## MR05-02

Preliminary

Cruise Report

August, 2005

Edited by

Dr. Takeshi Kawano

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## 1. Cruise Narrative

## 1.1 Highlight

| MR05-02  |
|--|
| P10  |
| Takeshi Kawano   |
| Ocean General Circulation Observational Research Program |
| Institute of Observational Research for Global Change    |
| Japan Agency for Marine-earth Science and Technology     |
| 2-15, Natsushima, Yokosuka, Japan 237-0061               |
|  |

| Ship :          | R/V MIRAI                     |
|-----------------|-------------------------------|
| Ports of Call : | Sekinehama – Hachinohe - Guam |
| Cruise Date :   | May 25, 2005 – July 2, 2005   |

## **1.2 Cruise Summary**

#### **Cruise Track**

Cruise Track and station locations are shown in Fig.1.1.

#### Number of Stations

A total of 124 stations were occupied using a Sea Bird Electronics 36 bottle carousel equipped with 12 liter Niskin X water sample bottles, a SBE911plus equipped with SBE35 deep ocean standards thermometer, SBE43 oxygen sensor, Seapoint sensors Inc. Chlorophyll Fluorometer and Benthos Inc. Altimeter and RDI Monitor ADCP.

#### Sampling and measurements

- 1) Measurements of temperature, salinity, oxygen ,current profile, fluorescence using CTD/O<sub>2</sub> with LADCP, fluorometer.
- Water sampling and analysis of salinity, oxygen, nutrients, CFC11,12, 113, total alkalinity, DIC, and pH. The sampling depth in db were 10, 50, 100, 150, 200, 250, 300, 400, 500, 600, 700, 800, 900, 1000, 1200, 1400, 1600, 1800, 2000, 2200, 2400, 2600, 2800, 3000, 3250, 3500, 3750, 4000, 4250, 4500, 4750, 5000, 5250, 5500, 5750 and sea bottom (minus 10db).
- 3) Water sampling of PON, <sup>14</sup>C, <sup>13</sup>C, <sup>15</sup>N and <sup>137</sup>Cs.
- 4) Surface water sampling for a biological study.
- 5) Underway measurements of pCO<sub>2</sub>, temperature, salinity, nutrients, surface current, bathymetry and meteorological parameters

## Floats, Drifters, Drifter

2 ARGO floats (APEX floats) were launched.



Fig.1.1 Cruise Track

## 1.3 Responsibility

The principal investigators responsible for major parameters are listed in Table.1.1.

## Table 1.1 List of principal investigator and person in charge on the ship

## Chief Scientist : Takeshi Kawano Chief Technologist : Kenichiro Sato

| Item                | Principal Investigator | Person in Charge on the Ship     |
|---------------------|------------------------|----------------------------------|
| Hydrography         | ·                      |                                  |
| CTDO                | Hiroshi Uchida         | Satoshi Ozawa                    |
| LADCP               | Shinya Kouketsu        | Shinya Kouketsu                  |
| BTL Salinity        | Takeshi Kawano         | Fujio Kobayashi                  |
| BTL Oxygen          | Ikuo Kaneko            | Takayoshi Seike                  |
| Nutrients           | Michio Aoyama          | Junko Hamanaka                   |
| DIC                 | Akihiko Murata         | Mikio Kitada                     |
| Alkalinity          | Akihiko Murata         | Fuyuki Shibata                   |
| pH                  | Akihiko Murata         | Taeko Ohama                      |
| CFCs                | Kenichi Sasaki         | Katsunori Sagishima              |
| $^{14}C$            | Yuichiro Kumamoto      | Akihiko Murata (collection only) |
| Cs                  | Michio Aoyama          | Akihiko Murata (collection only) |
| <sup>15</sup> N     | Hisayuki Y. Inoue      | Tomomi Takamura                  |
| Biology             | Ken Furuya             | Satoshi Kitajima                 |
| Underway            |                        |                                  |
| ADCP                | Yasushi Yoshikawa      | Hiroshi Imai                     |
| Bathymetry          | Hiroshi Imai           | Hiroshi Imai                     |
| Meteorology         | Kunio Yoneyama         | Hiroshi Imai                     |
| Thermo-Salinograph  | Takeshi Kawano         | Takayoshi Seike                  |
| Infrared Radiometer | Hajime Okamoto         | Hiroshi Imai                     |
| Sky Radiometer      | Tatsuo Endo            | Hiroshi Imai                     |
| Laser Radar         | Nobuo Sugimoto         | Hiroshi Imai                     |
| pCO <sub>2</sub>    | Akihiko Murata         | Mikio Kitada                     |
| Floats, Drifters    |                        |                                  |
| Argo float          | Nobuyuki Shikama       | Naoko Takahashi                  |

#### 1.4 Objective of the Cruise

#### 1.4.1 Objectives

It is well known that the oceans play a central role in determining global climate. However, heat and material transports in the ocean and their temporal changes have not yet been sufficiently quantified. Therefore, the global climate change is not understood satisfactorily. The purposes of this research are to evaluate heat and material transports including carbon, nutrients etc, in the North Pacific and to detect its long term changes and basin-scale biogeochemical changes since the 1990s.

P10 is the hydrographic section nominally along 149 degree east from Hokkaido, Japan, to the coast of Papua New Guinea. The P10 cruise was the first in two WHP re-visit cruise aboard R/V MIRAI in 2005 followed by P3.

The other objectives of this cruise are as follows;

- 1) to observe surface meteorological and hydrogical parameters as a basic data of the meteorology and oceangraphy,
- 2) to observe sea bottom topography, gravity and magnetic fields along cruise track to understand the dynamics of ocean plate and the accompanying geophysical activities,
- 3) to contribute to establishment of data base for model validation,
- 4) ARGO sensor calibration and its deployment in the western Pacific.

#### 1.4.2 Data Policy

Obtained data will be quality controlled and opened through GHPO and JAMSTEC within two years .

## 1.5 List of Cruise Participants

Cruise participants are listed in Table 1.2.

|                     | Table 1.2 Cruise Participants       |                     |
|---------------------|-------------------------------------|---------------------|
| Name                | Responsibility                      | Affiliation         |
| Hideyuki FUTAMURA   | Water Sampling                      | MWJ                 |
| Junko HAMANAKA      | Nutrients                           | MWJ                 |
| Miyo IKEDA          | Water Sampling                      | MWJ                 |
| Hiroshi IMAI        | Meteorology                         | GODI                |
| Tetsuya INABA       | Water Sampling                      | MWJ                 |
| Yoshiko ISHIKAWA    | Carbon                              | MWJ                 |
| Kenichi KATAYAMA    | Salinity                            | MWJ                 |
| Takeshi KAWAO       | Chief Scientist / Salinity          | IORGC/JAMSTEC       |
| Mikio KITADA        | Carbon                              | MWJ                 |
| Satoshi KITAJIMA    | Biology                             | University of Tokyo |
| Fujio KOBAYASHI     | Salinity                            | MWJ                 |
| Shinya KOUKETSU     | LADCP/ADCP                          | IORGC/JAMSTEC       |
| Asako KUBO          | Nutrients                           | MWJ                 |
| Kazuma KUDO         | Water Sampling                      | MWJ                 |
| Akihiko MURATA      | Carbon                              | IORGC/JAMSTEC       |
| Kimiko NISHIJIMA    | Dissolved Oxygen                    | MWJ                 |
| Tomohide NOGUCHI    | CTD                                 | MWJ                 |
| Taeko OHAMA         | Carbon                              | MWJ                 |
| Shinya OKUMURA      | Meteorology                         | GODI                |
| Kentaro OYAMA       | CTD                                 | MWJ                 |
| Ryo OYAMA           | Meteorology                         | GODI                |
| Satoshi OZAWA       | CTD                                 | MWJ                 |
| Katsunori SAGISHIMA | CFCs                                | MWJ                 |
| Kenichi SASAKI      | CFCs                                | MIO/JAMSTEC         |
| Kenichiro SATO      | Chief Technologist / Water Sampling | MWJ                 |
| Takayoshi SEIKE     | Dissolved Oxygen                    | MWJ                 |
| Fuyuki SHIBATA      | Carbon                              | MWJ                 |
| Naoko TAKAHASHI     | CTD                                 | MWJ                 |
| Tomomi TAKAMURA     | C-13                                | Hokkaido University |
| Ayumi TAKEUCHI      | Nutrients                           | MWJ                 |
| Tatsuya TANAKA      | Salinity                            | MWJ                 |
| Tomokazu TANIGUCHI  | Water Sampling                      | MWJ                 |
| Hiroshi UCHIDA      | LADCP/CTD                           | IORGC/JAMSTEC       |
| Satoshi UDA         | Water Sampling                      | MWJ                 |
| Masahide WAKITA     | CFCs                                | MIO/JAMSTEC         |
| Hideki YAMAMOTO     | CFCs                                | MWJ                 |
| Ai YASUDA           | Dissolved Oxygen                    | MWJ                 |
| Masashi YASUNAGA    | Water Sampling                      | MWJ                 |
| Atsushi YOSHIMURA   | Water Sampling                      | MWJ                 |
|                     | Clabel Ocean Development la         |                     |
| GODI                | Global Ocean Development Inc.       |                     |
| MWJ                 | Marine Works Japan Ltd.             | and Technology      |

Table 1.2 Cruise Participants

| GODI    | Global Ocean Development Inc.                         |
|---------|---|
| MWJ     | Marine Works Japan Ltd.                               |
| JAMSTEC | Japan Agency for Marine-earth Sceinece and Technology |
| IORGC   | Institute of Observational Research for Global Change |
| MIO     | Mutsu Institute of Oceanography                       |

#### 2.1 Meteorological observation

#### 2.1.1 Surface Meteorological Observation

| Kunio Yoneyama | (JAMSTEC) Principal Investigator / Not on-board: |
|----------------|--|
| Yasutaka Imai  | (Global Ocean Development Inc.)                  |
| Shinya Okumura | (Global Ocean Development Inc.)                  |
| Ryo Ohyama     | (Global Ocean Development Inc.)                  |

#### (1) Objectives

The surface meteorological parameters are observed as a basic dataset of the meteorology. These parameters bring us the information about the temporal variation of the meteorological condition surrounding the ship.

#### (2)Methods

The surface meteorological parameters were observed throughout the MR05-02 cruise, from 25 May 2005 to 30 June 2005. During this cruise, we used two systems for the observation.

#### 1) MIRAI Surface Meteorological observation (SMET) system

Instruments of SMET system are listed in Table 2.1.1-1 and measured parameters are listed in Table 2.1.1-2. Data was collected and processed by KOAC-7800 weather data processor made by Koshin-Denki, Japan. The data set consists of 6-second averaged data.

2) Shipboard Oceanographic and Atmospheric Radiation (SOAR) system

SOAR system designed by BNL (Brookhaven National Laboratory, USA) consists of major three parts.

i) Portable Radiation Package (PRP) designed by BNL – short and long wave downward radiation.

ii) Zeno Meteorological (Zeno/Met) system designed by BNL – wind, air temperature, relative humidity, pressure, and rainfall measurement.

iii) Scientific Computer System (SCS) designed by NOAA (National Oceanic and Atmospheric Administration, USA) – centralized data acquisition and logging of all data sets.

SCS recorded PRP data every 6 seconds and Zeno/Met data every 10 seconds. Instruments and their locations are listed in Table2.1.1-3, and measured parameters are listed in Table 2.1.1-4.

We have checked the following sensors, before and after the cruise for the quality control as post processing.

a) Young Rain gauge (SMET and SOAR)

Inspecting the linearity of output value from the rain gauge sensor to change input value by adding fixed quantity of test water.

b) Barometer (SMET and SOAR)

Comparing with the portable barometer value, PTB220CASE, VAISALA.

#### c) Thermometer (air temperature and relative humidity) (SMET and SOAR) Comparing with the portable thermometer value, HMP41/45, VAISALA.

(3) Preliminary results
Figures 2.1.1-1 show the time series of the following parameters;
Wind (SOAR)
Air temperature (SOAR)
Relative humidity (SOAR)
Precipitation (SMET)
Short/long wave radiation (SOAR)
Pressure (SOAR)
Sea surface temperature (SMET)
Significant wave height (SMET)

(4) Data archives

The raw data obtained during this cruise will be submitted to JAMSTEC Data Management Division. Corrected data sets will also be available from K. Yoneyama of JAMSTEC.

(5) Remarks

1) Sensor trouble for SOAR ORG precipitation measurement occurred at 06:00 UTC on 20 June. Therefore we replaced the sensor ORG-815 with ORG-115 at 04:30 UTC on 23 June.

2) Observation was stopped in the following periods for the maintenance.

June 21 02:10 - 02:22 UTC June 23 04:00 - 05:05 UTC June 24 02:00 - 07:20 UTC

3) Sea surface temperature was not acquired from 07:00UTC 25 May to 12:30 UTC 26 May, because we stopped pumping up surface water.

4) We did not install Fast rotating shadowband radiometer (FRSR) sensor during this cruise.

| Sensors                   | Туре             | Manufacturer 1       | Location(altitude from surface) |
|---------------------------|------------------|----------------------|---------------------------------|
| Anemometer                | KE-500           | Koshin Denki, Japan  | foremast (24 m)                 |
| Tair/RH                   | HMP45A           | Vaisala, Finland     |                                 |
| with 43408 Gill aspirated | radiation shield | R.M. Young, USA      | compass deck (21 m)             |
|                           |                  |                      | starboard side and port side    |
| Thermometer: SST          | RFN1-0           | Koshin Denki, Japan  | 4th deck (-1m, inlet -5m)       |
| Barometer                 | F-451            | Yokogawa, Japan      | captain deck (13 m)             |
|                           |                  |                      | weather observation room        |
| Rain gauge                | 50202            | R. M. Young, USA     | compass deck (19 m)             |
| Optical rain gauge        | ORG-115          | DRScTi, USA          | compass deck (19 m)             |
| Radiometer (short wave)   | MS-801           | Eiko Seiki, Japan    | radar mast (28 m)               |
| Radiometer (long wave)    | MS-202           | Eiko Seiki, Japan    | radar mast (28 m)               |
| Wave height meter         | MW-2             | Tsurumi-seiki, Japan | bow (10 m)                      |

Table 2.1.1-1 Instruments and installations of MIRAI Surface Meteorological observation system

|    | Parmeter                              | Units   | Remarks                       |
|----|---------------------------------------|---------|-------------------------------|
| 1  | Latitude                              | degree  |                               |
| 2  | Longitude                             | degree  |                               |
| 3  | Ship's speed                          | knot    | Mirai log, DS-30 Furuno       |
| 4  | Ship's heading                        | degree  | Mirai gyro, TG-6000, Tokimec  |
| 5  | Relative wind speed                   | m/s     | 6sec./10min. averaged         |
| 6  | Relative wind direction               | degree  | 6sec./10min. averaged         |
| 7  | True wind speed                       | m/s     | 6sec./10min. averaged         |
| 8  | True wind direction                   | degree  | 6sec./10min. averaged         |
| 9  | Barometric pressure                   | hPa     | adjusted to sea surface level |
|    |                                       |         | 6sec. averaged                |
| 10 | Air temperature (starboard side)      | degC    | 6sec. averaged                |
| 11 | Air temperature (port side)           | degC    | 6sec. averaged                |
| 12 | Dewpoint temperature (starboard side) | degC    | 6sec. averaged                |
| 13 | Dewpoint temperature (port side)      | degC    | 6sec. averaged                |
| 14 | Relative humidity (starboard side)    | %       | 6sec. averaged                |
| 15 | Relative humidity (port side)         | %       | 6sec. averaged                |
| 16 | Sea surface temperature               | degC    | 6sec. averaged                |
| 17 | Rain rate (optical rain gauge)        | mm/hr   | hourly accumulation           |
| 18 | Rain rate (capacitive rain gauge)     | mm/hr   | hourly accumulation           |
| 19 | Down welling shortwave radiation      | $W/m^2$ | 6sec. averaged                |
| 20 | Down welling infra-red radiation      | $W/m^2$ | 6sec. averaged                |
| 21 | Significant wave height (bow)         | m       | hourly                        |
| 22 | Significant wave height (aft)         | m       | hourly                        |
| 23 | Significant wave period (bow)         | second  | hourly                        |
| 24 | Significant wave period (aft)         | second  | hourly                        |

 Table 2.1.1-2
 Parameters of MIRAI Surface Meteorological observation system

| Table 2.1.1-3 Instrument and installation locations of SOAR system | Table 2.1.1-3 | Instrument and installation locations of SOAR system |
|--|---------------|--|
|--|---------------|--|

| Sensors (Zeno/Met)          | Туре             | Manufacturer     | Location (altitude from surface) |
|-----------------------------|------------------|------------------|----------------------------------|
| Anemometer                  | 05106            | R.M. Young, USA  | foremast (25 m)                  |
| Tair/RH                     | HMP45A           | Vaisala, Finland |                                  |
| with 43408 Gill aspirated   | radiation shield | R.M. Young, USA  | foremast (24 m)                  |
| Barometer                   | 61201            | R.M. Young, USA  |                                  |
| with 61002 Gill pressure    | port             | R.M. Young, USA  | foremast (24 m)                  |
| Rain gauge                  | 50202            | R. M. Young, USA | foremast (24 m)                  |
| Optical rain gauge          | ORG-815DA        | Osi, USA         | foremast(24 m) May25 -Jun24      |
|                             | ORG-115DA        | ScTi, USA        | foremast (24 m) Jun24 - Jul02    |
|                             |                  |                  |                                  |
| Sensors (PRP)               | Туре             | Manufacturer     | Location(altitude from surface)  |
| Radiometer (short wave)     | PSP              | Epply Labs, USA  | foremast (25 m)                  |
| Radiometer (long wave)      | PIR              | Epply Labs, USA  | foremast (25 m)                  |
| Fast rotating shadowband ra | diometer(FRSR)   | Yankee, USA      | foremast (25 m)                  |

|           | Parmeter                              | Units            | Remarks        |
|-----------|---------------------------------------|------------------|----------------|
| 1         | Latitude                              | degree           |                |
| 2         | Longitude                             | degree           |                |
| 3         | SOG                                   | knot             |                |
| 4         | COG                                   | degree           |                |
| 5         | Relative wind speed                   | m/s              |                |
| 6         | Relative wind direction               | degree           |                |
| 7         | Barometric pressure                   | hPa              |                |
| 8         | Air temperature                       | degC             |                |
| 9         | Relative humidity                     | %                |                |
| 10        | Rain rate (optical rain gauge)        | mm/hr            |                |
| 11        | Precipitation (capacitive rain gauge) | mm               | reset at 50 mm |
| 12        | Down welling shortwave radiation      | $W/m^2$          |                |
| 13        | Down welling infra-red radiation      | $W/m^2$          |                |
| <u>14</u> | Defuse irradiance                     | W/m <sup>2</sup> |                |

Table 2.1.1-4 Parameters of SOAR system

#### 2.1.2 Ceilometer Observation

| Kunio Yoneyama | (JAMSTEC) Principal Investigator / Not on-board |
|----------------|---|
| Yasutaka Imai  | (Global Ocean Development Inc.)                 |
| Shinya Okumura | (Global Ocean Development Inc.)                 |
| Ryo Ohyama     | (Global Ocean Development Inc.)                 |

#### (1) Objectives

The information on cloud base height and liquid water amount around cloud base is important to understand the process on formation of the cloud. As a methods to measure them, the ceilometer observation was carried out.

#### (2) Methods

We measured cloud base height and backscatter profile using ceilometer (CT-25K, VAISALA, Finland) throughout the MR05-02 cruise, from 25 May 2005 to 30 June 2005. Major parameters measured are 1) cloud base height in meters, 2) backscatter profiles, and 3) estimated cloud amount in octas.

Specifications of the system are as follows.

| Laser source:               | Indium Gallium Arsenide Diode                                |
|-----------------------------|--|
| Transmitting wavelength:    | 905±5 mm at 25 degC  |
| Transmitting average power: | 8.9 mW   |
| Repetition rate:            | 5.57 kHz   |
| Detector:                   | Silicon avalanche photodiode (APD)                           |
| Responsibility at 905 nm:   | 65 A/W   |
| Measurement range:          | 0 ~ 7.5 km   |
| Resolution:                 | 50 ft in full range  |
| Sampling rate:              | 60 sec   |
| Sky Condition:              | 0, 1, 3, 5, 7, 8 oktas (9: Vertical Visibility)              |
|                             | (0: Sky Clear, 1:Few, 3:Scattered, 5-7: Broken, 8: Overcast) |

On the archive dataset, cloud base height and backscatter profile are recorded with the resolution of 30 m (100 ft).

#### (3) Preliminary results

Figure 2.1.2-1 shows the time series of the first and the second lowest cloud base height.

#### (4) Data archives

The raw data obtained during this cruise will be submitted to JAMSTEC Data Management Division. The data are also available from K. Yoneyama of JAMSTEC.

#### (5) Remarks

Window cleaning : 26 May. 2005 04:32 UTC 29 May. 2005 02:15 UTC 04 Jun. 2005 00:49 UTC 11 Jun. 2005 00:19 UTC 18 Jun. 2005 23:28 UTC 24 Jun. 2005 23:58 UTC 29 Jun. 2005 23:05 UTC



Fig.2.1.1-1 Time series of surface meteorological parameters during the cruise



Fig.2.1.1-1 Continued



Fig.2.1.1-1 Continued



Fig.2.1.1-1 Continued



Fig.2.1.1-1 Continued



Fig.2.1.2-1 1st, 2nd and 3rd lowest cloud base height during the cruise.



#### 2.1.3 Surface Atmospheric Turbulent Flux Measurement

| Kunio Yoneyama  | (JAMSTEC) Principal Investigator / Not-onboard        |
|-----------------|---|
| Osamu Tsukamoto | (Okayama University) Not-onboard                      |
| Yasutaka Imai   | (Global Ocean Development Inc.) On-board collaborator |
| Shinya Okumura  | (Global Ocean Development Inc.) On-board collaborator |
| Ryo Ohyama      | (Global Ocean Development Inc.) On-board collaborator |

#### (1) Objective

In order to understand the air-sea interaction more, accurate measurements of surface heat and fresh water budgets are necessary as well as momentum exchange through the sea surface. In addition, the evaluation of surface flux of carbon dioxide is also indispensable for the study of global warming. Sea surface turbulent fluxes of momentum, sensible heat, latent heat, and carbon dioxide were measured by using the eddy correlation method that is thought to be most accurate and free from assumptions. These surface heat flux data are combined with radiation fluxes and water temperature profiles to derive the surface energy budget.

#### (2) Methods

The surface turbulent flux measurement system (Fig. 2.1.3-1) consists of turbulence instruments (Kaijo Co., Ltd.) and ship motion sensors (Kanto Aircraft Instrument Co., Ltd.). The turbulence sensors include a three-dimensional sonic anemometer-thermometer (Kaijo, DA-600) and an infrared hygrometer (LICOR, LI-7500). The sonic anemometer measures three-dimensional wind components relative to the ship. The ship motion sensors include a two-axis inclinometer (Applied Geomechanics, MD-900-T), a three-axis accelerometer (Applied Signal Inc., QA-700-020), and a three-axis rate gyro (Systron Donner, QRS-0050-100). LI7500 is a CO2/H2O turbulence sensor that measures turbulent signals of carbon dioxide and water vapor simultaneously.

These signals are sampled at 10 Hz by a PC-based data logging system (Labview, National Instruments Co., Ltd.). By obtaining the ship speed and heading information through the Mirai network system it yields the absolute wind components relative to the ground. Combining wind data with the turbulence data, turbulent fluxes and statistics are calculated in a real-time basis. These data are also saved in digital files every 0.1 second for raw data and every 1 minute for statistic data.

#### (3) Preliminary results

Data will be processed after the cruise at Okayama University.

#### (4) Data Archive

All data are archived at Okayama University, and will be open to public after quality check and correction by K. Yoneyama and/or O. Tsukamoto. Corrected data will be submitted to JAMSTEC Data Management Division.

Fig. 2.1.3-1 Turbulent flux measurement system on the top deck of foremast.



#### 2.1.4 Infrared radiometer

Hajime Okamoto (CAOS, Tohoku University): Principal Investigator Shinichi Otake (CAOS, Tohoku University): Student Nobuo Sugimoto (National Institute for Environmental Studies) Ichiro Matsui (National Institute for Environmental Studies) Akihide Kamei (National Institute for Environmental Studies) Toshiaki Takano (Chiba University)

#### (1) Objective

Infrared radiometer (hereafter IR) is used to derive temperature of cloud base and emissivity of thin clouds. Main objectives are to use study clouds and climate system in tropics by the combination of IR with active sensors such as lidar and 95GHz cloud radar. From these integrated approach, it is expected to extend our knowledge of clouds and climate system. Special emphasis is made to retrieve cloud microphysics in upper part of clouds, including sub-visual clouds that is recognized to be a key component for the exchange of water amount between troposphere and stratosphere

#### (2) Method

IR instrument directly provides broadband infrared temperature (9.6-10.5µm). General specifications of IR system (KT 19II, HEITRONICS)

| Temperature range | -100 to 100°C                                   |
|-------------------|---|
| Accuracy          | 0.5 °C  |
| Mode              | 24hours   |
| Time resolution   | 1 min.  |
| Field of view     | Less than $1^{\circ}$ (will be estimated later) |
| Spectral region   | 9.6-10.5µm                                      |

This is converted to broadband radiance around the wavelength region. This is further combined with the lidar or radar for the retrieval of cloud microphysics such as optical thickness at visible wavelength, effective particle size. The applicability of the retrieval technique of the synergetic use of radar/IR or lidar/IR is so far limited to ice clouds. The microphysics of clouds from hese techniques will be compared with other retrieval techniques such as radar/lidar one or radar with multi-parameter.

#### (3) Data archive

The data archive server is set inside Tohoku University and the original data and the results of the analyses will be available from us.

#### (4) Operations.

Basically the IRT is operated for 24 hours. In order to avoid the direct sun light entering the lens of the IRT, we asked to the staffs in MIRAI to use the shutter (cover) on the top of the lens. We also asked to use the shutter when the precipitation was expected.

## (6) preliminary data

The data obtained in June 1 was shown in the figure. The temperature below -20degC indicates the existence of cirrus clouds and should be analyzed by the combination of the lidar data. The temperature of beyond 10 degC suggests the warm clouds. In June 3, we were informed that the inside of the lens of the IRT got wet and dew was found under the lens after the precipitation. Therefore, we asked the staffs on the R/V Mirai to take some photos of the lens and also the data recorded by the IRT measurements to investigate the condition of the IRT.



Fig. 1 the results of the temperature by IRT on June 1 to 2, 2005.



Fig.2 The same as Fig.1 but for June 21.

Fig.2 shows the same history of temperature measurements but in June 21. We believe the IRT is now being dried and working properly.

#### 2.1.5 Studies on behaviors and climate influence of atmospheric aerosols over the ocean

| 2.1.5.1.1 | Name of research cruise: | Observational Research in the Western Pacific and adjacent |
|-----------|--------------------------|--|
|           |                          | seas   |
| 2.1.5.1.2 | Observational duration:  | From 25 May-02 July 2005 ( 39 days )                       |
| 2.1.5.1.3 | Area of ocean:           | Western Pacific and adjacent seas                          |

#### 2.1.5.2.1. Objective theme:

Investigation of horizontal distribution on the concentration and size distribution and optical properties of atmospheric aerosols at the surface and optical thickness of columnar aerosol over the ocean.

#### 2.1.5.2 .2. Objects:

To clear and solve the problems of horizontal distribution and optical properties of aerosols, some observations were carried out over the western North Pacific Ocean. Furthermore, collections of the data for calibration and validation to the remote sensing data were performed simultaneously

#### 2.1.5.3. Summery:

To obtain the data for calibration and validation between remote sensing and surface measurements over the ocean, a series of simultaneous observations has been carried out about optical properties like as scattering and absorption coefficients and radiative properties as optical properties of atmospheric aerosols, the concentration and size distribution of surface aerosols over the Western Pacific Ocean for 39 days from 25 May 2005 to 02 July 2005. In addition of that, a sky radiometer was examined for to a fully automated ship-borne instrument and improved to the practical usage on same board.

#### 2.1.5.4. Personnel

#### 2.1.5.4.1 Principal Investigator not on board

Tatsuo ENDOH (Tottori University of Environmental Studies) Professor

#### 2.1.5.4.2 On board scientists

Takeshi Kawano ( JAMSTEC ) Chief Scientist

#### 2.1.5.4.3 Co-workers not on board

Sachio OHTA (Engineering environmental resource laboratory, Graduate school of engineering, Hokkaido University) Professor

Tamio TAKAMURA (Center of environmental remote sensing science, Chiba University) Professor Teruyuki NAKAJIMA (Center of climate system research, University of Tokyo) Professor Nobuo SUGIMOTO (National Institute for Environmental Studies, Japan) Chief Research Scientist

#### 2.1.5.5.1 Objects/Introduction

One of the most important objects is the collection of calibration and validation data from the surface (Nakajima et al.1996, 1997 and 1999). It may be considered for the observation over the widely opening of the huge ocean to be desired ideally because of horizontal homogeneity. Furthermore, the back ground values of aerosol concentration are easily obtained over there (Ohta et al.1996, Miura et al. 1997 and Takahashi et al. 1996) and vertical profile of aerosol concentration are obtained by means of extrapolation up to the scale height. It is desired to compare the integrated value of these profile of aerosol concentration with optical thickness observed by the optical and radiative measurement (Hayasaka et al. 1998, Takamura et al.1994). Facing this object, the optical and radiative observations were carried out by mean of the Sky Radiometer providing more precise radiation data as the radiative forcing for global warming.

#### 2.1.5.5.2 Measuring parameters

Atmospheric optical thickness, Ångström coefficient of wave length efficiencies,

Direct irradiating intensity of solar, and forward up to back scattering intensity with scattering angles of 2-140degree and seven different wave lengths

GPS provides the position with longitude and latitude and heading direction of the vessel, and azimuth and elevation angle of sun. Horizon sensor provides rolling and pitching angles.

Concentration and size distribution of atmospheric aerosol.

#### 2.1.5.5.3 Methods

The instruments used in this work are shown as following in Table-1.

Sky Radiometer was measuring irradiating intensities of solar radiation through seven different filters with the scanning angle of 2-140 degree. These data will provide finally optical thickness, Ångström exponent, single scattering albado and size distribution of atmospheric aerosols with a kind of retrieval method.

Optical Particle Counter was measuring the size of large aerosol particle and counting the number concentration with laser light scattering method and providing the size distribution in 0.3,0.5,1.0,2.0 and 5.0 micron of diameter with real time series display graphically.

#### 2.1.5.5.4 Results

Information of data and sample obtained are summarized in Table-2. The sky radiometer has been going well owing to more calm and silent condition and circumstances about shivering problems provided by the R/V Mirai whose engines are supported by well defined cushions.

Therefore, measured values will be expected to be considerably stable and provide good calculated parameters in higher quality. However, some noise waves were found to interfere the 16,13 and 12channel marine bands of VHF from sky radiometer. Fortunately the origin and source were identified by using a VHF wide band receiver and the interference waves were kept by fairly separating from two VHF antennae and decreased to recovery of 100%.

Aerosols size distribution of number concentration have been measured by the Particle Counter and data obtained are displayed in real time by a kind of time series *in situ* with 5stages of size range of 0.3, 0.5, 1.0, 2.0, and 5.0 micron in diameter.

#### 2.1.5.5.5 Data archive

This aerosol data by the Particle Counter will be able to be archived soon and anytime. However, the data of other kind of aerosol measurements are not archived so soon and developed, examined, arranged and finally provided as available data after a certain duration. All data will archived at ILTS (Endoh), Hokkaido University, CCSR(Nakajima), University of Tokyo and CEReS (Takamura), Chiba University after the quality check and submitted to JAMSTEC within 3-year.

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## Data inventory Table-1. Information of obtained data inventory ( Method )

| Item, No.dat   | a Name | Instrument                      | Site position      |
|--|--------|---------------------------------|--------------------|
| Optical thickno<br>Ångström expo<br>and Aerosol Si<br>tribution. | onent  | Sky Radiometer(Prede,POM-01MK2) | roof of stabilizer |

#### Table-2. Data and Sample inventory

| Data/Samp        | le rate                      | site                  | object                              | name | state         | remarks           |
|------------------|------------------------------|-----------------------|-------------------------------------|------|---------------|-------------------|
| Sun&Sky<br>Light | 1/5min<br>(fine&<br>daytime) | roof of<br>stabilizer | optical thickness<br>Ångström expt. |      | land analysis | 25/05'05-02/07'05 |

#### 2.1.6 Lidar observations of clouds and aerosols

Nobuo Sugimoto, Ichiro Matsui, Atsushi Shimizu and Akihide Kamei (National Institute for Environmental Studies, not on board), operation was supported by GODI.

#### (1) Objectives

Objectives of the observations in this cruise is to study distribution and optical characteristics of ice/water clouds and marine aerosols using a two-wavelength lidar.

(2) Measured parameters

- · Vertical profiles of backscattering coefficient at 532 nm
- · Vertical profiles of backscattering coefficient at 1064 nm

#### (3) Method

Vertical profiles of aerosols and clouds were measured with a two-wavelength lidar. The lidar employs a Nd:YAG laser as a light source which generates the fundamental output at 1064 nm and the second harmonic at 532 nm. Transmitted laser energy is typically 100 mJ per pulse at 1064 nm and 50 mJ per pulse at 532 nm. The pulse repetition rate is 10 Hz. The receiver telescope has a diameter of 20 cm. The receiver has two detection channels to receive the lidar signals at 1064 nm and the at 532 nm. An analog-mode avalanche photo diode (APD) is used as a detector for 1064 nm, and photomultiplier tubes (PMTs) are used for 532 nm. The detected signals are recorded with a digital oscilloscope and stored on a hard disk with a computer. The lidar system was installed in the

radiosonde container on the compass deck. The container has a glass window on the roof, and the lidar was operated continuously regardless of weather.

#### (4) Results

Data obtained in this cruise has not been analyzed.

#### (5) Data archive

- raw data

lidar signal at 532 nm lidar signal at 1064 nm temporal resolution 15 min. vertical resolution 6 m. data period : May 26, 2005 – July 2, 2005 - processed data

cloud base height, apparent cloud top height cloud fraction boundary layer height (aerosol layer upper boundary height) backscatter coefficient of aerosols

## 2.1.7 Rain Sampling for Stable Isotopes

#### Kimpei Ichiyanagi (JAMSTEC) (Not on board)

#### (1) Objective

To determine rain water sources using a technique of stable isotope analysis

(2) Method

Rain water samples are collected in 6cc glass bottle with plastic cap. Stable isotopic composition for hydrogen and oxygen in water is determined by the Isotope Ratio Mass Spectrometry (IRMS). The IRMS used in this study is Finnigan MAT252 (Thermo Quest K. K.) with CO2 & H2 equilibration device.

(3) Preliminary results

During this cruise, we collect 32 samples in total. Table 2.1.7-1 lists the date and location of rain water samples. Analysis will be done after the cruise.

(4) Data archive

Original samples will be analyzed by IORGC. Inventory and analyzed digital data will be submitted to JAMSTEC Data Management Office.

| Sample No. | Date (UTC)          | Location (lat, lon) |
|------------|---------------------|---------------------|
| 01         | 07:02, May 27, 2005 | 42-00N, 143-55E     |
| 02         | 01:50, May 28, 2005 | 41-03N, 144-39E     |
| 03         | 23:20, May 30, 2005 | 38-17N, 146-43E     |
| 04         | 21:30, May 31, 2005 | 37-46N, 146-53E     |
| 05         | 19:40, Jun 2, 2005  | 36-00N, 148-08E     |
| 06         | 03:50, Jun 3, 2005  | 35-44N, 148-19E     |
| 07         | 22:40, Jun 3, 2005  | 34-59N, 148-44E     |
| 08         | 11:48, Jun 4, 2005  | 34-29N, 149-02E     |
| 09         | 21:55, Jun 4, 2005  | 34-00N, 149-19E     |
| 10         | 05:48, Jun 5, 2005  | 33-45N, 149-21E     |
| 11         | 21:00, Jun 5, 2005  | 32-51N, 149-20E     |
| 12         | 10:39, Jun 6, 2005  | 32-11N, 149-19E     |
| 13         | 21:40, Jun 6, 2005  | 31-10N, 149-20E     |
| 14         | 06:58, Jun 7, 2005  | 30-30N, 149-20E     |
| 15         | 20:10, Jun 12, 2005 | 21-09N, 149-20E     |
| 16         | 05:16, Jun 17, 2005 | 12-28N, 149-19E     |
| 17         | 08:37, Jun 18, 2005 | 09-43N, 149-20E     |
| 18         | 12:14, Jun 18, 2005 | 09-43N, 149-20E     |
| 19         | 11:50, Jun 19, 2005 | 07-52N, 149-06E     |
| 20         | 14:15, Jun 19, 2005 | 07-30N, 149-00E     |
| 21         | 23:58, Jun 19, 2005 | 06-31N, 148-29E     |
| 22         | 00:40, Jun 20, 2005 | 06-31N, 148-29E     |
| 23         | 22:27, Jun 20, 2005 | 04-30N, 147-39E     |
| 24         | 09:50, Jun 21, 2005 | 03-31N, 147-13E     |
| 25         | 23:52, Jun 21, 2005 | 02-30N, 146-52E     |
| 26         | 03:34, Jun 22, 2005 | 02-26N, 146-51E     |
| 27         | 15:46, Jun 22, 2005 | 01-49N, 146-40E     |
| 28         | 11:44, Jun 23, 2005 | 01-00N, 146-26E     |
| 29         | 21:53, Jun 26, 2005 | 02-45S, 145-22E     |
| 30         | 04:06, Jun 27, 2005 | 03-02S, 145-16E     |
| 31         | 05:07, Jun 27, 2005 | 03-08S, 145-14E     |
| 32         | 20:10, Jun 27, 2005 | 03-53S, 144-54E     |
|            | , ,                 | ,                   |

## Table 2.1.7-1Dates and locations to show when and where rain water were sampled.

#### 2.2.1 Navigation

| Yasutaka Imai  | (Global Ocean Development Inc.) |
|----------------|---------------------------------|
| Shinya Okumura | (Global Ocean Development Inc.) |
| Ryo Ohyama     | (Global Ocean Development Inc.) |

<u>Navigation:</u> Ship's position was measured by navigation system, made by Sena Co. Ltd, Japan. The system has two 12-channel GPS receivers (Leica MX9400N). GPS antennas located at Navigation deck, offset to starboard and portside, respectively. We switched them to choose better state of receiving when the number of GPS satellites decreased or HDOP increased. But the system sometimes lost the position while the receiving status became worse. The system also integrates gyro heading (Tokimec TG-6000), log speed (Furuno DS-30) and other navigation devices data on HP workstation. The workstation keeps accurate time using GPS Time server (Datum Tymserv2100) via NTP(Network Time Protocol). Navigation data was recorded as "SOJ" data every 60 seconds. The periods of losing the position are described in "Readme" file attached to SOJ data.

#### 2.2.2 Bathymetry

| Takeshi Matsumoto | <i>o</i> ( <i>Ryukyu Univ.</i> ) <i>Principal Investigator / Not on-board:</i> |
|-------------------|--|
| Yasutaka Imai     | (Global Ocean Development Inc.)  |
| Shinya Okumura    | (Global Ocean Development Inc.)  |
| Ryo Ohyama        | (Global Ocean Development Inc.)  |

Bathymetry: R/V MIRAI equipped a Multi Narrow Beam Echo Sounding system (MNBES), SEABEAM 2112.004 (SeaBeam Instruments Inc.) The main objective of MNBES survey is collecting continuous bathymetry data along ship's track to make a contribution to geological and geophysical investigations and global datasets. We carried out bathymetric survey during the MR05-02 cruise from CTD station P10N-143 on 26 May 2005 to CTD station P10-001 on 28 January 2005. Data interval along ship's track was max 17 seconds at 6,000 m. To get accurate sound velocity of water column for ray-path correction of acoustic multibeam, we used Surface Sound Velocimeter (SSV) data at the surface (6.2m) sound velocity, and the others depth sound velocity was calculated using temperature and salinity profiles from the nearest CTD data by the equation in Mackenzie (1981).

| System configuration and performan | ce of SEABEAM 2112.004, |
|------------------------------------|-------------------------|
| Frequency:                         | 12 kHz                  |
| Transmit beam width:               | 2 degree                |
| Transmit power:                    | 20 kW                   |
| Transmit pulse length:             | 3 to 20 msec.           |

| Transmit pulse length: | 3 to 20 msec.                                       |
|------------------------|---|
| Depth range:           | 100 to 11,000 m                                     |
| Beam spacing:          | 1 degree athwart ship                               |
| Swath width:           | 150 degree (max)                                    |
|                        | 120 degree to 4,500 m                               |
|                        | 100 degree to 6,000 m                               |
|                        | 90 degree to 11,000 m                               |
| Depth accuracy:        | Within $< 0.5\%$ of depth or $+/-1m$ , whichever is |
|                        | greater, over the entire swath.                     |
|                        | (Nadir beam has greater accuracy; typically within  |
|                        | < 0.2% of depth or +/-1m, whichever is greater)     |



Figure. 2.2.2-1 Depth of CTD line

# 2.2.3 Sea surface gravity Personnel

| Takeshi Matsumoto | (Ryukyu Univ.) Principal Investigator / Not on-board: |
|-------------------|---|
| Yasutaka Imai     | (Global Ocean Development Inc.)                       |
| Shinya Okumura    | (Global Ocean Development Inc.)                       |
| Ryo Ohyama        | (Global Ocean Development Inc.)                       |

#### Introduction

The difference of local gravity is an important parameter in geophysics and geodesy. We collected gravity data at the sea surface during the MR05-02 cruise from 25 May 2005 to 30 June 2005.

#### Parameters

Relative Gravity [mGal]

#### **Data Acquisition**

We have measured relative gravity using LaCoste and Romberg air-sea gravity system (LaCosat and Romberg Gravity Meters, Inc.) during this cruise. To convert the relative gravity to absolute one, we measured gravity, using portable gravity meter (Scintrex gravity meter CG-5M), at Sekinehama as reference points.

#### **Preliminary Results**

Absolute gravity shown in Table 2.2.3-1

| No. | Date        | UTC   | Port       | Absolute<br>Gravity | Sea<br>Level | Draft | Gravity<br>at Sensor *1 | L&R *2   |
|-----|-------------|-------|------------|---------------------|--------------|-------|-------------------------|----------|
|     |             |       |            | (mGal)              | (cm)         | (cm)  | (mGal)                  | (mGal)   |
| 1   | 2005/May/25 | 03:52 | Sekinehama | 98064.344           | 316          | 615   | 98065.36                | 12726.63 |
| 3   | 2005/Jul/3  | 00:03 | Guam       | -                   | 212          | 645   | -                       | 10852.17 |

#### Table 2.2.3-1

\*1: Gravity at Sensor= Absolute Gravity + Sea Level\*0.3086/100 + (Draft-530)/100\*0.0431

\*2: LaCoste and Romberg air-sea gravity system

#### **Data Archives**

Gravity data obtained during this cruise will be submitted to the JAMSTEC Data Management Division, and archived there.

#### Remarks

We did not collect data from 28 Jun 2005 00:40UTC to 28 Jun 2005 03:17UTC, due to the territorial waters of Papua New Guinea.

#### 2.2.4 On-board geomagnetic measurement

#### Personnel

| Takeshi Matsumoto | (Ryukyu Univ.) Principal Investigator / Not on-board: |
|-------------------|---|
| Yasutaka Imai     | (Global Ocean Development Inc.)                       |
| Shinya Okumura    | (Global Ocean Development Inc.)                       |
| Ryo Ohyama        | (Global Ocean Development Inc.)                       |

#### Introduction

Measurements of magnetic force on the sea are required for the geophysical investigations of marine magnetic anomaly caused by magnetization in upper crustal structure. We measured geomagnetic field using a three-component magnetometer during the MR05-02 cruise from 25 May 2005 to 30 June 2005.

#### Instruments on R/V Mirai

A shipboard three-component magnetometer system (Tierra Tecnica SFG1214) is equipped on-board R/V Mirai. Three-axis flux-gate sensors with ring-cored coils are fixed on the fore mast. Outputs of the sensors are digitized by a 20-bit A/D converter (1 nT/LSB), and sampled at 8 times per second. Ship's heading, pitch and roll are measured utilizing a ring-laser gyro installed for controlling attitude of a Doppler radar. Ship's position (GPS) and speed data are taken from LAN every second.

#### **Data Archives**

Magnetic force data obtained during this cruise will be submitted to the JAMSTEC Data Management Division, and archived there.

#### Remarks

1. We did not collect data from 28 Jun 2005 00:40UTC to 28 Jun 2005 03:17UTC, due to the territorial waters of Papua New Guinea.

 We collected the data for calibration following period. 12 Jun. 2005 04:52 – 05:19 UTC

#### 2.3 Acoustic Doppler Current Profiler (ADCP)

Yasushi Yoshikawa (JAMSTEC) Shinya Kouketsu (JAMSTEC) Yasutaka Imai (GODI) Shinya Okumura (GODI) Ryo Ohyama (GODI)

#### (1) Instruments and method

The instrument used was an RDI 76.8kHz unit, hull-mounted on the centerline and approximately 23m aft of the bow at the water line. On this cruise the firmware version was 5.59 and the data acquisition software was the RDI VMDAS Ver. 1.4. Operation was made from the first CTD station to the last CTD station. The instrument was used in the water-tracking mode during the most of operations, recording each ping raw data in 90 x 5m bins from about 23m to 735m in deep. Typical sampling interval was 3.5 seconds. Bottom track mode was added in the northernmost shallow water region. GPS gave the navigation data. Two kinds of compass data were recorded. One was the ship's gyrocompass which is connected the ADCP system directory and stored with the ADCP data. Current field based on the gyrocompass was used to check the operation and performance on board. Another compass used was the Inertial Navigation Unit (INU), DRU-H, Honeywell Inc. Its accuracy is 1.0mile (about 0.056degree) and had already set on zero bias before the beginning of the cruise. The INU compass data were stored independently, and will be combined with the ADCP data after the cruise.

The performance of the ADCP instrument was almost good throughout the cruise: on streaming, profiles usually reached to about 600m (652384pings of all 953103pings till Jun, 27). Profiles were rather bad on CTD station. The profiles did not reach so far, from 200m to 500m and the ADCP signal was weak typically at about 350m in deep. It is probably due to the babbles from the bow-thruster. Echo intensity was relatively weak in the sea south of 35N in the subtropical and tropical North Pacific.

#### (2) Data Processing

We processed ADCP data on this cruise as described below.

ADCP-coordinate velocities were converted to the earth-coordinate velocities using the ship heading, roll and pitch data form the INU. The earth-coordinate currents were obtaind by subtracting ship velocities from the earth-coordinate velocities. The ship velocities were obtained between the moving distance for 5minites, which were obtained GPS data. The noise of the position data of GPS were filtered out by 15-sec running mean. The errors of the estimated ship velocities are with in 10cm/s. The currents obtained on this cruise are shown in Figure 3.2.1 (shown at the depths of about 100, 200, and 500m).

After this cruise the parameters of the misalignment and scale factor will be evaluated by using the bottom track data obtained both in this cruise and in the engineering test cruise made just before this cruise. Depth correction will be made using the CTD data. We will make composite current field and show error estimation there. The ADCP data set will give two types of profiles: mean profiles at each CTD station and mean profiles on streaming between CTD stations.





#### 2.4 Thermo-salinograph

Takayoshi SEIKE<sup>1)</sup> and Takeshi KAWANO<sup>2)</sup> 1) Marine Works Japan Co. Ltd. 2) IORGC/JAMSTEC

#### (1) Objective

To measure salinity, temperature, dissolved oxygen, and fluorescence of near-sea surface water.

#### (2) Methods

The Continuous Sea Surface Water Monitoring System (Nippon Kaiyo Co. Ltd.) has six

kind of sensors and can automatically measure salinity, temperature, dissolved oxygen, fluorescence and particle size of plankton in near-sea surface water continuously, every 1-minute. This system is located in the "*sea surface monitoring laboratory*" on R/V MIRAI. This system is connected to shipboard LAN-system. Measured data is stored in a hard disk of PC every 1-minute together with time and position of ship, and displayed in the data management PC machine.

Near-surface water was continuously pumped up to the laboratory and flowed into the *Continuous Sea Surface Water Monitoring System* through a vinyl-chloride pipe. The flow rate for the system is controlled by several valves and was 12L/min except for fluorometer (about 0.3L/min). The flow rate is measured with two flow meters.

Specification of the each sensor in this system of listed below.

a) Temperature and Salinity sensor

SEACAT THERMOSALINOGRAPH

| Model:             | SBE-21, SEA-BIRD          | ELECTRON  | ICS, INC.                   |
|--------------------|---------------------------|-----------|-----------------------------|
| Serial number:     | 2126391-2641              |           |                             |
| Measurement range: | Temperature -5 to $+35$ , |           | Salinity0 to 6.5 S m-1      |
| Accuracy:          | Temperature 0.01          | 6month-1, | Salinity0.001 S m-1 month-1 |
| Resolution:        | Temperatures 0.001        | ,         | Salinity0.0001 S m-1        |

#### b) Bottom of ship thermometer

| Model:             | SBE 3S, SEA-BIRD ELECTRONICS, INC. |
|--------------------|------------------------------------|
| Serial number:     | 032175                             |
| Measurement range: | -5 to +35                          |
| Resolution:        | ± 0.001                            |
| Stability:         | 0.002 year-1                       |
|                    |                                    |

#### c) Dissolved oxygen sensor

| Model:             | 2127A, HAC       | H ULTRA ANALYTICS JAPAN, INC. |
|--------------------|------------------|-------------------------------|
| Serial number:     | 44733            |                               |
| Measurement range: | 0 to 14 ppm      |                               |
| Accuracy:          | <b>±</b> 1% at 5 | of correction range           |
| Stability:         | 1% month-1       |                               |

#### d) Fluorometer

| Model:           | 10-AU-005, TURNER DESIGNS       |
|------------------|---------------------------------|
| Serial number:   | 5562 FRXX                       |
| Detection limit: | 5 ppt or less for chlorophyll a |
| Stability:       | 0.5% month-1 of full scale      |

#### e) Particle Size sensor

| Model:             | P-05, Nippon Kaiyo LTD. |
|--------------------|-------------------------|
| Serial number:     | P5024                   |
| Measurement range: | 0.2681 mm to 6.666 mm   |
| Accuracy:          | ± 10% of range          |

| Reproducibility: | <b>±</b> 5% |
|------------------|-------------|
| Stability:       | 5% week-1   |

f) Flow meter

| Model:             | EMARG2W, Aichi Watch Electronics LTD. |
|--------------------|---------------------------------------|
| Serial number:     | 8672                                  |
| Measurement range: | 0 to 30 l min-1                       |
| Accuracy:          | ±1%                                   |
| Stability:         | ±1% day-1                             |

The monitoring Periods (UTC) during this cruise are listed below. 26-Mar-05 13:31 to 30-Jun-05 02:45

#### (4) Preliminary Result

Preliminary data of temperature (Bottom of ship thermometer), salinity at sea surface during this cruise are shown in Fig. 1, 2. They show the respective trend of each distribution on the ship's track every ten minutes.

We sampled about twice a day for salinity sensor calibration. All salinity samples were collected from the course of the system while on station or from regions with weak horizontal gradients. All samples were analyzed on the Guildline 8400B. The results were shown in Table 1.



Fig.1 Time series of temperature in the sea surface water.


Fig.2 Time series of salinity in the sea surface water.

 Table.1 Comparison between salinity data from Continuous Sea Surface Water Monitoring and bottle salinity.

| bottle samily. |            |               |                          |
|----------------|------------|---------------|--------------------------|
| Date [UTC]     | Time [UTC] | Salinity data | Bottle Salinity [PSS-78] |
| 27-Mar-05      | 22:52      | 32.9296       | 32.9317                  |
| 28-Mar-05      | 12:36      | 33.6424       | 33.6306                  |
| 28-Mar-05      | 22:55      | 33.3806       | 33.3756                  |
| 29-Mar-05      | 06:12      | 33.6521       | 33.6319                  |
| 29-Mar-05      | 22:46      | 33.3896       | 33.3984                  |
| 30-Mar-05      | 18:49      | 34.5657       | 34.5776                  |
| 30-Mar-05      | 22:54      | 34.4765       | 34.4939                  |
| 31-Mar-05      | 04:22      | 34.5199       | 34.5350                  |
| 31-Mar-05      | 22:40      | 34.4629       | 34.4929                  |
| 1-JUN-05       | 12:36      | 34.4079       | 34.4531                  |
| 1-JUN-05       | 22:51      | 34.4860       | 34.5147                  |
| 2-JUN-05       | 05:02      | 34.4708       | 34.4911                  |
| 3-JUN-05       | 02:53      | 34.5825       | 34.6117                  |
| 3-JUN-05       | 09:01      | 34.5986       | 34.6273                  |
| 4-JUN-05       | 02:47      | 34.6163       | 34.6446                  |
| 5-JUN-05       | 02:38      | 34.6549       | 34.6750                  |
| 5-JUN-05       | 15:56      | 34.6632       | 34.6873                  |
| 6-JUN-05       | 02:31      | 34.4601       | 34.5024                  |
| 6-JUN-05       | 15:43      | 34.3304       | 34.3552                  |
| 7-JUN-05       | 02:36      | 34.3558       | 34.3859                  |

| 7-JUN-05  | 16:51 | 34.8104 | 34.8351 |
|-----------|-------|---------|---------|
| 8-JUN-05  | 02:40 | 34.5198 | 34.5394 |
| 8-JUN-05  | 18:19 | 34.8639 | 34.8893 |
| 9-JUN-05  | 02:48 | 34.4874 | 34.5868 |
| 9-JUN-05  | 15:44 | 34.7581 | 34.8940 |
| 10-JUN-05 | 02:42 | 35.0075 | 35.0049 |
| 10-JUN-05 | 15:24 | 34.9980 | 35.0406 |
| 11-JUN-05 | 02:30 | 34.6205 | 34.6298 |
| 12-JUN-05 | 08:20 | 34.5390 | 34.5625 |
| 12-JUN-05 | 14:32 | 34.5394 | 34.5688 |
| 13-JUN-05 | 00:17 | 34.5725 | 34.6049 |
| 13-JUN-05 | 14:34 | 34.9744 | 35.0077 |
| 14-JUN-05 | 04:12 | 34.7980 | 34.8137 |
| 14-JUN-05 | 14:48 | 34.8969 | 34.9322 |
| 15-JUN-05 | 03:32 | 34.5539 | 34.5324 |
| 15-JUN-05 | 14:49 | 34.4052 | 34.4381 |
| 16-JUN-05 | 01:33 | 34.4143 | 34.4526 |
| 16-JUN-05 | 14:43 | 34.4642 | 34.5038 |
| 17-JUN-05 | 02:51 | 34.2650 | 34.3030 |
| 17-JUN-05 | 14:47 | 34.4193 | 34.4256 |
| 18-JUN-05 | 00:59 | 34.1001 | 34.1407 |
| 18-JUN-05 | 14:46 | 33.9444 | 33.9876 |
| 19-JUN-05 | 00:47 | 33.8548 | 33.8967 |
| 19-JUN-05 | 14:28 | 33.8954 | 33.9374 |
| 20-JUN-05 | 00:37 | 33.9928 | 34.0371 |
| 20-JUN-05 | 14:29 | 33.9209 | 33.9624 |
| 21-JUN-05 | 02:56 | 33.9359 | 33.9764 |
| 21-JUN-05 | 14:48 | 33.9013 | 33.9045 |
| 22-JUN-05 | 01:18 | 33.8159 | 33.9168 |
| 22-JUN-05 | 14:47 | 34.1404 | 34.2044 |
| 23-JUN-05 | 00:52 | 34.2102 | 34.2569 |
| 23-JUN-05 | 14:32 | 34.2208 | 34.2785 |
| 24-JUN-05 | 01:01 | 33.9716 | 34.0119 |
| 24-JUN-05 | 12:51 | 34.1161 | 34.1624 |
| 25-JUN-05 | 00:35 | 34.1160 | 34.1664 |
| 25-JUN-05 | 14:45 | 34.0914 | 34.1350 |
| 26-JUN-05 | 00:26 | 34.0454 | 34.1016 |
| 26-JUN-05 | 15:21 | 34.2297 | 34.2773 |
| 27-JUN-05 | 04:11 | 34.1533 | 34.1756 |
| 27-JUN-05 | 14:38 | 34.1362 | 34.2077 |
|           | •     |         |         |

# (4) Date archive

The data were stored on a magnetic optical disk, which will be submitted to the Data Management Office (DMO) JAMSTEC, and will be opened to public via "R/V MIRAI Data Web Page " in JAMSTEC homepage.

2.5. pCO<sub>2</sub> Akihiko Murata (JAMSTEC) Fuyuki Shibata (MWJ) Mikio Kitada (MWJ) Taeko Ohama (MWJ) Yoshiko Ishikawa (MWJ)

## 2.5.1 Objective

Concentrations of  $CO_2$  in the atmosphere are now increasing at a rate of 1.5 ppmv y<sup>-1</sup> owing to human activities such as burning of fossil fuels, deforestation, and cement production. It is an urgent task to estimate as accurately as possible the absorption capacity of the oceans against the increased atmospheric  $CO_2$ , and to clarify the mechanism of the  $CO_2$  absorption, because the magnitude of the anticipated global warming depends on the levels of  $CO_2$  in the atmosphere, and because the ocean currently absorbs 1/3 of the 6 Gt of carbon emitted into the atmosphere each year by human activities.

In this cruise, we wee aimed at quantifying how much anthropogenic  $CO_2$  is absorbed in the surface ocean in the North Pacific For the purpose, we measured  $pCO_2$  (partial pressures of  $CO_2$ ) in the atmosphere and surface seawater.

#### 2.5.2 Apparatus and performance

Concentrations of  $CO_2$  in the atmosphere and the sea surface were measured continuously during the cruise using an automated system with a non-dispersive infrared (NDIR) analyzer (BINOS<sup>TM</sup>). The automated system was operated by on one and a half hour cycle. In one cycle, standard gasses, marine air and an air in a headspace of an equilibrator were analyzed subsequently. The concentrations of the standard gas were 262.95, 320.44, 381.03 and 420.75 ppm. The standard gases will be recalibrated after the cruise.

The marine air taken from the bow is introduced into the NDIR by passing through a mass flow controller which controls the air flow rate at about 0.5 L/min, a cooling unit, a perma-pure dryer (GL Sciences Inc.) and a desiccant holder containing  $Mg(ClO_4)_2$ .

A fixed volume of the marine air taken from the bow is equilibrated with a stream of seawater that flows at a rate of 5-6L/min in the equilibrator. The air in the equilibrator is circulated with a pump at 0.7-0.8L/min in a closed loop passing through two cooling units, a perma-pure dryer (GL Science Inc.) and a desiccant holder containing  $Mg(ClO_4)_2$ .

## 2.5.3 Results

Concentrations of  $CO_2$  (xCO<sub>2</sub>) of marine air and surface seawater are shown in Fig. 1. From this figure, it is found that the ocean acted as a sink for atmospheric  $CO_2$  during the former half period of the cruise. However, it acted as a source for or almost equilibrated with atmospheric  $CO_2$  during the latter half period.



Date (UTC)

Figure 1. Temporal changes of concentrations of  $CO_2$  ( $xCO_2$ ) in atmosphere (green) and surface seawater (blue), and SST (red).

# 3. Hydrography

## 3.1 CTD/O<sub>2</sub> Measurements (2 July 2005)

Hiroshi Uchida, Masao Fukasawa (JAMSTEC), Satoshi Ozawa, Naoko Takahashi, Kentaro Oyama and Tomohide Noguchi (MWJ)

## 3.1.1 Winch arrangements

The CTD package was deployed using 4.5 Ton Traction Winch System (Dynacon, Inc., USA), which was installed on the R/V Mirai in April 2001. 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 (Ocean Cable and Communication Co.), 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.

### 3.1.2 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 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 were 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 and fluorometer, were also used with the SBE 9plus underwater unit. The SBE 35 position in regard to the SBE 3 is shown in Figure 3.1.1.

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 ( $54 \times 90$  cm) was attached to the frame (Figure 3.1.1).

## Summary of the system used in this cruise

Deck unit: SBE, Inc., SBE 11plus, S/N 0308 Under water unit:

SBE, Inc., SBE 9plus, S/N 79511 (Pressure sensor: S/N 0677) Temperature sensor: SBE, Inc., SBE 3, S/N 1464 (primary) SBE, Inc., SBE 3, S/N 1525 (secondary) Conductivity sensor: SBE, Inc., SBE 4, S/N 1203 (primary) SBE, Inc., SBE 4, S/N 3036 (secondary, from P10N\_143 to P10\_53) SBE, Inc., SBE 4, S/N 1088 (secondary, from P10\_52 to P10\_27) SBE, Inc., SBE 4, S/N 2854 (secondary, from P10\_26 to P10\_1) Oxygen sensor: SBE, Inc., SBE 43, S/N 0391 (primary, from P10N\_143 to P10N\_122) SBE, Inc., SBE 43, S/N 0767 (primary, from P10N\_121 to P10\_1) SBE, Inc., SBE 43, S/N 0390 (secondary) Pump: SBE, Inc., SBE 5T, S/N 3118 (primary) SBE, Inc., SBE 5T, S/N 3293 (secondary) Altimeter: Benthos Inc., PSA-916T, S/N 1157 Deep Ocean Standards Thermometer: SBE, Inc., SBE 35, S/N 0045 Fluorometer: Seapoint sensors, Inc., S/N 2579 (without fluorometer from P10N\_134 to132, P10N\_112 to P10\_68, and P10\_28 to 1) Carousel Water Sampler: SBE, Inc., SBE 32, S/N 0278 Water sample bottle: General Oceanics, Inc., 12-litre Niskin-X (no TEFLON coating)



Figure 3.1.1. The CTD package (left) and the SBE 35 position in regard to the SBE 3 temperature sensors (right).

## 3.1.3 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 0677, 2 July 2002
```

```
c_1 = -62072.94
c_2 = -1.176956
c_3 = 1.954420e-02
d_1 = 0.027386
d_2 = 0.0
t_1 = 30.05031
t_2 = -4.744833e-04
t_3 = 3.757590e-06
t_4 = 3.810700e-09
t_5 = 0.0
```

Pressure coefficients are first formulated into

$$\begin{split} c &= c_1 + c_2 * U + c_3 * U^2 \\ d &= d_1 + d_2 * U \\ t_0 &= t_1 + t_2 * U + t_3 * U^2 + t_4 * U^3 + t_5 * U^4 \end{split}$$

where U is temperature in degrees Celsius. The pressure temperature, U, is determined according to

 $U(^{\circ}C) = M * (12 \text{ bit pressure temperature compensation word}) - B$ The following coefficients were used in SEASOFT:

S/N 0677

M = 0.0128041B = -9.324136

(in the underwater unit system configuration sheet dated on 22 February 2002) Finally, pressure is computed as

P (psi) = c \*  $[1 - (t_0^2 / t^2)] * \{1 - d * [1 - (t_0^2 / t^2)]\}$ 

where t is pressure period ( $\mu$ sec). 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 be primarily an offset drift at all pressures rather

than a change of span slope. The pressure sensor hysterisis is typically 0.2 dbar. The following coefficients for the sensor drift correction were also used in SEASOFT through the software module SEACON:

*S/N 0677, 13 April 2005* slope = 0.9998953 offset = -0.44425

The drift-corrected pressure is computed as

Drift-corrected pressure (dbar) = slope \* (computed pressure in dbar) + offset Result of the pressure sensor calibration against the dead weight piston gauge is shown in Figure 3.1.2. Time drift of the pressure sensor based on the offset and the slope of the calibrations is also shown in Figure 3.1.3.



Figure 3.1.2. The residual pressures between the dead weight piston gauge and the CTD pressure (S/N 0677). Black line indicates the residual between the dead weight piston gauge and the calibration line for the CTD pressure.



Figure 3.1.3. Pressure sensor (S/N 0677) time drift of offset (upper panel) and slope (lower panel) based on laboratory calibrations.

## (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 °C. 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 3 thermometer has a nominal accuracy of 0.001 °C, typical stability of 0.0002 °C/month and resolution of 0.0002 °C at 24 samples per second. The premium temperature sensor, SBE 3plus, is a more rigorously tested and calibrated version of standard temperature sensor (SBE 3). A sensor is designated as an SBE 3plus only after demonstrating drift of less than 0.001 °C during a six-month screening period. In addition, the time response is carefully measured and verified to be 0.065  $\pm$  0.010 seconds.

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

S/N 1464 (primary), 19 April 2005 g = 4.84385804e-03 h = 6.80766786e-04 i = 2.69831319e-05 j = 2.13061451e-06  $f_0 = 1000.000$  S/N 1525 (secondary), 19 April 2005 g = 4.84608198e-03h = 6.75358139e-04 i = 2.65523364e-05 j = 2.13525896e-06 $f_0 = 1000.000$ 

Temperature (ITS-90) is computed according to

Temperature (ITS-90) =

 $1 \; / \; \{g + h \; \ast \; [\ln(f0 \; / \; f)] + i \; \ast \; [\ln^2(f0 \; / \; f)] + j \; \ast \; [\ln^3(f_0 \; / \; f)] \} - 273.15$ 

where f is the instrument frequency (kHz).

Time drift of the SBE 3 temperature sensors based on the laboratory calibrations is shown in Figure 3.1.4.



Figure 3.1.4. Time drift of SBE 3 temperature sensors (S/N 1464 and S/N 1525) 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:

S/N 1203 (primary), 19 April 2005 g = -4.05393563e+00 h = 4.93901550e-01 i = 1.74707654e-05 j = 2.56674141e-05CPcor = -9.57e-08 (nominal)

```
CTcor = 3.25e-06 (nominal)
S/N 3036 (secondary), 20 January 2005
         g = -1.03104164e+01
         h = 1.42680631e+00
         i = 2.61243729e-04
         j = 5.17689837e - 05
         CPcor = -9.57e-08 (nominal)
         CTcor = 3.25e-06 (nominal)
S/N 1088 (secondary), 10 March 2005
         g = -4.21020837e + 00
         h = 5.77013782e-01
         i = -1.87512042e - 04
         j = 4.10775826e - 05
         CPcor = -9.57e - 08 (nominal)
         CTcor = 3.25e-06 (nominal)
S/N 2854 (secondary), 22 June 2004
         g = -1.02670783e + 01
         h = 1.41649193e+00
         i = -3.19882205e-04
         i = 7.82222198e-05
         CPcor = -9.57e-08 (nominal)
         CTcor = 3.25e-06 (nominal)
```

Conductivity of a fluid in the cell is expressed as:

C (S/m) = (g + h \* f<sup>2</sup> + i \* f<sup>3</sup> + j \* f<sup>4</sup>) / [10 (1 + CTcor \* t + CPcor \* p)]

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

## (4) 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 hysterisis is largely eliminated in the upper ocean (1,000 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. The oxygen 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 1,000 hours.

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

S/N 0391 (primary), 8 April 2005 Soc = 0.3525

```
Offset = -0.4761
          TCor = 0.0010
          PCor = 1.350e - 04
S/N 0767 (primary), 11 February 2005
          Soc = 0.4320
          Offset = -0.4889
          TCor = 0.0002
          PCor = 1.350e - 04
S/N 0390 (secondary), 8 April 2005
          Soc = 0.3567
          Offset = -0.4965
          TCor = 0.0013
          PCor = 1.350e - 04
Oxygen (ml/l) is computed as
          Oxygen (ml/l) = {Soc * (v + Offset)} * exp(TCor * t + PCor * p) * Oxsat(t, s)
          Oxsat(t, s) = exp[A_1 + A_2 * (100 / t) + A_3 * ln(t / 100) + A_4 * (t / 100)
                    + s * \{B_1 + B_2 * (t / 100) + B_3 * (t / 100) * (t / 100)\}\}
          A_1 = -173.4292
          A_2 = 249.6339
          A_3 = 143.3483
          A_4 = -21.8482
          B_1 = -0.033096
          B_2 = -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.

## (5) 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.

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  $\mu$ watts, and contributes less than 200  $\mu$ K 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  $\mu$ K. 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., USA. The following coefficients were stored in EEPROM:

S/N 0045, 27 October 2002 (1st step: linearization)

 $a_0 = 5.84093815e-03$  $a_1 = -1.65529280e-03$ 

 $a_1 = 1.035222000 = 03$  $a_2 = 2.37944937e - 04$ 

 $a_3 = -1.32611385e-05$ 

 $a_4 = 2.83355203e - 07$ 

Linearized temperature (ITS-90) is computed according to

Linearized temperature (ITS-90) =

 $1 / \{a_0 + a_1 * [\ln(n)] + a_2 * [\ln^2(n)] + a_3 * [\ln^3(n)] + a_4 * [\ln^4(n)]\} - 273.15$ 

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 0045, 6 May 2005 (2nd step: fixed point calibration)

Slope = 1.000019

Offset = -0.000881

Temperature (ITS-90) is calibrated according to

Temperature (ITS-90) = Slope \* Linearized temperature + 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. Root mean square (rms) temperature noise for a SBE 35 in a Triple Point of Water cell is typically expressed as  $82 / NCYCLES^{1/2}$  in  $\mu K$ . In this cruise NCYCLES was set to 4 and the rms noise is estimated to be 0.04 m°C.

When using the SBE 911 system with SBE 35, the deck unit receives incorrect signal from the under water unit for confirmation of firing bottle #16. In order to correct the signal, a module (Yoshi Ver. 1, EMS Co. Ltd., JAPAN) was used between the under water unit and the deck unit.

Time drift of the SBE 35 based on the fixed point calibrations is shown in Figure 3.1.5.



Figure 3.1.5. SBE35 (S/N 0045) time drift based on laboratory fixed point calibrations (triple point of water, TPW and gallium melt point, GaMP) performed by SBE, Inc.

## (6) Altimeter

The Benthos PSA-916T Sonar Altimeter (Benthos, Inc., USA) determines the distance of the target from the unit by generating a narrow beam acoustic pulse and measuring the travel time for the pulse to bounce back from the target surface. The PSA-916T is the same as the standard PSA-916 Sonar Altimeter except it is housed in a corrosion-resistant titanium pressure case. It is O-ring-sealed and rated for operation in water depths up to 10,000 meters. In this unit, a 250 microseconds pulse at 200 kHz is transmitted 5 times in a second. The PSA-916T uses the nominal speed of sound of 1,500 m/s. Thus the unit itself, neglecting variations in the speed of sound, can be considered accurate to 5 % or 0.1 meter, whichever is greater. In the PSA-916T the jitter of the detectors is approximately 5 microseconds or +/- 0.4 cm total distance. Since the total travel time is divided by two, the jitter error is +/- 0.2 cm.

The following scale factors were used in SEASOFT:

```
S/N 1157
```

FSVolt \* 300 / FSRange = 15 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:

S/N 2579

Gain = 30 Offset = 0.0 Chlorophyll-a concentration is computed as Chlorophyll-a (µg/l) = (Voltage \* 30 / Gain) + Offset

## 3.1.4 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 Deep Ocean Standards Thermometer, altimeter and fluorometer. The SBE 9plus CTD (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 1.0 m/s to 200 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 1.2 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 multi-narrow beam sounder on board. For the up cast, the package was lifted at a rate of 1.0 m/s except for bottle firing stops. At each bottle firing stops, the bottle was fired 30 seconds after the stop and the package was stayed 5 seconds in order to sample temperature by the Deep Ocean Standards Thermometer. At 200 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 Nisken-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 data acquisition software. Temperature, conductivity, salinity, oxygen and descent rate profiles were displayed in real-time with the package depth and altimeter reading. Temperature, salinity and oxygen difference between primary and secondary sensor were also displayed in order to monitor the status of the sensors.

## Data acquisition software

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

## (2) Data collection problems

At station P10N\_142, bottle #1 was not fired at the beginning of the up cast. The cast was aborted and the Y-cable was replaced.

At station P10N\_137, the primary temperature showed abnormal values at depths between 450 and 430 dbar in the up cast. The connecting cable and connector for the primary temperature sensor was checked and cleaned.

At station P10N\_122, the primary oxygen sensor was replaced because the difference between the sensor output and the bottle oxygen was gradually becoming greater (40  $\mu$ mol/kg near bottom).

At station P10N\_113, the primary temperature data was slightly noisy during up cast. And at station P10N\_112, the primary temperature signal was lost near bottom. The connecting cable for the temperature sensor was replaced after the cast.

At station P10N\_101 and 100, the secondary temperature and conductivity were very noisy from the up cast of P10N\_101 because of something in the secondary TC duct. The TC duct was well flushed after the cast.

At station P10\_62, the CTD signal was lost at 1,270 dbar in the down cast and the cast was aborted. The second cast was carried out after re-connecting the armored cable and pigtail.

At station P10\_53, the secondary conductivity was abnormally biased near bottom. The conductivity sensor was replaced after the cast.

At station P10\_27, the secondary conductivity was abnormally biased near bottom. The conductivity sensor was replaced after the cast.

#### (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 computer. Raw data are acquired from instruments and are stored as unmodified data. The conversion module DATCNV uses the instrument configuration and calibration coefficients to create a converted engineering unit data file that is operated on by all SEASOFT post processing modules. Each SEASOFT module that modifies the converted data file adds proper information to the header of the converted file permitting tracking of how the various oceanographic parameters were obtained. The converted data is stored in rows and columns of ascii numbers. The last data column is a flag field used to mark scans as good or bad.

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 5.27b

DATCNV converted the raw data to scan number, pressure, depth, temperatures, conductivities, oxygen voltage, descent rate, altitude and fluorescence. 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, descent rate, altitude and fluorescence were averaged over 4.4 seconds. Then, salinity, potential temperature, density ( $\sigma_{\theta}$ ) and oxygen were computed.

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 and the secondary conductivity for 1.73 scans (1.75/24 = 0.073 seconds). 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 all variables.

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.

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

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 start 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 to check 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-dbar 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 density ( $\sigma_{\theta}$ ).

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

As for a 1-dbar-pressure bin averaged the data less than 10 scans, data of the bin was eliminated. As for remaining spikes in the Fluorometer data near surface, those data quality flags were set to 4. Remaining spikes in the salinity data were manually eliminated for raw data. When the data was eliminated over 1 dbar, the data gap was linearly interpolated with a quality flag of 6. Remaining spikes in the oxygen data are going to be eliminated after the cruise.

## 3.1.5 Post-cruise calibration

## (1) Pressure

The CTD pressure sensor drift in the period of the 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 deck pressure. The atmospheric pressure was measured at the captain deck (20 m high from the base line) and sub-sampled one-minute interval for a meteorological data. Time series of the CTD deck pressure is shown in Figure 3.1.6.

The CTD pressure sensor drift is estimated from the deck pressure obtained above. Mean of the pre- and the post-casts data over the whole period for gave an estimation of the pressure sensor offset from the pre-cruise calibration. Mean residual pressure between the dead weight piston gauge and the calibrated CTD data at 0 dbar of the pre-cruise calibration is subtracted from the mean deck pressure. Offset of the pressure data is estimated to be -0.40 dbar (Table 3.1.1). So the post-cruise calibration is not deemed necessary for the pressure sensors.

Table 3.1.1. Offset of the pressure data. Mean and standard deviation are calculated from time series of the average of the pre- and the post-cast deck pressures.

| S/N  | Mean deck       | Standard         | Residual pressure | Estimated offset |
|------|-----------------|------------------|-------------------|------------------|
|      | Pressure (dbar) | deviation (dbar) | (dbar)            | (dbar)           |
| 0677 | -0.42           | 0.05             | -0.02             | -0.40            |



Figure 3.1.6. Time series of the CTD deck pressure. Pink dot indicates atmospheric pressure anomaly. Blue and green dots indicate pre- and post-cast deck pressures, respectively. Red dot indicates an average of the pre- and the post-cast deck pressures.

## (2) Temperature (preliminary)

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 are going to be performed immediately after the cruise. In this report the CTD temperature data is preliminarily calibrated using the SBE 35 data.

The discrepancy between the CTD temperature and the standard thermometer (SBE 35) is considered to be a function of pressure and time. Since the pressure sensitivity is thought to be constant in time at least during observation period, the CTD temperature is calibrated as

Calibrated temperature =  $T - (c_0 * P + c_1 * t + c_2)$ where T is CTD temperature in °C, P is pressure in dbar, t is time in days from pre-cruise calibration date of CTD temperature and  $c_0$ ,  $c_1$ , and  $c_2$  are calibration coefficients. The best fit sets of coefficients are determined by minimizing the sum of absolute deviation from the SBE 35 data. The MATLAB<sup>®</sup> function FMINSEARCH is used to determine the sets. The FMINSEARCH uses the simplex search method (Lagarias et al., 1998). This is a direct search method that does not use

numerical or analytic gradients.

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

The number of data used for the calibration and the mean absolute deviation from the SBE 35 are listed in Table 3.1.2 and the calibration coefficients are listed in Table 3.1.3. The results of the post-cruise calibration for the CTD temperature are summarized in Table 3.1.4 and shown in Figure 3.1.7 and 3.1.8.

Table 3.1.2. Number of data used for the calibration (pressure >= 1,950 dbar) and mean absolute deviation (ADEV) between the CTD temperature and the SBE 35. The SBE 35 data should be verified by the post-cruise laboratory calibration.

| S/N  | Number of data | ADEV (m°C) | Note |  |
|------|----------------|------------|------|--|
| 1464 | 1586           | 0.10       |      |  |
| 1525 | 1583           | 0.10       |      |  |

| S/N  | $c_0$ (°C/dbar) | c <sub>1</sub> (°C/day) | c <sub>2</sub> (°C) |
|------|-----------------|-------------------------|---------------------|
| 1464 | -1.0013e-7      | 2.4017e-6               | 0.56e-3             |
| 1525 | -7.9037e-9      | 2.8765e-6               | 0.29e-3             |

 Table 3.1.3.
 Calibration coefficients for the CTD temperature sensor.

Table 3.1.4.Difference between the CTD temperature and the SBE 35 after the post-cruise<br/>calibration. Mean and standard deviation (Sdev) are calculated below and above 1,950<br/>dbar. Number of data used is also shown.

| S/N  | Pressu | Pressure >= 1,950 dbar |            |      | Pressure < 1,950 dbar |            |  |  |
|------|--------|------------------------|------------|------|-----------------------|------------|--|--|
|      | Num    | Mean (m°C)             | Sdev (m°C) | Num  | Mean (m°C)            | Sdev (m°C) |  |  |
| 1464 | 1586   | 0.00                   | 0.14       | 2171 | -0.35                 | 8.3        |  |  |
| 1525 | 1583   | 0.00                   | 0.13       | 2153 | -0.52                 | 6.3        |  |  |

# (3) Salinity and dissolved oxygen

The CTD salinity and dissolved oxygen are going to be calibrated using in-situ salinity and dissolved oxygen data obtained from sampled water after the sampled data is quality controlled and the CTD temperature is calibrated. Difference between uncorrected CTD salinity and bottle salinity is shown in Figure 3.1.9. Difference between uncorrected CTD oxygen and bottle oxygen is also shown in Figure 3.1.10.

# **3.1.6 Preliminary results**

Date, time and locations of the CTD casts are listed in station summary file (49MR0502\_1\_sum.txt). Vertical section of potential temperature and salinity are shown in Figure 3.1.11 and Figure 3.1.12. Uncorrected CTD data is preliminarily used.

### References

- Budeus, G. and W. Schneider (1998): In-situ temperature calibration: A remark on instruments and methods, *Intl. WOCE Newsletter*, 30, 16-18.
- Lagarias, J.C., J.A. Reeds, M.H. Wright and P. E. Wright (1998): Convergence properties of the Nelder-Mead simplex method in low dimensions, *SIAM Journal of Optimization*, 9, 112-147.
- Larson, N. and A. Pederson (1996): Temperature measurements in flowing water: Viscous heating of sensor tips, 1<sup>st</sup> IGHEM Meeting, Montreal, Canada.

(http://www.seabird.com/technical\_references/paperindex.htm)



Figure 3.1.7. Difference between the CTD temperature (primary) and the Deep Ocean Standards thermometer (SBE 35). Blue and red dots indicate before and after the post-cruise calibration using the SBE 35 data, respectively. Lower two panels show histogram of the difference after the calibration. The SBE 35 data should be verified by the post-cruise laboratory calibration.



Figure 3.1.8. Same as Figure 3.1.7, but for the secondary CTD temperature.



Figure 3.1.9. Difference between the CTD salinity and the bottle salinity. Time series for deeper than 1,000 dbar (upper two panel) and vertical distribution (lower two panel) are shown for primary and secondary sensors.



Figure 3.1.10. Difference between the CTD oxygen and the bottle oxygen. Time series for deeper than 1,000 dbar (upper two panel) and vertical distribution (lower two panel) are shown for primary and secondary sensors.



Figure 3.1.11. Vertical section of potential temperature. Uncorrected CTD data is used.



Figure 3.1.12. Vertical section of CTD salinity. Uncorrected CTD data is used.

# 3.2 Bottle Salinity

Fujio Kobayashi (MWJ) Kenichi Katayama (MWJ) Tatsuya Tanaka (MWJ) Takeshi Kawano (JAMSTEC)

## 3.2.1 Objectives

1. To measure bottle salinity obtained by CTD casts, bucket sampling, and EPCS

2. To calibrate CTD salinity

# 3.2.2 Instrument and Method

## 3.2.2.1 Salinity Sample Collection

Seawater samples were collected with 12 liter Niskin-X bottles, bucket, and the EPCS. The salinity sample bottle of the 250ml brown grass bottle with screw cap was used to collect the sample water. Each bottle was rinsed three times with sample water, and was filled with sample water to the bottle shoulder. Its cap was also thoroughly rinsed. The bottle was stored more than 12 hours in 'AUTOSAL ROOM' before the salinity measurement.

The kind and number of samples are shown as follows ;

| Samples          | Number of Samples |
|------------------|-------------------|
| Samples for CTD  | 4,570             |
| Samples for EPCS | 60                |
| Total            | 4,630             |

Table 3.2.3.1 number of samples

## 3.2.2.2 Instruments and Method

The salinity analysis was carried out on R/V MIRAI during the cruise of MR05-02 using the salinometer (Model 8400B "AUTOSAL"; Guildline Instruments Ltd.: S/N 62556) with additional peristaltic-type intake pump (Ocean Scientific International, Ltd.). We also used two pairs of precision digital thermometers (Model 9540; Guildline Instruments Ltd.). One thermometer monitored an ambient temperature and the other monitored a bath temperature.

The specifications of AUTOSAL salinometer and thermometer are shown as follows ;

| Salinometer (Model 8400B "A | AUTOSAL"; Guildline Instruments Ltd.)         |
|-----------------------------|---|
| Measurement Range           | : 0.005 to 42 (PSU)                           |
|                             |   |
| Accuracy                    | : Better than $\pm 0.002$ (PSU) over 24 hours |
|                             | without restandardization                     |
| Maximum Resolution          | : Better than $\pm 0.0002$ (PSU) at 35 (PSU)  |
| Thermometer (Model 9540;    | Guildline Instruments Ltd.)                   |
| Measurement Range           | : -180 to +240 deg C                          |
| Resolution                  | : 0.001                                       |

| Limits of error | ± deg C | : | 0.01 (24 hours @ 23 deg C    | <b>±</b> 1 deg C) |
|-----------------|---------|---|------------------------------|-------------------|
| Repeatability   |         | : | ± 2 least significant digits |                   |

The measurement system was almost same as Aoyama *et al.* (2003). The salinometer was operated in the air-conditioned ship's laboratory 'AUTOSAL ROOM' at a bath temperature of 24 deg C, very stable and varied within 24 deg C +/- 0.002 deg C on rare occasion.

The measurement for each sample was done with a double conductivity ratio that is defined as median of 31 times reading of the salinometer. Data collection was started in 5 seconds after filling sample into the cell and it took about 10 seconds to collect 31 readings by a personal computer. Data were taken for the sixth and the seventh filling of the cell. In case the difference between the double conductivity ratio of these two fillings is smaller than 0.00002, the average value of these double conductivity ratio was used to calculate the bottle salinity with the algorithm for practical salinity scale, 1978 (UNESCO, 1981). If the difference was greater than or equal to 0.0003, we measured eighth filling of the cell. In case the double conductivity ratio of eighth filling did not satisfy the criteria above, we measured ninth and tenth filling of the cell and the median of the double conductivity ratios of five fillings are used to calculate the bottle salinity.

The measurement was conducted about 16hours per day (typically from 7:00 to 23:00) and the cell was cleaned with ethanol or soap or both after the measurement of the day.

# 3.2.3 Preliminary Result

# 3.2.3.1 Stand Seawater

Standardization control of the salinometer with serial number of 62556 was set to 491. During the measurement, the STANDBY of 62556 was 5509 +/- 0001 and ZERO was 0.00001. We used IAPSO Standard Seawater batch P145 which conductivity ratio was 0.99981 (double conductivity ratio is 1.99962) as the standard for salinity. We measured 179 bottles of P145. There were 5 bad bottles which conductivities are extremely high or low. Data of these 5 bottles are not taken into consideration hereafter.

Fig.3.2.3.1 shows the history of double conductivity ratio of the Standard Seawater batch P145. During this cruise, we did flushing cell twice using ultrasonic washing machine for cleaning the cell. The average of double conductivity ratio from Stn.143 to Stn.071 was 1.99962 and the standard deviation was 0.00001, which is equivalent to 0.0002 in salinity. The average from Stn.070 to Stn.023 was 1.99963 and the standard deviation was 0.00001. We reduce 0.00001 to the measured double conductivity ratio during this period. The average of double conductivity ratio from Stn.022 to Stn.001 was 1.99962 and the standard deviation was 0.00001, which is equivalent to 0.0002 in salinity.

The specifications of SSW used in this cruise are shown as follows;

| Standard seawater (SSW) |   |            |  |  |  |  |  |  |
|-------------------------|---|------------|--|--|--|--|--|--|
| batch                   | : | P145       |  |  |  |  |  |  |
| conductivity ratio      | : | 0.99981    |  |  |  |  |  |  |
| salinity                | : | 34.993     |  |  |  |  |  |  |
| preparation date        | : | 15-Jul2004 |  |  |  |  |  |  |



Fig. 3.2.3.1 The history of double conductivity ratio of the Standard Seawater batch P145

## 3.2.3.2 Sub-Standard Seawater

We also used sub-standard seawater, which was deep-sea water filtered by pore size of 0.45 micrometer, stored in a 20 liter container made of polyethylene, and stirred for at least 24 hours before measuring. It was measured every six samples in order to check the possible sudden drift of the salinometer. During the whole measurements, there was no detectable sudden drift of the salinometer.

The specifications of SUB used in this cruise are shown as follows ;

Sub standard seawater (SUB) sampling cruise ID : MR04-ENG sampling depth : 5,000dbar filtration date : 29-May-2004 sampling cruise ID : MR04-05 sampling depth : 2,000dbar filtration date : 10-Sep.-2004

## 3.2.3.3 Replicate and Duplicate Samples

We took 666 pairs of replicate and 55 pairs of duplicate samples. Fig.3.2.3.2 (a) and (b) shows the histogram of the absolute difference between replicate samples and duplicate samples, respectively. There were 6 bad measurements and 18 questionable measurements of replicate samples and 6 questionable measurements of duplicate samples. Excluding these measurements, the standard deviation of the absolute deference of 642 pairs of replicate samples was 0.0002 in salinity and that of 48 pairs of duplicate samples was 0.0002 in salinity.



**Replicate Samples** 

Fig. 3.2.3.2 (a) The histogram of the difference between replicate samples

# **Duplicate Samples**



Fig. 3.2.3.2 (b) The histogram of the absolute difference between duplicate samples

# 3.2.3.4 Figures

We measured 4,630 samples during this cruise. As a preliminary result, we will show a several figures without any interpretation. Fig.3.2.4.3 shows a vertical section of bottle salinity, vertical profile of bottle salinity and Sigma4-Salinity diagram produced by Ocean Data View.

## 3.2.4 Further data quality check

All data will be checked once again in detail with other parameters such as dissolved oxygen and nutrients.

## **3.2.5 Reference**

- Aoyama, M., T. Joyce, T. Kawano and Y. Takatsuki: Standard seawater comparison up to P129. Deep-Sea Research, I, Vol. 49, 1103 ~ 1114, 2002
- UNESCO: Tenth report of the Joint Panel on Oceanographic Tables and Standards. UNESCO Technical Papers in Marine Science, 36, 25 pp., 1981



Fig. 3.2.4.3 Vertical section, vertical profile of bottle salinity and Sigma4-Salinity diagram

# 3.3 Bottle Oxygen (2-July-2005)

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# 3.3.1 Objectives

Dissolved oxygen is a significant tracer for the ocean circulation study. Recent studies in the North Pacific indicated that dissolved oxygen concentration in intermediate layers decreased in basin wide scale during the past decades. The causes of the decrease, however, are still unclear. During MR05-02, we measured dissolved oxygen concentration from surface to bottom layers at all the hydrocast stations. The stations from 29°N to 4°S reoccupied WHP P10 stations in 1993. Our purpose is to evaluate decadal change of dissolved oxygen in the western Pacific.

# 3.3.2 Reagents

Pickling Reagent I: Manganous chloride solution (3M)
Pickling Reagent II: Sodium hydroxide (8M) / sodium iodide solution (4M)
Sulfuric acid solution (5M)
Sodium thiosulfate (0.025M)
Potassium iodate (0.001667M)
CSK standard of potassium iodate: Lot ASE8280, Wako Pure Chemical Industries Ltd., 0.0100N

# 3.3.3 Instruments

Burette for sodium thiosulfate;

APB-510 manufactured by Kyoto Electronic Co. Ltd. /  $10 \text{ cm}^3$  of titration vessel Burette for potassium iodate;

APB-410 manufactured by Kyoto Electronic Co. Ltd. / 20 cm<sup>3</sup> of titration vessel Detector; Automatic photometric titrator manufactured, Kimoto Electronic Co. Ltd.

## 3.3.4 Seawater sampling

Following procedure is based on a determination method in the WHP Operations Manual (Dickson, 1996). Seawater samples were collected from Niskin sampler bottles attached to the CTD-system. Seawater for bottle oxygen measurement was transferred from the Niskin sampler bottle to a volume calibrated glass flask (ca. 100 cm<sup>3</sup>). Three times volume of the flask of seawater was overflowed. Sample temperature was measured by a thermometer during the overflowing. Then two reagent solutions (Reagent I, II) of 0.5 cm<sup>3</sup> each were added immediately into the sample flask and the stopper was inserted carefully into the flask. The sample flask was then shaken vigorously to mix the contents and to disperse the precipitate finely throughout. After the precipitate has settled at least halfway down the flask, the flask was shaken again vigorously to disperse the precipitate. The sample flasks containing pickled samples were stored in a laboratory until they were titrated.

#### 3.3.5 Sample measurement

At least two hours after the re-shaking, the pickled samples were measured on board. A magnetic stirrer bar and 1 cm<sup>3</sup> sulfuric acid solution were added into the sample flask and stirring began. Samples were titrated by sodium thiosulfate solution whose molarity was determined by potassium iodate solution (section 3.3.6). Temperature of sodium thiosulfate during titration was recorded by a thermometer. During this cruise we measured dissolved oxygen concentration using two sets of the titration apparatus, DOT-1 and DOT-2. Dissolved oxygen concentration ( $\mu$ mol kg<sup>-1</sup>) was calculated by the sample temperature during the sampling, CTD salinity, flask volume, and titrated volume of the sodium thiosulfate solution.

### 3.3.6 Standardization

Concentration of sodium thiosulfate titrant (ca. 0.025M) was determined by potassium iodate solution. Pure potassium iodate was dried in an oven at 130°C. 1.7835 g potassium iodate weighed out accurately was dissolved in deionized water and diluted to final volume of 5 dm<sup>3</sup> in a calibrated volumetric flask (0.001667M). 10 cm<sup>3</sup> of the standard potassium iodate solution was added to a flask using a volume-calibrated dispenser. Then 90 cm<sup>3</sup> of deionized water, 1 cm<sup>3</sup> of sulfuric acid solution, and 0.5 cm<sup>3</sup> of pickling reagent solution II and I were added into the flask in order. Amount of titrated volume of sodium thiosulfate gave the molarity of the sodium thiosulfate titrant. Table 3.3-1 shows result of the standardization during this cruise. Error (C.V.) of the each standardization was less than 0.08 % (n = 5).

#### **3.3.7** Determination of the blank

The oxygen in the pickling reagents I ( $0.5 \text{ cm}^3$ ) and II ( $0.5 \text{ cm}^3$ ) was assumed to be  $3.8 \times 10^{-8}$  mol (Dickson, 1996). The blank from the presence of redox species apart from oxygen in the reagents (the pickling reagents I, II, and the sulfuric acid solution) was determined as follows. 1 and 2 cm<sup>3</sup> of the standard potassium iodate solution were added to two flasks respectively. Then 100 cm<sup>3</sup> of deionized water, 1 cm<sup>3</sup> of sulfuric acid solution, and 0.5 cm<sup>3</sup> of pickling reagent solution II and I were added into the two flasks in order. The blank was determined by difference between the two times of the first ( $1 \text{ cm}^3$  of KIO<sub>3</sub>) titrated volume of the sodium thiosulfate and the second ( $2 \text{ cm}^3$  of KIO<sub>3</sub>) one. The results of the blank determination are also shown in Table 3.3-1. The averaged blank of DOT-1 and DOT-2 were -0.007 and -0.010 cm<sup>3</sup>, respectively.

| Date      |   | KIO <sub>3</sub> | DOT-         | 1 (cm <sup>3</sup> ) |        | DOT-2 $(cm^3)$ |       |        | Samples      |
|-----------|---|------------------|--------------|----------------------|--------|----------------|-------|--------|--------------|
| (UTC)     | # | bottle           | $Na_2S_2O_3$ | E.P.                 | blank  | $Na_2S_2O_3$   | E.P.  | blank  | (Stations)   |
| 2005/5/26 |   | 20050420-01      | 20050523-1   | 3.959                | -0.006 | 20050523-2     | 3.961 | -0.011 | 135-143      |
| 2005/5/28 |   | 20050420-02      | 20050523-1   | 3.960                | -0.005 | 20050523-2     | 3.961 | -0.008 | 131-134      |
| 2005/5/29 |   | 20050420-03      | 20050523-3   | 3.957                | -0.008 | 20050523-4     | 3.961 | -0.011 | 127-130      |
| 2005/5/30 | 1 | 20050420-04      | 20050523-3   | 3.960                | -0.006 | 20050523-4     | 3.964 | -0.008 | 123-126      |
| 2005/5/31 | 1 | 20050420-05      | 20050529-1   | 3.959                | -0.006 | 20050529-2     | 3.961 | -0.009 | 119-122      |
| 2005/6/2  |   | 20050420-06      | 20050529-1   | 3.959                | -0.006 | 20050529-2     | 3.959 | -0.009 | 115-118      |
| 2005/6/3  |   | 20050420-07      | 20050529-3   | 3.959                | -0.007 | 20050529-4     | 3.960 | -0.008 | 111-114      |
| 2005/6/4  |   | 20050420-08      | 20050529-3   | 3.958                | -0.006 | 20050529-4     | 3.961 | -0.009 | 107-110      |
| 2005/6/5  |   | 20050420-13      | 20050603-1   | 3.954                | -0.007 | 20050603-2     | 3.957 | -0.011 | 103-106      |
| 2005/6/6  |   | 20050420-14      | 20050603-1   | 3.956                | -0.006 | 20050603-2     | 3.956 | -0.011 | 99-102       |
| 2005/6/7  |   | 20050420-15      | 20050603-3   | 3.956                | -0.007 | 20050603-4     | 3.958 | -0.011 | 96,X02,97,98 |
| 2005/6/8  |   | 20050420-16      | 20050603-3   | 3.955                | -0.008 | 20050603-4     | 3.959 | -0.009 | 69-73,95     |
| 2005/6/10 | 2 | 20050420-17      | 20050609-1   | 3.953                | -0.009 | 20050609-2     | 3.955 | -0.010 | 66,X03,67,68 |
| 2005/6/10 |   | 20050420-17      | 20050609-1   | 3.961                | -0.008 | 20050609-2     | 3.960 | -0.011 | 67           |
| 2005/6/11 |   | 20050420-18      | 20050609-1   | 3.953                | -0.005 | 20050609-2     | 3.955 | -0.010 | 62-65        |
| 2005/6/13 |   | 20050420-19      | 20050609-3   | 3.952                | -0.008 | 20050609-4     | 3.954 | -0.009 | 58-61        |
| 2005/6/14 |   | 20050420-20      | 20050609-3   | 3.954                | -0.008 | 20050609-4     | 3.956 | -0.010 | 54-57        |
| 2005/6/16 |   | 20050420-25      | 20050613-1   | 3.951                | -0.007 | 20050613-2     | 3.953 | -0.009 | 50-53        |
| 2005/6/17 |   | 20050420-26      | 20050613-1   | 3.953                | -0.006 | 20050613-2     | 3.954 | -0.009 | 46-49        |
| 2005/6/18 |   | 20050420-27      | 20050613-3   | 3.953                | -0.008 | 20050613-4     | 3.954 | -0.010 | 42,X04,44,45 |
| 2005/6/19 | 3 | 20050420-28      | 20050613-3   | 3.953                | -0.008 | 20050613-4     | 3.954 | -0.008 | 36-41        |
| 2005/6/20 | 5 | 20050420-29      | 20050618-1   | 3.960                | -0.008 | 20050618-2     | 3.962 | -0.010 | 31-35        |
| 2005/6/21 |   | 20050420-30      | 20050618-1   | 3.960                | -0.007 | 20050618-2     | 3.962 | -0.010 | 27-30        |
| 2005/6/22 |   | 20050420-32      | 20050618-3   | 3.960                | -0.009 | 20050618-4     | 3.962 | -0.010 | 23-26        |
| 2005/6/23 |   | 20050420-31      | 20050618-3   | 3.959                | -0.009 | 20050618-4     | 3.960 | -0.010 | 18-22        |
| 2005/6/25 |   | 20050420-40      | 20050622-1   | 3.958                | -0.007 | 20050622-2     | 3.960 | -0.010 | 12-17        |
| 2005/6/26 | 4 | 20050420-39      | 20050622-1   | 3.957                | -0.005 | 20050622-2     | 3.959 | -0.010 | 5-11         |
| 2005/6/27 |   | 20050420-38      | 20050622-3   | 3.957                | -0.009 | 20050622-4     | 3.961 | -0.008 | 1-4          |

Table 3.3-1 Results of the standardization and the blank determinations during MR05-02.

# Batch number of the KIO<sub>3</sub> standard solution.

# 3.3.8 Reagent blank

The blank determined in the section 3.3.7, pure water blank  $(V_{blk, dw})$  can be represented by equation 1,

$$V_{blk, dw} = V_{blk, ep} + V_{blk, reg}$$
(1)

where

 $V_{blk, ep}$  = blank due to differences between the measured end-point and the equivalence point;  $V_{blk, reg}$  = blank due to oxidants or reductants in the reagent.

Here, the reagent blank ( $V_{blk, reg}$ ) was determined by following procedure. 1 cm<sup>3</sup> of the standard potassium iodate solution and 100 cm<sup>3</sup> of deionized water were added to two flasks. 1 cm<sup>3</sup> of sulfuric acid solution, and 0.5 cm<sup>3</sup> of pickling reagent solution II and I each were added into the first flask in order. Then into the second flask, two times volume of the reagents (2 cm<sup>3</sup> of sulfuric acid solution, and 1.0 cm<sup>3</sup> of pickling reagent solution II and I each) was added. The reagent blank was determined by difference between the first (2 cm<sup>3</sup> of the total reagent volume added) titrated volume of the sodium thiosulfate and the second (4 cm<sup>3</sup> of the total reagent volume added) one. We also carried out experiments for three and four times volume of the reagents. The results are shown in Figure 3.3-1.



Figure 3.3-1 Blank (cm<sup>3</sup>) due to redox species apart from oxygen in the reagents

The relation between the reagent blank  $(V_{blk, reg})$  and the volume of the reagents  $(V_{reagent})$  is expressed by equation 2,

$$V_{blk, reg} = -0.0020 V_{reagent} + 0.0005$$
(2)

There was no difference between the results of DOT-1 and DOT-2.  $V_{blk, reg}$  was estimated to be about -0.004 cm<sup>3</sup>, suggesting that about 0.02 µmol of reductants was contained in every 2 cm<sup>3</sup> of the reagents added. In other words, the difference of the pure water blank ( $V_{blk, dw}$ ) between DOT-1 and DOT-2, determined in the section 3.3.7, was due to the difference of the end-point blank ( $V_{blk, ep}$ ) between the two titration apparatus (-0.003 and -0.006 cm<sup>3</sup> for DOT-1 and DOT-2, respectively).

## 3.3.9 Sample blank

Blank due to redox species other than oxygen in the sample  $(V_{blk, spl})$  can be a potential source of measurement error. Total blank during the seawater measurement, seawater blank  $(V_{blk, sw})$  can be represented by equation 3,

$$V_{blk, sw} = V_{blk, spl} + V_{blk, ep} + V_{blk, reg}$$
(3).

If the end-point blank  $(V_{blk, ep})$  is identical in pure water and in seawater, the difference between the
seawater blank and the pure water one gives the sample blank (V<sub>blk, spl</sub>),

$$\mathbf{V}_{\text{blk, sw}} - \mathbf{V}_{\text{blk, dw}} = \mathbf{V}_{\text{blk, spl}}$$
(4).

 $V_{blk, spl}$  was determined by following procedure. Seawater sample was collected in the volume calibrated glass flask (ca. 100 cm<sup>3</sup>) without the pickling. Then 1 cm<sup>3</sup> of the standard potassium iodate solution, 1 cm<sup>3</sup> of sulfuric acid solution, and 0.5 cm<sup>3</sup> of pickling reagent solution II and I each were added into the flask in order. Additionally a flask contained 1 cm<sup>3</sup> of the standard potassium iodate solution, 100 cm<sup>3</sup> of deionized water, 1 cm<sup>3</sup> of sulfuric acid solution, and 0.5 cm<sup>3</sup> of pickling reagent solution II and I were prepared. The difference the titrant volumes between the seawater flask and the deionized water one gave the sample blank (V<sub>blk, spl</sub>).

| Station: P10N-097 |             |                       | Station: P10-019 |           |                       |  |
|-------------------|-------------|-----------------------|------------------|-----------|-----------------------|--|
| 30                | ).5°N / 149 | 3°E                   | 0.3°N / 146.2°E  |           |                       |  |
| Sample No.        | CTD Pres.   | Sample blank          | Sample No.       | CTD Pres. | Sample blank          |  |
| (Niskin No.)      | dbar        | µmol kg <sup>-1</sup> | (Niskin No.)     | dbar      | µmol kg <sup>-1</sup> |  |
| 35                | 51          | 0.5                   | 35               | 51        | 0.4                   |  |
| 33                | 151         | 0.6                   | 33               | 150       | 0.7                   |  |
| 31                | 249         | 0.6                   | 31               | 251       | 0.7                   |  |
| 29                | 402         | 0.7                   | 29               | 401       | 0.9                   |  |
| 27                | 602         | 0.6                   | 27               | 601       | 0.7                   |  |
| 25                | 800         | 0.6                   | 25               | 801       | 0.7                   |  |
| 23                | 1001        | 0.6                   | 23               | 1001      | 0.7                   |  |
| 21                | 1400        | 0.7                   | 21               | 1400      | 0.7                   |  |
| 17                | 2200        | 0.7                   | 19               | 1802      | 0.7                   |  |
| 15                | 2599        | 0.7                   | 17               | 2200      | 0.7                   |  |
| 13                | 3000        | 0.7                   | 15               | 2600      | 0.7                   |  |
| 11                | 3499        | 0.6                   | 13               | 2999      | 0.7                   |  |
| 9                 | 4002        | 0.7                   | 11               | 3499      | 0.7                   |  |
| 7                 | 4502        | 0.7                   | 1                | 3770      | 0.9                   |  |
| 5                 | 4999        | 0.7                   |                  |           |                       |  |
| 3                 | 5500        | 0.7                   |                  |           |                       |  |
| 1                 | 6251        | 0.7                   |                  |           |                       |  |

Table 3.3-2 Results of the sample blank determinations during MR05-02.

During this cruise we measured vertical profiles of the sample blanks at two stations (Table 3.3-2) using DOT-1 system. The sample blank ranged from 0.4 to 0.9  $\mu$ mol kg<sup>-1</sup> and its vertical and horizontal variations are small. There are a few reports of the sample blank estimation of oxygen analysis in the open ocean. Our results agree with reported values ranged from 0.4 to 0.8  $\mu$ mol kg<sup>-1</sup> (Culberson *et al.*, 1991). If we ignore that the sample blank introduces systematic errors into the oxygen calculations, but these errors are expected to be the same for all investigators and not to affect the comparison of results from different investigators (Culberson, 1994).

#### 3.3.10 Replicate sample measurement

Replicate samples were taken at every CTD cast. Total amount of the replicate sample pairs in good measurement (flag=2) was 452. The standard deviation of the replicate measurement was 0.11  $\mu$ mol/kg and there was no significant difference between DOT-1 and DOT-2 measurements. The standard deviation was calculated by a procedure (SOP23) in DOE (1994). Figure 3.3-2 is plots of oxygen difference in the replicate measurement as a function of station sequential number and indicates the improvement of measurement skill during the cruise. There found large differences during the primary stage of the cruise. If we exclude the data at the initial ten stations from the calculation of standard deviation, it decreases to 0.09  $\mu$ mol/kg.



Figure 3.3-2 Difference in the replicate measurements against station sequential number.

As shown in Figure 3.3-3, the layers of replicate sampling are localized at the surface layer, 1200, 3000 and 5000 dbar depths. Since scattering of the plots somewhat depend on depths, we classified replicate data in the following categories: surface (<20 dbar), intermediate (500-1500dbar) and deep (>1500dbar) layers. Standard deviation for each category is 0.16, 0.11, and 0.07  $\mu$ mol/kg, respectively.



Figure 3.3-3 Difference in the replicate measurements against sampling depth (pressure).

# 3.3.11 Duplicate sample measurement

We also collected seawater samples from two Niskin samplers that were fired at same depth (duplicate sampling). Duplicate samples were taken at 49 stations in the deep layer below 2000 dbar, and 48 duplicate sample pairs were obtained successfully. From Figure 3.3-4, variation in



Figure 3.3-4 Difference in the duplicate measurements against station sequential number.

measurement resolution is not clear during the period of this cruise. The standard deviation of the total duplicate measurement was about 0.11  $\mu$ mol/kg. This value is roughly close to the standard deviation of the replicate measurement for the intermediate and deep layers (>500dbar). Thus, we conclude that our measurement resolution of bottle oxygen is about 0.1  $\mu$ mol/kg or less for

MR05-02 cruise.

## 3.3.12 CSK standard measurements

The CSK standard solution is a commercial potassium iodate solution (0.0100 N) for analysis of oxygen in seawater. During this cruise, we measured concentration of the CSK standard solution (Lot ASE8280) against our KIO<sub>3</sub> standard in order to confirm accuracy of our oxygen measurement on board (Table 3.3-3). Averaged values of DOT-1 and DOT-2 were 0.009999  $\pm$  0.000002 N and 0.009999  $\pm$  0.000002 N respectively, which indicates that there was no systematic difference between DOT-1 and DOT-2 measurements. The averaged value of the CSK standard solution was so close to the certified value (0.0100 N) that we did not correct sample measurements with the CSK standard measurements. Additionally, we also measured another batch of the CSK standard solution, Lot TCK8677 that was also measured during our last cruise in 2003 (MR03-K04). We found that the measurements of the two batches of the CSK standard agreed well, suggesting there was no systematic difference between our oxygen measurements in 2003 and in 2005.

| Date (UTC) | KIO3 batch#             | DOT-1     |           | DOT-2     |           |
|------------|-------------------------|-----------|-----------|-----------|-----------|
| Date (UTC) | KIO <sub>3</sub> Datch# | Conc. (N) | error (N) | Conc. (N) | error (N) |
| 2005/6/2   | ASE8280-1               | 0.009997  | 0.000003  | 0.010002  | 0.000003  |
| 2005/6/11  | ASE8280-2               | 0.010002  | 0.000003  | 0.009997  | 0.000003  |
| 2005/6/21  | ASE8280-3               | 0.009999  | 0.000003  | 0.009997  | 0.000003  |
| 2005/6/27  | ASE8280-4               | 0.0099999 | 0.000005  | 0.009999  | 0.000003  |
| Aver       | rage                    | 0.0099999 | 0.000002  | 0.009999  | 0.000002  |
|            |                         |           |           |           |           |
| 2005/6/11  | TCK8677                 | 0.009999  | 0.000003  | 0.009997  | 0.000003  |

Table 3.3-3 Results of the CSK standard measurements.

## 3.3.13 Quality control flag assignment

Quality flag values were assigned to oxygen 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). Measurement flags of 2, 3, 4, and 5 have been assigned (Table 3.3-4). For the choice between 2 (good), 3 (questionable) or 4 (bad), we basically followed a flagging procedure as listed below:

- a. On a station-by-station basis, bottle oxygen and difference between bottle oxygen and CTD oxygen at the time of rosette sampling were plotted against CTD pressure. Any points not lying on a generally smooth trend were noted.
- b. Dissolved oxygen was then plotted against potential temperature for several stations. If a datum deviated from a group of plots, it was flagged 3 or 4.
- c. If the bottle flag was 4 (Did not trip correctly), a datum was noted and flagged 4, respectively. In case of the bottle flag 3 (Leaking), a datum was flagged based on steps a and b.

Before the publishing of these data, as a post-cruise quality control for bottle oxygen, we will carry out one more pass of flagging with the data at all stations. The following steps will be added.

- d. Vertical sections against depth and potential density will be drawn. If a datum is anomalous on the section plots, datum flag will be degraded from 2 to 3, or from 3 to 4.
- e. In the relationships between oxygen and other properties, data flagged 3 and 4 will be examined

once more and upgraded if necessary.

| Flag | Definition           |      |
|------|----------------------|------|
| 2    | Good                 | 3746 |
| 3    | Questionable         | 8    |
| 4    | Bad                  | 14   |
| 5    | Not report (missing) | 14   |
|      | Total                | 3782 |

Table 3.3-4 Summary of assigned quality control flags.

References

- Culberson, A.H. (1994) Dissolved oxygen, in WHPO Pub. 91-1 Rev. 1, November 1994, Woods Hole, Mass., USA.
- Culberson, A.H., G. Knapp, M.C. Stalcup, R.T. Williams, F. Zemlyak (1991) A comparison of methods for the determination of dissolved oxygen in seawater, WHPO Pub. 91-2, August 1991, Woods Hole, Mass., USA.
- Dickson, A. (1996) Determination of dissolved oxygen in sea water by Winkler titration, in WHPO Pub. 91-1 Rev. 1, November 1994, Woods Hole, Mass., USA.
- DOE (1994) Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water; version 2. A.G. Dickson and C. Goyet (eds), ORNL/CDIAC-74.
- Joyce, T., and C. Corry, eds., C. Corry, A. Dessier, A. Dickson, T. Joyce, M. Kenny, R. Key, D. Legler, R. Millard, R. Onken, P. Saunders, M. Stalcup, contrib. (1994) Requirements for WOCE Hydrographic Programme Data Reporting, WHPO Pub. 90-1 Rev. 2, May 1994 Woods Hole, Mass., USA.

#### **3.4 Nutrients**

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#### 3.4.1 Objectives

The objectives of nutrients analyses during the R/V Mirai MR0502 cruise along 149E line in the Western North Pacific are as follows;

Describe the present status of nutrients in the present in good traceability.

The target nutrients are nitrate, nitrite, phosphate and silicate (Although silicic acid is correct, we use silicate because a term of silicate is widely used in oceanographic community.)

Study the temporal and spatial variation of nutrients based on the previous high quality

experiments data of WOCE, GOESECS, IGY and so on.

Study of temporal and spatial variation of nitrate: phosphate ratio, so called Redfield ratio.

Obtain more accurate estimation of total amount of nitrate, phosphate and silicate in the interested area.

Provide more accurate nutrients data for physical oceanographers to use as tracers of water mass movement.

#### 3.4.2 Equipment and techniques

#### 3.4.2.1 Analytical detail using TRAACS 800 systems (BRAN+LUEBBE)

The phosphate analysis is a modification of the procedure of Murphy and Riley (1962).

Molybdic acid is added to the seawater sample to form phosphomolybdic acid which is in turn reduced to phosphomolybdous acid using L-ascorbic acid as the reductant.

Nitrate + nitrite and nitrite are analyzed according to the modification method of Grasshoff (1970).

The sample nitrate is reduced to nitrite in a cadmium tube inside of which is coated with metallic copper. The sample stream with its equivalent nitrite is treated with an acidic, sulfanilamide reagent and the nitrite forms nitrous acid which reacts with the sulfanilamide to produce a diazonium ion. N1-Naphthylethylene-diamine added to the sample stream then couples with the diazonium ion to produce a red, azo dye. With reduction of the nitrate to nitrite, both nitrate and nitrite react and are measured; without reduction, only nitrite reacts. Thus, for the nitrite analysis, no reduction is performed and the alkaline buffer is not necessary. Nitrate is computed by difference.

The silicate method is analogous to that described for phosphate. The method used is essentially that of Grasshoff et al. (1983), wherein silicomolybdic acid is first formed from the silicic acid in the sample and added molybdic acid; then the silicomolybdic acid is reduced to silicomolybdous acid, or "molybdenum blue," using ascorbic acid as the reductant.

The flow diagrams and regents for each parameter are shown in Figures 3.4.1-3.4.4.



# **Nitrate Reagents**

Imidazole (buffer), 0.06M (0.4% w/v)

Dissolve 4g imidazole,  $C_3H_4N_2$ , in ca. 900ml DIW; add 2ml concentrated HCl; make up to 1000ml with DIW. After mixing, 1ml Triton(R)X-100 (50% solution in ethanol) is added.

Sulfanilamide, 0.06M (1% w/v) in 1.2M HCl

Dissolve 10g sulfanilamide,  $4-NH_2C_6H_4SO_3H$ , in 1000ml of 1.2M (10%) HCl. After mixing, 1ml Triton(R)X-100 (50% solution in ethanol) is added.

N-1-Napthylethylene-diamine dihydrochloride, 0.004 M (0.1% w/v)

Dissolve 1 g NEDA,  $C_{10}H_7NHCH_2CH_2NH_2 \cdot 2HCl$ , in 1000ml of DIW; containing 10ml concentrated HCl. Stored in a dark bottle.



# **Nitrite Reagents**

Sulfanilamide, 0.06M (1% w/v) in 1.2M HCl Dissolve 10g sulfanilamide,  $4-NH_2C_6H_4SO_3H$ , in 1000ml of 1.2M (10%) HCl. After mixing, 1ml Triton(R)X-100 (50% solution in ethanol) is added.

N-1-Napthylethylene-diamine dihydrochloride , 0.004 M (0.1% w/v) Dissolve 1 g NEDA,  $C_{10}H_7NHCH_2CH_2NH_2 \cdot 2HCl$ , in 1000ml of DIW; containing 10ml concentrated HCl. Stored in a dark bottle.



# **Silicic Acid Reagents**

Molybdic acid, 0.06M (2% w/v) Dissolve 15g Disodium Molybdate(VI) Dihydrate, Na<sub>2</sub>MoO<sub>4</sub> • 2H<sub>2</sub>O, in 1000ml DIW containing 6ml H<sub>2</sub>SO<sub>4</sub>. After mixing, 20ml sodium dodecyl sulphate (15% solution in water) is added.

Oxalic acid, 0.6M (5% w/v) Dissolve 50g Oxalic Acid Anhydrous, HOOC: COOH, in 1000ml of DIW.

Ascorbic acid, 0.01M (3% w/v)

Dissolve 2.5g L (+)-Ascorbic Acid,  $C_6H_8O_6$ , in 100ml of DIW. Stored in a dark bottle and freshly prepared before every measurement.



# **Phosphate Reagents**

Stock molybdate solution, 0.03M (0.8% w/v)

Dissolve 8g Disodium Molybdate(VI) Dihydrate,  $Na_2MoO_4 \cdot 2H_2O$ , and 0.17g Antimony Potassium Tartrate,  $C_8H_4K_2O_{12}Sb_2 \cdot 3H_2O$ , in 1000ml of DIW containing 50ml concentrated  $H_2SO_4$ .

# Mixed Reagent

Dissolve 0.8g L (+)-Ascorbic Acid,  $C_6H_8O_6$ , in 100ml of stock molybdate solution. After mixing, 2ml sodium dodecyl sulphate (15% solution in water) is added. Stored in a dark bottle and freshly prepared before every measurement.

# PO4 dilution

Dissolve Sodium Hydrate, NaCl, 10g in ca. 900ml, add 50ml Acetone and 4ml concentrated  $H_2SO_4$ , make up to 1000ml. After mixing, 5ml sodium dodecyl sulphate (15% solution in water) is added.

# 3.4.2.2 Sampling procedures

Sampling of nutrients followed that oxygen, trace gases and salinity. Samples were drawn into two of virgin 10 ml polyacrylates vials without sample drawing tubes. These were rinsed three times before filling and vials were caped immediately after the drawing. The vials are put into water bath at 26 deg. C in 10 minutes before use to stabilize the temperature of samples.

No transfer was made and the vials were set an auto sampler tray directly. Samples were analyzed after collection basically within 17 hours.

#### 3.4.2.3 Data processing.

Raw data from TRAACS800 were treated as follows;

Check baseline shift.

Check the shape of each peak and positions of peak values taken, and then change the positions of peak values taken if necessary.

Carriover correction and baseline drift correction were applied to peak heights of each samples followed by sensitivity correction.

Baseline correction and sensitivity correction were done basically using liner regression.

Load pressure and salinity from CTD data to calculate density of seawater.

Calibration curves to get nutrients concentration were assumed second order equations.

#### 3.4.3 Nutrients standards

## 3.4.3.1 In-house standards

#### 3.4.3.1.1 Volumetric Laboratory Ware.

All volumetric glass- and plastic (PMP)-ware used were gravimetrically calibrated. Plastic volumetric flasks were gravimetrically calibrated at the temperature of use within 2-3 K.

#### Volumetric flasks.

Volumetric flasks of Class quality (Class A) are used because their nominal tolerances are 0.05% or less over the size ranges likely to be used in this work. Class A flasks are made of borosilicate glass, and the standard solutions were transferred to plastic bottles as quickly as possible after they are made up to volume and well mixed in order to prevent excessive dissolution of silicic acid from the glass. High quality plastic (polymethylpentene, PMP, or polypropylene) volumetric flasks were gravimetrically calibrated and used only within 3-4 K of the calibration temperature.

The computation of volume contained by glass flasks at various temperatures other than the calibration temperatures were done by using the coefficient of linear expansion of borosilicate crown glass.

Because of their larger temperature coefficients of cubical expansion and lack of tables constructed for these materials, the plastic volumetric flasks were gravimetrically calibrated over the temperature range of intended use and used at the temperature of calibration within 3-4 K. The weights obtained in the calibration weightings were corrected for the density of water and air buoyancy.

#### Pipettes and pipettors.

All pipettes have nominal calibration tolerances of 0.1% or better. These were gravimetrically calibrated in order to verify and improve upon this nominal tolerance.

## 3.4.3.1.2 REAGENTS, GENERAL CONSIDERATIONS

#### **General Specifications.**

All reagents were of very high purity such as "Analytical Grade," "Analyzed Reagent Grade" and others. And assay of nitrite was determined according JISK8019 and assays of nitrite salts were 98.9%. We use that value to adjust the weights taken.

For the silicate standards solution, we use commercial available silicon standard solution for atomic absorption spectrometry of 1000mg  $L^{-1}$ . Since this solution is alkaline solution of 0.5 M KOH, an aliquot of 40ml solution were diluted to 500ml as B standard together with an aliquot of 20ml of 1M HCl. Then the pH of B standard for silicate prepared to be 6.9.

#### Ultra pure water.

Ultra pure water (MilliQ water) freshly drawn was used for preparation of reagents, higher concentration standards and for measurement of reagent and system blanks.

#### Low-Nutrient Seawater (LNSW).

Surface water having low nutrient concentration was taken and filtered using  $0.45 \,\mu m$  pore size membrane filter. This water is stored in 20 liter cubitainer with paper box. The concentrations of nutrient of this water were measured carefully in March 2005.

## 3.4.3.1.3 Concentrations of nutrients for A, B and C standards

Concentrations of nutrients for A, B and C standards are set as shown in Table 3.4.1. The C standard is prepared according recipes as shown in Table 3.4.2. All volumetric laboratory tools were calibrated prior the cruise as stated in chapter (i). Then the actual concentration of nutrients in each fresh standard was calculated based on the ambient, solution temperature and determined factors of volumetric lab. wares.

Table 3.4.1: Nominal concentrations of nutrients for A, B and C standards

|                      | Α     | В    | C-1 | C-2 | C-3 | C-4 | C-5 |
|----------------------|-------|------|-----|-----|-----|-----|-----|
| NO <sub>3</sub> (µM) | 45000 | 900  | 0   | 9   | 27  | 45  | 54  |
| $NO_2(\mu M)$        | 4000  | 20   | 0   | 0.2 | 0.6 | 1.0 | 1.2 |
| $SiO_2(\mu M)$       | 36000 | 2880 | 0   | 29  | 86  | 143 | 172 |
| PO <sub>4</sub> (µM) | 3000  | 60   | 0   | 0.6 | 1.8 | 3.0 | 3.6 |

#### Table 3.4.2: Working calibration standard recipes

| C-STD | B-1 STD | B-2 STD | MAT   |
|-------|---------|---------|-------|
| C-1   | 0 ml    | 0 ml    | 60 ml |
| C-2   | 5 ml    | 5 ml    | 50 ml |
| C-3   | 15 ml   | 15 ml   | 30 ml |
| C-4   | 25 ml   | 25 ml   | 10 ml |
| C-5   | 30 ml   | 30 ml   | 0 ml  |

B-1 STD: Mixture of nitrate, silicate and phosphate

B-2 STD: Nitrite

#### 3.4.3.1.4 Renewal of in-house standard solutions.

In-house standard solutions as stated in (iii) were renewed as shown in Table 3.4.3.

| $NO_3$ , $NO_2$ , $SiO_2$ , $PO_4$                                    | Renewal                      |
|---|------------------------------|
| A-1 Std. (NO <sub>3</sub> )   | maximum 1 month              |
| A-2 Std. (NO <sub>2</sub> )   | maximum 1 month              |
| A-3 Std. (SiO <sub>2</sub> )  | commercial prepared solution |
| A-4 Std. (PO <sub>4</sub> )   | maximum 1 month              |
| B-1 Std.  |                              |
| (mixture of NO <sub>3</sub> , SiO <sub>2</sub> , PO <sub>4</sub> )    | 3 days                       |
| <b>B-2 Std.</b> (NO <sub>2</sub> )                                    | 6 days                       |
|   |                              |
|   |                              |
| C Std   | Renewal                      |
| C-1 ~ C-5 Std (mixture of B1  | Renewal<br>24 hours          |
|   |                              |
| C-1 ~ C-5 Std ( mixture of B1   |                              |
| C-1 ~ C-5 Std ( mixture of B1<br>and B2 Std.)                         | 24 hours                     |
| C-1 ~ C-5 Std ( mixture of B1<br>and B2 Std.)<br>Reduction estimation | 24 hours<br>Renewal          |

Table 3.4.3: Timing of renewal of in-house standards.

# 3.4.3.2 RMNS

To get the more accurate and high quality nutrients data to achieve the objectives stated above, huge numbers of the bottles of the reference material of nutrients in seawater (hereafter RMNS) are prepared (Aoyama et al., submitted). In the previous world wide expeditions, such as WOCE cruises, the higher reproducibility and precision of nutrients measurements were required (Joyce and Corry, 1994). Since no standards were available for the measurement of nutrients in seawater at that time, the requirements were described in term of reproducibility. The required reproducibility was 1%, 1-2%, 1-3% for nitrate, phosphate and silicate, respectively. Although nutrient data from the WOCE one-time survey was of unprecedented quality and coverage due to much care in sampling and measurements, the differences of nutrients concentration at crossover points are still found among the expeditions (Aoyama and Joyce, 1996, Mordy et al., 2000, Gouretski and Jancke, 2001). For instance, the mean offset of nitrate concentration at deep waters was 0.5  $\mu$ mol kg<sup>-1</sup> for 345 crossovers at world oceans, though the maximum was 1.7  $\mu$ mol kg<sup>-1</sup> (Gouretski and Jancke, 2001). At the 31 crossover points in the Pacific WHP one-time lines, the WOCE standard of reproducibility

for nitrate of 1% was fulfilled at about half of the crossover points and the maximum difference was 7% at deeper layers below 1.6 deg. C in potential temperature (Aoyama and Joyce, 1996).

#### 3.4.3.3 RMNS preparation

#### **RMNS** preparation and homogeneity for previous lots.

The study on reference material for nutrients in seawater (RMNS) on the seawater base has been carried out to establish traceability on nutrient analyses in seawater since 1994 in Japan. Autoclaving to produce RMNS has been studied (Aminot and Kerouel, 1991, 1995) and autoclaving was used to stabilize the samples for the 5th intercompariosn exercise in 1992/1993 (Aminot and Kirkwood, 1995). Aminot and Kerouel (1995) concluded that nitrate and nitrite were extremely stable throughout their 27 months storage experiment with overall standard deviations lower than 0.3% (range 5-50  $\mu$ mol 1<sup>-1</sup>) and 0.8% (range 0.5-5  $\mu$ mol 1<sup>-1</sup>), respectively. For phosphate, slight increase by 0.02-0.07  $\mu$ mol 1<sup>-1</sup> per year was observed due to the leaching from the container glass. The main source of nutrient variation in seawater is believed to be microorganism activity, hence, production of RMNS depends on biological inactivate the biological activity is acceptable for RMNS preparation.

In the R/V Mirai BEAGLE2003 cruise, which was around the world cruise along ca. 30 deg. S and conducted in 2003 and 2004, RMNS was analyzed at about 500 stations throughout cruises. The results of BEAGLE2003 cruise will be available soon. (Databook of BEAGLE2003, in press)

The seawater for RMNS production was sampled in the North Pacific Ocean at the depths of surface where the nutrients are almost depleted and 1500-2000 meters depth where the nutrients concentrations are the maximum. The seawater was gravity-filtered through a membrane filter with a pore size of 0.45  $\mu$ m (Millipore HA). The latest procedure of autoclaving for RMNS preparation is that the seawater in a stainless steel container of 40 liters was autoclaved at 120 deg. C, 2 hours, 2 times during two days. The filling procedure of autoclaved seawater was basically same throughout our study. Following cooling at room temperature in two days, polypropylene bottle of 100 ml capacity were filled by the autoclaved seawater of 90 ml through a membrane filter with a pore size of 0.2  $\mu$ m (Millipore HA) at a clean bench in a clean room. The polypropylene caps were immediately tightly screwed on and a label containing lot number and serial number of the bottle was attached on all of the bottles. Then the bottles were vacuum-sealed to avid potential contamination from the environment.

#### **RMNSs for this cruise**

RMNS lots BC,AV,AX,AY and BA, which covers full range of nutrients concentrations in the western North Pacific are prepared as packages. These packages were renewed daily and analyzed every 2-6 runs on the same day. 150 bottles of RMNS lot AZ are prepared to use every analysis at every hydrographic station. These RMNS assignment were completely done based on random number. The RMNS bottles were stored at a room, REGENT STORE, where the temperature was maintained around 26-28 deg. C.

#### 3.4.3.4 The homogeneity of RMNSs

The homogeneity of lot BC and analytical precisions are shown in Table 3.4.4. These are for the assessment of the magnitude of homogeneity of the RMNS bottles those are used during the cruise.

As shown in Table3.4.4, the homogeneity of RMNS lot BC for nitrate and silicate are the same magnitude of analytical precision derived from fresh raw seawater. The homogeneity for phosphate, however, exceeded the analytical precision at some extent.

|           | Nitrate | Phosphate | Silicate |
|-----------|---------|-----------|----------|
|           | CV%     | CV%       | CV%      |
| BC        | 0.22    | 0.32      | 0.19     |
| (AH)      | (0.39%) | (0.83%)   | (0.13)   |
| (K)       | (0.3%)  | (1.0%)    | (0.2%)   |
| Precision | 0.22%   | 0.22%     | 0.12%    |

Table 3.4.4:Homogeneity of lot BC and previous lots derived from simultaneous 30 samplesmeasurements and analytical precision onboard R/V Mirai in May 2005.

Note:  $N=30 \ge 2$ 

#### 3.4.4 Quality control

## 3.4.4.1 Precision of nutrients analyses during the cruise

Precision of nutrients analyses during the cruise was evaluated based on the 12 measurements, which are measured every 12 samples, during a run at the concentration of C-5. We also evaluated the reproducibility based on the replicate analyses of five samples in each run. Summary of precisions are shown in Table 3.4.5. As shown in Table 3.4.5 and Figures 3.4.5-3.4.7, the precisions for each parameter are generally good considering the analytical precisions estimated from the simultaneous analyses of 60 samples in May 2005. Analytical precisions previously evaluated were 0.22% for phosphate, 0.22% for nitrate and 0.12% for silicate, respectively. During this cruise, analytical precisions were 0.12% for phosphate, 0.09% for nitrate and 0.08% for silicate in terms of median of precision, respectively. Then we can conclude that the analytical precisions for phosphate, nitrate and silicate were maintained or better throughout this cruise comparing the pre-cruise evaluations. The time series of precision are shown in Figures 3.4.5-3.4.7.

|         | Nitrate | Phosphate | Silicate |  |
|---------|---------|-----------|----------|--|
|         | CV%     | CV%       | CV%      |  |
| Median  | 0.09    | 0.11      | 0.07     |  |
| Mean    | 0.09    | 0.12      | 0.08     |  |
| Maximum | 0.17    | 0.29      | 0.19     |  |
| Minimum | 0.03    | 0.05      | 0.03     |  |
| Ν       | 126     | 126       | 126      |  |

Table 3.4.5: Summary of precision based on the replicate analyses of 12 samples in each run through out cruise.



Figure: 3.4.5 Time series of precision of nitrate



Figure: 3.4.5 Time series of precision of nitrate



Figure: 3.4.6 Time series of precision of phosphate



Figure: 3.4.7 Time series of precision of silicate

## 3.4.4.2 Carry over

We can also summarize the magnitudes of carry over throughout the cruise. These are as shown in Table 3.4.6.

|         | Table 3.4.6: Summary of carry over through out cruise. |           |          |  |  |  |  |
|---------|--|-----------|----------|--|--|--|--|
|         | Nitrate  | Phosphate | Silicate |  |  |  |  |
|         | %  | %         | %        |  |  |  |  |
| Median  | 0.30   | 0.24      | 0.21     |  |  |  |  |
| Mean    | 0.30   | 0.25      | 0.21     |  |  |  |  |
| Maximum | 0.50   | 0.71      | 0.38     |  |  |  |  |
| Minimum | 0.10   | 0.00      | 0.03     |  |  |  |  |
| Ν       | 126  | 126       | 126      |  |  |  |  |

| Table 3.4.6: Summary of carry over through out cruise. |
|--|
|--|

# 3.4.4.3 Evaluation of trueness of nutrients concentrations using RMNSs

| Uncertainties of phos   | phate measurer   | nent are expre  | essed eq. (2).            |           |        |   |
|-------------------------|------------------|-----------------|---------------------------|-----------|--------|---|
| Uncertainties           | (%)              | =               | -0.11                     | +         | 1.032  | / |
| Cphos                   |                  |                 | • •                       | ••• (2)   |        |   |
| Where Cphos is ph       | osphate concen   | tration in mic  | ro mol kg <sup>-1</sup> . |           |        |   |
|                         |                  |                 |                           |           |        |   |
| Uncertainties of silica | ate measuremen   | nt are expresse | ed eq. (3).               |           |        |   |
| Uncertainties (%) =     | = 0.095 + 4.92 / | Csilicate ·     | •••••                     | • • • • • | •• (3) |   |

Where Csilicate is silicate concentration in micro mol kg<sup>-1</sup>.

Then, three columns to show the uncertainties of nutrients measurement were created in the sea file of this cruise.



Figure: 3.4.8: Time series of nitrate concentration for RMNSs



Figure: 3.4.9: Same as Figure 3.4.8, but for phosphate



Figure: 3.4.10: Same as Figure 3.4.8, but for silicic acid

# 3.4.5 Cruise-to-cruise traceability

Cruise-to-cruise traceability was examined based on the results of the previous results of RMNSs obtained among several cruises and laboratory analyses. As shown in table 3.4.7, the nutrients concentration of RMNSs were in good agreement among experiments.

|            | Table 3 | .4.7: Cruise | to cruise tra | cerbility |       |
|------------|---------|--------------|---------------|-----------|-------|
| Cruise/Lab |         |              | RM Lots       |           |       |
| Cruise/Lab | AX      | AV           | BC            | AZ        | AH    |
|            |         |              | Nitrate       |           |       |
| BEAGLE2003 |         |              |               |           | 35.3  |
| RY0501     | 21.8    |              |               | 41.9      | 35.5  |
| MR0501     | 21.5    | 33.4         |               |           | 35.5  |
| Pre-MR0502 |         |              | 40.8          |           |       |
| KANSO2005  | 21.4    | 33.2         | 40.5          | 41.9      | 35.9  |
| MR0502     | 21.5    | 33.4         | 40.7          | 42.3      |       |
|            |         | 1            | Phosphate     |           |       |
| BEAGLE2003 | —       |              | nospilate     |           | 2.10  |
| RY0501     | 1.52    |              |               | 2.99      | 2.10  |
| MR0501     | 1.62    | 2.52         |               | 2.77      | 2.00  |
| Pre-MR0502 | 1.02    | 2.02         | 2.78          |           | 2.13  |
| KANSO2005  | 1.59    | 2.48         | 2.72          | 3.01      | 2.03  |
| MR0502     | 1.61    | 2.52         | 2.78          | 3.01      |       |
|            |         |              | C11:4-        |           |       |
|            | -       |              | Silicate      |           |       |
| BEAGLE2003 |         |              |               |           | 133.8 |
| RY0501     | 59.9    |              |               | 135.6     | 133.8 |
| MR0501     | 59.4    | 157.7        |               |           | 135.5 |
| Pre-MR0502 |         |              | 160.7         |           |       |
| KANSO2005  | 59.5    | 156.6        | 159.5         | 136.3     | 135.4 |
| MR0502     | 59.5    | 157.9        | 159.9         | 137.1     |       |

## 3.4.6 Problems/improvements occurred and solutions.

As shown in Figure 3.4.7, the precisions of silicate concentration reached to 0.15-0.19% at several stations before station 118, of which serial number of the station is 26. The cause of relatively higher precisions was attributed to be larger ambient temperature variability up to 1 deg. C around 30 minutes interval. We re-arranged a setting of room temperature control to be more stable and got less room temperature variability around 0.5 deg. C. Then we can see much better precision of silicate analyses after re-arrangement as shown in Figure 3.4.7.

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#### Appendix 1

- 1. Section of Nitrate (Tentative value)
- 2. Section of Phosphate (Tentative value)
- 3. Section of Silicate (Tentative value)







# 3.5 Chlorofluorocarbons

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#### 3.5.1 Objectives

Chlorofluorocarbons (hereafter CFCs) are chemically and biologically stable gases that have been artificially synthesized at 1930's or later. The atmospheric CFCs can slightly dissolve in sea surface water and then circulate in the ocean. Three chemical species of CFCs, namely CFC-11 (CCl3F), CFC-12 (CCl2F2) and CFC-113 (C2Cl3F3), can be used as transient tracers for decadal scale circulation of the ocean. We determined these CFCs concentrations in seawater on board.

#### 3.5.2 Apparatus

Dissolved CFCs are detected by an electron capture detector – gas chromatograph attached with a purging & trapping system.

| Table 3-5-1 Instruments  |                        |  |  |  |  |  |
|--|------------------------|--|--|--|--|--|
| Gas Chromatograph:   | GC-14B (Shimadzu Ltd.) |  |  |  |  |  |
| Detector:  | ECD-14 (Shimadzu Ltd)  |  |  |  |  |  |
| Analytical Columr  | Analytical Column:     |  |  |  |  |  |
| Pre column: Silica Plot capillary columns [i.d.: 0.53 mm, length: 4 m, film thickness: 6 µm] |                        |  |  |  |  |  |
| Main column: Connected two capillary columns (Pola Bond-Q [i.d.: 0.53 mm, length: 7 m,       |                        |  |  |  |  |  |
| film thickness: 10 µm] followed by Silica Plot [i. d.: 0.53 mm, length: 22 m, tick: 6 µm])   |                        |  |  |  |  |  |
|  |                        |  |  |  |  |  |

# 3.5.3 Procedures 3.5.3.1 Sampling

Seawater sub-samples for CFCs measurement were collected from 12 litter Niskin bottles to 300ml glass bottle. The bottle was filled by nitrogen gas before sampling. Two times of the bottle volumes of seawater sample were overflowed. The bottles filled by seawater sample were kept in water bathes roughly controlled on sample temperature. The CFCs concentrations were determined as soon as possible after sampling (within 24 hr in maximum). These procedures were needed in order to minimize contamination from atmospheric CFCs.

Air samples for CFCs measurement were collected to 100ml glass cylinder attached magnesium perchlorate dryer tube at the navigation deck on R/V "MIRAI".

# 3.5.3.2 Analysis

The CFCs analytical system is modified from the original design of Bullister and Weiss (1988). Constant volume of sample water (50ml) is taken into the purging & trapping system. Dissolved CFCs are de-gassed by N2 gas purge and concentrated in a trap column cooling to -45 degree centigrade. The CFCs are desorbed by heating the trap column to 140 degree centigrade within 1.5 minutes, and lead into an electron capture detector - gas chromatograph (ECD-GC). The analytical conditions are listed following table in detail.

|                   | 5          |   |  |  |  |  |
|-------------------|------------|---|--|--|--|--|
| Temperature       |            |   |  |  |  |  |
| Analytical Colu   | umn:       | 95 deg-C  |  |  |  |  |
| Detector (ECD     | ):         | 240 deg-C   |  |  |  |  |
| Trap column:      |            | -45 deg-C (at adsorbing) & 140 deg-C (at desorbing) |  |  |  |  |
|                   |            |   |  |  |  |  |
| Mass flow rate of | f nitrogen | gas (99.9999%)                                      |  |  |  |  |
| Carrier gas:      |            | 20 ml/min   |  |  |  |  |
| Detector Make     | UP:        | 16 ml/min   |  |  |  |  |
| Back flush gas:   | :          | 20 ml/min   |  |  |  |  |
| Sample purge gas: |            | 200 ml/min  |  |  |  |  |
|                   |            |   |  |  |  |  |
| Standard gas (Jap | oan Fine P | Products co. ltd.)                                  |  |  |  |  |
| Base gas:         | Nitrogen   |   |  |  |  |  |
| CFC-11: 300 ppt ( |            | (v/v)   |  |  |  |  |
| CFC-12:           | 160 ppt (  | (v/v)   |  |  |  |  |
| CFC-113:          | 30 ppt (v  | /v)   |  |  |  |  |
|                   |            |   |  |  |  |  |

Table 3-5-2 Analytical conditions of dissolved CFCs in seawater.

## 3.5.3.3 Performance

The analytical precisions are estimated from replicate sample analyses. The precisions were calculated to be  $\pm 0.012 \text{ pmol/kg}$  (n = 220),  $\pm 0.007 \text{ pmol/kg}$  (n = 219) and  $\pm 0.007 \text{ pmol/kg}$  (n = 218) for CFC-11, -12 and -113, respectively. The standard gases used in this cruise will be calibrated to SIO scale standard gases after the cruise, and then the data will be corrected.

## 3.5.4 Results

Penetration depths of CFCs were around 1500 m at northern region (higher than 30 degree North) and shallower than 1000 m at low latitude. CFC-113 maximum was found around 500 - 1000 m between 35 degree-N and 20 degree-N. We detected significant increase in CFCs around 250 - 1000 m in this decade (Fig 3-5-1)





Fig. 3-5-1 Comparison between CFC-12 distributions of WOCE P10 data (a) and this cruise (b). Shallower part (<1500 m) is expanded. Distribution of difference in CFC-12 concentration between two observations is plotted (c).

#### 3.5.5 Data archive

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

#### 3.5.6 Reference

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3.6. Carbon items Akihiko Murata (JAMSTEC) Fuyuki Shibata (MWJ) Mikio Kitada (MWJ) Taeko Ohama (MWJ) Yoshiko Ishikawa (MWJ)

#### 3.6.1 Objectives

Concentrations of  $CO_2$  in the atmosphere are now increasing at a rate of 1.5 ppmv y<sup>-1</sup> owing to human activities such as burning of fossil fuels, deforestation, and cement production. It is an urgent task to estimate as accurately as possible the absorption capacity of the oceans against the increased atmospheric  $CO_2$ , and to clarify the mechanism of the  $CO_2$  absorption, because the magnitude of the anticipated global warming depends on the levels of  $CO_2$  in the atmosphere, and because the ocean currently absorbs 1/3 of the 6 Gt of carbon emitted into the atmosphere each year by human activities.

In this cruise, we were aimed at quantifying how much anthropogenic  $CO_2$  is absorbed in the North Pacific Ocean, especially in North Pacific Intermediate Water. For the purpose, we measured  $CO_2$ -system parameters such as dissolved inorganic carbon ( $C_T$ ), total alkalinity ( $A_T$ ) and pH.

#### 3.6.2 Apparatus

 $(1) C_{T}$ 

Measurements of  $C_T$  was made with two total  $CO_2$  measuring systems (systems A and B; Nippon ANS, Inc.), which are slightly different from each other. The systems comprise of a sea water dispensing system, a  $CO_2$  extraction system and a coulometer (Model 5012, UIC Inc.).

The seawater dispensing system has an auto-sampler (6 ports), which takes seawater in a 300 ml borosilicate glass bottle and dispenses the seawater to a pipette of nominal 20 ml volume by

PC control. The pipette was kept at 20 °C by a water jacket, in which water from a water bath set at 20 °C is circulated.

CO<sub>2</sub> dissolved in a seawater sample is extracted in a stripping chamber of the CO<sub>2</sub> extraction system by adding phosphoric acid (10 % v/v). The stripping chamber is made approx. 25 cm long and has a fine frit at the bottom. To degass CO<sub>2</sub> as quickly as possible, a heating wire kept at 40 °C is rolled from the bottom to a 1/3 height of the stripping chamber. The acid is added to the stripping chamber from the bottom of the chamber by pressurizing an acid bottle for a given time to push out the right amount of acid. The pressrizing is made with nitrogen gas (99.9999 %). After the acid is transferred to the stripping chamber, a seawater sample kept in a pipette is introduced to the stripping chamber by the same method as in adding an acid. The seawater reacted with phosphoric acid is stripped of CO<sub>2</sub> by bubbling the nigrogen gas through a fine frit at the bottom of the stripping chamber. The CO<sub>2</sub> stripped in the chamber is carried by the nitrogen gas (flow rates of 130 ml min<sup>-1</sup> and 140 ml min<sup>-1</sup> for systems A and B, respectively) to the coulometer through a dehydrating module. For system A, the module consists of two electric dehumidifiers (kept at 1 – 2 °C) and a chemical desiccant.

The measurement sequence such as system blank (phosphoric acid blank),  $2 \% CO_2$  gas in a nitrogen base, seawater samples (6) was programmed to repeat. The measurement of  $2 \% CO_2$  gas was made to monitor response of coulometer solutions (from UIC, Inc.).

#### $(2) A_T$

Measurement of  $A_T$  was made using a titration system (Nippon ANS, Inc.). The system comprise of a water dispensing unit, an auto-burette (Metrohm), a pH meter (Thermo Electron), and a pair of electrodes (Reference electrode: REF201 (Rodiometer), Glass pH Electrode: pHG201-7 (Radiometer)), or combination electrodes (ROSS 8102BN: Thermo Electron Corporation), which is automatically controlled by a PC.

A seawater of approx. 40 ml is transferred from a sample bottle (brosilicate glass bottle; 130 ml) into a water-jacketed (25 °C), and is introduced into a water-jacketed (25 °C) titration cell. The seawaters are titrated by a acid titrant, which was 0.05 M HCl in 0.65 M NaCl in this cruise.

Calibration of the acid titrant was made by measuring  $A_T$  of 5 solutions of  $Na_2CO_3$  in 0.7 M NaCl solutions. The computed  $A_Ts$  were approx. 0, 100, 1000, 2000 and 2500 µmol kg<sup>-1</sup>. The measured values of  $A_T$  (calculated by assuming 0.05 M) should be a linear function of the  $A_T$  contributed by the  $Na_2CO_3$ . The line was fitted by the method of least squares. Theoretically, the slope should be unity. If the measured slope is not equal to one, the acid normality should be adjusted by dividing initial normality by the slope, and the whole set of calculations is repeated until the slope = 1

Calculation of A<sub>T</sub> was made based on a modified Gran approach.

#### (3) pH

Measurement of pH was made by a pH measuring system (Nippon ANS, Inc.), which adopts a method for the spectrophotometric determination. The system comprises of a water dispensing unit and a spectrophotometer (Carry 50 Scan, Varian). For an indicator, *m*-cresol purple (2 mM) was used.

Seawater is transferred from borosilicate glass bottle (300 ml) to a sample cell in the

spectrophotometer. The length and volume of the cell are 8 cm and 13 ml, respectively, and the sample cell is kept at  $25.00 \pm 0.05$  °C in a thermostated compartment. First, absorbances of seawater only are measured at three wavelengths (730, 578 and 434 nm). Then the indicator is injected and circulated for about 3 or 3.5 minutes. to mix the indicator and seawater sufficiently. After the pump is stopped, the absorbances of seawater + indicator are maeasured at the same wavelengths. The pH was calculated based on the following equation (Clayton and Byrne, 1993):

$$pH = pK_2 + \log\left(\frac{A_1 / A_2 - 0.00691}{2.2220 - 0.1331(A_1 / A_2)}\right)$$

where  $A_1$  and  $A_2$  indicate absorbances at 578 and 434 nm, respectively, and  $pK_2$  is calculated as a function of water temperature and salinity.

#### Reference

Clayton T.D. & R.H. Byrne (1993) Spectrophotometric seawater pH measurements: total hydrogen ion concentration scale calibration of m-cresol purple and at-sea results. Deep-Sea Research 40, 2115-2129.

## 3.6.3 Performances

(1)  $C_T$ 

The two systems had worked well during the leg without a major malfunction. Replicate analysis was made for 3 - 4 pair samples at each water column. The repeatability for systems A and B were estimated to be 0.8 (n = 117 pairs) and 1.7 (n = 94 pairs) µmol kg<sup>-1</sup>, respectively. The combined result was 1.2 µmol kg<sup>-1</sup> (n = 211 pairs).

#### $(2) A_{T}$

The systems conducted a high speed titration (5 - 6 min.) compared to systems used in previous studies. A few replicate samples were taken on every station. The repeatability was estimated to be  $1.8 \mu$ mol kg<sup>-1</sup> (n = 212 pairs).

#### (3) pH

The system had worked well with no troubles. The average of absolute differences between replicate samples was 0.0008 pH unit (n = 207 pairs).

#### 3.6.4 Results

Cross sections of C<sub>T</sub>, A<sub>T</sub> and pH along the observation line are illustrated in Fig. 1.



Fig. 1 Distributions of C<sub>T</sub>, A<sub>T</sub> and pH along the observation line

# 3.7 Samples taken for other chemical measurement

# 3.7.1 Carbon-14, carbon-13 (2-July-2005)

## Yuichiro KUMAMOTO

Japan Agency for Marine Earth Science and Technology

# 3.7.1.1 Objective

In order to investigate water circulation and carbon cycle in the western Pacific, seawater for carbon-14 (C-14; radiocarbon) and carbon-13 (C-13; stable carbon isotope) of total dissolved inorganic carbon (TDIC) was collected by the hydrocasts from surface to bottom.

#### 3.7.1.2 Sample collection

The sampling stations and number of samples are summarized in Table 3.7.1-1. All samples for carbon isotope ratios were collected at 19 stations using 12 liter Niskin bottles. The seawater

sample was siphoned into a 250 cm<sup>3</sup> glass bottle with enough seawater to fill the glass bottle 3 times. Immediately after sampling, 10 cm<sup>3</sup> of seawater was removed from the bottle and poisoned by 0.1 cm<sup>3</sup>  $\mu$ l of saturated HgCl<sub>2</sub> solution. Then the bottle was sealed by a glass stopper with Apiezon grease M and stored in a cool and dark space on board.

#### 3.7.1.3 Sample preparation and measurements

In our laboratory, dissolved inorganic carbon in the seawater samples will be stripped cryogenically and split into three aliquots: radiocarbon measurement (about 200  $\mu$ mol), C-13 measurement (about 100  $\mu$ mol), and archive (about 200  $\mu$ mol). The extracted CO<sub>2</sub> gas for radiocarbon will be then converted to graphite catalytically on iron powder with pure hydrogen gas. The C-13 of the extracted CO<sub>2</sub> gas will be measured using Finnigan MAT252 mass spectrometer. The carbon-14 in the graphite sample will be measured by Accelerator Mass Spectrometry (AMS).

| Table 3.7.1-1. The sampling stations and number of samples for carbon isotope ratios. |             |                       |                            |  |  |
|---|-------------|-----------------------|----------------------------|--|--|
| Station   | No. samples | No. replicate samples | Max. sampling pressure /db |  |  |
| P10N-136  | 19          | 1                     | 2001.7                     |  |  |
| P10N-130  | 36          | 2                     | 5404.4                     |  |  |
| P10N-120  | 19          | 1                     | 2000.0                     |  |  |
| P10N-110  | 36          | 2                     | 6211.2                     |  |  |
| P10N-100  | 19          | 1                     | 2000.4                     |  |  |
| P10-073   | 36          | 2                     | 6333.4                     |  |  |
| P10-068   | 19          | 1                     | 2001.7                     |  |  |
| P10-064   | 36          | 2                     | 5811.2                     |  |  |
| P10-060   | 19          | 1                     | 1999.4                     |  |  |
| P10-056   | 35          | 2                     | 5484.1                     |  |  |
| P10-051   | 19          | 1                     | 2000.2                     |  |  |
| P10-047   | 36          | 2                     | 5909.5                     |  |  |
| P10-040   | 19          | 1                     | 2000.5                     |  |  |
| P10-034   | 31          | 2                     | 4242.0                     |  |  |
| P10-029   | 19          | 1                     | 2002.5                     |  |  |
| P10-024   | 31          | 2                     | 4548.4                     |  |  |
| P10-017   | 33          | 2                     | 4775.7                     |  |  |
| P10-010   | 12          | 1                     | 727.8                      |  |  |
| P10-005   | 20          | 1                     | 2173.1                     |  |  |
| Total   | 494         | 28                    |                            |  |  |

Table 3.7.1-1. The sampling stations and number of samples for carbon isotope ratios.

# 3.7.2 Radionuclides (draft as of 30 June, 2005)

# Michio Aoyama (Meteorological Research Institute / Japan Meteorological Agency, Principal Investigator)

# 3.7.2.1 Objectives

- 1) Study more about present distribution of 137Cs in the subtropical gyre originated mainly from atmospheric nuclear weapons tests conducted in the 1960s.
- 2) Provide detail artificial radionuclides database for general criculation model validation

# 3.7.2.2 Target radionuclides

Main target radionuclides are 137Cs, and Pu..

# 3.7.2.3 Sampling procedures

Sampling of seawater samples of radionuclides in water column were done followed that all parameters. The additional bottles were available by chance, then, the samples volumes for water column varied from 6 liter to 20 liter. Samples were drawn into 10 or 20 liter cubitainers from the Niskin bottles. Concentrated Nitric Acid was added to the samples to keep pH1.6.

Surface water samples were drawn through intake pump below several meters from the surface. Seawater of 85 liter were collected for 137Cs and Pu.

# 3.7.2.4 Samples accomplished during the cruise

A total of 7 samples were collected for surface sample. At the 7 stations, a total of 50 samples were collected for water column.

# 3.7.2.5 Problem occurred and solutions.

No problem occurred.

# 3.7.2.6 Sampling summary

| St<br>ation# |    | Lat.    |     | Long.   | Sampling layer        | Number of layers |
|--------------|----|---------|-----|---------|-----------------------|------------------|
| 64           | 22 | 30.00 N | 149 | 20.00 E | Sur, 100-600,800,1000 | 9 layers         |
| 62           | 21 | 10.00 N | 149 | 20.00 E | Sur, 100-600,800,1000 | 9 layers         |
| 60           | 19 | 50.00 N | 149 | 20.00 E | Sur, 100-600,800,1000 | 9 layers         |
| 58           | 18 | 30.00 N | 149 | 20.00 E | Sur, 100-600,800,1000 | 9 layers         |
| 56           | 17 | 10.00 N | 149 | 20.00 E | Sur, 100-600,800      | 8 layers         |
| 54           | 15 | 50.00 N | 149 | 20.00 E | Sur, 100-600          | 7 layers         |
| 52           | 14 | 30.00 N | 149 | 20.00 E | Sur, 100-600          | 7 layers         |

# 3.7.3 C-13, N-15

Tomomi Takamura and Hisayuki Y. Inoue (not on board) Graduate School of Environmental Science, Hokkaido University, Kita 10 Nishi 5, Kita-Ku, Sapporo, Hokkaido 060-0810, Japan

#### (1) Objective

While the ocean is known as one of the major sinks for atmospheric  $CO_2$ , the magnitude of the oceanic  $CO_2$  uptake is unclear. It is necessary to clarify how and to what extent the carbonate system in the ocean affects the atmospheric  $CO_2$  concentration via the changes in air-sea  $CO_2$  flux. The air-sea  $CO_2$  flux is conventionally estimated by the products of the gas transfer velocity, solubility of  $CO_2$ , and the difference in partial pressure of  $CO_2$  in surface seawater (p $CO_2$ sw) and that in overlying air (p $CO_2$ air). The p $CO_2$ sw is changed by the following factors: biological activities, the ocean dynamics (lateral transport, vertical mixing) and thermodynamic effects derived from changes in surface sea temperature and salinity. In the western North Pacific Subtropical Gyre (NPSG), the p $CO_2$ sw variations were mostly caused by the change in DIC as well as the effect of thermodynamics. But the contribution of biological activities and the ocean dynamics to the DIC change is still unclear.

In this cruise, we collect water samples for measurements of  $\delta^{13}$ C of dissolved inorganic carbon (DIC) and  $\delta^{15}$ N of suspended particulate nitrogen. The objective of these collections of samples is to describe the oceanic CO<sub>2</sub> system in the western North Pacific and clarify the effect of biological activities to CO<sub>2</sub> system in this region.

# (2) Sampling and Methods

# (a) $\delta^{13}C$ of DIC:

Seawater samples for analysis of  $\delta^{13}$ C of DIC were taken from Niskin bottles on CTD/carousel sampler at the total of 23 hydrographic stations (~2000m). Seawater samples were collected in 100 ml glass bottles with butyl gum cap and sealed by aluminum cap. The samples were poisoned with 100 µl of saturated mercuric chloride solution and preserve at room temperature.

# (b) $\delta^{15}$ N of suspended particulate nitrogen

For measurements of  $\delta^{15}$ N of suspended particulate nitrogen, surface seawater sample was taken by using a bucket from broadside. In order to isolate the suspended particulate matter, about 20 liters of water were filtered through pre-combusted (450°C, 4 hours) GF/F filters (Whatman; 47 mm diameter). Filters are stored in a refrigerator (<-20°C) until isotopic analysis will be made.

## (3) Results

Measurements of  $\delta^{13}$ C of DIC and  $\delta^{15}$ N of suspended particulate nitrogen will be made at the laboratory in Hokkaido University in the near future.

# **3.7.4** Distribution of diazotrophs, its rate of nitrogen fixation, and nutrients (This observation was not done in the EEZ and TW of Papua New Guinea)

#### Satoshi Kitajima and Ken Furuya

Department of Aquatic Bioscience, Graduate School of Agricultural and Life Sciences University of Tokyo

## (1) **Objective**

Cyanobacteria are taxonomically, physiologically and ecologically diverse, and dominant phytoplankters in the subtropical and tropical ocean. Spatial distribution of planktonic cyanobacteria has been well studied in the western subtropical and tropical Pacific Ocean, and their importance in nitrogen fixation is repeatedly emphasized. Particularly, some new diazotrophs, such as unicellular cyanobacteria or proteobacteria have been found in the subtropical and tropical ocean. Our results obtained during MR04-07 suggested importance of these unicellular diazotrophs. Nitrogen fixation is controlled by environmental factors such as availability of nutrients. In this cruise, we examined the correlation between nitrogen fixation rates, nutrients, and phytoplankton assemblages.

## (2) Sampling and Methods

For measurement of nitrogen fixation rate, 1800 mL of seawater were collected by a bucket at the surface layer of stations between 37 to  $3^{\circ}$  N. The seawater was poured into three or five - 1200 mL PET bottle, then placed in an on-deck incubator under natural sunlight with running near surface water pumped up from 5 m depth. Samples were spiked with 10% acetylene and return to the incubator. Subsampling was done at 0 (initial) and 24 hours after the acetylene addition to measure ethylene production using a gas chromatograph (GC-17A, Shimadzu). The ethylene production was converted to an amount of fixed nitrogen with a ratio of C<sub>2</sub>H<sub>2</sub>: N<sub>2</sub> = 1:4. After the sampling, seawater left in the vial was fixed for later microscopic observation. Nitrogen fixation by *Trichodesmium*, and *R. intracellularis* collected with horizontal hauls of a plankton net were also measured at selected stations.

Along with the nitrogen fixation rate measurements, following determination and sample preparation were made; flow cytometric count of *Synechococcus*, and *Prochlorococcus*, chlorophyll *a*, algal pigments by HPLC, microscopic observation of *Trichodesmium*, *R. intracellularis* associated with diatoms, unicellular cyanobacteria. Chlorophyll *a* and nitrogen fixation rate has already measured on board.

# (3) Future Works

Samples and specimens prepared during the cruise will be analyzed and examined. Following determinations will be on land: flow cytometric analysis fixed with 1% glutaraldehyde, pigments analysis prepared by a gentle filtration (< 18 mmHg) of particles on GF/F filters, nutrients analysis. These samples were immediately frozen and transferred to land laboratory. Samples taken with plankton net and fixed seawater samples will be also brought back to land laboratory to make further study.

## **3.8 LADCP**(Lowered Acoustic Doppler Current Profiler)

Shinya Kouketsu (JAMSTEC) Yasushi Yoshikawa (JAMSTEC)

## 3.8.1 Instrument and method

Direct flow measurement from sea surface to the bottom was carried out using a lowered acoustic Doppler current profiler (LADCP). The instrument used was the RDI Workhorse Monitor 307.2kHz unit (RD Instruments, USA). The instrument was attached on the CTD/RMS frame, orientating downward. The CPU firmware version was 16.05. The firmware was updated at station P10-002 to version 16.27.

One ping raw data were recorded. Settings for the collecting data are listed in Table 3.8.1. A total of 128 operations were made with the CTD observations. The performance of the LADCP instrument was good in northern stations (in the subarctic region of North Pacific). Profiles were obtained over 100m distance from LADCP in shallow depth and almost 60m in deeper depth. On the other hand in southern stations (in the subtropical region of North Pacific) the performance was bad. In the deeper depth, good quality data were obtained only 3 or 4 bins, which means the LADCP could observe only about 25m. It would due to a weak echo intensity, which agreed with ship's ADCP. Data transfer errors were often occurred during upload process from the LADCP to PC.

| Station            | 143-50,<br>48,47 | 49      | 46      | 45      | 44,X04         | 42-            |
|--------------------|------------------|---------|---------|---------|----------------|----------------|
| Bin length         | 8m               | 8m      | 12m     | 12m     | 12m            | 16m            |
| Bin number         | 24               | 20      | 16      | 20      | 16             | 10             |
| Standard deviation | 2cm/s            | 2cm/s   | 1.6cm/s | 1.6cm/s | 1.6cm/s        | 1.4cm/s        |
| Ping interval      | 1.2sec           | 1sec    | 1.2sec  | 1.2sec  | 1.2sec         | 1sec           |
| Percent Good       | Collect          | Collect | Collect | Collect | Not<br>collect | Not<br>collect |



#### **3.8.2 Preliminary results**

Vertical profiles of velocity field are obtained by integrating vertical velocity shears from the surface to the bottom. The detailed method is described in Fischer and Visbeck (1993). In the integration of upcasts, the first bin data from the LADCP are not used because the data were greatly influenced by the turbulent velocity by the CTD frame. The GPS navigation data are used

in the calculation of the reference velocities and the bottom-track data are used for the correction of the reference velocities. Shipboard ADCP data are not included in the calculation. At this stage the CTD data are used for the sound speed and depth calculation. Figure 3.8.1 and 3.8.2 show the results of the cross-section velocity in the subarctic North Pacific (eastward is positive) and the eastward velocity in equatorial zone, where the difference between the upcast and downcast velocity profiles are not so large. The major currents in the Western Pacific such as the Kuroshio Extension (P10N-116-114), the Equatorial Under Current (around P10-18), and New Guinea Coastal Under Current (P10-002) appeared in the figures. These currents also appeared in the ship-board ADCP current fields. But, in the subtropical region, the difference between the upcast and downcast velocity profiles is so much large. It is probably due to the short range of the LADCP signal, which makes the shears suspicious. In the estimation of the velocity from LADCP data, it is the biggest problem that there is less information of the CTD frame motion, which is only determined from bottom track data and GPS data.

After this cruise, we will re-estimate the velocity profiles by the inversion method described in Visbeck (2002). The reliability of the LADCP velocities will be considered comparing with the velocity profiles from ship-board ADCP and the velocity shears by the hydrographical data. We tested setting bins to 16m long in the tropical region. By this setting referred in Visbeck (2002), we will investigate whether the reliable velocity profile can be obtained in the subtropical region.

#### Reference

Fischer, J., and M. Visbeck (1993): Deep velocity profiling with self-contained ADCPs., *J. Atmos. Oceanic Technol.*, 10, 764-773.

Visbeck, M. (2002): Deep velocity profiling using Lowered Acoustic Doppler Current Profilers: Bottom track and inverse solutions. *J. Atmos. Oceanic Technol.*, 19, 794-807.



# 4. Floats and Drifters

# 4.1 Argo floats

| Nobuyuki Shikama | (IORGC): Principal Investigator (not on board) |
|------------------|--|
| Hiromichi Ueno   | (IORGC): not on board                          |
| Mizue Hirano     | (IORGC): not on board                          |
| Naoko Takahashi  | (MWJ): Technical Staff                         |

# 4.1.1 Objectives

The objective of deployment is to clarify the structure and temporal/spatial variability of water masses in the North Pacific such as the North Pacific Tropical Water.

The profiling floats launched in this cruise measure vertical profiles of temperature and salinity automatically every ten days. The data from the floats will enable us to understand the phenomenon mentioned above with time/spatial scales much smaller than in previous studies.

## 4.1.2 Parameters

· water temperature, salinity, and pressure

## 4.1.3 Methods

#### 4.1.3.1 Profiling float deployment

We launched 2 APEX floats manufactured by Webb Research Ltd. These floats equip an SBE41 CTD sensor manufactured by Sea-Bird Electronics Inc.

The floats usually drift at a depth of 1000 dbar (called the parking depth), diving to a depth of 2000 dbar and rising up to the sea surface by decreasing and increasing their volume and thus changing the buoyancy in ten-day cycles. During the ascent, they measure temperature, salinity, and pressure. They stay at the sea surface for approximately nine hours, transmitting the CTD data to the land via the ARGOS system, and then return to the parking depth by decreasing volume. The status of floats and their launches are shown in Table 4.1-1.

# 4.1.4 Data archive

The real-time data are provided to meteorological organizations, research institutes, and universities via Global Data Assembly Center (GDAC: http://www.usgodae.org/argo/argo.html, http://www.coriolis.eu.org/) and Global Telecommunication System (GTS), and utilized for analysis and forecasts of sea conditions.

Table 4.1-1 Status of floats and their launches

| Float                   |  |  |  |  |  |
|-------------------------|--|--|--|--|--|
| Float Type              | APEX floats manufactured by Webb Research Ltd.                 |  |  |  |  |
| CTD sensor              | SBE41 manufactured by Sea-Bird Electronics Inc.                |  |  |  |  |
| Cycle                   | 10 days (approximately 9 hours at the sea surface)             |  |  |  |  |
| ARGOS transmit          | 30 sec   |  |  |  |  |
| interval                |  |  |  |  |  |
| Target Parking Pressure | 1000 dbar  |  |  |  |  |
| Sampling layers         | 110 (1950, 1900, 1850, 1800, 1750, 1700, 1650, 1600,           |  |  |  |  |
|                         | 1550, 1500, 1450, 1400, 1350, 1300, 1250, 1200, 1150,          |  |  |  |  |
|                         | 1100, 1050, 1000, 975, 950, 925, 900, 875, 850, 825, 800,      |  |  |  |  |
|                         | 775, 750, 725, 700, 675, 650, 625, 600, 580, 560, 540, 520,    |  |  |  |  |
|                         | 500, 490, 480, 470, 460, 450, 440, 430, 420, 410, 400, 390,    |  |  |  |  |
|                         | 380, 370, 360, 350, 340, 330, 320, 310, 300, 290, 280, 270,    |  |  |  |  |
|                         | 260, 250, 240, 230, 220, 210, 200, 195, 190, 185, 180, 175,    |  |  |  |  |
|                         | 170, 165, 160, 155, 150, 145, 140, 135, 130, 125, 120, 115,    |  |  |  |  |
|                         | 110, 105, 100, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, |  |  |  |  |
|                         | 35, 30, 25, 20, 15, 10, 4 dbar)                                |  |  |  |  |

Launches

| Float | ARGOS  | Date     | and  | Date       | and  | Location of Launch | l  | CTD    | St. |
|-------|--------|----------|------|------------|------|--------------------|----|--------|-----|
| S/N   | PTT ID | Time     |      | Time       |      |                    |    | No.    |     |
|       |        | of Reset |      | of Launch  |      |                    |    |        |     |
|       |        | (UTC)    |      | (UTC)      |      |                    |    |        |     |
| 1575  | 23732  | 15:03,   | Jun. | 17:09, Jun | . 13 | 19-50.14           | N, | P10-60 |     |
|       |        | 13       |      |            |      | 149-19.62 E        |    |        |     |
| 223   | 6497   | 19:37,   | Jun. | 23:44, Jun | . 15 | 15-15.25           | N, | P10-53 |     |
|       |        | 15       |      |            |      | 149-20.00 E        |    |        |     |