DISTRIBUTION OF pCO_2 AND $\delta^{13}C$ IN THE AIR AND SURFACE SEA WATER IN THE SOUTHERN OCEAN, SOUTH OF AUSTRALIA

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Abstract: Distribution of pCO_2 and $\delta^{13}C$ in the air over the ocean and in the surface sea water of the Southern Ocean was determined during the cruise of BIOMASS (November 1983 to February 1984). In the study area, south of Australia, pCO_2 in the air was nearly constant (~342 ppm) throughout the cruise but pCO_2 in the surface sea water varied considerably ranging from 300 to 356 ppm. In general, pCO_2 in the surface sea water tended to increase from north to south, and it was relatively higher than that in the air in higher latitudes. The average value in the south of 5°S was $-7.97\permil$ for $\delta^{13}C$ and 341.7 ppm for pCO_2 of atmospheric CO_2. These results indicate that atmospheric CO_2 over the ocean is not isotopic equilibrium with the surface sea water and kinetic fractionation must be considered for understanding $\delta^{13}C$ of atmospheric CO_2.

1. Introduction

Recent increase of the atmospheric CO_2 concentration has attracted the great public concerns as one of the triggers for the global climatic change in the near future. The increasing rate of the atmospheric CO_2, however, does not reflect directly the estimated amount of the CO_2 release through the combustion of fossil fuel. The amount of the increase in the air is estimated to be 55% of all fossil CO_2 produced during the period from 1959 to 1978 (ROTTY, 1983).

The exchange of CO_2 among the main terrestrial carbon reservoirs (atmosphere, biosphere and hydrosphere) controls the material balance of CO_2 in the earth's environment, but little is known about the magnitude of the contribution of CO_2 exchanges between air/sea or air/biota to the change of atmospheric CO_2.

The measurement of the partial pressure of CO_2, pCO_2, in the surface sea water is one of the essential requirements for understanding the global carbon cycle. Based on the IGY data, KEELING (1968) has constructed a rough sketch of pCO_2 distribution in the world oceans, and later MIYAKE *et al.* (1974) have given a horizontal distribution of pCO_2 in the Pacific Ocean in detail.

The results of these works indicate that pCO_2 in the surface sea water was supersaturated with respect to pCO_2 in the air in the equatorial region and undersaturated in the subtropical region except in the area where upwelling occurs. It is often treated that water in high latitudes is a sink of the excess CO_2 by the direct ventilation of intermediate and deep waters to the surface air (SIEGENTHALER, 1983), whereas the Antarctic Ocean has been reported to be supersaturated with respect to the atmosphere as given by TORII *et al.* (1959) and MIYAKE and SUGIMURA (1969).

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The seasonal, secular and regional trends of pCO_2 in the Southern Ocean, however, still remain ambiguous. During the Southern Cross Cruise (KH-68-4, November 1968 to February 1969), pCO_2 in the surface sea water and air over the ocean in the south of New Zealand was measured by one of the authors, SUGIMURA (MIYAKE *et al.*, 1974), but there has been no information on the pCO_2 and $\delta^{13}C$ values in the air and sea water in the south of Australia up to the present.

In the present paper, the authors intend to report the results of measurements of pCO_2 in the air and surface sea water together with $\delta^{13}C$ in the air mainly from 5° to 65°S along 150°E. The results clearly indicate that the Southern Ocean water is not equilibrated with the atmosphere with respect to both pCO_2 and $\delta^{13}C$.

2. Samples and Method of Analysis

The measurements of pCO_2 in the air and surface sea water, and the sampling of air for the measurement of $\delta^{13}C$ were carried out on board the R. V. HAKUHO MARU which belongs to the Ocean Research Institute, University of Tokyo, during the cruise of BIOMASS 1983–1984 (KH-83-4) along the course from the western North Pacific to the Southern Ocean and back home through the Indian Ocean. The track of the cruise is illustrated in Fig. 1.
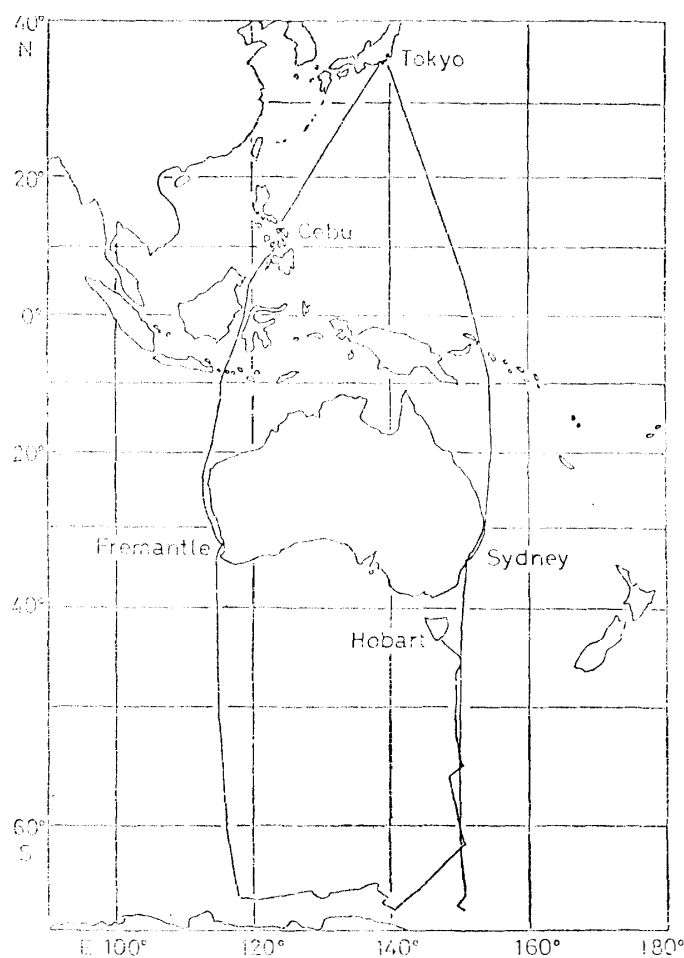

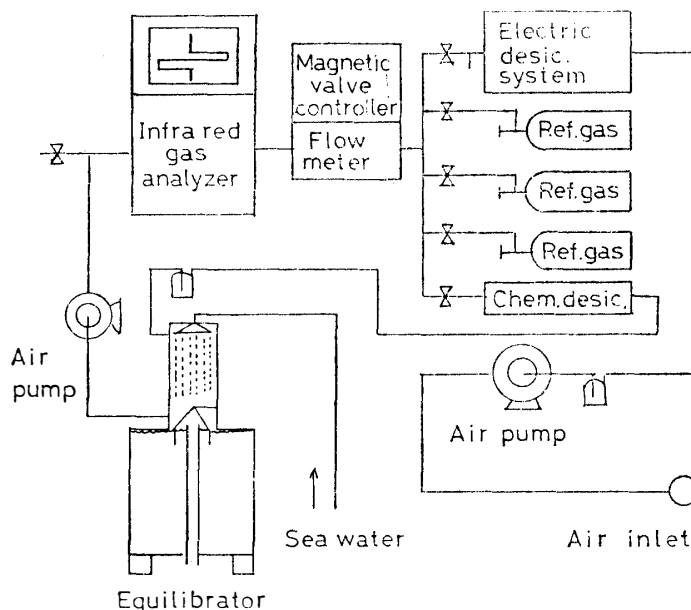Fig. 1. Track of BIOMASS 1983 cruise (November 1983 to February 1984).

Fig. 2.　A schematic diagram of the CO_2 measurement system in the air and the surface sea water.

The continuous records of pCO_2 in the air and sea water were taken in the round trip from Tokyo (November 1983) to Tokyo (February 1984).　The schematic drawing of the instrument used for the measurements of pCO_2 in the air and surface sea water is given in Fig. 2.　Sea water was pumped up continuously from 5 m below the sea surface (bottom of the ship) and introduced into an equilibrator in a closed circuit consisting of a diaphragm air pump, an electric dehumidifier, with chemical desiccant and gas exchange column.　Correction was made for the observed pCO_2 value of the surface sea water following eq. 1 (GORDON and JONES, 1973) which is caused by the warming of sea water sample through the inner piping.

$$\frac{\delta pCO_2}{\delta T} = 4.4 \times 10^{-2}\, pCO_2 - 4.6 \times 10^{-6}(pCO_2)^2,\qquad\qquad (1)$$

where T is the temperature of the sea water and the value of pCO_2 is expressed as mole fractions in parts of CO_2 per million parts of dry air (ppm).

The air sample was collected about 5m above the sea level at the bow of the vessel with a rate of $5\,l\,min^{-1}$.　About one-tenth of the sample air was introduced into the sample cell of a non-dispersive infrared gas analyzer (Beckman model 315A).　For the calibration of the instrument, three different concentrations of working standard gases (CO_2/N_2) were used: two (250 and 450ppm) were passed through five minutes each every hour and the rest (350 ppm) every two or three days to confirm the calibration curve used for the conversion from mV to ppm.　The working standard gases were calibrated against the primary standard gases (CO_2/Air) prepared by the gravimetric method. The primary standard gases were standardized against the WMO standard (1981 mole fraction, supplied from the Scripps Institution of Oceanography).　The accuracy of the measurement was estimated to be ± 0.6 ppm by a duplicate analysis of the same air sample.

For the measurement of carbon isotopic ratio, sample air was collected intermittently in a plastic bag with continuous monitoring of pCO_2 from Tokyo to Cebu, Philippines. Within several hours after sampling, CO_2 in the air was concentrated in a trap with fritted glass disk immersed in liquid nitrogen under the reduced pressure. The CO_2 deposited in the trap was purified by the cryogenic distillation and transferred into a sample tube.

The isotopic composition of carbon was measured on a tripple ion collector mass spectrometer (Finnigan Mat 250) at the Meteorological Research Institute. The results of the measurement were expressed as the per mil deviation from the PDB standard:

$$\delta^{13}C = \left[\frac{(^{13}C/^{12}C)_{sample}}{(^{13}C/^{12}C)_{PDB}} - 1 \right] \times 10^3. \qquad (2)$$

The instrument was calibrated against the international reference standard NBS-20 ($\delta^{13}C = -1.06‰$). A duplicate analysis of the same standard and the sample air revealed that the standard deviation of the analytical results was $\pm 0.05‰$ for the observed $\delta^{13}C$ value.

Correction due to N_2O which is trapped at the same time with CO_2 and interferes the isotopic measurement is not given in this report because of the unknown concentrations of N_2O in maritime air. On our mass spectrometer, the beam intensity of mass 44 ion of N_2O^+ was about 71% to that of CO_2^+ at equal inlet pressure (INOUE and SUGIMURA, 1984). The ionization efficiency of N_2O is lower than that of CO_2 (MOOK and VAN DER HOEK, 1983). If N_2O concentration is 0.3 ppm, the correction of $0.23‰$ is given for the observed $\delta^{13}C$ value (CRAIG and KEELING, 1963).

3. Results and Discussion

The results of the determination of pCO_2 value in the surface sea water along 150°E are shown in Fig. 3. During the back and forth cruises along the line from 45 to 65°S, pCO_2 in the surface sea water was measured repeatedly in the same area three times within 30 days. As seen in the figure, pCO_2 in the surface sea water increased from north to south, and it is relatively higher than that in the air (~ 342 ppm) in high latitudes. The partial pressure of CO_2 in the surface sea water changed at the subtropical convergence (47°S), the subantarctic front (49°S) and polar front (56.5°S). As is well-known, the water temperature decreased from north to south along the observation line but pCO_2 in the surface sea water increased significantly from the subtropical to the polar front.

Following the geographical location of oceanographic fronts, the area was divided into four sections and the average value of pCO_2 in the surface sea water in each area is given in Table 1. In the circumpolar water, the pCO_2 value in the surface water varied significantly from place to place. An example of the distribution of pCO_2 is shown in Fig. 4 along 65°S from 115 to 150°E. As seen in the figure, the pCO_2 vlaue ranged from 330 to 380 ppm and it is noted that most of the surface sea water was supersaturated with respect to the atmospheric CO_2 (341.7 ppm).

Therefore, it can be said that the Antarctic Ocean acts as a source of CO_2 at least during the early summer in the south of Australia region. A fairly uniform distribu-
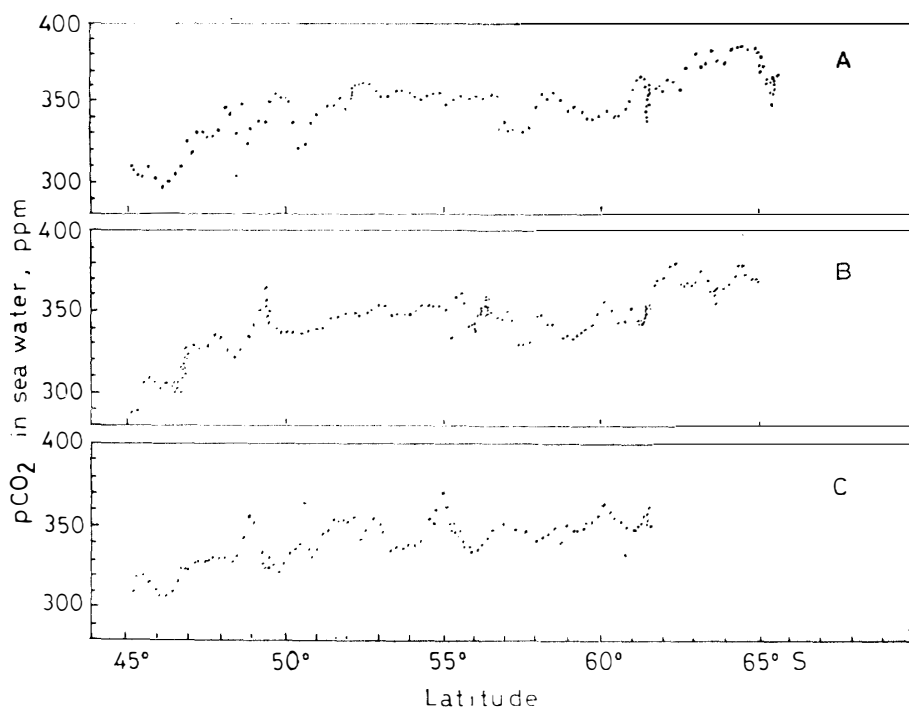
Fig. 3.   Distribution of pCO₂ in the surface sea water along 150° E in the Southern Ocean.
A: southward traverse, B: northward traverse, C: southward traverse.

Table 1.   The average values of pCO₂ in the surface sea water in the Southern
Ocean divided into four areas based on geographic locations of
oceanographic fronts along 150° E (unit ppm).

	45–47°S	47–49°S	49–56.5°S	56.5°S–
A	300. 8±10. 3	332. 6±8. 7	350. 0± 9. 0	356. 4±14. 3
B	309. 7±10. 0	328. 6±4. 3	348. 5± 7. 2	
C	314. 5± 7. 1	334. 0±8. 3	342. 9±10. 4	355. 8± 8. 7

A: Southward traverse, B: northward traverse, C: southward traverse.

tion of inorganic nutrients with depth strongly indicates that the enhanced vertical mixing and biological activity in this region may be responsible for maintaining relatively high pCO_2 values.

Zonal mean values of pCO_2 and $\delta^{13}C$ in the air from 5°S to the Antarctic Ocean are given in Table 2.   The area was divided into four parts tentatively.   As seen in the table, pCO_2 in the air in the southern hemisphere showed a fairly uniform distribution in the meridional direction with the average value of 341 to 342 ppm.   The $\delta^{13}C$ value of the atmospheric CO_2 in the southern hemisphere tended to increase from -8.03 to $-7.88‰$ with latitude.

Thus, the relationship between pCO_2 and $\delta^{13}C$ of CO_2 in the air over the ocean is different from that in the continental and forest air, where $\delta^{13}C$ of the atmospheric CO_2 is linearly correlated with the reciprocal of pCO_2 (FREYER, 1979; KEELING, 1958, 1961; INOUE and SUGIMURA, 1984).

Variations in CO_2 in the forest air are caused by air/biota CO_2 exchange and that
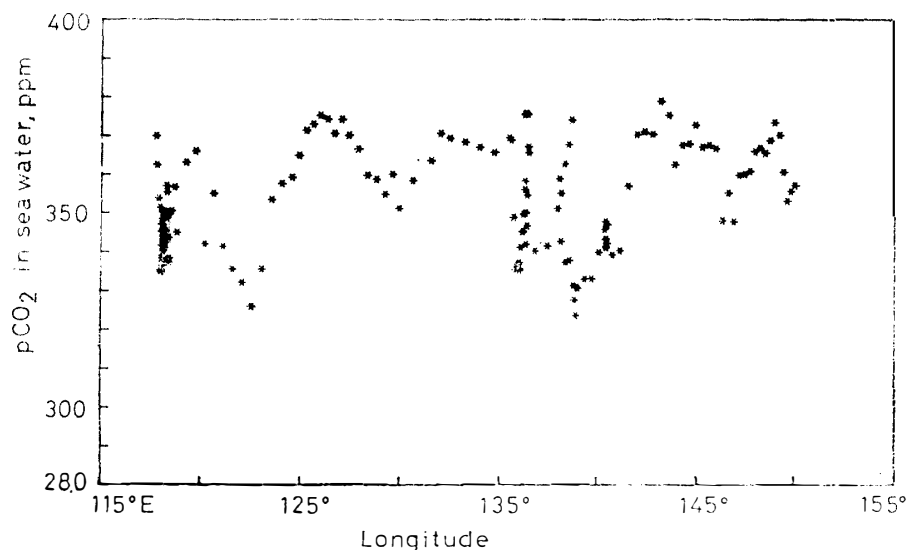
Fig. 4.   Distribution of pCO₂ in the surface sea water around 65° S, south of Australia.

Table 2.   The average value of pCO₂ and δ¹³C in the air over the South
Pacific and the Southern Ocean.

Area	pCO₂ (ppm)	δ¹³C (‰)	Sample number
5–40°S	341.8±0.5	−8.03±0.09	6
40–50°S	341.5±0.5	−8.08±0.13	4
50–60°S	341.7±0.4	−7.98±0.16	6
60°S–	341.6±0.9	−7.88±0.24	10

in the continental air by fossil fuel CO_2. The reason of the difference of the relation-ship in the marine air from the "single mixing relation" in the forest and continental air is a problem for the further study, but it may be related to some other process of carbon cycle; such as air/sea exchange.

In general, carbon isotopic composition in the air CO_2 changes when the exchange of CO_2 takes place between the air and the sea water. The equilibrium fractionation factor of carbon isotopes between the air and the sea water increases with decreasing temperature (INOUE and SUGIMURA, 1985a; KROOPNICK, 1974).

Considering the meridional distribution of the $\delta^{13}C$ value in the air CO_2 over the ocean, there are about 30K difference of temperature in the north-south direction. Thus the $\delta^{13}C$ value in the air CO_2 is expected to vary from $-8.6‰$ at 273.2K to $-5.1‰$ at 303.2 K in equilibrium under the condition that $\delta^{13}C$ of ΣCO_2 in the sea water is 2‰.

However, as seen in Table 2, the $\delta^{13}C$ value in the air CO_2 is fairly constant with latitude, and it is deviated negatively in the tropical to subantarctic area and positively in the antarctic from the expected value under the isotopic equilibrium between the air and the sea water at given temperature.

The results of previous studies (KEELING et al., 1979; MOOK et al., 1983) indicate that $\delta^{13}C$ of the air CO_2 in a remote area has been decreasing with the increase of CO_2, and further, $\delta^{13}C$ of the atmospheric CO_2 in almost all ocean area tends to increase the deviation from the isotopic equilibrium value with that of ΣCO_2 (KROOPNICK, 1985) in the surface sea water.

Therefore, equilibrium process cannot explain the observed results of $\delta^{13}C$ and CO_2 in the air over the ocean.

For further treatment of carbon cycle, we must consider the kinetic isotope exchange process between the air and the sea water. The result of recent study (INOUE and SUGIMURA, 1985a) indicates that the kinetic isotope fractionation factor of ^{13}C from the air to the sea water is larger than that of the sea to the air, and the estimated value of carbon isotopic ratio of CO_2 passing through the air/sea interface is given to be $-10‰$ for air-to-sea and $-8‰$ for sea-to-air, when the CO_2 exchange takes place between the air ($\delta^{13}C = -8‰$) and the surface sea water ($\delta^{13}C = 2‰$) at 288.2 K.

It appeared that for the purpose of qualitative explanation of the observed $\delta^{13}C$ value in the air over the ocean, the process of kinetic exchanging is much more reasonable than equilibrium process as regarded for a long time by many researchers.

4. Conclusion

The Antarctic Ocean cannot be treated simply as a sink of excess CO_2 released by the increased human activities in recent years (SIEGENTHALER, 1983) because pCO_2 in the surface sea water was higher than that in the air at least during the early summer in the south of Australia region.

The results of carbon isotopic measurement of atmospheric CO_2 indicate that CO_2 exchange between the air and the sea water must be considered under the concept of kinetic exchange process based on the difference in pCO_2 between the air and the sea water.

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