text{pHsamp} = \text{pHTRIS} + \frac{(E_{\text{TRIS}} - E_{\text{samp}})}{\text{ER}} \]

where ER indicates electrode response, which is calculated as follows:

\[ \text{ER} = \frac{(E_{\text{AMP}} - E_{\text{TRIS}})}{(\text{pH}_{\text{TRIS}} - \text{pH}_{\text{AMP}})} \]

ER value should be equal to the ideal Nernst value as follows:

\[ \text{ER} = \frac{RT \ln(10)}{F} = 59.16 \text{ mV} / \text{pH unit at 25°C} \]
**Preliminary Results**

Figure 3.5.1 shows the vertical distribution of pH from St.WC09 to St.WC01. Absolute differences of duplicate measurements were plotted sequentially to evaluate the precision of the measurements (Fig.3.5.2). The average and repeatability (1 std) were 0.001 and 0.001 pH unit, respectively.

**Data Archive**

All data was submitted to JAMSTEC Data Management Office (DMO) and is currently under its control.

**References**


![Figure 3.5.1: Vertical Distribution of pH from St. WC09 to St. WC01.](image)

**FIGURE 3.5.1: VERTICAL DISTRIBUTION OF PH FROM ST. WC09 TO ST. WC01.**
FIGURE 3.5.2: DIFFERENCES OF DUPLICATE MEASUREMENTS.
3.6 Total Alkalinity

Personnel

Akihiko Murata (JAMSTEC): Principal Investigator
Fuyuki Shibata (MWJ)
Taeko Ohama (MWJ)

Objective

Global warming due to an increase of CO₂ in the atmosphere is now regarded as a social problem. Therefore understanding of CO₂ cycling is an urgent task. Because the ocean plays a major role in absorbing atmospheric CO₂, accurate estimation of CO₂ absorption by the ocean is highly important.

Total alkalinity (TAlk) is defined as the number of moles of hydrogen ion equivalent to the excess of proton acceptors over proton donors in 1 kg of seawater. TAlk is one of the CO₂-system parameters (other parameters are total CO₂, pCO₂ and pH), and is required to measure as accurate as possible to detect changes of anthropogenic CO₂ in the ocean, and to use it as a tracer of oceanic circulation.

In the present survey, TAlk was measured to detect changes of anthropogenic CO₂ in the North Pacific subtropical gyre.

Measured Parameters

Total alkalinity (TAlk)

Methods

1. Seawater sampling

Seawater samples for TAlk measurement were collected by 12L Niskin bottles at 9 stations. Seawater was sampled into 125 ml glass bottles, which was previously soaked in 5% non-phosphoric acid detergent (pH = 13) solution for 3 hours at least and was cleansed by fresh water and Milli-Q deionized water 3 times each. A sampling tube was connected to a drain of Niskin bottles. The glass bottles were filled from the bottom smoothly, and seawater was overflowed for 6 seconds. The glass bottles were sealed with a plastic screw cap, and were stored in a refrigerator at approximately 5 degree C until analysis.

2. Seawater analysis

For TAlk measurement by potentiometry, we used two TAlk measuring systems (TA-1000), which were made by Nihon ANS Ltd, and were hereafter denoted as A and B, respectively. A TAlk measuring system has 6 units: a water circulation-titration device, an auto-sampler, an auto-burette (Metrohm), a pH meter (Thermo Orion), a thermostat bath and a PC. With the systems, first, approximately 42ml of a seawater sample was transferred into a water-jacketed pipette from a glass bottle. After that, the seawater sample was transferred into a titration cell. In the titration cell, samples were titrated with a titrant of 0.05M hydrochloric acid mixed with 0.65M sodium chloride. The whole titration procedure was carried out automatically.

We analyzed samples of WC9, WC8, WC7, WC6, WC4 and WC3 stations with TA1000-A, and WC5, WC2 and WC1 stations with TA1000-B. The acid used for the titration was calibrated by measuring TAlk of 4 different concentrations of Na₂CO₃ (0 to 2500 µmol/L) in 0.7N NaCl solutions. The Gran-plot method was applied to
calculate TAlk.

Results
Four duplicate samples were taken on every station. The absolute differences between the duplicate samples were plotted on a range control chart, separately for TA1000-A and -B (see Figures 3.6.1 and 3.6.2). The averaged differences and the standard deviation of TA1000-A were 2.38 and 2.09 μmol/kg (n=24), respectively. Those for TA1000-B were 3.75 and 3.31 μmol/kg (n=12).

Data Archive
All data will be submitted to JAMSTEC Data Management Office (DMO) and will be under its control.

FIGURE 3.6.1: RANGE CONTROL CHART OF TA-1000-A.

FIGURE 3.6.2: RANGE CONTROL CHART OF TA-1000-B.
3.7 Chlorofluorocarbons

Personnel
Ken’ichi Sasaki (Japan Marine Science and Technology Center): Principal Investigator
Katsunori Sagishima (Marine Works Japan Ltd.)

Objectives
Chlorofluorocarbons (hereafter CFCs) are the artificially formed gas. CFC-11 (CCl3F), CFC-12 (CCl2F2) and other CFCs are very useful chemical tracers to clarify the water movement. We determine CFC-11 and CFC-12 concentrations in seawater on board.

Methods
Dissolved CFCs concentrations in seawater were determined with the electron capture detector - gas chromatograph (ECD-GC) attached the purge and trapping system. This Procedure was based on Bullister and Weiss (1988).

1) Sampling
Seawater samples for CFCs measurement were collected from 12 litter Niskin bottles to N2 purged 300ml glass bottle. Three times bottle/cylinder volumes of seawater sample were overflowed to minimize contamination with atmospheric CFCs.

Air samples for CFCs measurement were collected to 100ml glass cylinder at the navigation deck on R/V “MIRAI”.

2) Analysis
The CFCs analytical system was modified from the original design of Bullister and Weiss (1988). Sample volume was 150ml. The trap used to hold CFCs consists of a length of 1/8 in. o.d. SS tubing packed with 5 cm of Porapak T (80/100 mesh). Trapping and desorbing temperature were -45 deg-C and 130 deg-C, respectively. The trapped gas was transformed to GC system directly. Analytical conditions were bellow (Table 3.7.1).
TABLE 3.7.1: INSTRUMENTS AND ANALYTICAL CONDITIONS.

<table>
<thead>
<tr>
<th>Instruments</th>
<th>GC-14B (Shimazu Ltd.)</th>
<th>ECD-14 (Shimazu Ltd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Chromatograph:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Detector:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pre column:</td>
<td>Pola PLOT – QHT (i.d.: 0.53mm, length: 1m, tick: 6.0µm)</td>
<td></td>
</tr>
<tr>
<td>Main column:</td>
<td>Pola PLOT – QHT (i.d.: 0.53mm, length: 30m, tick: 6.0µm)</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oven:</td>
<td>140 deg-C (constant)</td>
<td></td>
</tr>
<tr>
<td>Detector:</td>
<td>250 deg-C</td>
<td></td>
</tr>
<tr>
<td>Trapping &amp; desorbing:</td>
<td>-45 deg-C &amp; 130 deg-C</td>
<td></td>
</tr>
<tr>
<td>Gas flow</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Column flow:</strong></td>
<td><strong>3.0 ml/min</strong></td>
<td></td>
</tr>
<tr>
<td>Detector Make UP:</td>
<td>14.5 ml/min</td>
<td></td>
</tr>
<tr>
<td>Column Purge:</td>
<td>8.4 ml/min</td>
<td></td>
</tr>
</tbody>
</table>

**Data Archive**
All data will be submitted to JAMSTEC Data Management office (DMO) and under its control.

**Reference**
3.8 Carbon-14 and -13

18 December 2006

(1) Personnel
Yuichiro Kumamoto (IORGC, JAMSTEC)
Fuyuki Shibata (MWJ)

(2) Introduction
MR03-K02 cruise was carried out aboard the R/V MIRAI in the western North Pacific Ocean in May – June of 2003. One of the main purposes of this cruise is investigation of material transports by the abyssal water flowing into the North Pacific through the Wake Island Passage. This is the final report of δ^{13}C and Δ^{14}C measurements of dissolved inorganic carbon (DIC). Our preliminary reports are replaced by this final report.

(3) Sample collection
The sampling stations are summarized in Table 3.8.1. A total of 330 seawater samples, including 11 replicate samples, were collected between surface (about 10 m depth) and near bottom at nine stations using 12-liter X-Niskin bottles. The seawater in the X-Niskin bottle was siphoned into a 250 cm³ glass bottle with enough seawater to fill the glass bottle 2 times. Immediately after sampling, 10 cm³ of seawater was removed from the bottle and poisoned by 50 µl of saturated HgCl₂ solution. Then the bottle was sealed by a glass stopper with Apiezon M grease and stored in a cool and dark space on board.

Table 3.8.1  The sampling locations, date, number of samples, and maximum sampling pressure.

<table>
<thead>
<tr>
<th>Station</th>
<th>Date (UTC)</th>
<th>Latitude (°N)</th>
<th>Longitude (°E)</th>
<th>Number of samples</th>
<th>Number of replicates</th>
<th>Max. sampling pressure (db)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC1</td>
<td>5/30/03</td>
<td>12.771</td>
<td>170.248</td>
<td>35</td>
<td>0</td>
<td>5449</td>
</tr>
<tr>
<td>WC2</td>
<td>5/30/03</td>
<td>13.208</td>
<td>170.417</td>
<td>35</td>
<td>0</td>
<td>5487</td>
</tr>
<tr>
<td>WC3</td>
<td>5/30/03</td>
<td>13.631</td>
<td>170.550</td>
<td>35</td>
<td>0</td>
<td>5601</td>
</tr>
<tr>
<td>WC4</td>
<td>5/29/03</td>
<td>14.127</td>
<td>170.746</td>
<td>36</td>
<td>0</td>
<td>5719</td>
</tr>
<tr>
<td>WC5</td>
<td>5/29/03</td>
<td>14.616</td>
<td>170.861</td>
<td>36</td>
<td>0</td>
<td>5758</td>
</tr>
<tr>
<td>WC6</td>
<td>5/29/03</td>
<td>15.048</td>
<td>171.086</td>
<td>36</td>
<td>0</td>
<td>5767</td>
</tr>
<tr>
<td>WC7</td>
<td>5/28/03</td>
<td>15.516</td>
<td>171.251</td>
<td>36</td>
<td>0</td>
<td>5703</td>
</tr>
<tr>
<td>WC8</td>
<td>5/28/03</td>
<td>15.971</td>
<td>171.413</td>
<td>35</td>
<td>0</td>
<td>5625</td>
</tr>
<tr>
<td>WC9</td>
<td>5/27/03</td>
<td>16.419</td>
<td>171.581</td>
<td>35</td>
<td>11</td>
<td>5562</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td>319</td>
<td>11</td>
<td></td>
</tr>
</tbody>
</table>

(4) Sample preparation
In our laboratory, DIC in the seawater samples were stripped cryogenically and split into three aliquots: Accelerator Mass Spectrometry (AMS) ^14C measurement (about 200 µmol), ^13C measurement (about 100 µmol), and archive (about 200 µmol). Efficiency of the CO₂ stripping from seawater sample was more than 95 % that was calculated from concentration of DIC in the seawater samples. The stripped CO₂ gas for ^14C was then converted to graphite catalytically on iron powder with pure hydrogen gas. Yield of graphite powder from CO₂ gas was estimated to be more than 70 % by weighing of sample graphite powder. Details of these preparation procedures were described by Kumamoto et al. (2000).
(5) Sample measurements

δ^{13}C of the sample CO₂ gas was measured using Finnigan MAT252 mass spectrometer. The δ^{13}C value was calculated by a following equation:

\[
\delta^{13}C (\text{‰}) = (R_{\text{sample}} / R_{\text{standard}} - 1) \times 1000. 
\]

where \( R_{\text{sample}} \) and \( R_{\text{standard}} \) denote \(^{13}\text{C} / ^{12}\text{C} \) ratios of the sample CO₂ gas and the standard CO₂ gas, respectively. The working standard gas was purchased from Oztech Gas Co. with assigned δ^{13}C value of -3.64 ‰ versus VPDB (Lot No. SHO-873C). The gas has been calibrated relative to the appropriate internationally accepted IAEA primary standards. Δ^{14}C in the graphite sample was measured in AMS facilities of Institute of Accelerator Analysis Ltd in Shirakawa (Pelletron 9SDH-2, NEC) and Japan Atomic Energy Agency (3 MV Tandetron, HVEE) in Mutsu, Japan. The Δ^{14}C value was calculated by:

\[
\delta^{14}C (\text{‰}) = (R_{\text{sample}} / R_{\text{standard}} - 1) \times 1000, 
\]

\[
\Delta^{14}C (\text{‰}) = \delta^{14}C - 2 (\delta^{13}C + 25) (1 + \delta^{14}C / 1000),
\]

where \( R_{\text{sample}} \) and \( R_{\text{standard}} \) denote, respectively, \(^{14}\text{C} / ^{12}\text{C} \) ratios of the sample and the international standard, NIST Oxalic Acid SRM4990-C (HOxII). \( R_{\text{standard}} \) was corrected for decay since A.D. 1950 (Stuiver and Polach, 1977; Stuiver, 1983). Equation 3 is normalization for isotopic fractionation. When quality of δ^{13}C data was not "good", Δ^{14}C was calculated by interpolated δ^{13}C value from data at just above and below layers. Finally Δ^{14}C value was corrected for radiocarbon decay between the sampling and the measurement. Individual errors of δ^{13}C were given by standard deviation of repeat measurements. Errors of Δ^{14}C were derived from larger of the standard deviation of repeat measurements and the counting error. Means of the δ^{13}C and Δ^{14}C errors were calculated to be 0.003 ‰ and 3.4 ‰ that probably correspond to "repeatabilities" of our δ^{13}C and Δ^{14}C measurements, respectively. It should be noted that these errors did not include error due to sample preparation.

(6) Replicate measurements

Nine pairs of replicate samples were collected at Station WC9. Results of the replicate samples are shown in Table 3.8.2. The standard deviation of the δ^{13}C and Δ^{14}C replicate analyses in good measurement was calculated to be 0.017 ‰ (n = 8) and 3.3 ‰ (n = 11), respectively. The results of replicate measurements suggested that "repeatabilities" of our δ^{13}C and Δ^{14}C measurements including errors due to the sample preparation were less than 0.02 ‰ and 3.5 ‰, respectively.
Table 3.8.2 Summary of replicate analyses

<table>
<thead>
<tr>
<th>Station</th>
<th>Btl</th>
<th>δ¹³C / ‰</th>
<th>Error</th>
<th>E.W.Mean</th>
<th>Uncertainty</th>
<th>Δ¹⁴C / ‰</th>
<th>Error</th>
<th>E.W.Mean</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC9</td>
<td>12</td>
<td>0.061</td>
<td>0.001</td>
<td>0.061</td>
<td>0.006</td>
<td>-226.7</td>
<td>3.5</td>
<td>-227.7</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.069</td>
<td>0.004</td>
<td></td>
<td></td>
<td>-228.7</td>
<td>3.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WC9</td>
<td>11</td>
<td>0.089</td>
<td>0.001</td>
<td>0.090</td>
<td>0.015</td>
<td>-227.1</td>
<td>3.4</td>
<td>-224.7</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.110</td>
<td>0.005</td>
<td></td>
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<td>-222.1</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>WC9</td>
<td>10</td>
<td>0.151</td>
<td>0.003</td>
<td>0.156</td>
<td>0.005</td>
<td>-222.6</td>
<td>3.4</td>
<td>-221.3</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.158</td>
<td>0.002</td>
<td></td>
<td></td>
<td>-219.9</td>
<td>3.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WC9</td>
<td>9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-219.8</td>
<td>3.5</td>
<td>-223.6</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-227.4</td>
<td>3.5</td>
<td></td>
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</tr>
<tr>
<td>WC9</td>
<td>8</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-212.2</td>
<td>3.5</td>
<td>-214.1</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-215.9</td>
<td>3.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WC9</td>
<td>7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-204.8</td>
<td>3.5</td>
<td>-202.6</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-200.4</td>
<td>3.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WC9</td>
<td>6</td>
<td>0.282</td>
<td>0.004</td>
<td>0.304</td>
<td>0.030</td>
<td>-200.9</td>
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<td>-197.3</td>
<td>5.0</td>
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<td>0.325</td>
<td>0.004</td>
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<td></td>
<td>-193.8</td>
<td>3.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WC9</td>
<td>5</td>
<td>0.346</td>
<td>0.003</td>
<td>0.353</td>
<td>0.018</td>
<td>-198.2</td>
<td>3.5</td>
<td>-195.9</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.371</td>
<td>0.005</td>
<td></td>
<td></td>
<td>-193.5</td>
<td>3.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WC9</td>
<td>4</td>
<td>0.400</td>
<td>0.002</td>
<td>0.400</td>
<td>0.002</td>
<td>-190.9</td>
<td>3.5</td>
<td>-190.5</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.399</td>
<td>0.003</td>
<td></td>
<td></td>
<td>-190.1</td>
<td>3.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WC9</td>
<td>3</td>
<td>0.415</td>
<td>0.004</td>
<td>0.415</td>
<td>0.003</td>
<td>-181.8</td>
<td>3.8</td>
<td>-179.7</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
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<td>0.415</td>
<td>0.004</td>
<td></td>
<td></td>
<td>-177.8</td>
<td>3.6</td>
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<td></td>
</tr>
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<td>WC9</td>
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<td>0.403</td>
<td>0.005</td>
<td>0.434</td>
<td>0.030</td>
<td>-185.7</td>
<td>3.5</td>
<td>-183.3</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.445</td>
<td>0.003</td>
<td></td>
<td></td>
<td>-180.9</td>
<td>3.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. Standard deviation of several time measurements
b. Error weighted mean of the replicate pair
c. Larger of the standard deviation and the error weighted standard deviation of the replicate pair
d. Larger of the standard deviation and the counting error

(7) Quality control flag assignment

Quality flag values were assigned to all δ¹³C and Δ¹⁴C 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). Δ¹⁴C measurements of 142 seawater samples collected at stations WC2, WC4, WC6, and WC8 have not finished yet because of a lack of funding (flag 1). Except those unmeasured samples, measurement flags of 2, 3, 4, and 6 have been assigned (Table 3.8.3). For the choice between 2 (good), 3 (questionable) or 4 (bad), we basically followed a flagging procedure that described by Key et al. (1996) as listed below:

a. On a station-by-station basis, a datum was plotted against pressure. Any points not lying on a generally smooth trend were noted.

b. δ¹³C (Δ¹⁴C) was then plotted against dissolved oxygen (silicate) concentration and deviant points noted. If a datum deviated from both the depth and oxygen (silicate) plots, it was flagged 3.
c. Vertical sections against depth were prepared using the Ocean Data View (Schlitzer, 2006). If a datum was anomalous on the section plots, datum flag was degraded from 2 to 3, or from 3 to 4.

Table 3.8.3 Summary of assigned quality control flags

<table>
<thead>
<tr>
<th>Flag</th>
<th>Definition</th>
<th>Number</th>
<th>$\delta^{13}$C</th>
<th>$\Delta^{14}$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Not reported</td>
<td></td>
<td>0</td>
<td>142</td>
</tr>
<tr>
<td>2</td>
<td>Good</td>
<td></td>
<td>291</td>
<td>163</td>
</tr>
<tr>
<td>3</td>
<td>Questionable</td>
<td></td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>Bad</td>
<td></td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>Replicate</td>
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<td>8</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td></td>
<td>319</td>
<td>319</td>
</tr>
</tbody>
</table>

(8) Data Summary

Figure 3.8.1 shows transects of $\delta^{13}$C and $\Delta^{14}$C. In deep and bottom waters, there are no obvious differences in vertical profiles of $\delta^{13}$C and $\Delta^{14}$C among all the stations. We compared our deep $\delta^{13}$C and $\Delta^{14}$C data with historical ones (Kroopnick, 1985; Key et al., 2004) at stations closed to our observation line and found no systematic shifts between them. In the thermocline, there were some variations in $\delta^{13}$C and $\Delta^{14}$C by stations. In the upper thermocline (500 m depth), $\Delta^{14}$C in northern stations were higher than those in southern stations. At the two southernmost stations, WC1 and WC2, $\delta^{13}$C in the lower thermocline (500 - 1,000 m depth) were relatively high.
Figure 3.8.1 Transects of $\delta^{13}C$ (a) and $\Delta^{14}C$ (b) in dissolved inorganic carbon along the Wake Island Passage in 2003.

References


Kroopnick, P.M., 1985. The distribution of $^{13}C$ of $\Sigma CO_2$ in the world oceans, Deep-Sea Research, 32, 57-84.


3.10 CTD Measurements

Personnel

Hiroshi Uchida (JAMSTEC): Principal Investigator
Satoshi Ozawa (MWJ): Operation Leader
Miki Yoshiike (MWJ)
Tomoyuki Takamori (MWJ)

3.10.1 Winch arrangements

The CTD package was deployed using a 4.5 Ton Traction Winch System (Dynacon, Inc., USA), which was installed on the R/V Mirai in April 2001 and moved its position several meters to stern side in April 2003. The CTD Traction Winch System with the Heave Compensation Systems (Dynacon, Inc., USA) is designed to reduce cable stress resulting from load variation caused by wave or vessel motion. The system is operated passively by providing a nodding boom crane that moves up or down in response to line tension variations. Primary system components include a complete CTD Traction Winch System with up to 10 km of 9.53 mm armored cable rocker and Electro-Hydraulic Power Unit, nodding-boom crane assembly, two hydraulic cylinders and two hydraulic oil/nitrogen accumulators mounted within a single frame assembly. The system also contains related electronic hardware interface and a heave compensation computer control program.

3.10.2 Overview of the equipment

The CTD system, SBE 911plus system (Sea-Bird Electronics, Inc., USA), is a real time data system with the CTD data transmitted from a SBE 9plus underwater unit via a conducting cable to the SBE 11plus deck unit. The SBE 11plus deck unit is a rack-mountable interface which supplies DC power to the underwater unit, decodes the serial data stream, formats the data under microprocessor control, and passes the data to a companion computer. The serial data from the underwater unit is sent to the deck unit in RS-232 NRZ format using a 34,560 Hz carrier-modulated differential-phase-shift-keying (DPSK) telemetry link. The deck unit decodes the serial data and sends them to a personal computer (Hewlett Packard Vectra VL, Intel(r) Celeron(tm), Windows98 2nd edition) to display, at the same time, to storage in a disk file using SBE SEASOFT software.

The SBE 911plus system acquires data from primary, secondary and auxiliary sensors in the form of binary numbers corresponding to the frequency or voltage outputs from those sensors at 24 samples per second. The calculations required to convert from raw data to engineering units of the parameters are performed by the SBE SEASOFT in real-time. The same calculations can be carried out after the observation using data stored in a disk file.

The SBE 911plus system controls the 36-position SBE 32 Carousel Water Sampler. The Carousel accepts 12-litre water sample bottles. Bottles are fired through the RS-232C modem connector on the back of the SBE 11plus deck unit while acquiring real time data. The 12-litre Niskin-X water sample bottle (General Oceanics, Inc., USA) is equipped externally with two stainless steel springs. The external springs are ideal for applications such as the trace metal analysis because the inside of the sampler is free from contaminants from springs.

SBE’s temperature (SBE 3) and conductivity (SBE 4) sensor modules were used with the SBE 9plus underwater unit fixed by a single clamp and “L” bracket to the lower end cap. The conductivity cell entrance is co-planar
with the tip of the temperature sensor’s protective steel sheath. The pressure sensor is mounted in the main housing of the underwater unit and is ported to outside through the oil-filled plastic capillary tube. A compact, modular unit consisting of a centrifugal pump head and a brushless DC ball bearing motor contained in an aluminum underwater housing pump (SBE 5T) flushes water through sensor tubing at a constant rate independent of the CTD’s motion. Motor speed and pumping rate (3,000 rpm) remain nearly constant over the entire input voltage range of 12-18 volts DC. Flow speed of pumped water in standard TC duct is about 2.4 m/s. SBE’s dissolved oxygen sensor (SBE 43) was placed between the conductivity sensor module and the pump. Auxiliary sensors, Deep Ocean Standards Thermometer (SBE 35), altimeter, fluorometer and Transmissometer were also used with the SBE 9plus underwater unit. The SBE 35 position in regard to the SBE 3 is shown in Figure 3.10.1.

It is known that the CTD temperature data is influenced by the motion (pitching and rolling) of the CTD package. In order to reduce the motion of the CTD package, a heavy stainless frame (total weight of the CTD package without sea water in the bottles is about 1,000 kg) was used and an aluminum plate was attached to the frame (see Appendix C).

**Summary of the system used in this cruise:**

**Deck unit:**
- SBE, Inc., SBE 11plus, S/N 0344

**Underwater unit:**
- SBE, Inc., SBE 9plus, S/N 0357 (Pressure sensor: S/N 42423)

**Temperature sensor:**
- SBE, Inc., SBE 3plus, S/N 4188, (primary)
- SBE, Inc., SBE 3plus, S/N 4216, (secondary)

**Conductivity sensor:**
- SBE, Inc., SBE 4-02/0, S/N 1088, (primary)
- SBE, Inc., SBE 4-04/0, S/N 1203, (secondary)

**Oxygen sensor:**
- SBE, Inc., SBE 43, S/N 0390, (primary)
- SBE, Inc., SBE 43, S/N 0391, (secondary)

**Pump:**
- SBE, Inc., SBE 5T, S/N 3575, (primary)
- SBE, Inc., SBE 5T, S/N 3576, (secondary)

**Altimeter:**
- Benthos, Inc., PSA-900D, S/N 1026

**Deep Ocean Standards Thermometer:**
- SBE, Inc., SBE 35, S/N 0022

**Fluorometer:**
- Seapoint Sensors, Inc., S/N 2148

**Transmissometer:**
- WET Labs, Inc., C Star Transmissometer, S/N CST-207RD

**Carousel Water Sampler:**
- SBE, Inc., SBE 32, S/N 0278

**Water sample bottle:**
- General Oceanics, Inc., 12-litre Niskin-X
3.10.3 Pre-cruise calibration

1) Pressure
The Paroscientific series 4000 Digiquartz high pressure transducer (Paroscientific, Inc., USA) uses a quartz crystal resonator whose frequency of oscillation varies with pressure induced stress with 0.01 per million of resolution over the absolute pressure range of 0 to 15,000 psia (0 to 10,332 dbar). Also, a quartz crystal temperature signal is used to compensate for a wide range of temperature changes at the time of an observation. The pressure sensor (MODEL 415K-187) has a nominal accuracy of 0.015 % FS (1.5 dbar), typical stability of 0.0015 % FS/month (0.15 dbar/month) and resolution of 0.001 % FS (0.1 dbar).

Pre-cruise sensor calibrations were performed at SBE, Inc., USA. The following coefficients were used in the SEASOFT:

S/N 42423 May 17, 1994
  c1 = -69582.91
  c2 = -1.619244
  c3 = 2.34327e-02
  d1 = 0.029679
  d2 = 0
Pressure coefficients are first formulated into
\[
c = c_1 + c_2 \times U + c_3 \times U^2 \\
d = d_1 + d_2 \times U \\
t_0 = t_1 + t_2 \times U + t_3 \times U^2 + t_4 \times U^3 + t_5 \times U^4
\]

where \( U \) is temperature in degrees Celsius. The pressure temperature, \( U \), is determined according to
\[
U \text{ (degC)} = M \times (12 \text{ bit pressure temperature compensation word}) - B
\]

The following coefficients were used in SEASOFT:
- \( M = 0.01161 \)
- \( B = -8.32759 \)

(in the underwater unit system configuration sheet dated on May 24, 1994)

Finally, pressure is computed as
\[
P \text{ (psi)} = c \times [1 - (t_0^2 / t^2)] \times \{1 - d \times [1 - (t_0^2 / t^2)]\}
\]

where \( t \) is pressure period (microsec). Since the pressure sensor measures the absolute value, it inherently includes atmospheric pressure (about 14.7 psi). SEASOFT subtracts 14.7 psi from computed pressure above automatically.

Pressure sensor calibrations against a dead-weight piston gauge (Bundenberg Gauge Co. Ltd., UK; Model 480DA, S/N 23906) are performed at JAMSTEC (Yokosuka, Kanagawa, JAPAN) by Marine Works Japan Ltd. (MWJ), usually once in a year in order to monitor sensor time drift and linearity. The pressure sensor drift is known to primarily be an offset drift at all pressures rather than a change of span slope. The pressure sensor hysteresis is typically 0.2 dbar. The following coefficients for the sensor drift correction were also used in SEASOFT:

S/N 42423 April 18, 2003
- slope = 0.9999112
- offset = -0.0295469

The drift-corrected pressure is computed as
\[
\text{Drift-corrected pressure (dbar)} = \text{slope} \times \text{(computed pressure in dbar)} + \text{offset}
\]

Result of the pressure sensor calibration against the dead weight piston gauge is shown in Figure 3.10.2.

2) Temperature (SBE 3)

The temperature sensing element is a glass-coated thermistor bead in a stainless steel tube, providing a pressure-free measurement at depths up to 10,500 (6,800) meters by titanium (aluminum) housing. The sensor output frequency ranges from approximately 5 to 13 kHz corresponding to temperature from –5 to 35 degC. The output frequency is inversely proportional to the square root of the thermistor resistance, which controls the output of a patented Wien Bridge circuit. The thermistor resistance is exponentially related to temperature. The SBE 3F thermometer has a nominal accuracy of 0.001 degC, typical stability of 0.0002 degC/month and resolution of 0.0002 degC at 24 samples per second. The premium temperature sensor, SBE 3plus, is a more rigorously tested and calibrated version of standard temperature sensor (SBE 3F). A sensor is designated as an SBE 3plus only after demonstrating drift of less than 0.001 degC during a six-month screening period. In addition, the time response is carefully measured and verified to be 0.065 ± 0.010 seconds.

Pre-cruise sensor calibrations were performed at SBE, Inc., USA. The following coefficients were used in SEASOFT:

S/N 4188 (primary)  April 05, 2003  (SBE 3plus, aluminum)

\[
g = 4.39869443\times10^{-3}
\]
\[
h = 6.45278631\times10^{-4}
\]
\[
i = 2.2599059\times10^{-5}
\]
\[
j = 1.88773787\times10^{-6}
\]
\[
f_0 = 1000.000
\]

S/N 4216 (secondary)  April 05, 2003  (SBE 3plus, aluminum)

\[
g = 4.35980548\times10^{-3}
\]
\[
h = 6.46149426\times10^{-4}
\]
\[
i = 2.29065636\times10^{-5}
\]
\[
j = 1.95269986\times10^{-6}
\]
\[ f_0 = 1000.000 \]

Temperature (ITS-90) is computed according to

\[
\text{Temperature (ITS-90)} = \frac{1}{g + h \cdot \ln(f_0 / f) + i \cdot \ln^2(f_0 / f) + j \cdot \ln^3(f_0 / f)} - 273.15
\]

where \( f \) is the instrument frequency (kHz).

Time drift of the SBE 3 temperature sensors based on the laboratory calibrations is shown in Figure 3.10.3.

**FIGURE 3.10.3: TIME DRIFT OF SBE 3 TEMPERATURE SENSORS (S/N 4188 AND S/N 4216) BASED ON LABORATORY CALIBRATIONS PERFORMED BY SBE, INC.**

3) Conductivity (SBE 4)

The flow-through conductivity sensing element is a glass tube (cell) with three platinum electrodes to provide in-situ measurements at depths up to 10,500 meters. The impedance between the center and the end electrodes is determined by the cell geometry and the specific conductance of the fluid within the cell. The conductivity cell composes a Wien Bridge circuit with other electric elements of which frequency output is approximately 3 to 12 kHz corresponding to conductivity of the fluid of 0 to 7 S/m. The conductivity cell SBE 4 has a nominal accuracy of 0.0003 S/m, typical stability of 0.0003 S/m/month and resolution of 0.00004 S/m at 24 samples per second.

Pre-cruise sensor calibrations were performed at SBE, Inc., USA. The following coefficients were used in SEASOFT:
Conductivity of a fluid in the cell is expressed as:

$$C \text{ (S/m)} = \frac{g + h \cdot f^2 + i \cdot f^3 + j \cdot f^4}{[10 \cdot (1 + CTcor \cdot t + CPcor \cdot p)]}$$

where \(f\) is the instrument frequency (kHz), \(t\) is the water temperature (degC) and \(p\) is the water pressure (dbar). The value of conductivity at salinity of 35, temperature of 15 degC (IPTS-68) and pressure of 0 dbar is 4.2914 S/m.

### 4) Deep Ocean Standards Thermometer

The Deep Ocean Standards Thermometer (SBE 35) is an accurate, ocean-range temperature sensor that can be standardized against Triple Point of Water and Gallium Melt Point cells and is also capable of measuring temperature in the ocean to depths of 6,800 m. The SBE 35 communicates via a standard RS-232 interface at 300 baud, 8 bits, no parity. The SBE 35 can be used with the SBE 32 Carousel Water Sampler and SBE 911plus CTD system. The SBE 35 makes a temperature measurement each time a bottle fire confirmation is received, and stores the value in EEPROM. Calibration coefficients stored in EEPROM allow the SBE 35 to transmit data in engineering units. Commands can be sent to SBE 35 to provide status display, data acquisition setup, data retrieval, and diagnostic test.

Temperature is determined by applying an AC excitation to reference resistances and an ultrastable aged thermistor with a drift rate of less than 0.001 °C/year. Each of the resulting outputs is digitized by a 20-bit A/D converter. The reference resistor is a hermetically sealed, temperature-controlled VISHAY. The switches are mercury wetted reed relays with a stable contact resistance. AC excitation and ratiometric comparison using a common processing channel removes measurement errors due to parasitic thermocouples, offset voltages, leakage currents, and gain errors. Maximum power dissipated in the thermistor is 0.5 µwatts, and contributes less than 200 µK of overheat error.

The SBE 35 communicates via a standard RS-232 interface at 300 baud, 8 bits, no parity. The SBE 35 can be
used with the SBE 32 Carousel Water Sampler and SBE 911plus CTD system. The SBE 35 makes a
temperature measurement each time a bottle fire confirmation is received, and stores the value in EEPROM.
Calibration coefficients stored in EEPROM allow the SBE 35 to transmit data in engineering units.
Commands can be sent to SBE 35 to provide status display, data acquisition setup, data retrieval, and diagnostic
test using terminal software.

Following the methodology used for standards-grade platinum resistance thermometers (SPRT), the calibration
of the SBE 35 is accomplished in two steps. The first step is to characterize and capture the non-linear
resistance vs temperature response of the sensor. The SBE 35 calibrations are performed at SBE, Inc., in a
low-gradient temperature bath and against ITS-90 certified SPRTs maintained at Sea-Bird’s primary temperature
metrology laboratory. The second step is frequent certification of the sensor by measurements in
thermodynamic fixed-point cells. Triple point of water (TPW) and gallium melt point (GaMP) cells are
appropriate for the SBE 35. The SBE 35 resolves temperature in the fixed-point cells to approximately 25 µK.
Like SPRTs, the slow time drift of the SBE 35 is adjusted by a slope and offset correction to the basic non-linear
calibration equation.

Pre-cruise sensor calibrations were performed at SBE, Inc. in Bellevue, Washington, USA. The following
coefficients were stored in EEPROM:

S/N 0022   October 12, 1999 (1st step: linearization)
            a0 = 4.320725498e-3
            a1 = -1.189839279e-3
            a2 = 1.836299593e-3
            a3 = -1.032916769e-5
            a4 = 2.225491125e-7

Temperature (ITS-90) is computed according to

\[
\text{Temperature (ITS-90)} = \frac{1}{a0 + a1 \cdot \ln(n) + a2 \cdot \ln^2(n) + a3 \cdot \ln^3(n) + a4 \cdot \ln^4(n)} - 273.15
\]

where n is the instrument output. Then the SBE 35 is certified by measurements in thermodynamic fixed-point
cells of the TPW (0.0100 °C) and GaMP (29.7646 °C). Like SPRTs, the slow time drift of the SBE 35 is
adjusted by periodic recertification corrections.

S/N 0022   26 March, 2003 (2nd step: fixed point calibration)
            Slope = 1.000012
            Offset = 0.000052

Temperature (ITS-90) is calibrated according to

\[
\text{Temperature (ITS-90)} = \text{Slope} \times \text{Linearized temperature} + \text{Offset}
\]

The SBE 35 has a time constant of 0.5 seconds. The time required per sample = 1.1 * NCYCLES + 2.7
seconds. The 1.1 seconds is total time per an acquisition cycle. NCYCLES is the number of acquisition
cycles per sample. The 2.7 seconds is required for converting the measured values to temperature and storing
average in EEPROM. RMS temperature noise for an SBE 35 in a Triple Point of Water cell is typically expressed as \( \frac{82}{\sqrt{\text{NCYCLES}}} \) in micro K. In this cruise NCYCLES was set to 4 (acquisition time was 4.4 seconds) and the RMS noise was 0.000041 degrees C.

Time drift of the SBE 35 based on the fixed point calibrations is shown in Figure 3.10.4.

![Figure 3.10.4: Time Drift of SBE 35 (S/N 0022) Based on Laboratory Fixed Point Calibrations (Triple Point of Water, TPW and Gallium Melt Point, GAMP) Performed by SBE, Inc.](image)

5) Oxygen (SBE 43)
The SBE 43 oxygen sensor uses a Clark polarographic element to provide in-situ measurements at depths up to 7,000 meters. Calibration stability is improved by an order of magnitude and pressure hysteresis is largely eliminated in the upper ocean (1000 m) compared with the previous oxygen sensor (SBE 13). Continuous polarization eliminates the wait-time for stabilization after power-up. Signal resolution is increased by on-board temperature compensation. This Sensor is also included in the path of pumped sea water. The oxygen sensor determines the dissolved oxygen concentration by counting the number of oxygen molecules per second (flux) that diffuse through a membrane, where the permeability of the membrane to oxygen is a function of temperature and ambient pressure. Computation of dissolved oxygen in engineering units is done in SEASOFT software. The range for dissolved oxygen is 120 % of surface saturation in all natural waters; nominal accuracy is 2 % of saturation; typical stability is 2 % per 1000 hours.

Pre-cruise sensor calibrations were performed at SBE, Inc., USA. The following coefficients were used in SEASOFT:
S/N 430390 (primary)  April 07, 2003
   Soc = 3.7710e-001
   TCor = 0.0014
   PCor = 1.350e-04
   Offset = -0.5027

S/N 430391 (secondary)  April 07, 2003
   Soc = 4.0140e-001
   TCor = 0.0014
   PCor = 1.350e-04
   Offset = -0.4827

Oxygen (ml/l) is computed as

$$\text{Oxygen (ml/l)} = \text{Soc} \times (v + \text{offset}) \times \exp(\text{TCor} \times t + \text{PCor} \times p) \times \text{Oxsat}(t, s)$$

$$\text{Oxsat}(t, s) = \exp[A1 + A2 \times (100 / t) + A3 \times \ln(t / 100) + A4 \times (t / 100) + s \times (B1 + B2 \times (t / 100) + B3 \times (t / 100) \times (t / 100))]$$

- $A1 = -173.4292$
- $A2 = 249.6339$
- $A3 = 143.3483$
- $A4 = -21.8482$
- $B1 = -0.033096$
- $B2 = -0.00170$

where p is pressure in dbar, t is absolute temperature and s is salinity in psu. Oxsat is oxygen saturation value minus the volume of oxygen gas (STP) absorbed from humidity-saturated air.

6) Altimeter
The Benthos PSA-900 Programmable Sonar Altimeter (Benthos, Inc., USA) determines the distance of the target from the unit in almost the same way as the Benthos 2110. PSA-900 also uses the nominal speed of sound of 1500 m/s. But, PSA-900 compensates for sound velocity errors due to temperature. In a PSA-900 operating at a 350 microsecond pulse at 200 kHz, the jitter of the detectors can be as small as 5 microseconds or approximately 0.4 centimeters total distance. Since the total travel time is divided by two, the jitter error is 0.25 centimeters. The unit (PSA-900D) is rated to a depth of 6,000 meters.

The following scale factors were used in SEASOFT:

- $FS\text{Volt} \times 300 / FS\text{Range} = 10$
- Offset = 0.0

7) Fluorometer
The Seapoint Chlorophyll Fluorometer (Seapoint sensors, Inc., USA) is a high-performance, low power
instrument to provide in-situ measurements of chlorophyll-a at depths up to 6,000 meters. The instrument uses modulated blue LED lamps and a blue excitation filter to excite chlorophyll-a. The fluorescent light emitted by the chlorophyll-a passes through a red emission filter and is detected by a silicon photodiode. The low level signal is then processed using synchronous demodulation circuitry which generates an output voltage proportional to chlorophyll-a concentration.

The following coefficients were used in SEASOFT through the software module SEACON as user defined polynomial:

S/N 2148 (unknown calibration date)

Gain = 5.0 (Gain setting = 30X 0-5 ug/l)
Offset = 0.0

Chlorophyll-a concentration is computed as

\[
\text{Chlorophyll-a (ug/l)} = \left( \frac{\text{Voltage} \times \text{Range}}{\text{Gain}} \right) + \text{Offset}
\]

8) Transmissometer
The C-Star Transmissometer (WET Labs, Inc., USA) measures light transmittance at a single wavelength over a known path. In general, losses of light propagating through water can be attributed to two primary causes: scattering and absorption. By projecting a collimated beam of light through the water and placing a focused receiver at a known distance away, one can quantify these losses. The ratio of light gathered by the receiver to the amount originating at the source is known as the beam transmittance. Suspended particles, phytoplankton, bacteria and dissolved organic matter contribute to the losses sensed by the instrument. Thus, the instrument provides information both for an indication of the total concentrations of matter in the water as well as for a value of the water clarity.

The following coefficients were used in SEASOFT:

S/N CST-207RD May 19, 1998

\[
M = 19.6410 \\
B = -1.3940 \\
\text{Path length (m)} = 0.25
\]

The beam transmittance (Tr) is computed as

\[
\text{Tr} (%) = M \times \text{voltage} + B
\]

3.10.4 Data collection and processing
1) Data collection
CTD measurements were made using a SBE 9plus CTD equipped with two pumped temperature-conductivity (TC) sensors. The TC pairs were monitored to check drift and shifts by examining the differences between the
two pairs. Dissolved oxygen sensor was placed between the conductivity sensor module and the pump. Auxiliary sensors included altimeter, Deep Ocean Standards Thermometer, Fluorometer and Transmissometer. The SBE 9plus (sampling rate of 24 Hz) was mounted horizontally in a 36-position carousel frame.

CTD system was powered on at least two minutes in advance of the operation and was powered off at least two minutes after the operation in order to acquire pressure data on ship’s deck.

The package was lowered into the water from the starboard side and held 10 m beneath the surface for about one minute in order to activate the pump. After the pump was activated the package was lifted to the surface and lowered at a rate of 0.5 m/s to 100 m then the package was stopped in order to operate the heave compensator of the crane. The package was lowered again at a rate of 1.0 m/s or 1.2 m/s to the bottom. The position of the package relative to the bottom was monitored by the altimeter reading. Also the bottom depth was monitored by the SEABEAM multibeam sounder on board. For the up cast, the package was lifted at a rate of 1.0 m/s or 1.2 m/s except for bottle firing stops. At each bottle firing stops, the bottle was fired after waiting 30 seconds and the package was stayed 5 seconds in order to sample temperature by the Deep Ocean Standards Thermometer. At 100 m from the surface, the package was stopped in order to stop the heave compensator of the crane.

Water samples were collected using a 36-bottle SBE 32 Carousel Water Sampler with 12-litre Niskin-X bottles. Before a cast taken water for CFCs, the 36-bottle frame and Niskin-X bottles were wiped with acetone.

The SBE 11plus deck unit received the data signal from the CTD. Digitized data were forwarded to a personal computer running the SEASAVE module of the SEASOFT data acquisition software. Temperature, salinity, oxygen and descent rate profiles were displayed in real-time with the package depth and altimeter reading.

The following software was used in this cruise.

SBE, Inc., SEASAVE-Win32, version 5.27b

2) Data collection problems
When operating the SBE 911 system with SBE 35, it was found that the deck unit (SBE 11plus) frequently could not receive correct signal for confirmation of firing bottle #16. This problem occurred at station TR1 (750 dbar), WC9, WC7, WC5 (2,000 dbar), WC6, WC2 (1,800 dbar), WC1 (Bottom), TC1 and TC2 (no water sample). These bottle firing times are estimated using SBE 35 data and the bottle data are created after the cruise.

After the cruise, it was found that the altimeter setting was incorrect (FSVolt * 300 / FSRange = 5) during the cruise. The altimeter reading showed a distance twice of a true distance. So the altimeter reading was corrected after the cruise.

3) Data processing
SEASOFT consists of modular menu driven routines for acquisition, display, processing, and archiving of oceanographic data acquired with SBE equipment, and is designed to work with a compatible personal
The following are the SEASOFT data processing module sequence and specifications used in the reduction of CTD data in this cruise.

**Data processing software**

SBE, Inc., SEASOFT-Win32, version 5.29b

DATCNV converted the raw data to scan number, pressure, depth, temperatures, conductivities, oxygen, oxygen voltage. DATCNV also extracted bottle information where scans were marked with the bottle confirm bit during acquisition. The duration was set to 4.4 seconds, and the offset was set to 0.0 seconds.

ROSSUM created a summary of the bottle data. The bottle position, date, time were output as the first two columns. Scan number, pressure, depth, temperatures, conductivities, oxygen voltage, and altitude were averaged over 4.4 seconds.

ALIGNCTD converted the time-sequence of conductivity and oxygen sensor outputs into the pressure sequence to ensure that all calculations were made using measurements from the same parcel of water. For a SBE 9plus CTD with the ducted temperature and conductivity sensors and a 3,000-rpm pump, the typical net advance of the conductivity relative to the temperature is 0.073 seconds. So, the SBE 11plus deck unit was set to advance the primary conductivity for 1.73 scans (1.75/24 = 0.073 seconds). As a result, the secondary conductivity was advanced 0.073 seconds relative to the temperature. Oxygen data are also systematically delayed with respect to depth mainly because of the long time constant of the oxygen sensor and of an additional delay from the transit time of water in the pumped plumbing line. This delay was compensated by 6 seconds advancing oxygen sensor output (oxygen voltage) relative to the temperature.

WILDEDIT marked extreme outliers in the data files. The first pass of WILDEDIT obtained an accurate estimate of the true standard deviation of the data. The data were read in blocks of 1000 scans. Data greater than 10 standard deviations were flagged. The second pass computed a standard deviation over the same 1000 scans excluding the flagged values. Values greater than 20 standard deviations were marked bad. This process was applied to pressure, temperatures, conductivities and oxygen voltage.

WFILTER performed a median filter to remove spikes in the Fluorometer and Transmissometer data. A median value was determined from a window of 49 scans.

CELLTM used a recursive filter to remove conductivity cell thermal mass effects from the measured conductivity. Typical values used were thermal anomaly amplitude alpha = 0.03 and the time constant 1/beta = 7.0.

FILTER performed a low pass filter on pressure with a time constant of 0.15 seconds. In order to produce zero
phase lag (no time shift) the filter runs forward first then backwards.

SECTION selected a time span of data based on scan number in order to reduce a file size. The minimum number was set to be the starting time when the CTD package was beneath the sea-surface after activation of the pump. The maximum number was set to be the end time when the package came up from the surface. Data for estimation of the CTD pressure drift were prepared before SECTION.

LOOPEDIT marked scans where the CTD was moving less than the minimum velocity of 0.0 m/s (traveling backwards due to ship roll).

DERIVE was used to compute oxygen.

BINAVG averaged the data into 1-bar pressure bins. The center value of the first bin was set equal to the bin size. The bin minimum and maximum values are the center value plus and minus half the bin size. Scans with pressures greater than the minimum and less than or equal to the maximum were averaged. Scans were interpolated so that a data record exists every dbar.

DERIVE was re-used to compute salinity, potential temperature, and sigma-theta.

SPLIT was used to split data into the down cast and the up cast.

3.10.5 Post-cruise calibration

1) Pressure
The CTD pressure sensor drift in the period of this cruise is estimated from the pressure readings on the ship deck. For best results the Paroscientific sensor has to be powered for at least 10 minutes before the operation and carefully temperature equilibrated. However, CTD system was powered only several minutes before the operation at most of stations. In order to get the calibration data for the pre- and post-cast pressure sensor drift, the CTD deck pressure is averaged over first and last two minutes, respectively. Then the atmospheric pressure deviation from a standard atmospheric pressure (14.7 psi) is subtracted from the CTD pressure. The atmospheric pressure was measured at the captain deck (20 m high from the base line) and averaged over one minute for a meteorological data.

The CTD pressure sensor drift is estimated from the deck pressure obtained above. An average of the pre- and the post-casts data over the whole period of this cruise gave an estimation of –0.73 dbar and the root-mean-square difference of 0.21 dbar. And the pre-cruise calibration (April 2003) shows that residual pressure between the Dead Weight Tester and the drift corrected CTD data at 0 dbar was –0.57 dbar. Therefore the pressure sensor drift from the pre-cruise calibration is estimated as –0.16 dbar. So the post-cruise calibration is not deemed necessary for this pressure sensor.
2) Temperature
The CTD temperature sensor (SBE 3) is made with a glass encased thermistor bead inside a needle. The needle protects the thermistor from seawater. If the thermistor bead is slightly large of specification it receives mechanical stress when the needle is compressed at high pressure (Budeus and Schneider, 1998). The pressure sensitivity for a SBE 3 sensor is usually less than +2 m°C / 6000 dbar. It is somewhat difficult to measure this effect in the laboratory and it is one of the primary reasons to use the SBE 35 at sea for critical work. Also SBE 3 measurements may be affected by viscous heating (about +0.5 m°C) that occurs in a TC duct and does not occur for un-pumped SBE 35 measurements (Larson and Pederson, 1996). Furthermore the SBE 35 calibrations have some uncertainty (about 0.2 m°C) and SBE 3 calibrations have some uncertainty (about 1 m°C). So the practical corrections for CTD temperature data can be made by using a SBE 35, correcting the SBE 3 to agree with the SBE 35 (a linear pressure correction, a viscous heating correction and an offset for drift and/or calibration uncertainty).

Post-cruise sensor calibration for the SBE 35 was performed at SBE, Inc., USA.
S/N 0022, 19 November 2003 (2nd step: fixed point calibration)
Slope = 1.000018
Offset = 0.000116

Offset of the SBE 35 data from the pre-cruise calibration are estimated to be −0.1 m°C for temperature less than 4 °C. So the post-cruise correction of the SBE 35 temperature data is not deemed necessary for the SBE 35.
The discrepancy between the CTD temperature and the SBE 35 is considered to be a function of pressure and time. Effect of the viscous heating is assumed to be constant. Since the pressure sensitivity is thought to be constant in time at least during observation period and observation period (3 days) is too short to estimate time drift during the period, the CTD temperature is calibrated as

\[ \text{Calibrated temperature} = T - (c_0 \times P + c_1) \]

where \( T \) is CTD temperature in °C, \( P \) is pressure in dbar, and \( c_0 \) and \( c_1 \) are calibration coefficients. The best fit sets of coefficients are determined by minimizing the sum of absolute deviation from the SBE 35 data. The fortran subroutine DMINF1 of the Scientific Subroutine Library II (Fujitsu Ltd., JAPAN) is used to determine the sets. The DMINF1 uses the revised quasi-Newton method.

The calibration is performed for the secondary temperature (S/N 4216) data. The CTD data created by the software module ROSSUM are used. The deviation of CTD temperature from the SBE 35 temperature at depth shallower than 2,000 dbar is large for determining the coefficients with sufficient accuracy since the vertical temperature gradient is too large in the regions. So the coefficients are determined using the data for the depth deeper than 1,950 dbar.

The number of data used for the calibration (from station WC9 to WC1), the mean absolute deviation from the SBE 35 and the calibration coefficients are listed in Table 3.10.1. Mean and standard deviation of the difference between the CTD temperature and the SBE 35 after the post-cruise calibration are listed in Table 3.10.2. The results of the post-cruise calibration for the CTD temperature are summarized in Table 3.10.3 and shown in Figure 3.10.6.

**TABLE 3.10.1: CALIBRATION COEFFICIENTS FOR THE CTD TEMPERATURE (SECONDARY).**

<table>
<thead>
<tr>
<th>S/N</th>
<th>Number</th>
<th>ADEV (°C)</th>
<th>( c_0 ) (°C/dbar)</th>
<th>( c_2 ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4216</td>
<td>141</td>
<td>0.18</td>
<td>6.9351e-8</td>
<td>0.11e-3</td>
</tr>
</tbody>
</table>

**TABLE 3.10.2: DIFFERENCE BETWEEN THE CTD TEMPERATURE AND THE SBE 35 AFTER THE POST-CRUISE CALIBRATION. MEAN AND STANDARD DEVIATION (SDEV) ARE CALCULATED FOR THE DATA BELOW AND ABOVE 1,950 DBAR.**

<table>
<thead>
<tr>
<th>S/N</th>
<th>Pressure &lt; 1,950 dbar</th>
<th>Pressure &gt;= 1,950 dbar</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Num</td>
<td>Mean (°C)</td>
</tr>
<tr>
<td>4216</td>
<td>276</td>
<td>0.40</td>
</tr>
</tbody>
</table>
3) Salinity
The discrepancy between the CTD salinity and the bottle salinity is considered to be a function of conductivity and pressure. The CTD salinity is calibrated as

Calibrated salinity = S – (c_0 * P + c_1 * C + c_2 * C * P + c_3)

where S is CTD salinity, P is pressure in dbar, C is conductivity in S/m and c_0, c_1, c_2 and c_3 are calibration coefficients. The best fit sets of coefficients are determined by minimizing the sum of absolute deviation with a weight from the bottle salinity data. The fortran subroutine DMINF1 of the Scientific Subroutine Library II (Fujitsu Ltd., JAPAN) is used to determine the sets. The weight is given as a function of pressure as

Weight = min[10, exp{log(10) * P / PR}]

where PR is threshold of pressure (1,000 dbar). When pressure is large (small), the weight is large (small) at maximum (minimum) value of 10 (1).

The calibration is performed for the salinity derived from the secondary temperature and secondary conductivity sensors. The CTD data created by the software module ROSSUM are used after the post-cruise calibration for the CTD temperature. The calibration coefficients are determined for grouped stations.

The results of the post-cruise calibration for the CTD salinity are summarized in Table 3.10.4 and shown in Figure 3.10.7. And the calibration coefficients and the number of the data (NUM) used for the calibration are listed in Table 3.10.5.

<table>
<thead>
<tr>
<th>Station</th>
<th>Num</th>
<th>c0</th>
<th>c1</th>
<th>c2</th>
<th>c3</th>
</tr>
</thead>
<tbody>
<tr>
<td>TR1</td>
<td>23</td>
<td>-4.80974e-5</td>
<td>4.99536e-4</td>
<td>1.64214e-2</td>
<td>-6.20274e-3</td>
</tr>
<tr>
<td>WC1-9</td>
<td>299</td>
<td>5.32578e-6</td>
<td>-4.71760e-4</td>
<td>-1.54552e-6</td>
<td>2.49370e-3</td>
</tr>
<tr>
<td>TC1-2</td>
<td>31</td>
<td>-3.73661e-6</td>
<td>-6.81139e-3</td>
<td>-2.85383e-7</td>
<td>2.80237e-2</td>
</tr>
</tbody>
</table>

TABLE 3.10.4: DIFFERENCE BETWEEN THE CTD SALINITY AND THE BOTTLE SALINITY AFTER THE POST-CRUISE CALIBRATION. MEAN AND STANDARD DEVIATION (SDEV) ARE CALCULATED FOR THE DATA BELOW AND ABOVE 1,000 DBAR.

<table>
<thead>
<tr>
<th>Pressure &lt; 1,000 dbar</th>
<th>Pressure &gt;= 1,000 dbar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Num</td>
<td>Mean</td>
</tr>
<tr>
<td>179</td>
<td>-0.0013</td>
</tr>
</tbody>
</table>

TABLE 3.10.5: CALIBRATION COEFFICIENTS FOR THE CTD SALINITY. THE NUMBER OF DATA (NUM) USED FOR THE CALIBRATION IS ALSO SHOWN.
FIGURE 3.10.7: DIFFERENCE BETWEEN THE CTD SALINITY (SECONDARY) AND THE BOTTLE SALINITY. OPEN AND CLOSED CIRCLES INDICATE BEFORE AND AFTER THE POST-CRUISE CALIBRATION USING THE BOTTLE SALINITY DATA, RESPECTIVELY. LOWER TWO PANELS SHOWS HISTOGRAM OF THE DIFFERENCE AFTER THE CALIBRATION.
4) Oxygen

The CTD oxygen is calibrated using the oxygen model (see section 3.10.3) as

\[
\text{Calibrated oxygen (ml/l)} = \text{Soc} \times (v + \text{offset}) \times \exp(T\text{Cor} \times t + P\text{Cor} \times p) \times \text{Oxsat}(t, s)
\]

where \( p \) is pressure in dbar, \( t \) is absolute temperature and \( s \) is salinity in psu. \( \text{Oxsat} \) is oxygen saturation value minus the volume of oxygen gas (STP) absorbed from humidity-saturated air (see section 3.10.3). \( \text{Soc}, \text{offset}, \text{TCor} \) and \( \text{PCor} \) are the calibration coefficients. The best fit sets of coefficients are determined by minimizing the sum of absolute deviation with a weight from the bottle oxygen data. The fortran subroutine DMINF1 of the Scientific Subroutine Library II (Fujitsu Ltd., JAPAN) is used to determine the sets. The weight is given as a function of pressure as

\[
\text{Weight} = \min\{10, \exp\{\log(10) \times P / \text{PR}\}\}
\]

where \( \text{PR} \) is threshold of pressure (1,000 dbar). When pressure is large (small), the weight is large (small) at maximum (minimum) value of 10 (1).

The calibration is performed for the output from the secondary oxygen sensor. The down-cast CTD data sampled at same pressure of the CTD data created by the software module ROSSUM are used after the post-cruise calibration for the CTD temperature and salinity. The coefficients are basically determined for each station.

The results of the post-cruise calibration for the CTD oxygen are summarized in Table 3.10.6 and shown in Figure 3.10.8. And the calibration coefficients and the number of the data (NUM) used for the calibration are listed in Table 3.10.7.

**TABLE 3.10.6: DIFFERENCE BETWEEN THE CTD OXYGEN AND THE BOTTLE OXYGEN AFTER THE POST-CRUISE CALIBRATION. MEAN AND STANDARD DEVIATION (SDEV) ARE CALCULATED FOR THE DATA BELOW AND ABOVE 1,000 DBAR.**

<table>
<thead>
<tr>
<th>Pressure &lt; 1,000 dbar</th>
<th>Pressure &gt;= 1,000 dbar</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Num</strong></td>
<td><strong>Mean (umol/kg)</strong></td>
</tr>
<tr>
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FIGURE 3.10.8: DIFFERENCE BETWEEN THE CTD OXYGEN (SECONDARY) AND THE BOTTLE OXYGEN. OPEN AND CLOSED CIRCLES INDICATE BEFORE AND AFTER THE POST-CRUISE CALIBRATION USING THE BOTTLE OXYGEN DATA, RESPECTIVELY. LOWER TWO PANELS SHOWS HISTOGRAM OF THE DIFFERENCE AFTER THE CALIBRATION.
3.10.6 Results
Date, time and locations of the CTD casts are listed in SUM (station summary) file (see Appendix A). In total 12 CTD casts were carried out. Vertical section of temperature, salinity and dissolved oxygen are shown in Section 1.5.

References