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THE LAST 41.000 YEARS FLUCTUATION IN ATMOSPHERIC CO_2 CONCENTRATION INFERRED FROM THE CHANGES IN OXYGEN AND CARBON STABLE ISOTOPES RATIOS OF MARINE SEDIMENTS

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ABSTRACT

The past atmospheric CO_2 concentrations were reconstructed based on the results of measurements of stable oxygen and carbon isotopic ratios of fossil foraminifer and total organic carbon contained in marine sediment taken from the Okinawa Trough, East China Sea. In this study, we utilized two models of Popp *et al* and Rau *et al*. for the reconstruction. The results show that the whole trends of the changes in CO_2 concentrations are very similar, even when it is compared to the atmospheric CO_2 concentration of air trapped in ice core from southern pole. Changes in atmospheric CO_2 concentrations are interpreted as a consequence of fluctuation in ocean surface water utilization of CO_2 by marine organism and those are closely related to glacial-interglacial (cold-warm) fluctuations between maximum and minimum values through most Quaternary.

Key words: reconstruction, atmospheric CO_2 concentrations, stable isotopes, marine sediment

ABSTRAK

Rekonstruksi terhadap perubahan konsentrasi CO_2 yang terkandung dalam udara telah dilakukan berdasarkan hasil pengukuran rasio isotop stabil oksigen dan karbon dalam fosil foraminifera dan total karbon organik yang terkandung dalam sedimen dasar laut dari Okinawa Trough, Laut Cina Timur. Dalam studi ini, dipakai model dari Popp *et al*. dan Rau *et al*. untuk rekonstruksi. Hasil studi menunjukkan bahwa kedua tren dari perubahan kandungan CO_2 udara sangat mirip, bahkan bila dibandingkan dengan kandungan CO_2 udara yang terperangkap dalam inti es di Kutup Selatan sekalipun. Perubahan kandungan CO_2 udara diinterpretrasikan sebagai akibat fluktuasi konsumsi CO_2 di permukaan air laut oleh mikro-organisme yang juga sangat erat hubungannya dengan fluktuasi glasial-interglasial (dingin-panas) antara suhu udara bumi maksimum dan minimum sepanjang masa Kuarter.

Kata kunci: rekonstruksi, kandungan CO_2 udara, isotop stabil, endapan laut

INTRODUCTION

Climates and isotopes affect everybody. The vagaries of weather may have become accentuated by the famous greenhouse effect. This is a suspected warming up of the world due to rising levels of carbon dioxide in the atmosphere caused by the burning of fossil fuels. Due to the role of carbon dioxide in global heat balance and climate, it is interesting to study how and by what mechanisms atmospheric CO_2 levels have changed in the past and how they will change in the future.

This study reveals the down-core changes in oxygen and carbon stable isotope ratios of carbonate and bulk sedimentary organic carbon and utilized the data for reconstructing past variation of atmospheric CO_2 concentration.

Stable Isotopes and Environmental Changes

Stable isotope ratio of elements contained in the ocean sediment have been widely used in the world for inferring past environmental changes. Utility of oxygen isotope composition ($^{18}O/^{16}O$ ratio or $\delta^{18}O$) in foraminiferal shells as indicator of past climate change was pioneered by Emiliani. He showed that oxygen isotopic composition in foraminiferal test has oscillated in response to glacial-interglacial (cold-warm) fluctuations between maximum and minimum values through most Quaternary. Martinson *et al.* created a high resolution of 0 to 300,000 year chronostratigraphy. They used orbital theory to create a continuous, high resolution oxygen isotope stratigraphy. Their work is now widely used by marine geologist for age dating of ocean sediment cores.

Stable carbon isotopic ratio ($^{13}C/^{12}C$ or $\delta^{13}C$) contained in either inorganic material (e.g. foraminiferal test) or in organic material can also be utilized as a paleoproxy, i.e. for identification of water mass and as indicator of seawater circulation, and for reconstruction of surface water productivity and carbon cycle **[13, 14]**.

Total dissolved CO_2 in the production zone of the surface waters are typically enriched in ^{13}C because of preferential fixation of ^{12}C into organic matter during photosynthesis which makes marine plant organic matter about 20 per mil depleted in $\delta^{13}C$ (Sackett *et al.*, 1965). Because of the organic material tends to sink and is oxidized at depth, releasing fixed carbon back to water as CO_2, the deeper water is richer in ^{12}C than surface water (Kroopnick, 1985). Consequently, the deeper water dwelling planktonic foraminiferal shells acquire correspondingly lower $\delta^{13}C$ than shallower ones.

Carbon Isotopic Ratio and CO_2 Concentration

Field observation indicates that variation in oceanic and atmospheric CO_2 concentration may be recorded as changes in marine organic matter $\delta^{13}C$ within the sedimentary record **[10]**. Laboratory and field studies have shown that the $\delta^{13}C$ of the bulk organic fraction of plankton or seston (δ^{13}Corg) generally decreases as the dissolved molecular CO_2 concentration (CO_2(aq)) increases **[11]**.

Popp *et al*. shown a possibility that $\delta^{13}C$ of marine biologic compounds could be utilized as a "CO_2 paleobarometer". Because the partial pressure of CO_2 influences the mechanism of photosynthetic fractionation of carbon isotopes, consequently, the past atmospheric CO_2 concentration could be estimated from carbon isotopic ratios contained in marine organism.

If organic matter preserved in the marine sedimentary record is isotopically representative of the organic matter produced by past plankton communities, its $\delta^{13}C$ within chronologically-defined strata could be determined and its variation in plankton $\delta^{13}C$ could be reconstructed. However, the problems arise when a number of factors complicate this approach. One factor is the origin of the organic matter, whether the organic matter is marine or terrestrial origin. Also, during organic matter sinking down to the ocean bottom and during its residence in sediment, the isotopic composition of bulk plankton organic matter may be altered **[11,15]**.

Experimental and field observations strongly suggest that there is a significant relationship between the $\delta^{13}C$ values of marine total organic carbon (TOC) in marine sediments and the concentration of dissolved CO_2 ($CO_{2(aq)}$) in ambient surface water **[4,9,10]**.

MATERIAL AND METHODS

This study used marine sediment core (piston core PN-3) collected from the Okinawa Trough (28°05.98' N, 127°20.55' E; water depth 1058 m; core length 430 cm), during the MASFLEX 1994 cruise by the research vessel *Bosei Maru* (Figure 1). This core consists of homogeneous grayish olive to gray colored silt with the top 15 cm being brownish black (oxidized layer) (Figure 2). Fine grained sand layer found at 280 cm and 380 cm, and Mollusca shell fragments at 180 cm, 220 cm and 410 cm from the top core (Figure 2).

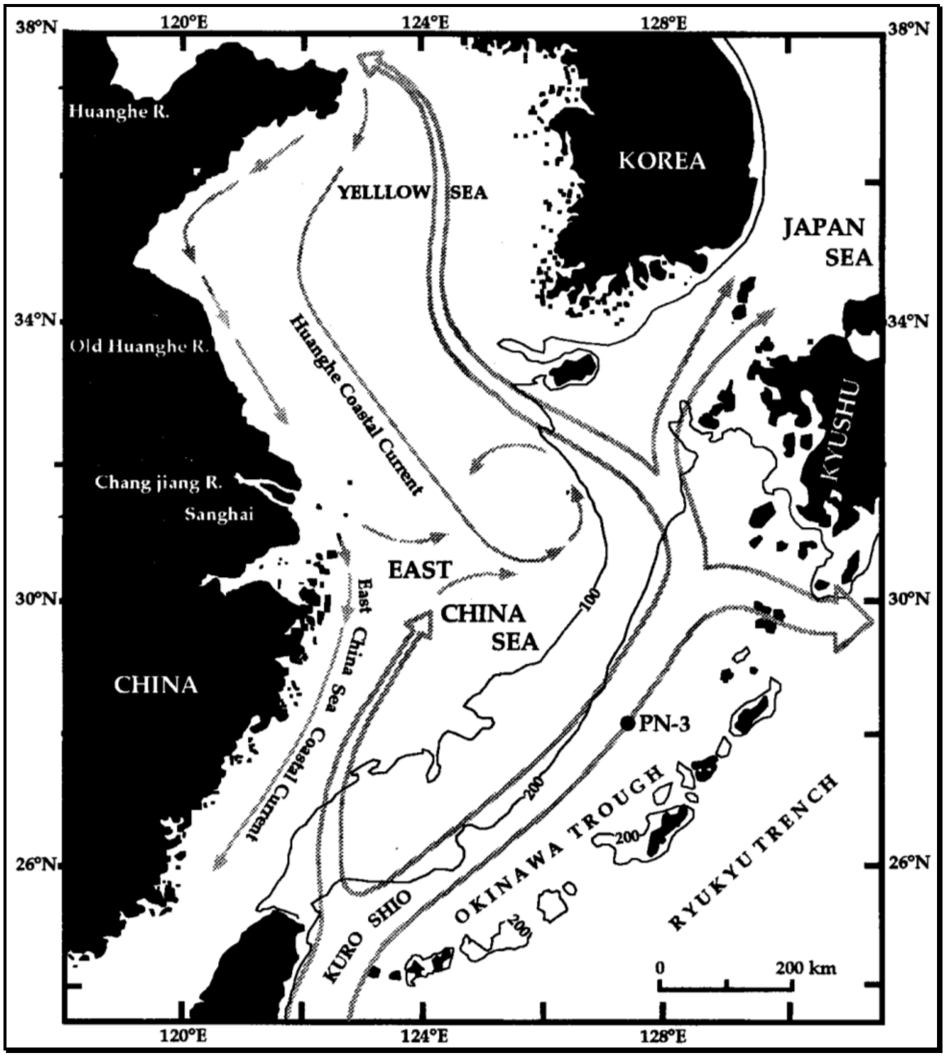


Figure 1. Location of piston core PN-3

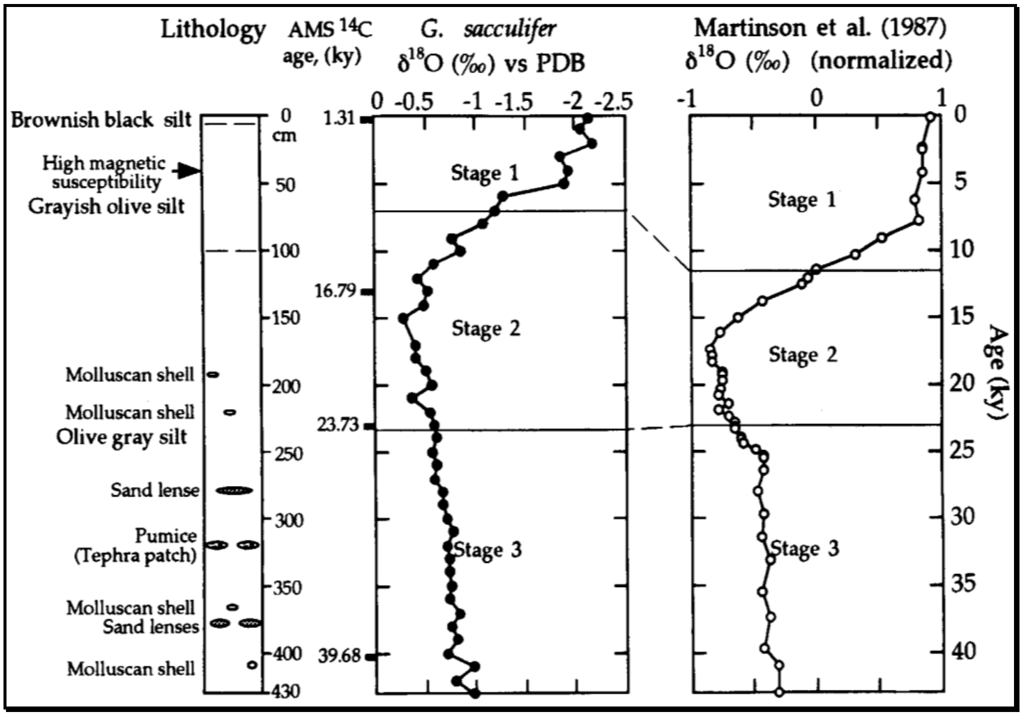


Figure 2. Lithology of core PN-3 (left), oxygen isotope record of *G. Sacculifer* (middle), and standard curve by Martinson *et al.* (right)

Oxygen and carbon isotope analyses were carried out on a planktonic foraminiferal species *Globigerinoides sacculifer*, using 30-40 specimens of 355-425 micron diameter. Isotopic measurement was carried out using a Finnigan MAT 251 mass spectrometer. The oxygen and carbon isotopic data are reported in δ notation relative to PDB standard. Ten replicate measurements of *Sholnhofen* Limestone sub-standard gave a precision of 0.03‰ for oxygen and 0.01‰ for carbon.

The δ notation expresses:

$$\delta = [\{^{13}C/^{12}C \text{ or } ^{18}O/^{16}Os - ^{13}C/^{12}C \text{ or } ^{18}O/^{16}Ost\}: ^{13}C/^{12}C \text{ or } ^{18}O/^{16}Ost] \times 1000\ ‰ .... (1)$$

subscripts s and st indicate sample and standard, respectively.

About 350-400 specimens of *G. sacculifer* of 300-500 μm in diameter were used for the AMS ^{14}C measurement. Sample preparation and graphite target preparation were performed at Laboratory of Geosphere Science Hokkaido University, Japan using a batch preparation method (Kitagawa *et al.*, 1993) and the AMS ^{14}C measurement was carried out at Dating and Material Research Center Nagoya University, Japan (Table 1).

For the organic matter analyses, 750 mg of the powdered sediments were decalcified with 1 N HCl solution for several hours, centrifuged and washed with distilled water. The carbonate free sediments were freeze-dried and crushed into powder. These were then used for quantitative analysis of organic carbon content using a sealed tube combustion method described by Minagawa *et al*.[8]. Organic carbon isotopic composition was also analyzed using a Finnigan MAT 251 mass spectrometer. The standard deviation of five replicate measurements of $\delta^{13}C_{org}$ was 0.07‰.

Table 1. Age control points for core PN-3

Depth in core (cm)	AMS ^{14}C age (ky)	Calibrated age (ky)
6.5	1.42 ± 0.08	1.31
70.0	-	12.00*
138.5	14.63 ± 0.12	16.79
228.5	20.47 ± 0.34	23.73
233.5	-	24.10*
406.0	35.40 ± 0.97	39.68

*) Ages at 70 and 233.5 cm depth are based on oxygen isotope stages ½ and 2/3 boundaries, respectively [7]

The obtained isotopic data were then used for reconstruction of atmospheric CO_2 concentration by employing two models [9,10]. According to Popp *et al.*, values of $CO_2(aq)$ concentration (in micro mol/l) were estimated using a formula :

$$CO_2(aq) = 10 \exp [(\varepsilon_p - 3.4)/-17] \quad (2)$$

where ε_p is isotope effect associated with photosynthetic fixation of carbon, and its values were determined from equation :

$$\varepsilon_p = 1000[(\delta_p+1000)/(\delta_d+1000)-1] \quad (3)$$

where δ_p (‰) and δ_d are the carbon isotopic compositions of primary photosynthate and of $CO_2(aq)$, respectively. Values of δ_d were estimated from the $\delta^{13}C$ record of the surface dwelling planktonic foraminifer *Globigerinoides ruber* assuming that this species depleted in ^{13}C relative to total dissolved CO_2 (ΣCO_2) by a constant of about 0.5‰. Then, $\delta_{\Sigma CO2}$ value is:

$$\delta_{\Sigma CO2} = \delta_{G.\ rubber} + 0.5 \quad (4)$$

The value of δ_d determined by equation:

$$\delta_d = \delta_{\Sigma CO2} - \varepsilon_{b(a)} \quad (5)$$

where $\varepsilon_{b(a)}$ is temperature dependent carbon isotope fractionation between $CO_2(aq)$ and bicarbonate that has values range from –9.54 to –8.86‰.
While the model proposed by Rau *et al.* [10] is based on an empirical relationship between plankton $\delta^{13}C$ (‰) and $CO_2(aq)$ as observed in the South Atlantic and Southern Ocean :

$$[CO_2(aq)] = (\delta^{13}Corg + 12.6)/-0.8 \quad (6)$$

The $CO_2(aq)$ concentration derived by both approaches (equations 2 and 6) were then converted to CO_2 partial pressure values (PCO_2, micro atm) using Henry's Law :

$$PCO_2 = CO_2(aq)/\alpha \quad (7)$$

where α is solubility constant

RESULTS AND DISCUSSION

Age Assignment of Core PN-3

The first and very important step in reconstructing paleoenvironment is to confirm whether the marine sediment is chronologically-defined strata or not. The next step is age dating. Results of $\delta^{18}O$ measurements on *G. sacculifer* are shown in Table 2. The $\delta^{18}O$ stages 1/2 and 2/3 were well defined using a high resolution $\delta^{18}O$ standard curve [7]. After correcting for reservoir age [1], all AMS ^{14}C ages were calibrated to the calendar year age, using the calibration curve of Stuiver and Pearson [12] for ^{14}C age younger than 8 ky and the calibration equation of Bard *et al*. [2] for ^{14}C ages older than 8 ky (Table 1). The calibrated ^{14}C ages are consistent with the $\delta^{18}O$ stratigraphy (Figure 2). We estimate that core PN-3 records continuous deposition during the past 40 ky. The age of each sample is interpolating and extrapolating between six control points (Table 1).

Reconstruction of the Past Atmospheric CO_2 Concentrations

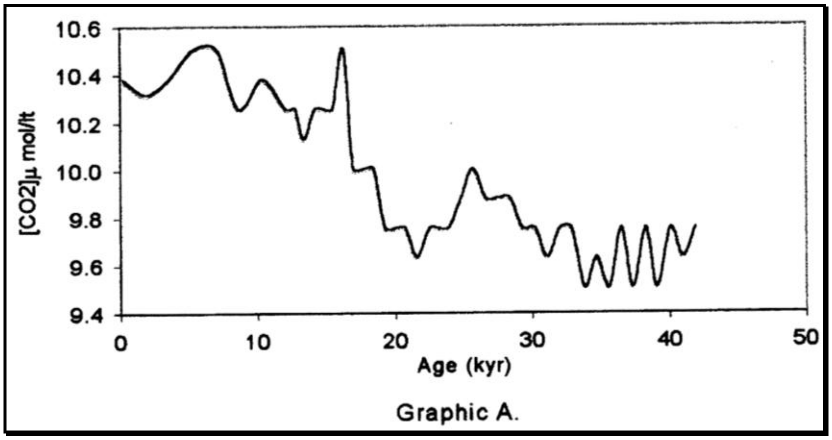
The records of the isotope measurements are shown in Tables 2. For estimation of CO_2 concentration using the model of Popp *et al*. [9], *Globogerinoides sacculifer* are employed as surface dwelling planktonic foraminifer instead of *Globigerinoides ruber*. Based on the records of C/N ratio, $\delta^{15}N$, and $\delta^{13}C$ values of bulk organic matter contained in PN-3, it had clearly been defined that organic matter contained in PN-3 is marine origin [14]. Accordingly, carbon isotopic ratios of total organic carbon in core PN-3 could be used for estimation of CO_2 concentration instead of marine plankton. Calculations of CO_2 concentrations are presented in Table 3 and Figure 3.

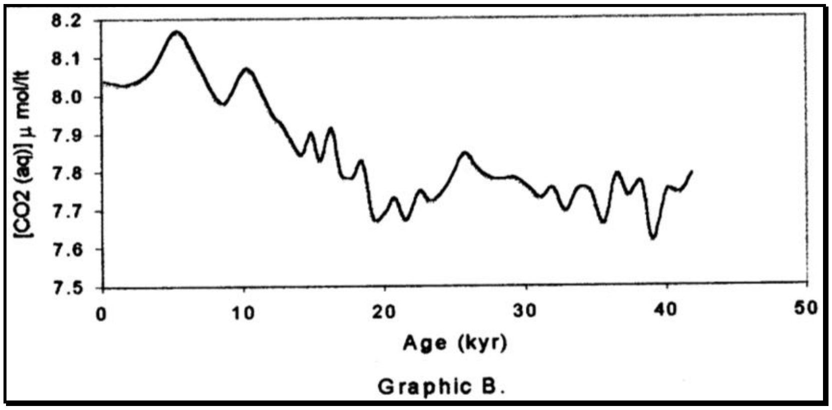
Table 2. Oxygen isotope ratio of the *Globigerinoides sacculifer* for core PN-3

Depth (cm)	Age (ky)	*G. sacculifer* $\delta^{18}O$ (‰, PDB)	Depth (cm)	Age (ky)	***G. sacculifer*** $\delta^{18}O$ (‰, PDB)
2	0.2	-2.14	220	23.1	-0.54
10	1.8	-2.05	230	13.8	-0.58
20	3.5	-2.18	240	24.7	-0.62
30	5.3	-1.85	250	25.6	-0.57
40	7.0	-1.92	260	26.5	-0.60
50	8.6	-1.88	270	27.4	-0.58
60	10.3	-1.28	280	28.3	-0.66
70	12.0	-1.21	290	29.2	-0.67
80	12.7	-0.07	300	30.1	-0.72
90	13.3	-0.77	310	31.0	-0.76
100	14.1	-0.86	320	31.9	-0.72
110	14.8	-0.59	330	32.8	-0.73
120	15.4	-0.43	340	33.7	-0.74
130	16.2	-0.52	350	34.6	-0.75
140	16.9	-0.49	360	35.5	-0.74
150	17.7	-0.29	370	36.4	-0.83
160	18.4	-0.80	380	37.3	-0.75
170	19.2	-0.41	390	38.2	-0.81
180	20.0	-0.41	400	39.0	-0.72
190	20.7	-0.51	410	40.0	-0.97
200	21.5	-0.57	420	40.9	-0.78
210	22.4	-0.38	430	41.8	-1.07

Table 3. Calculation of the past CO_2 concentrations ($[CO_2(aq)]$) recorded in core PN-3

Age (ky)	δp ($\delta^{13}C_{org}$)	$\delta^{13}C_{G.sac.}$ (‰)	δd (‰)	ε_p (‰)	$[CO_2(aq)]$ (µmol/lt)	
					Popp *et al.*('89)	Rau *et al.*('91)
0.200	-20.900	2.130	11.490	-32.022	8.030	10.375
1.800	-20.850	2.160	11.520	-32.001	8.020	10.313
3.500	-20.900	2.190	11.550	-32.079	8.060	10.375
5.300	-21.000	2.310	11.670	-32.293	8.160	10.500
7.000	-21.000	2.090	11.450	-32.083	8.060	10.500
8.600	-20.800	2.100	11.460	-31.894	7.970	10.250
10.300	-20.900	2.200	11.560	-32.089	8.070	10.375
12.000	-20.800	2.040	11.400	-31.837	7.950	10.250
12.700	-20.800	1.980	11.340	-31.780	7.920	10.250
13.300	-20.700	2.000	11.360	-31.700	7.880	10.125
14.100	-20.800	1.800	11.160	-31.607	7.840	10.250
14.800	-20.800	1.930	11.290	-31.732	7.900	10.250
15.400	-20.800	1.760	11.120	-31.569	7.820	10.250
16.200	-21.000	1.750	11.110	-31.757	7.910	10.500
16.900	-20.600	1.880	11.240	-31.486	7.780	10.000
17.700	-20.600	1.860	11.220	-31467	7.780	10.000
18.400	-20.600	1.960	11.320	-31.563	7.820	10.000
19.200	-20.400	1.820	11.180	-31.231	7.670	9.750
20.000	-20.400	1.860	11.220	-31.269	7.690	9.750
20.700	-20.400	1.950	11.310	-31.355	7.720	9.750
21.500	-20.300	1.920	11.280	-31.228	7.670	9.625
22.400	-20.400	1.990	11.350	-31.394	7.740	9.750
23.100	-20.400	1.930	11.290	-31.336	7.720	9.750
23.800	-20.400	1.960	11.320	-31.365	7.730	9.750
24.700	-20.500	1.970	11.330	-31.473	7.780	9.875
25.600	-20.600	2.010	11.370	-31.611	7.840	10.000
26.500	-20.500	2.030	11.390	-31.531	7.800	9.875
27.400	-20.500	1.970	11.330	-31.473	7.780	9.875
28.300	-20.500	1.960	11.320	-31.464	7.770	9.875
29.200	-20.400	2.070	11.430	-31.470	7.780	9.750
30.100	-20.400	2.020	11.380	-31.422	7.760	9.750
31.000	-20.300	2.050	11.410	-31.352	7.720	9.750
31.900	-20.400	2.010	11.370	-31.413	7.750	9.625
32.800	-20.400	1.870	11.230	-31.279	7.690	9.750
33.700	-20.200	2.210	11.570	-31.407	7.750	9.750
34.600	-20.300	2.090	11.450	-31.391	7.740	9.625
35.500	-20.200	2.000	11.360	-31.206	7.660	9.500
36.400	-20.400	2.090	11.450	-31.489	7.790	9.750
37.250	-20.200	2.170	11.530	-31.368	7.730	9.500
38.200	-20.400	2.040	11.400	-31.422	7.760	9.750
39.000	-20.200	1.900	11.260	-31.110	7.610	9.500
40.000	-20.400	1.990	11.350	-31.394	7.740	9.750
40.900	-20.300	2.080	11.440	-31.381	7.740	9.625
41.800	-20.400	2.090	11.450	-31.489	7.790	9.750





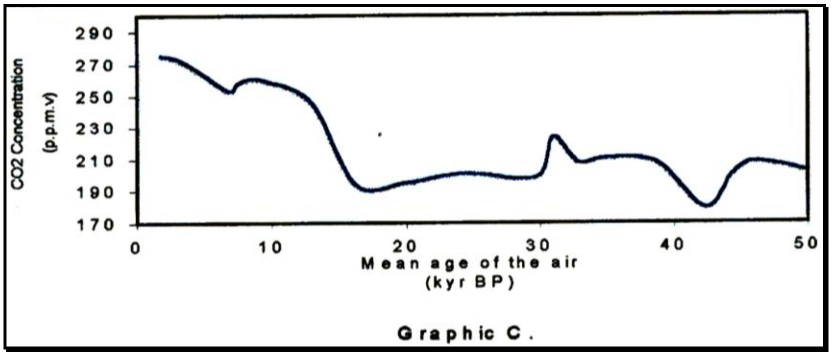


Figure 3. Variations of past CO_2 concentration in the surface water of the Okinawa Trough, East China Sea for the last 41000 years. A) using formula of Popp *et al.*[9], B) using formula of Rau *et al.* [10], and comparing to C) Atmospheric CO_2 concentration of air trapped in the ice core from the southern pole [3].

As shown in Figure 3, there is a significance discrepancy in a value between CO_2 concentration calculated by Popp *et al*. [9] and Rau *et al*. [10]. This is may be caused by different in utilizing species of foraminifer as a representation of ΣCO_2 of surface water. Furthermore, in this research, isotope effect due to temperature changes in surface water is neglected.

However, the whole trends of the changes in CO_2 concentrations estimated by both models [9,10] are very similar. Comparing to the fluctuation of atmospheric CO_2 concentrations of air trapped in ice core from southern pole [3] (Figure 3 C), both trends are also similar. There are lower values during glacial (before 12000 years ago) and higher during interglacial period (about the last 12000 yrs).

The similar trends of the fluctuation of the CO_2 concentrations indicate that the past global climate changes recorded in the ice core from southern pole are also well preserved in deep marine sediments from the Okinawa Trough, East China Sea. The lower values of CO_2 concentrations during glacial time suggest that there was increase in utilization of CO_2 in sea surface caused by increasing biological productivity in surface water. On the other hand, the higher values during the last 12000 years are interpreted as decreasing consumption of CO_2 (by marine organism) in ocean surface water.

The fluctuations of utilization of CO_2 in surface water are related to glacial-interglacial (cold-warm) fluctuations between maximum and minimum values through most Quaternary. During glacial (cold) period, the continental ice sheet was increased, then causing sea level change about 100m lower then in interglacial (warm) period. Consequently, during glacial period the area of continent became wider and supply of nutrient to the ocean increase. The increasing supply of nutrient to the ocean is interpreted as a reason of increasing productivity in surface water during glacial period. The higher surface productivity during glacial period in the Okinawa Trough has clearly been recorded as higher accumulation rate of total organic carbon investigated in core PN-3[14].

CONCLUSION

Global climate changes were expressed by fluctuations in past atmospheric CO_2 concentrations during the last 41.000 years have been reconstructed from total organic carbon $\delta^{13}C$ recorded in a sediment core PN-3 taken from the Okinawa Trough. These fluctuations of CO_2 concentrations are very similar to the past atmospheric CO_2 concentrations recorded in the ice core from southern pole. This indicates that past global climate changes recorded in the ice core from southern pole are also well preserved in deep marine sediments from the Okinawa Trough, East China Sea.

Instead of $\delta^{13}C$ of marine organism (plankton), carbon isotopic composition of marine origin total organic carbon could be used for inferring past environmental changes, especially for reconstructing past CO_2 concentration.

The changes in atmospheric CO_2 concentrations are interpreted as a result of fluctuation in utilization of CO_2 by marine organism in ocean surface water.

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