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Oceanic pCO_2 Measurements with a Multi-Layered, Composite Hollow-Fiber Membrane

By Hisayuki Yoshikawa Inoue, Masao Ishii, Hidekadzu Matsueda

Geochemical Research Department, Meteorological Research Institute, Tsukuba, Japan

Masayoshi Yoshimoto and Yoshikazu Morita

Research and Investigation Bureau, Institute for Sea Training, Ministry of Transport, Yokohama, Japan

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Abstract

In order to measure the CO_2 mixing ratios in air equilibrated with seawater ($xCO_2{}^S$), we tested a multi-layered composite hollow-fiber membrane (MHF) module aboard the TS Hokuto-maru in the North Pacific in January–February 1996 and July–August 1996. The MHF module is much smaller (300 cm^3) than the currently used shower-head type equilibrator (110 dm^3 installation volume). The mean difference in $xCO_2{}^S$ ($\Delta xCO_2{}^S$) values between the two systems determined 14 minutes apart was 1.6 ppm with a standard deviation of 2.2 ppm ($n = 73$) for the southbound cruise in January, and -1.9 ppm with a standard deviation of 1.8 ppm ($n = 103$) for the northbound cruise in February, 1996.

The difference in average $\Delta xCO_2{}^S$ between the two legs was mainly caused by the effect of water temperature difference between the shower-head type equilibrator and the MHF module. By taking into account the effect on $xCO_2{}^S$ of water-temperature difference between the two equilibrators, the mean $\Delta xCO_2{}^S$ was as low as 0.1 ppm ($n = 732$) with a standard deviation of 3.7 ppm for the cruise in July–August 1996. These results indicate that no systematic difference exists between the two equilibrators. The MHF has potential for future use as an equilibrator that is compact and easy to install.

1. Introduction

CO_2 exchange between the sea and the air plays an important role in determining the atmospheric CO_2 level. The net CO_2 flux is calculated by the product of the gas transfer coefficient and the difference in CO_2 fugacity (or partial pressure) between the sea and the air. Since the 1980s, we have conducted research on the sources and sinks of CO_2 in the western North Pacific (Inoue *et al.*, 1995) and the central/western equatorial Pacific (Inoue and Sugimura 1992; Ishii and Inoue 1995; Inoue *et al.*, 1996). We observed CO_2 mixing ratios in "dry" air equilibrated with seawater ($xCO_2{}^S$) semi-continuously, and then calculated the partial pressure of CO_2 (pCO_2) as:

$$pCO_2 = xCO_2{}^S \times (P - e) \quad (1)$$

where P is the atmospheric pressure at the sea surface and e is the saturated water vapor pressure of seawater. The amount of $xCO_2{}^S$ data collected on research vessels has increased, but the data are still too limited to elucidate temporal variations in CO_2 flux between the sea and the air on basin-wide scales.

For underway oceanic CO_2 measurements, different types of equilibrators have been used (see for example, Körtzinger *et al.*, 1996 and references cited therein). These are classified as "shower type" equilibrators, "bubble type" equilibrators, "laminar flow type" equilibrators, and "disk" equilibrators (Sabine *et al.*, 1994). Some of these equilibrators have large dimensions and need to be handled with care.

Our oceanic CO_2 measuring system consists of two racks (58 cm × 70 cm × 160 cm), a shower-head type equilibrator (water bath 12 dm^3; gas exchange column 1.4 dm^3) made of acrylic framed by plastic materials (35 cm W × 40 cm L × 90 cm H), an NDIR analyzer (BINOS 4.1) placed in an acrylic box (54 cm W × 63 cm L × 20 cm H), four working standard gases in aluminum cylinders (48 dm^3), and spare-parts boxes. It is necessary to have

Corresponding author: Hisayuki Y. Inoue, Geochemical Research Division, Meteorological Research Institute, 1-1 Nagamine, Tsukuba, 305-0052, Japan. E-mail: hyoshika@mri-jma.gp.jp

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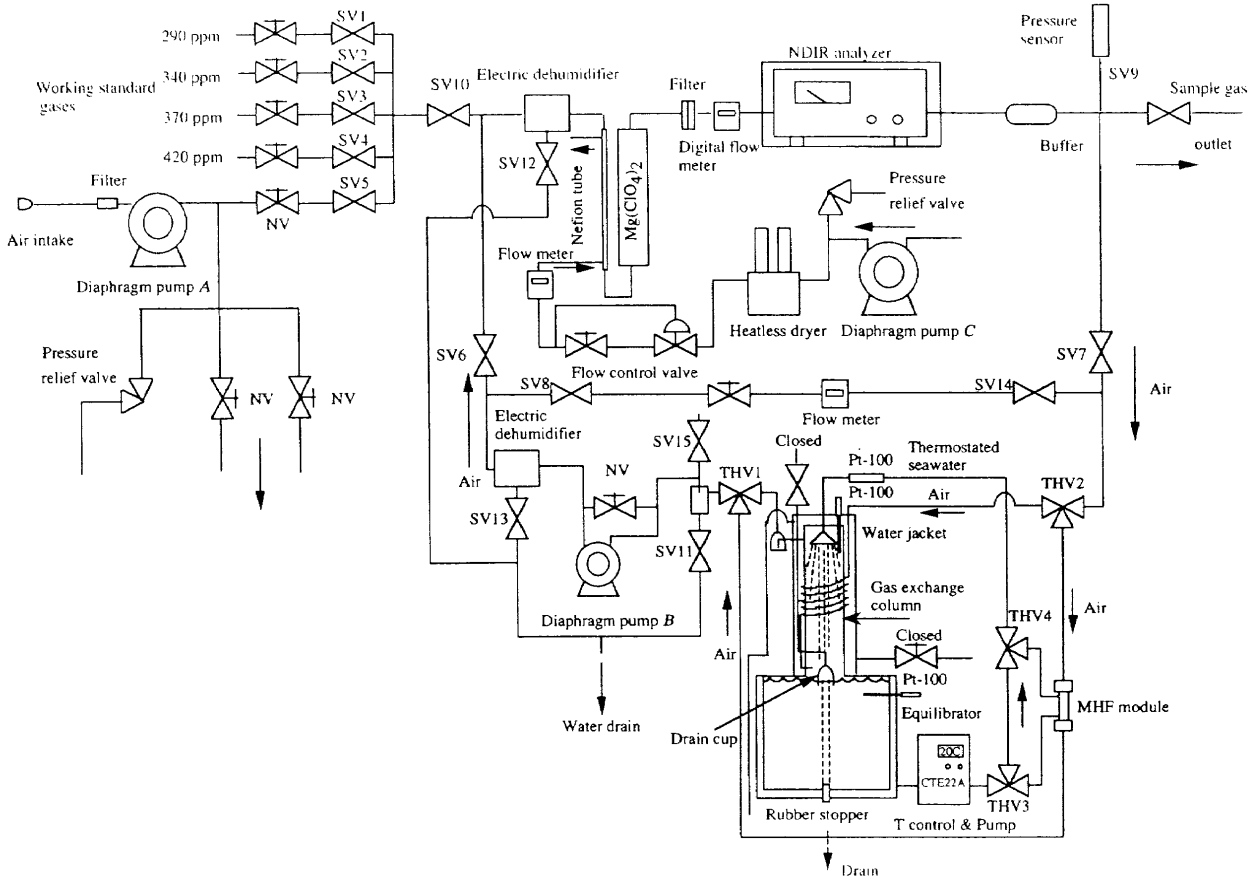

Fig. 1. Schematic diagram of the system for the comparison of xCO_2 in seawater. SV denotes 2-way solenoid valve, THV denotes 3-way solenoid valve, and NV a needle valve. For the laboratory experiment, the drain pipe was removed from the shower-head type equilibrator (dotted line). During experiments, dry air produced by a heatless dryer (Molecular Sieve 5A, CKD Co., Ltd.) was supplied to the outside of the Nefion tubing at the rate of 0.6 dm^3 min^{-1}. The dew point of the air sample at the outlet of the Nefion tubing was designed to be as low as $-40°C$. Aboard ship we did not use the heatless dryer used in the laboratory experiment; dry air passing through the sample cell of the NDIR analyzer was supplied to the Nefion tubing to remove water molecules from gas samples prior to their entering the $Mg(ClO_4)_2$ column.

a source/sink of fresh seawater and a place large enough to install the system. At the moment, we are planning to conduct $xCO_2{}^S$ measurements on ships of opportunity with unattended systems as is done in the Atlantic (Lefevre *et al.*, 1998).

To make a system that is compact and easy to install on board, we first examined whether a multi-layered composite hollow-fiber membrane module (MHF module, Mitsubishi Rayon Co., Ltd.) could be used as an equilibrator. The MHF module that we examined has small dimensions (4.8 cm O.D. × 20 cm L) with a large membrane area (0.6 m^2). The MHF has a three-layered structure in which a non-porous thin membrane with gas permselectivity is sandwiched between two porous membranes. Gases dissolved in water are added to or removed from the water by permeating the non-porous thin membrane of the MHF. The driving force of this permeation is the difference in fugacity for each gas component between the inside and outside of this membrane. Saito *et al.* (1995) have deployed a system that has a membrane tube made of gas-permeable poly-tetra fluoroethylene (PTFE) as the equilibrator. The equilibrator was designed to be immersed directly in seawater and, in order to measure $xCO_2{}^S$ aboard a ship, requires the separation of sample seawater from contaminated room air.

In this paper, we report $xCO_2{}^S$ data using the shower-head type equilibrator and the MHF module in the laboratory and aboard the TS Hokuto-maru (Institute for Sea Training, Ministry of Transport) in the North Pacific in January–February 1996 and July–August 1996.

2. Experiment

2.1 Working standards

To measure $xCO_2{}^S$, four working standards were calibrated against our secondary standards. Sec-

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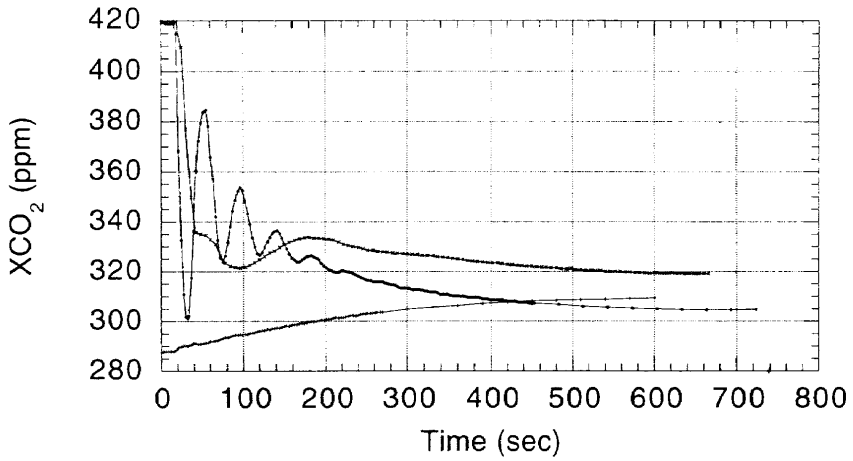

Fig. 2. Examples of xCO_2 variation in closed air when the MHF module or the shower-head type equilibrator was used as the equilibrator. Surface seawater (11 dm^3) taken at 0°, 165°W (34.80 psu) in December 1992 was thermostated at 20°C (Yamato-Komatsu CTE22A), and introduced into the two equilibrators at the rate of 2 dm^3 $^{-1}$. Prior to the experiment, pH was adjusted by adding HCl or NaOH dissolved in seawater. The flow rate of the air in the closed circuit was 0.55 to 0.57 dm^3 min^{-1}. Solid circles indicate MHF module, + symbols the addition of HCl, MHF module, and x symbols the shower-head type equilibrator.

ondary standards were calibrated twice a year against our primary standards (MRI87 scale) that were prepared gravimetrically by Nippon Sanso Co., Ltd. (Tanaka *et al.*, 1987; Inoue and Matsueda, 1996). The Japan Meteorological Agency (JMA) has cylinders that were measured on the basis of the WMO mole-fraction scale. Since 1990, we have sent our cylinders to the JMA to compare the MRI87 scale with the WMO scale at least once a year. The relationship between the two scales is given by

$$xCO_2^{WMO} = 5.451 + 0.9741\left(xCO_2^{MRI87}\right) + 2.7966 \times 10^{-5}\left(xCO_2^{MRI87}\right)^2, \quad (2)$$

where the superscript WMO means the WMO 1985 mole-fraction scale. The correlation coefficient is higher than 0.9999 ($n = 14$), and the standard error of estimate is smaller than 0.1 ppm. In this study we report $xCO_2{}^S$ on the basis of the xCO_2^{WMO} scale as determined by Eq. (2).

2.2 Laboratory experiments

As a first step, we examined the compatibility of the $xCO_2{}^S$ data from the two equilibrator types in our laboratory (Fig. 1). The time required to establish equilibrium depends on the difference in CO_2 mixing ratios in the air from the equilibrium value, as long as we use the equipment in the same conditions. We estimated the time needed to establish an equilibrium for air-sea CO_2 exchange in the MHF module. After introducing 420 ppm of CO_2 working gas in the space (400 cm^3) among the solenoid valves (SV) 6, 7, 9, 10, and 12, air was circulated in a closed circuit (600 cm^3) consisting of an electric dehumidifier, a chemical desiccant column ($Mg(ClO_4)_2$), a NDIR analyzer, a diaphragm pump and a series of solenoid valves, and the MHF module (MHF0504) at the rate of 0.6 dm^3 min^{-1}. Seawater (11 dm^3), taken at 0°, 165°W (34.80 psu) in December 1992, was thermostated at 20°C and introduced into the MHF module and the gas exchange column of the shower-head type equilibrator (2 dm^3 min^{-1}) during CO_2 exchange between the seawater and the air.

Figure 2 shows examples of the CO_2 exchange between air and seawater in the closed loop when the MHF module or the shower-head type equilibrator was used. Because of the relatively slow mixing rate of the air in the closed loop and of CO_2 exchange between the seawater and the air in the MHF module, the $xCO_2{}^S$ oscillated at first with a cycle of ca. 1 min while approaching the equilibrium value. The peak-to-trough amplitude of the xCO_2 decreased with time, and became negligibly small 7 min after the beginning of the experiment. To examine the MHF response against step changes, a small amount of HCl was added to the seawater sample. Seven minutes after the addition of HCl, the xCO_2 showed an almost constant value (Fig. 2). When the shower-head type equilibrator was used, the xCO_2 approached equilibrium value faster than in the MHF module. The experiments indicated that 12 minutes was required for the air in the closed circuit to reach the equilibrium value.

Next, we tested for any side-effects of the MHF module on $xCO_2{}^S$ measurements. We compared $xCO_2{}^S$ that was measured using the two equilibrator types (Table 1). By switching the three-way solenoid valves (THV1-4), measurements of $xCO_2{}^S$ were made every 14 minutes. During the circulation

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Table 1. $xCO_2{}^S$ when the MHF module and the shower-head type equilibrator (Shw-H) were used alternately as the equilibrator. $xCO_2{}^S$ of thermostated seawater samples (20°C, 11 dm^3) was determined every 14 minutes

	Experiment 1		Experiment 2	
	$xCO_2{}^S$	Equilibrator	$xCO_2{}^S$	Equilibrator
1	327.4	Shw-H	330.7	Shw-H
2	327.4	MHF	330.8	MHF
3	327.6	Shw-H	331.2	Shw-H
4	328.1	MHF	331.4	MHF

of the air for measurement of $xCO_2{}^S$, the pressure in the NDIR analyzer's cell was slightly higher than that in the ambient air, and was lower in the equilibrator. To measure the $xCO_2{}^S$ in the gas sample precisely, the temperature and pressure of the gas sample in the NDIR's analyzer cell should be the same as those of working standards. To attain this condition, we stopped the gas flow and opened SV 9. For measurements of working standards and $xCO_2{}^S$, we closed all valves except SV 9 and switched off diaphragm pump B (open-ended configuration). We allowed 25 seconds prior to integrating the output voltage of the NDIR analyzer over 1 minute. After integration we started the air circulation again by opening SV 6 and 7, and closing SV 9.

The results showed that there was no systematic difference in $xCO_2{}^S$ between the two equilibrators, although the $xCO_2{}^S$ increased by 0.7 ppm in each experiment. The small increase was probably caused by room-air contamination because we adopted an open-ended configuration. Within the limitations revealed by laboratory experiments, the present results indicate the feasibility of using the MHF as an equilibrator aboard ship.

2.3 Shipboard observations

In order to examine their compatibility, measurements of $xCO_2{}^S$ using the MHF module and the shower-head type equilibrator were made on the TS Hokuto-maru during its cruise between Japan and Australia in January–February 1996 and between Japan and the USA in July–August 1996 (Fig. 3). We installed our system in an experimental room close to the ship's engine where the air temperature was higher than 30°C. The $xCO_2{}^S$ was measured using a system similar to that described in Fig. 1. The MHF module manufacturer recommends that seawater flow inside the tubing (200 μm I.D.) to conduct the gas exchange. However, to avoid clogging by particulates, we passed seawater outside the tubing and air inside the tubing. During a 1-h cycle, 4 working standards, ambient air, and air equilibrated with seawater were introduced into the NDIR analyzer's cell. We allocated 23 minutes forthe measurement of working standards, 8 minutes for that of the ambient air, and 28 minutes for that of air equilibrated with seawater. During the measurements of the ambient air, air for measurement of $xCO_2{}^S$ was circulated in the closed loop by opening SV 8 and 14 via the shower-head type equilibrator. In this manner, the air was able to establish an equilibrium except in the air among SV 6, 7, 9, 10, and 12. After integration of output voltages of the NDIR analyzer, we closed SV 8 and 14, and opened SV 6 and 7. Then we circulated air at a flow rate of 0.6 dm^3 min^{-1} for 12 minutes. Signal integration was commenced as described (Section 2.2). After measurements of $xCO_2{}^S$ in the air passing through the shower-head type equilibrator, we switched the three-way THV 1 and 2, and circulated air for 12 minutes in the MHF module. Air in this closed circuit was expected to be equal to, or close to, equilibrium; its volume was about two-thirds (400 cm^3) of that used for the laboratory experiment. Thus, a circulation time of 12 minutes was enough to measure $xCO_2{}^S$ using the MHF module when the $xCO_2{}^S$ in surface seawater varied little. As a result, $xCO_2{}^S$ data were taken about 14 minutes apart. During each $xCO_2{}^S$ measurement, the TS Hokuto-maru moved about 7 km (at a speed of 16–17 knots).

The temperature increase between the shower-head type equilibrator and the sea surface temperature (SST) was typically 0.35°C for cruises of the TS Hokuto-maru. To calculate the pCO_2 in surface seawater, we used Eq. (3) given by Millero (1995):

$$\ln(pCO_2(T_s)) = \ln(pCO_2(T_{eq})) + B(T_s - T_{eq}) + C(T_s^2 - T_{eq}^2) \quad (3)$$

where T is the seawater temperature, B is a function of salinity and the ratio between total alkalinity and total dissolved inorganic carbon (X), C is a constant, and subsrcipt s means the surface and eq the equilibrator. On the basis of measurements in the western North Pacific aboard the vessel R/V Ryofu-maru (Japan Meteorological Agency), we assumed a constant salinity of 34.5 psu, and $X = 1.188$. From in-situ pCO_2, we calculated the $xCO_2{}^S$ by Eq. (1).

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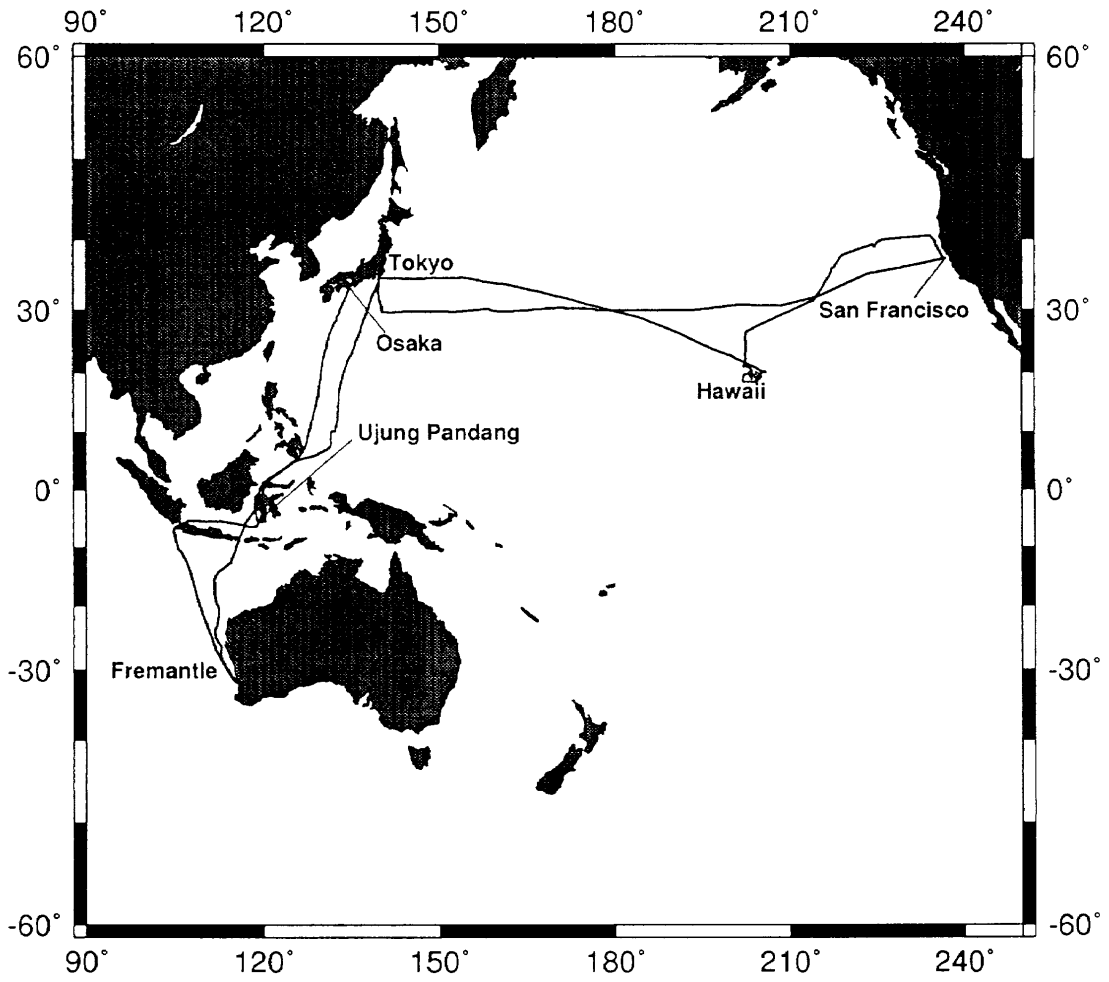

Fig. 3. Cruise tracks of the TS Hokuto-maru (Institute for Sea Training, Ministry of Transport) in January–February 1996 and July–August 1996 (GMT used). In January–February 1996, the cruise of the TS Hokuto-maru was from Osaka to Fremantle (Australia), and from Fremantle to Tokyo via Ujung Pandang (Indonesia). In July–August 1996, the cruise was from Tokyo to San Francisco via Hawaii, and from San Francisco to Tokyo.

3. Results and discussion

3.1 Results from the TS Hokuto-maru cruise between Japan and Australia in January–February 1996

During the cruise of the TS Hokuto-maru between Japan and Australia in January–February 1996 (Fig. 3), we compared the $xCO_2{}^S$ values from the two equilibrator types. Figure 4 shows the latitudinal distribution of $xCO_2{}^S$ when the shower-head type equilibrator was used. As reported earlier (Poisson *et al.*, 1993; Inoue *et al.*, 1995), the subtropics exhibit relatively small natural variability in $xCO_2{}^S$ on small spatial scales during the winter season (and large variability during the summer season). In January 1996, $xCO_2{}^S$ ranged from 300 to 330 ppm between 32°N and 14°N. The minimum $xCO_2{}^S$ occurred near 29°N–30°N at an SST of 21°C, and $xCO_2{}^S$ increased from there southward with increasing SST. In February 1996, the $xCO_2{}^S$ ranged from 290 ppm to 350 ppm, with the same pattern as that observed in January 1996. At 30°N the $xCO_2{}^S$ reached a minimum at an SST of 18°C, and increased southward with increasing SST.

The difference between two successive $xCO_2{}^S$ measurements using the two equilibrators taken 14 minutes apart ($\Delta xCO_2{}^S$) was plotted against latitude (Fig. 4). Almost all values of $\Delta xCO_2{}^S$ were positive ($1.6 \pm 2.2, n = 73$) for the southbound cruise in January 1996 and negative ($-1.9 \pm 1.8, n = 103$) for the northbound cruise in February 1996 (Table 2). Direct comparison of $xCO_2{}^S$ would include the contributions of small spatial-scale and basin-wide-scale variability. In order to eliminate the small spatial-scale variations, we fitted $xCO_2{}^S$ data to a smoothing function (Kaleidagraph Reference Guide, 1995) as also shown in Fig. 4. We used the equations of the smoothing function to determine the

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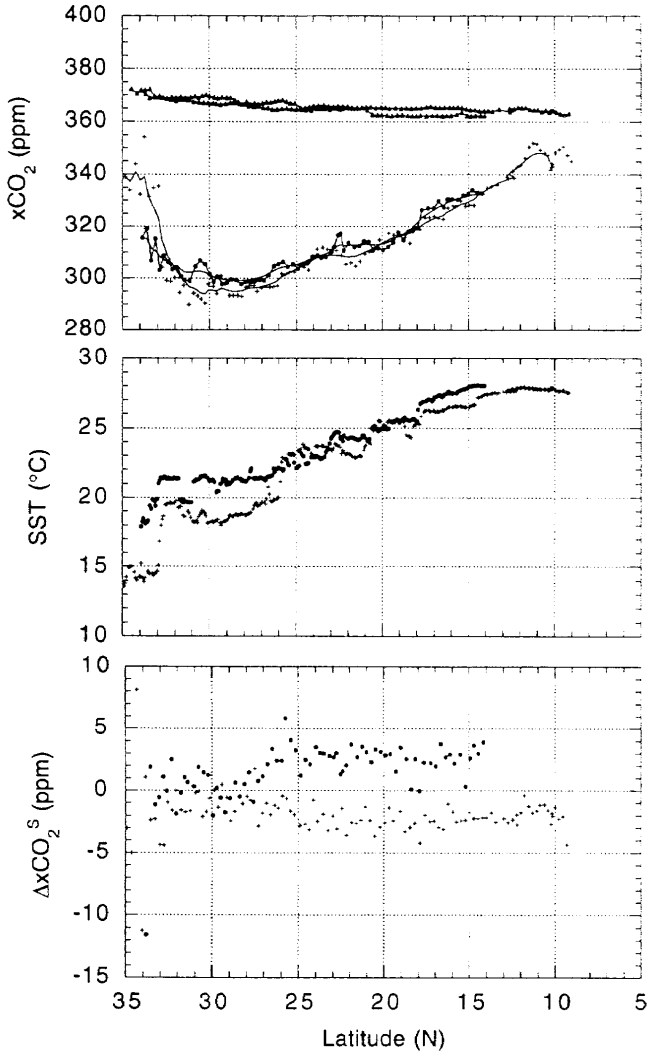

Fig. 4. Latitudinal distribution of $xCO_2{}^S$ and SST, and of $\Delta xCO_2{}^S$ in the western North Pacific, January–February 1996. In upper panel, solid triangles: atmospheric CO_2 in the southbound cruise, open triangles: atmospheric CO_2 in the northbound cruise, and solid circles $xCO_2{}^S$ in the southbound cruise and + symbols $xCO_2{}^S$ in the northbound cruise. In the middle and lower panel, solid circles indicate SST and $\Delta xCO_2{}^S$ in the southbound cruise, and + symbols SST and $\Delta xCO_2{}^S$ in the northbound cruise.

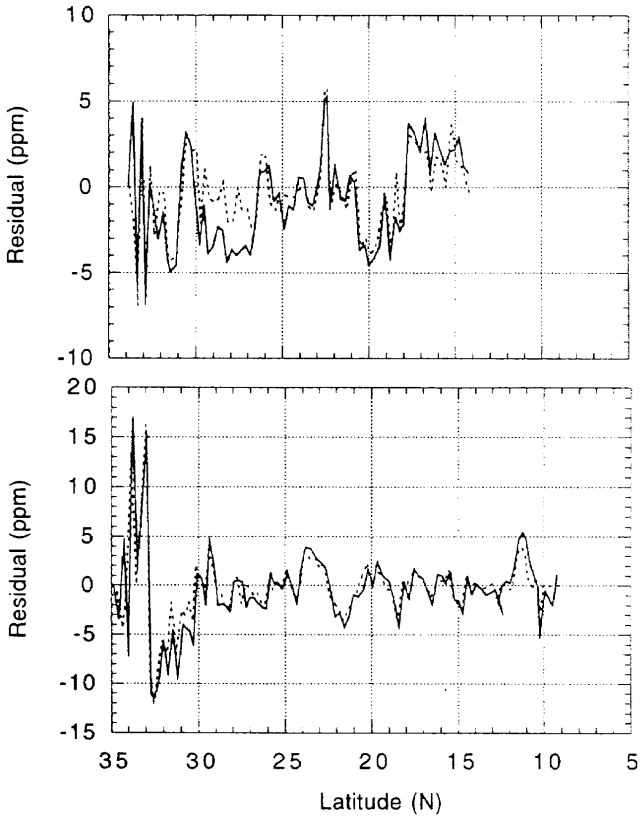

Fig. 5. Differences (residual) between the observed $xCO_2{}^S$ and the corresponding smoothed curves. Upper panel shows the difference for the southbound cruise, and the lower panel the northbound cruise. Solid line indicates the difference when the shower-head type equilibrator was used and the dotted line the MHF module.

$\Delta xCO_2{}^S$ obtained using the two different equilibrators. Figure 5 shows the difference between the observed $xCO_2{}^S$ and the corresponding smooth fit. The standard deviation of the difference between the observed $xCO_2{}^S$ and the corresponding smooth fit was almost the same for the two types of equilibrator (Table 3). This suggests nearly equal inertia of the two equilibrators against natural $xCO_2{}^S$ variability on spatial scales of several kilometers in the western North Pacific. The average difference between smoothed data was 2.1 ppm with a standard deviation of 2.2 ppm ($n = 73$) for the southbound cruise, and -1.7 ppm with a standard deviation of 1.3 ppm ($n = 103$) for the northbound cruise (Table 2).

The $\Delta xCO_2{}^S$ was plotted against $xCO_2{}^S$ (Fig. 6) and SST (Fig. 7). These figures show that $\Delta xCO_2{}^S$ is not correlated with either $xCO_2{}^S$ or SST. The difference in $\Delta xCO_2{}^S$ levels between the two legs suggests that $\Delta xCO_2{}^S$ does not depend on $xCO_2{}^S$, SST or the MHF module.

During the cruises of the TS Hokuto-maru, we simply assumed that the temperature of the seawater samples supplied to the two equilibrators was the same. One reason for the difference in $\Delta xCO_2{}^S$ in each leg could be a temperature difference between the two equilibrators. The observed $xCO_2{}^S$ difference corresponds to a difference in seawater temperature of -0.1 to 0.2°C, if there is no natural variability of $xCO_2{}^S$.

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Table 2. The difference in CO_2 mixing ratios in the air ($\Delta xCO_2{}^S$) and a standard deviation ($1-\sigma$) determined by using a shower-head type equilibrator and the MHF module aboard the TS Hokuto-maru in the western North Pacific in January–February 1996

Departure	Arrival		Mean $\Delta xCO_2{}^S$ (ppm)	$1-\sigma$ (ppm)	No
Osaka	Fremantle	Observed data	1.6	2.2	73
		Smoothed data	2.1	2.2	73
Ujung Pandang	Tokyo	Observed data	−1.9	1.8	103
		Smoothed data	−1.7	1.3	88
Total		Observed data	−0.5	2.6	176
		Smoothed data	−0.1	2.5	176

Table 3. The standard deviation of the difference between observed $xCO_2{}^S$ values and corresponding smooth fit during the TS Hokuto-maru cruises in January–February 1996 and July–August 1996. (Shw-H = shower-head type equilibrator)

January–February 1996

Departure-Arrival	Shw-H	MHF-module	No
Osaka-Fremantle	2.6	2.4	73
Ujung Pandang-Tokyo	4.1	3.4	103

July–August 1996

Departure-Arrival	Shw-H	MHF-module	No
Tokyo-Hawaii	3.4	3.1	242
Hawaii-San Francisco	2.1	2.3	134
San Francisco-Tokyo	5.8	5.8	355

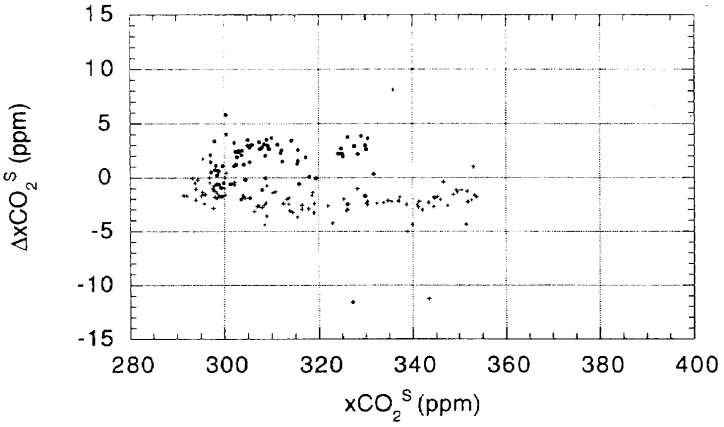

Fig. 6. $\Delta xCO_2{}^S$ plotted against $xCO_2{}^S$ when the shower-head type equilibrator was used in the western North Pacific in January–February 1996. Solid circles indicate southbound cruise and + symbols the northbound cruise.

3.2 Results from the TS Hokuto-maru cruise between Tokyo and San Francisco, July–August 1996

During the cruise of TS Hokuto-maru between Tokyo and San Francisco in July–August 1996 (Fig. 3), we tried to keep the water flow rate constant by adjusting the position of the valves. We measured seawater temperature at the outlet of the MHF module as well as at the inlet of the shower-head type equilibrator twice a day using a mercury thermometer. The seawater temperature at the outlet of the MHF module during the cruise was 0.1–0.15°C higher than that at the inlet of the shower-head type equilibrator. This corresponds to a temperature correction of 0.4–0.6 % for $xCO_2{}^S$ in seawater.

Figure 8 indicates the longitudinal $xCO_2{}^S$ distri-

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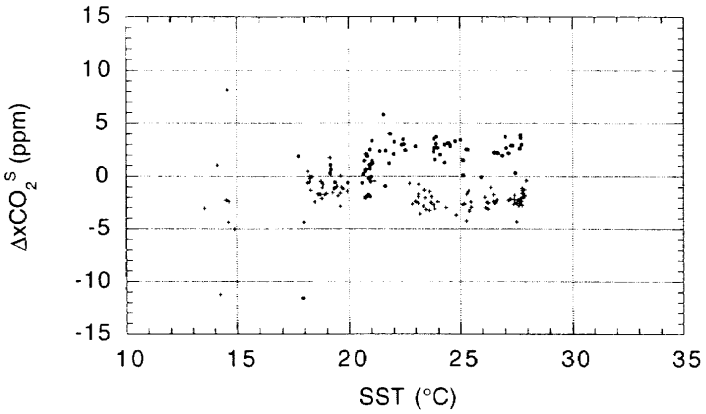

Fig. 7. $\Delta xCO_2{}^S$ plotted against SST when the shower-head type equilibrator was used in the western North Pacific in January–February 1996. Solid circles indicate southbound cruise and + symbols the northbound cruise.

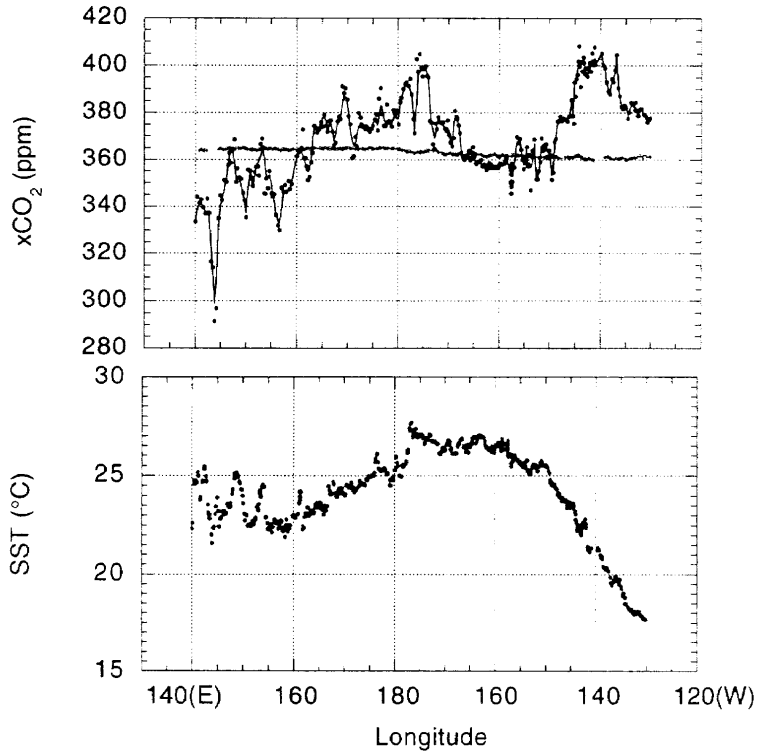

Fig. 8. Longitudinal distribution of $xCO_2{}^S$ when the shower-head type equilibrator was used (upper panel) and SST (lower panel) in the North Pacific (from Tokyo to San Francisco) in July–August 1996. In the upper panel, solid circles indicate $xCO_2{}^S$, + symbols xCO_2 in the ambient air, and solid line the smoothed $xCO_2{}^S$.

bution between Osaka and San Francisco via Hawaii in July–August 1996 when the shower-head type equilibrator was used. The $xCO_2{}^S$ exhibited large variability and ranged across the basin from 290 to 410 ppm. In the area of the Kuroshio Front, the value of $xCO_2{}^S$ was lower than that of the air. Between 34°N, 160°E and 26°E, 168°W, $xCO_2{}^S$ varied considerably (350 to 410 ppm), while in the area between 26°N, 168°W and 22°N, 155°W, $xCO_2{}^S$ was relatively constant (350 to 360 ppm) and nearly equal to that of the air (362 ppm). This distribution seems to follow the same pattern as that observed along 165°E in July–August 1987 (Murphy *et al.*, 1994; Landrum *et al.*, 1996). From Hawaii to San Francisco, $xCO_2{}^S$ ranged from 345 to 410 ppm. From 27°N, 158°W to 38°N, 140°W, $xCO_2{}^S$ increased by 60 ppm with decreasing SST, and showed a broad maximum at 140°W. East of 140°W, $xCO_2{}^S$ decreased with decreasing SST. Figure 8 illustrates the large variability of $xCO_2{}^S$, reflecting the com-

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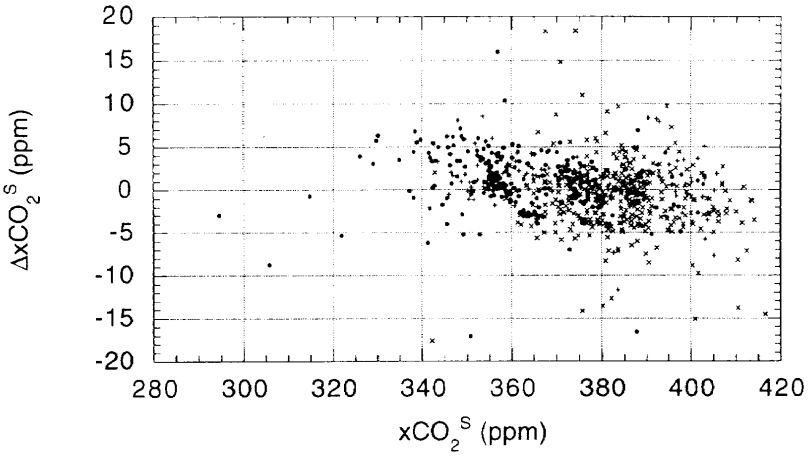

Fig. 9. $\Delta xCO_2{}^S$ plotted against $xCO_2{}^S$ when the shower-head type equilibrator was used during the TS Hokuto-maru cruise in the North Pacific in July-August 1996. Solid circles indicate the cruise from Tokyo to Hawaii, + symbols the cruise from Hawaii to San Francisco, and x symbols the cruise from San Francisco to Tokyo.

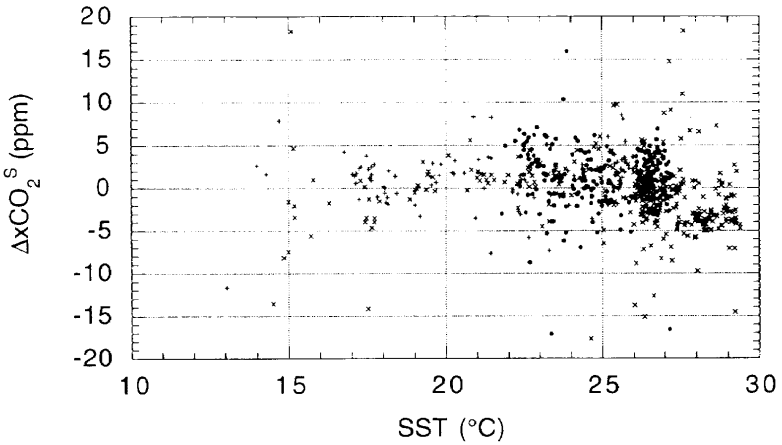

Fig. 10. $\Delta xCO_2{}^S$ plotted against SST when the shower-head type equilibrator was used during the TS Hokuto-maru cruise in the North Pacific in July–August 1996. Solid circles indicate the cruise from Tokyo to Hawaii, + symbols the cruise from Hawaii to San Francisco, and x symbols the cruise from San Francisco to Tokyo.

Table 4. The difference in CO_2 mixing ratios in the air ($\Delta xCO_2{}^S$) and a standard deviation ($1-\sigma$) determined by using a shower-head type equilibrator and the MHF module aboard the MS Hokuto-maru in the North Pacific July–August 1996

Departure	Arrival		Mean $\Delta xCO_2{}^S$ (ppm)	$1-\sigma$ (ppm)	No
Tokyo	Hawaii	Observed data	1.0	3.5	242
		Smoothed data	1.2	3.0	242
		Same T*	0.1	5.4	
Hawaii	San Francisco	Observed data	1.0	2.5	134
		Smoothed data	1.1	2.2	134
		Same T*	−1.2	2.8	
San Francisco	Tokyo	Observed data	−0.9	4.0	355
		Smoothed data	−1.2	3.6	355
		Same T*	−3.1	4.0	
Total		Observed data	0.1	3.7	732
		Smoothed data	0.0	3.4	732
		Same T*	−1.7	4.5	732

*: Same T assumes the same water temperature in the shower-head type equilibrator and the MHF module.

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plexity of the thermodynamic effects, biological processes, and ocean dynamics (Poisson *et al.*, 1993). A discussion of the distribution and factors controlling the carbonate system in surface seawater is beyond the scope of this paper.

All $\Delta xCO_2{}^S$ data taken aboard the TS Hokuto-maru in July–August 1996 were plotted against $xCO_2{}^S$ (Fig. 9) and SST (Fig. 10). Both figures show the same result as observed in January–February 1996: $\Delta xCO_2{}^S$ did not correlate with $xCO_2{}^S$ or SST. If we calculate $xCO_2{}^S$ by assuming the same water temperature in both equilibrators as we did in Section 3.1, the average $\Delta xCO_2{}^S$ for each leg ranged from -3.1 ppm to 0.1 ppm with an average of -1.7 ppm (Table 4). The average $\Delta xCO_2{}^S$ for all available data was 0.1 ppm with a standard deviation of 3.7 ppm ($n = 732$, Table 4). By accounting for temperature differences between the two equilibrators, the average $\Delta xCO_2{}^S$ for each leg ranged from -1 ppm to 1.2 ppm and that of total $\Delta xCO_2{}^S$ became 0.1 ppm. The average $\Delta xCO_2{}^S$ calculated by smoothing both sets of $xCO_2{}^S$ data was 0 ppm with a standard deviation of 3.4 ppm ($n = 732$). The standard deviation between observed $xCO_2{}^S$ and smoothed values measured using the two systems was nearly the same as observed in January–February 1996 (Table 3).

The results indicate that the MHF module can be used as an equilibrator as long as seawater temperature is controlled and measured carefully. With respect to our underway pCO_2 measuring system, the present MHF module has a relatively slow rates of CO_2 exchange between the seawater and the air. The next larger MHF has an area of 2.4 m^2, which will allow us to measure $xCO_2{}^S$ at time intervals of a few minutes.

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中空糸膜を用いた海洋二酸化炭素の測定

井上 (吉川) 久幸・石井雅男・松枝秀和
(気象研究所)
吉本誠義・森田良和
(運輸省航海訓練所)

1996年1月～2月にかけて日本–オーストラリア、7月～8月にかけて日本–アメリカ間を航行した大成丸 (運輸省　航海訓練所) で中空糸膜モジュールを用いて海水と平衡になった乾燥空気中の二酸化炭素混合比 (xCO_2^S) の測定を試みた。中空糸膜モジュールは、全容積が 300 cm^3と現在用いているシャワーヘッド型平衡器 (設置に 110 dm^3必要) に比べて小さく、設置が容易である。中空糸膜モジュールを用いて測定したxCO_2^Sは温度計測を行うことにより従来のシャワーヘッド型平衡器の結果と良い一致を示した。14 分離れて測定したxCO_2^Sの差は、0.1 ppm ($n = 732$) であり標準偏差は 3.7 ppm であった。このことは二つの平衡器間にシステマティックな差がないことを示しており、中空糸膜が平衡器として将来使用できることが分かった。

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