Geochemical Evidence for Spatial Paleoproductivity Variations in the Northwest Pacific (Shikoku Basin) during the Last Glacial Maximum

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A geochemical study of three piston cores (ST.4, ST.6 and ST.20) taken from the Northwest Pacific (eastern edge of Shikoku Basin) provides information about changes in surface water paleoproductivity and sedimentation during the last 127 kys. Paleoproductivity variations were estimated on the basis of total organic carbon content and carbonate mass accumulation rate. The paleoproductivity based on total organic carbon shows significant spatial variations between glacial and interglacial periods. During the last glacial maximum (LGM) paleoproductivity increased about 1.5 times with deglaciation decrease compared with those of the Holocene at inner side of the Shikoku Basin (ST.4 and ST.6). On the other hand, paleoproductivity at outer side of Shikoku Basin (ST.20) indicating not distinctive increase but deglaciation increase. The C/N ratios fall below 10 for cores ST.4 and ST.6, but C/N ratios between 100 ka and 80 ka in ST.20 which show around 10 or larger values suggest a predominance of marine organic carbon with some admixture of terrigenous materials. The carbonate mass accumulation rate of three cores show different patterns of calcareous record with respect to organic carbon based paleoproductivity variation. In the inner side of Shikoku Basin (ST.4 and ST.6) the carbonate mass accumulation rate decreased during last glacial maximum, and significant increase of carbonate mass accumulation rate is recognized at outer side of Shikoku Basin (ST.20). Thus, this set of data reveals that spatial paleoproductivity variations between inner and outer side of Shikoku Basin during the glacial and interglacial periods.

INTRODUCTION

Understanding spatial and temporal variations in paleoproductivity is of critical importance for investigating global climate changes. In fact, the variations in oceanic productivity have been thought to be at least partly responsible for fluctuation in atmospheric CO_2 during the last several tens of thousand of years as recorded in polar ice cores (Barnola *et al.*, 1987; Neftel *et al.*, 1982). This clearly demonstrates that the estimate of modern and past biological productivity is essential to our understanding of global carbon system and global environmental change (Berger *et al.*, 1989). Atmospheric CO_2 change largely depends on the exchange rate of CO_2 between atmosphere and ocean reservoirs, and dissolved CO_2, which is controlled by biogenic primary production of the surface ocean, is

regarded as one of the prime factor responsible for climate change (Broecker and Peng, 1982; Samthein *et al.*, 1988; Santhein and Zahn, 1987). Estimates of surface production using trace elements such as sedimentary barium and biogenic barium in sediments trap experiment (Dymond *et al.*, 1992; Breymann *et al.*, 1992; Van Os *et al.*, 1994) also support the importance of oceanic paleoproductivity variations in understanding global environmental change.

Even though shelf and slope environments with their enhanced surface-water productivity are of major importance to the global carbon budget, productivity variation in these areas is not studied as vigorously as those in the open ocean. However, quantitative estimates of productivity in shallow, local and upwelling areas are essential to develop comprehensive quantitative global carbon budget
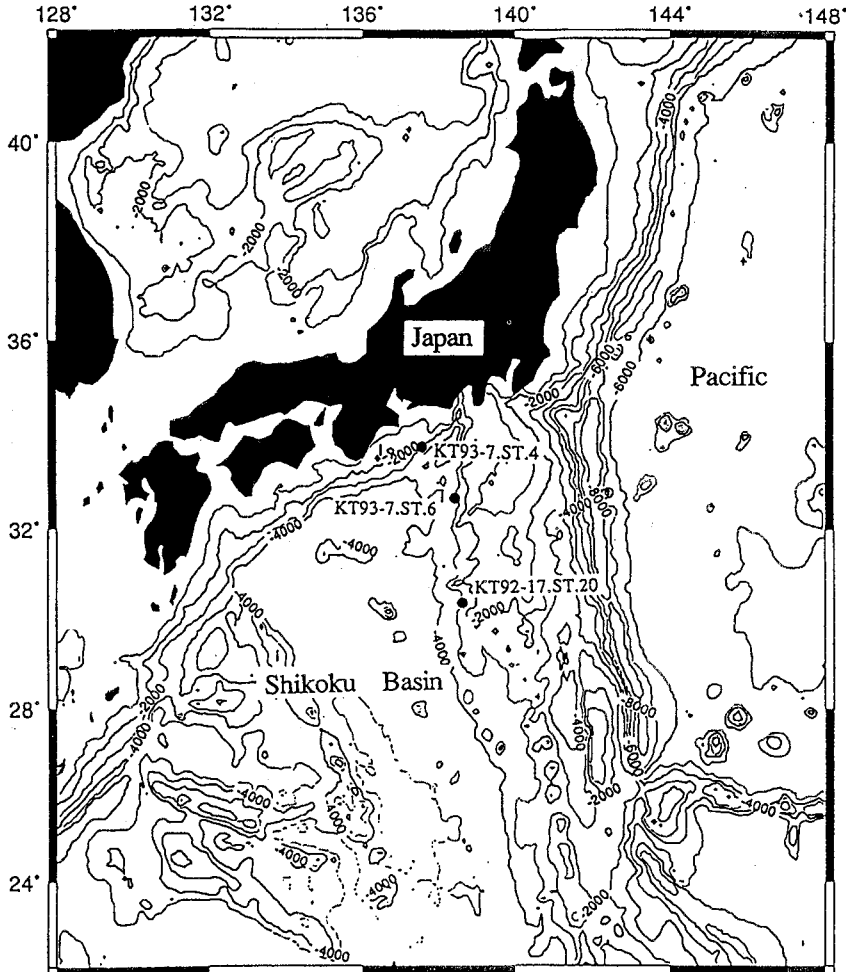
Fig. 1. Location of the three piston cores (ST.4, ST.6 and ST.20) used in this study.

models. Productivity in these area is extremely sensitive to climatic variation and is responsible for about 50% of world primary production even though they only comprise 10% of the area of world oceans (Berger *et al.*, 1987). Thus, paleoproductivity in shelf and slope area shares a key with open ocean to grasp cause and effect of the long term climatic change.

In this study, we examine spatial and temporal paleoproductivity variations at hemipelagic area on the basis of total organic carbon and mass accumulation rate of carbonate during the last 127,000 yrs. We also speculate the nature of organic carbon recorded in three cores based on C/N (total organic carbon/ total nitrogen) ratio.

GEOLOGICAL SETTING AND OCEANOGRAPHIC CONDITIONS

Three piston cores (ST.4, ST.6 and ST.20) studied here were taken during the KT93-7 and KT92-17 by the R/V *Tansei Maru* cruise of Ocean Research Institute, Univ. of Tokyo. These cores were situated on the eastern edge of the Shikoku Basin, to the west the Izu-Bonin Arc (Fig. 1). These sites are characterized by relatively high sedimentation rate due to the steep slope of bathymetry and by moderate biogenic sediments of open ocean. Thus, this location is thought to be suitable for our study as a representative region of Shikoku Basin as well as local paleoceanographic environmental changes since

Table 1. Location, water depth and length of the cores used in this study

Core ID	Latitude (N)	Longitude (E)	Water depth (m)	Length (cm)
KT93-7. ST.4	33°45.2'	137°35.5'	2274	370
KT93-7. ST.6	32°39.8'	138°27.3'	3272	607
KT93-17. ST.20	30°22.6'	138°38.9'	3280	875

the three cores are located across the Kuroshio pathyway with North-South transect line of the Shikoku Basin.

The Kuroshio current, a major North Pacific western boundary current and principal subsurface current system of this region, overlies these three sites. The Kuroshio current has repeatedly changed its course between glacial and interglacial time, causing significant oceanographic environmental change in this region (Chinzei et al., 1987). Judging from the cored site and its depth as well as oceanographic condition, and from the sediment character which is thought to be hemipelagic, it is suggested that this site is most suitable to examine spatiotemporal paleoproductivity variations during the glacial to interglacial periods. The core location, water depths, and core lengths are listed in Table 1.

MATERIALS AND METHODS

Sediment samples were taken every 2.4 cm using plastic sample cubes. X-ray photographs of whole cores and bulk density analysis were performed for all samples (Murayama et al., 1994). A total of 188 samples (approximately 10 cm-interval) were analyzed for stable oxygen and carbon isotopes, total organic carbon content and its C/N ratio, and carbonate content.

For the stable oxygen and carbon isotope analyses, we selected about 50 specimens of *Globorotalia inflata*, which dwelled in subsurface water and secreted calcitic tests in near isotopic equilibrium with ambient water. The selected foraminifera tests were cleaned, crushed and analyzed using Finnigan MAT-251 mass-spectrometer at Hokkaido University. The oxygen and carbon isotopic data are reported relative to the Peedee belemnite (PDB) standard.

Untreated powdered samples of dried bulk sediments were analyzed using CHN analyzer (Yana-gimoto-MT 2 type) to produce total carbon (TC; carbonate carbon plus organic carbon). For total organic carbon (TOC) determinations, we treated the sample with 1N HCl to dissolve inorganic carbon and than inorganic carbon-free sediment samples were conducted TOC content. Inorganic carbon content was calculated by subtracting TOC from TC. After determining total organic carbon content, paleoproductivity are calculated using the formula of Sarthein et al. (1987) as follows:

$$\text{Paleoproductivity(g cm}^{-2}/\text{yr})$$
$$= 15.9 \times C^{0.66} \times S_B^{0.66} \times DBD^{0.66} \times S_{B-C}^{-0.71} \times Z^{0.32}$$

where the C is organic carbon content(%), S_B is sedimentation rate, DBD is dry bulk density, S_{B-C} is organic carbon-free sedimentation rate, and the Z is water depth. Thus, this equation is based on the assumption that the organic carbon accumulation rate is mainly a function of primary production, water depth and of the sedimentation rates (Sarthein et al., 1987).

In calculating mass accumulation rate (MAR), we used linear sedimentation rate (LSR-cm/kry) which was determined based on oxygen isotopic results and ^{14}C age dating, and dry bulk density as follows:

MAR (bulk) = LSR* DBD or (WBD-1.023*PO/100)

where, WBD is wet bulk density (g/cm^3), PO is porosity.

Thus, mass accumulation rates (MAR) of carbonate is calculated as follows

Carbonate-MAR = Carbonate content(%)*LSR* DBD *0.01

where, LSR = linear sedimentation rate (cm/kyr)

DBD = dry bulk density (g/cm^3)

As far as organic carbon and carbonate analysis is

concerned, an estimated error was confirmed within 2% by the pure carbonate materials.

RESULTS AND DISCUSSION

Stratigraphy

Age was determined using mainly oxygen isotopic results and several AMS (accelerator mass spectrometry) ^{14}C age analyses. Simplified lithology, oxygen isotope stratigraphy and AMS ^{14}C age points are illustrated in Fig. 2. All of the oxygen isotope results are compared with the standard isotopic curve (Martinson et al, 1987). A volcanic ash layer is located at 196-202 cm in core ST.20 which, based on lithology and glass refractive index analysis, corresponds to the AT tuff. This AT (Aira-Tn ash) tuff layer is widespread in and around all of the Japan Islands and its age was determined to be 24, 330±225 yr.B.P (Murayama et al, 1993). Using several AMS ^{14}C age data in core ST.6 and ST.20, AT tuff layer, and oxygen isotopic data, the oldest age for core ST.6 and ST.20 is approximately 65 ka

and 127 ka, respectively (Fig. 2). Oxygen and carbon isotopic results are only referred to determine the age of core ST.4. The relatively short length of core ST.4 makes isotopic stage identification difficult, but we infer that the age of bottom of this core is the stage 3 boundary at 40 ka. The absence of any absolute age control points in core ST.4 indicates an uncertain chronology. Age control points and calculated sedimentation rates on three piston core are shown in Table 2.

Paleoproductivity variations

Marine organic carbon and its variation through time may give information about changes in surface productivity. Since surface water productivity influences on the exchange of carbon dioxide between ocean and atmosphere, changes in biologically derived productivity may affect the concentration of atmospheric CO_2 and hence influence the global climate (Berger et al., 1989). Paleoproductivity values of the world ocean show wide range depending on the region. During the
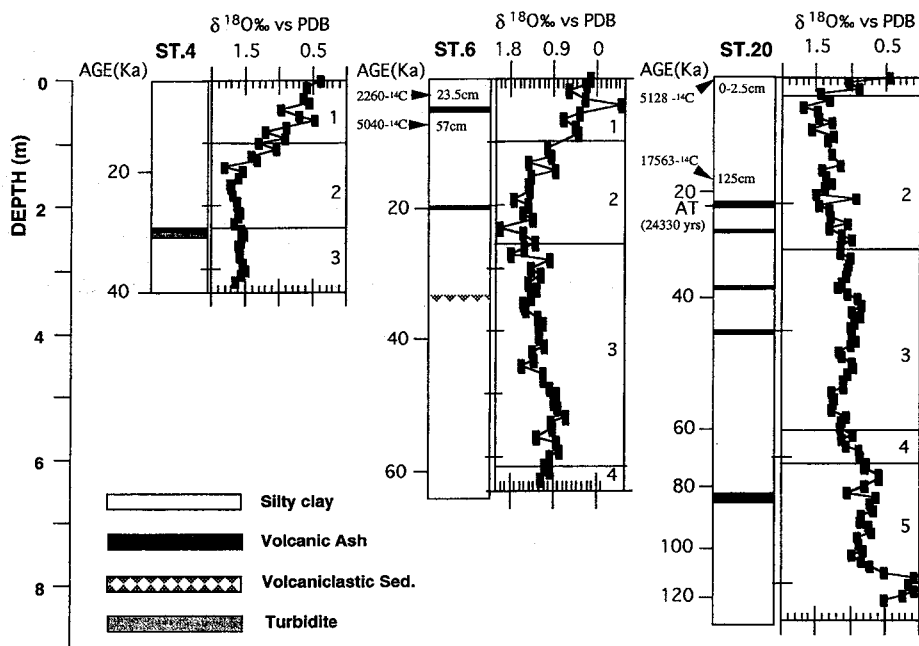

Fig. 2. Simplified lithology and planktonic foraminiferal $\delta^{18}O$ values of the three cores. Isotopic events are shown referring to Martinson et al. (1987).

Table 2. Age control points and sedimentation rates. The AMS 14-C ages dated on planktonic foraminifera, G. inflata

	Depth (cm)	Dating Methods	Ages (ka)	S.R (cm/kyr)*
ST.4	145	δ-18O	18	8.05
	330	δ-18O	40	8.4
ST.6	23.5	AMS-14C	2.26±0.8	10.39
	57	AMS-14C	5.04±0.8	12.05
	607	δ-18O	62	9.65
ST.20	0-2.3	AMS-14C	5.22±0.3	
	125	AMS-14C	17.56±0.7	9.93
	198.0-208.0	AT ash	24.30±0.23	10.83
	511.6-513.9	δ-18O	58.96	9.04
	609.1-611.4	δ-18O	73.91	6.52
	657.3-659.6	δ-18O	79.25	9.02
	687.4-689.7	δ-18O	90.95	2.57
	849.9-852.2	δ-18O	123.82	4.94

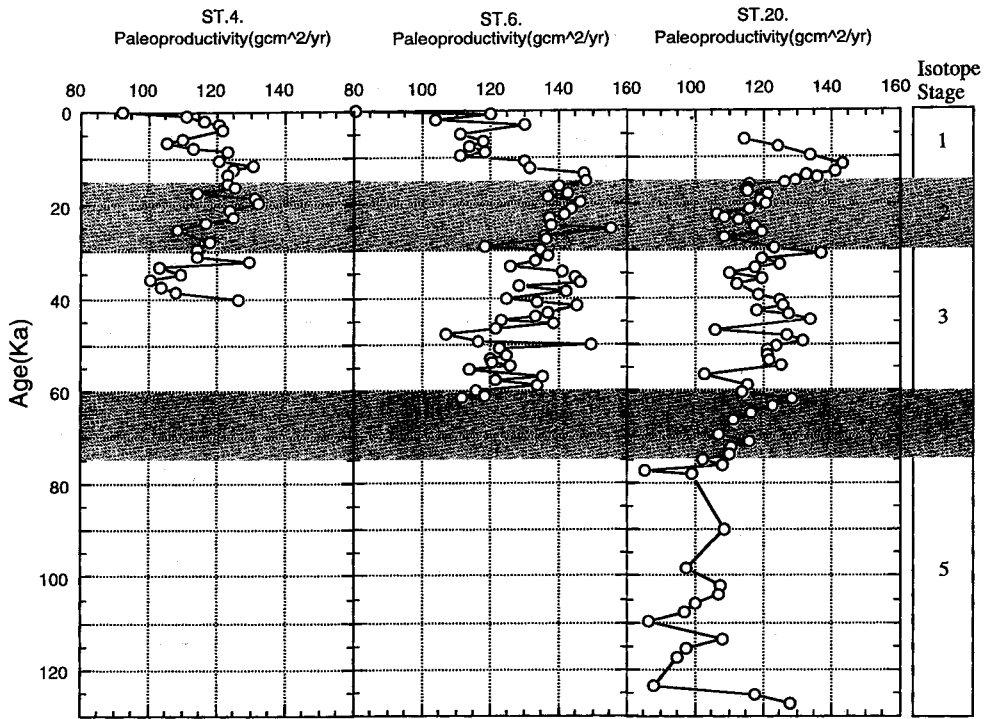*S.R; sedimentation rate (cm/kyr)

Fig. 3. Paleoproductivity variation during the past 127 ka showing increasing paleoproductivity during last glacial maximum at ST.4 and ST.6, and showing glacial decrease at ST.20. Dashed area represent glacial period.

last glacial period, surface biological productivity increased as much as two times off Northwest Africa (Muller and Suess, 1979) and also in the South China Sea (Thunell et al., 1992). Extremely high paleoproductivity, as much as three times higher than the present productivity level, was reported in coastal equatorial upwelling zone off Northwest Africa during glacial period (Sarnthein and Zahn, 1987). The present productivity of the world open ocean ranges from 80 to 100 g/cm^2/yr (Muller and Suess, 1979). Estimated paleoproductivity variation during the Holocene in our study area falls

within and/or is slightly higher than other published paleoproductivity values of the world ocean implying reasonable paleoproductivity estimations (Muller and Suess, 1979).

Two of the cores (inner side of Shikoku Basin - ST.4 and ST.6) show increases of paleoproductivity approximately over than 50% during the last glacial period with sharp decrease during deglaciation periods (Fig. 3). On the other hand, paleoproductivity of the ST.20 (outer side) does not show the last glacial increase but deglaciation increase. The paleoproductivity variations at ST.4 and ST.6 are, at least, coincident with global productivity variations; glacial increase and interglacial decrease in both low and intermediate latitudes (CLIMAP, 1976). Thus, paleoproductivity variation of in the study area indicates that paleoproductivity of Shikoku Basin follows global productivity pattern, and this pattern probably superimporsed on local environmental change since the productivity at ST.20 indicating different paleoproductivity pattern between inner and outer side of Shikoku Basin (Fig. 3). The paleoproductivity of ST.6 is higher than that of ST.4, but has same trend. This may result from more vigorous current circulation and/or abiotically driven biological pump (Ittekkot, 1993) through this time in this region. The last deglaciation interval in ST.20 shows an increased paleoproductivity suggesting slightly fertile surface paleoceanographic conditions among ST.4, 6 and ST.20 (Fig. 3).

C/N ratios and OCSR diagram

The most important factors controlling the organic carbon deposition are 1) an increase production of marine organic carbon, 2) an increase preservation of organic carbon, and 3) an increase in the supply of terrigenous organic carbon. The weight ratio of total organic carbon to total nitrogen (C/N ratio) is frequently used to characterize various types of organic matter (Bordowskiy, 1965; Muller, 1977; Stein, 1991). Although marine orginic carbon usually shows a relatively constant range of C/N ratio, terrigenous organic carbon shows a high value of C/
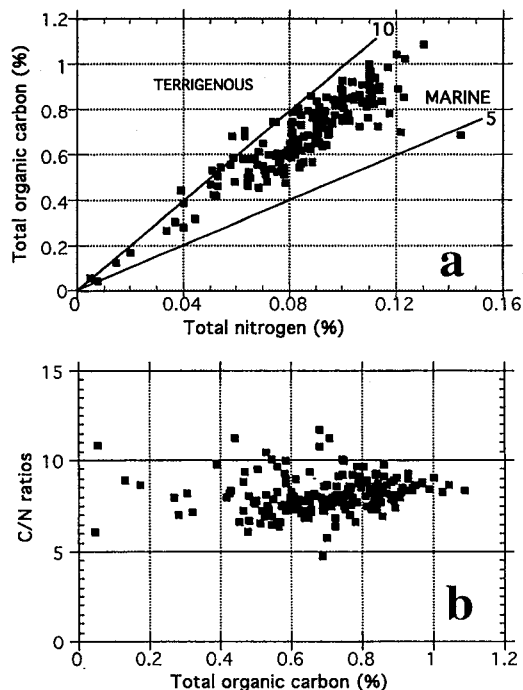

Fig. 4. a) Most of the C/N ratios fall between 10 and 5 indicating marine organic source except for several data points which around 80 to 100 ka in core ST.20. b) Relationship between C/N ratio and total organic carbon. Increasing organic carbon is not related C/N ratios indicating terrigenous organic carbon input has not significantely affected total organic carbon.

N ratio, usually 5 to 10 in marine organic carbon and higher than 10 in terrestial organic carbon (Stein, 1991). The origin of the organic carbon in our cores was investigated by the C/N ratios. The organic carbon and C/N plots of the three cores are shown in Fig. 4a and 4b. The C/N ratio indicates that most of these organic carbon was derived from a marine source as it is in the range of 10 and 5. This implies the surface biogenic-derived productivity (Fig. 4a). In core ST.20, C/N ratios over 10 between 100 ka and 80 ka suggest relatively large amount of terrigenous organic carbon was input. Despite this, terrigenous organic carbon input did not significantly affect the total organic carbon content because an increase in organic carbon is not related with the high C/N ratio. Most of the organic carbon varies between 5 and 10 implying a predominantly marine source (Fig. 4b).
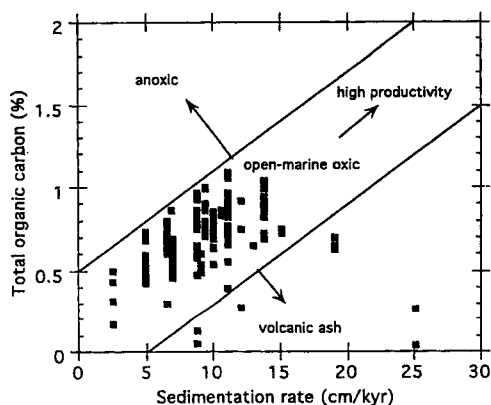
Fig. 5. OCSR diagram for three piston core shows total organic carbon increasing as function of linear sedementaion rate except for several volcanic ash horizon.

The sediment organic carbon content is not only dependent on the ocean surface productivity, water depth and sedimentation rate, but also on preservation, origin, diagenic history of the organic matter. To decide which of these mechanisms is the most important in our case, we used the organic carbon/sedimentation rate (OCSR) diagram to interpret our data (Stein, 1990). Estimated TOC values for linear sedimentation rates are plotted (Fig. 5). As shown in Fig. 5, almost all the data show the positive correlation except several ash layers which show a low organic carbon content with a high sedimentation rate. Even though organic carbon content is low in volcanic ash layer, the entire distribution of TOC indicates normal paleoceanographic conditions. This OCSR diagram may support our interpretation that the change in marine organic carbon deposition reflect changes in surface-water productivity. It also shows increased surface productivity during the glacial period and reduced productivity during the degalciation at ST.4 and ST.6, and swiched paleoproductivity excursion at ST.20 (glacial decrease and interglacial increase).

The organic carbon, settling from surface water, is likely to be oxidized during and after the transportation to the ocean floor, and only small portion (about less than 1%) of organic carbon is preserved in the underlying sediment (e.g., Emerson and Hedgo, 1988). This extremely small amount of or-

ganic matter available is thus not ideal for estimating exact paleoproductivity variation within glacial to intergalcial time scale. As far as more accurate paleoproductivity estimation is concerned, more reliable paleoproductivity proxy elements needed to be developed.

Carbonate content and its mass accumulation rate (MAR)

The carbonate content of deep-sea sediment can provide information on paleoclimatic changes and it plays an important role in the global carbon cycle over a relatively long time scale (Farrel and Prell, 1989; 1991). The preservation and distribution of $CaCO_3$ in sediments can be controlled by variation of surface biological production, dilution by terrigenous input (Arrhenius, 1952), however it is usually controlled by dissolution (e.g., Berger, 1973). The carbonate content in sediment is still used not only for the direct estimation of overall surface productivity but also in interpreting paleoceanographic and paleoclimatic shifts in open ocean (e.g., Farrell and Prell, 1991; Baumann et al., 1993) since its preservation has fluctuated markedly in conjunction with climatic cycle (Kawahata, 1994).

Calcareous nannoplankton as well as planktonic and benthic foraminifera is the main source of carbonate in sediments. In a pelagic setting, carbonate production is proportional to total organic carbon (Broecker and Peng, 1982) and the TOC is generally considered to reflect a surface primary productivity, thus carbonate content can also be used as an indicator of surface calcareous productivity. The biogenic carbonate in sediments can be easily dissolved with water depth increase and it can be also diluted by fine fraction material carried by such as bottom water current. Thus, to estimate quantitative variation of carbonates accurately it is needed that mass accumulation rate (MAR) must be considered whether it is real proxy or not.

The carbonate MAR for these three core are shown in Fig. 6. The oscillation of carbonate MAR can be produced either by oceanic calcareous productivity and dilution of carbonate or preferential
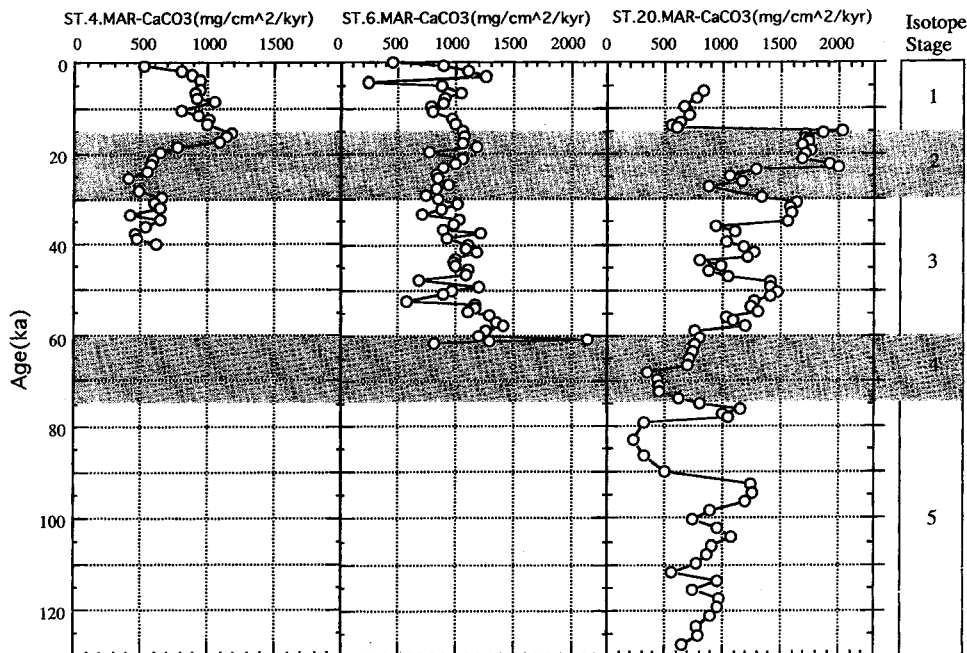
Fig. 6. Variation in CaCO₃ (g/cm²/kyr) mass accumulation rate from the three cores. Quantitative mass accumulation rate of carbonate during the last glacial maximum period is recognized. Dashed area represent glacial period.

dissolution during interglacial periods. Distinctive variations of carbonate mass accumulation are recognized throughout the core. The highest carbonate MAR is present during the stage 2 at ST.20 and the lowest value are occur at the 80-90 ka in which terrigenous organic matter is predominantly situated. The smoothest variation in carbonate MAR recognized at ST.6 may be attributed to either dilution effect or increase in dissolution.

Usually high productivity results in high carbonate preservation in normal shallow and intermediate o-cean setting. The carbonate MAR of ST.4 indicates less surface productivity, but the shallow environment might suggest high surface productivity. This paradox must be reassessed by other tracers. One of possible explanation of this trend is the dilution (by horizontal flux) of terrigenous materials in both of ST.6 and ST.20. Ahagon et al. (1995) explained increased horizontal flux of particles, based on a mass balance calculated by excess-²³⁰Th flux at the ST.20 during the last glacial maximum. Secondary transportation including excess - Th flux can be expected in accordance with the lo-

cation of both cores which are situated on the western edge of Izu-Bonin Arc.

CONCLUSIONS

We estimated paleoproductivity variations on the basis of organic carbon, mass accumulation rate of carbonate for three cores recovered from the Northwest Pacific (Shikoku Basin). From these analyses, the following conclusions can be drawn:

1. Estimated paleoproductivity based on algorithms of Santhein et al. (1987) of the surface water shows significant variations during the last 127 ka. High paleoproductivity in inner side of Shikoku Basin and low paleoproductivity at the outer side of Shikoku Basin are recognized during the last glacial maximum. Thus, spatial paleoproductivity variation is a prevailing feature of this area. During the last glacial maximum paleoproductivity shows more than 1.5 times increase over those of the Holocene.

2. Total organic carbon/total nitrogen (C/N) ratios and organic carbon/sedimentation rate (OCSR) resu-

Its suggest a relatively stable and continuous uniform surface productivity variation, even though some admixture of terrigenous organic carbon was recognized between 80 and 100 ka in core ST.20.

3. The mass accumulation rate (MAR) of carbonate from the three cores shows a apposite calcareous production pattern with respect to organic carbon based paleoproductivity variation, and also shows a increased mass accumulation rate toward the outside of the Shikoku Basin.

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