

## Sedimentary Excess Barium from a Core of the Northwest Pacific Ocean: Geochemical Proxy

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A geochemical study on a hemipelagic core sediment taken from the northwest Pacific Ocean (eastern edge of the Shikoku Basin) was conducted to use of excess barium (Ba(ex)) for evaluate the paleoceanographic changes. Also, the excursion of sedimentary Ba(ex) was compared with those of biogenic opal, carbonate and organic carbon content in the sediment during the last glacial and interglacial periods. The calculated Ba(ex) derived from the major and minor element shows a distinctive glacial-interglacial variations, and the mass accumulation rate (MAR) of Ba(ex) shows coincident variations with the MARs of biogenic fractions. Especially, strong positive correlation ( $r^2=0.85$ ) between the MAR of Ba(ex) and the MAR of biogenic carbonate is recognized. Based on the strong positive correlation ( $r^2=0.85$ ) between the MAR of Ba(ex) and the MAR of carbonate content, we estimated the degree of carbonate dissolution rate during the glacial and interglacial periods. Assuming the proportional variation and the refractory nature of barium exist between two factors, the variation of index Ca/Ba ratio in sediment indicates the degree of carbonate dissolution. Sedimentary Ca/Ba ratios index clearly show a striking fluctuation between the glacial and interglacial periods with higher positive correlation during glacial and lower correlation during interglacial. This fact indicates enhanced carbonate dissolution during interglacial period. Thus, the sedimentary Ca/Ba ratio in sedimentary records can be used as one of the useful tools for estimation of the relative degree of carbonate dissolution. The excursion of Ba(ex) and the sedimentary Ca/Ba ratio follows the typical pacific carbonate dissolution type (enhanced dissolution during interglacial and reduced dissolution during glacial time) as suggested by previous work (*e.g.*, Wu *et al.*, 1990). Variation in sedimentary Ca/Ba ratio thus strongly supports that glacial-interglacial fluctuation in carbonate dissolution has been prevailed in the northwest Pacific Ocean.

### INTRODUCTION

In understanding global environmental changes it has been considered one of the fundamental focus to grasp the carbonate dissolution as well as biogenic productivity variations of the ocean. The variations in carbonate dissolution and ocean productivity are thought to be responsible for fluctuation in atmospheric carbon dioxide as recorded in ice core (Neftel *et al.*, 1982; Barnola *et al.*, 1987; Sarnthein *et al.*, 1988; Dehairs *et al.*, 1990; Archer and Maier-Reimer, 1994). Thus, it is very clear that carbonate dissolution record and modern and past bio-productivity in the ocean are important tools in understanding global carbon system and its present and past effect on the environmental

changes on the ocean (*e.g.*, Berger *et al.*, 1973; Farrell and Prell, 1989).

Recently developed proxy element of barium for paleoproductivity reconstruction has been called for great concern because the barium has a striking correlation with organic matter in settling particles (Dymond *et al.*, 1992; Francois *et al.*, 1995). It has been used as a tool for monitoring global environmental changes (Schmitz, 1987; Gingele and Dahmke, 1994; Mcmanus *et al.*, 1998). Also, the results of the excess barium (Ba(ex)) at the Southern Ocean show a striking fluctuation with biogenic silica suggesting a possible proxy element for the biogenic silica production (Bishop, 1988; Nurnberg *et al.*, 1997). On the other hand, the barium concentration in foraminiferal calcite was to be proportional variations to the sea water Ca concentration (Lea and Boyle, 1989). This result thus indicates that barium content in the sediment can be an important tool for understanding the

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deep ocean water history and a possible productivity proxy elements even though the mechanism for the formation of Ba(ex) is not well known (Dehairs *et al.*, 1980; Bishop, 1988).

The amounts of preserved biogenic carbonate are thought to be the consequence of dissolution, surface productivity and dilution by terrigenous materials. Even though the carbonate dissolution has an important key in understanding ocean history as well as chemistry, many problems still exist in understanding carbonate dissolution. These problems are dissolution, diagenesis and some relation between productivity and preservation. Few reports exist on accumulation rate of barium in terms of other biogenic tracer such as biogenic carbonate and biogenic opal. Considering the refractory nature of barite in sediment, it would provide powerful tool for carbonate dissolution as far as barite has a certain proportional variation with biogenic fractions in hemipelagic setting.

The main objective of this study is to elucidate whether sedimentary barium can be a proxy element or not at the oligotrophic area, and how we can use barium as a proxy element at the neritic and hemipelagic sediment. From the Ba(ex) estimation by sedimentary barium, we also speculate entire paleoceanographic variation during the penultimate interglacial period with other records of total carbon and biogenic opal.

## GEOLOGICAL SETTING AND OCEANOGRAPHIC CONDITION

A piston core (ST 20) studied here was taken during the KT92-17 cruise by the R/V *Tansei maru* of the Ocean Research Institute, the University of Tokyo. This core was situated on the western edge of the Shikoku Basin and the western side of a core site appear Izu-Bonin Arc, where high rate of sediment

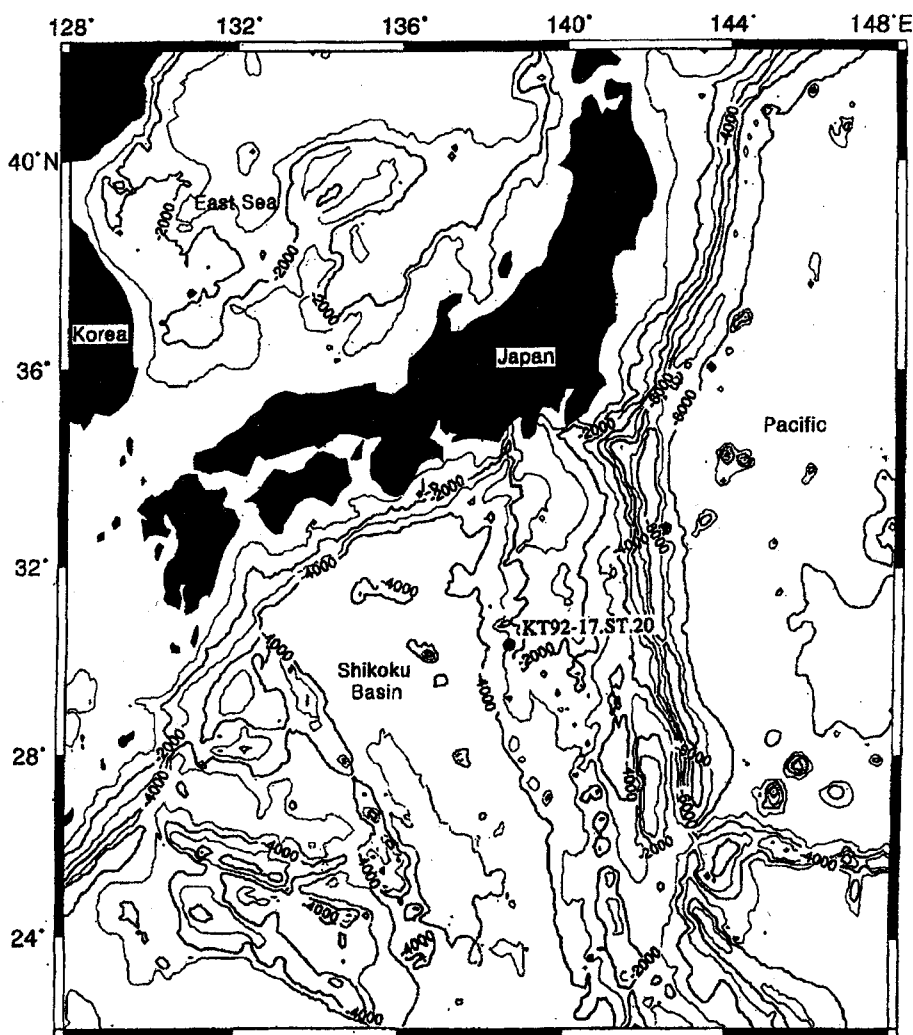


Fig. 1. Site map showing the coring sites.

transportation to the study area is expected (Fig. 1). The Kuroshio current has repeatedly changed its courses during glacial and interglacial time, causing significant environmental change in this region (Chinzei *et al.*, 1987).

One of the most important things of this area is that transitional site of water depth and rather complicated bathymetry. Due to the rather complicated circumstance, sediment of the core is composed of typical hemipelagic sediment with intermittent turbidite and volcanic ash (Ahagon, 1997). Considering the water depth (3280 meter), the carbonate recorded in sediment lattice be expected to have been affected by variable degree of dissolution, but not seriously, since the water depth is shallower than the carbonate compensation depth (CCD).

## METHOD AND MATERIALS

Sediment sub-samples were taken at every 10 cm interval by cube sampler, and dry bulk density (DBD; g/cm<sup>3</sup>) was measured directly (Hyun, 1997). Roughly selected cube sediment samples were analyzed for total carbon (TC) using a Yanagimoto MT-2 CHN analyzer after drying at 105°C for more than 24hr. Total organic carbon (TOC) are analyzed from the same sample which was treated 1N hydrochloric acid. Inorganic carbon was calculated from weight difference between TC and TOC, and the carbonate content was calculated as follows:

$$\text{Carbonate content (\%)} = \text{Inorganic carbon (\%)} \times 8.33$$

The content of the biogenic opal was determined by the direct dissolution by alkaline extraction using molybdate-blue spectrophotometry (Mortlock and Froelich, 1989). Major and minor elements were analyzed by X-ray fluorescence (XRF). Basically, each of samples was analyzed at the same layer to get comparative results for each analysis. The MAR of each fraction was calculated using LSR (linear sedimentation rate; cm/kyr) which was determined by oxygen isotope and several <sup>14</sup>C age control points and DBD. The oxygen isotope was determined from planktonic foraminifera, *Globorotalia inflata*, at the Hokkaido University. The analytical error for biogenic fractions is thought to be within 5%. The major and minor elements typically exhibit errors < 1% on both standards and unknown samples (Hyun *et al.*, 1999). Biogenic materials (carbonate, organic matters and opal) and isotopic age in this core have already been reported elsewhere (Hyun *et al.*, 1998).

## DETERMINATION OF EXCESS BARIUM (Ba(ex))

Because the bulk sedimentary barium can be classified into several fractions such as siliclastic sediment related barium (bounded in terrigenous materials), carbonate-bound barium, organic matter bounded barium and biogenic barium. Most fraction of barium is believed to be related with terrigenous materials in the case of hemipelagic sediments (Dymond, 1981). Thus, it is necessary to elaborate aluminosilicate-related barium from total barium concentration in order to estimate the accurate Ba(ex) concentration. In this study, we defined the total barium as carbonate-free barium concentration, and confirmed Ba(ex) as a barium which are calculated using following formula.

$$\text{Ba(ex)} = \text{Ba(total)} - (120 \text{ ppm} \times \% \text{opal}/100) - (452 \text{ ppm} \times \% \text{aluminosilicate}/100)$$

where, the amount of aluminosilicate materials is calculated by subtraction of biogenic fractions from total sediments(100), *i.e.*, 100 - (TOC content(%) + carbonate content(%) + biogenic opal content(%)).

The constant of 120 ppm is derived from the diatom culture observation (Dehairs *et al.*, 1980). Dymond *et al.* (1992) used the 0.0075 as a typical average value of Ba/Al in aluminosilicate matrix in testing barium for reconstructing paleoproductivity. But they suggested that the constant 0.0075 can be adjusted for specific provenance. Other authors used different Ba/Al ratio of 0.0019 in calculating biogenic barium at the Mediterranean Sea (van Os *et al.*, 1994), and Nurnberg *et al.* (1997) used the 0.0067 at the Atlantic sector of the Southern Ocean. Because the Ba/Al ratio is highly variable, we did not use this ratio, instead we used average barium concentration as a standard values included in aluminosilicate lattice directly.

The sediment of the Shikoku Basin likely to be affected by detrital materials from Japanese Island and aeolian dust from China continent (especially Manking) (Rea and Janecek, 1982; Dersch and Stein, 1994). The concentration of barium from Manking and Japanese Island are about 480 ppm and 452 ppm, respectively (Table 1). The average concentration of crustal barium is 425ppm (Taylor *et al.*, 1964). When we consider the sediment of the Shikoku Basin as a mixture of these three sources, average concentration of the three sources is 452 ppm. Using this average value, we determined Ba(ex) concentration in this study.

**Table 1.** Barium to aluminium ratio from the several sources

Al <sub>2</sub> O <sub>3</sub> (%)	Ba(ppm)	Sources	Ba/Al	References
		Aluminosilicate detritus	0.0075	Dymond <i>et al.</i> (1992)
		Mediterranean	0.0019	van Os <i>et al.</i> (1994)
15.4	480	Losses(Namking)	0.0058	Taylor <i>et al.</i> (1983)
11.4	810	Losses(Iowa)	0.0134	Taylor <i>et al.</i> (1983)
7.78	200	Losses(Kaiserstuhl)	0.0048	Taylor <i>et al.</i> (1983)
15.56	425	Crustal average	0.0051	Taylor <i>et al.</i> (1964)
16.56	250	Basalt average	0.00779	Taylor <i>et al.</i> (1964)
		Losses (Japanese Island)	0.007-0.008	Kanamori <i>et al.</i> (1991)
14.5	452	Japanese Island	0.00598	Togashi <i>et al.</i> (1995)
16.25	873.3	ST.20	0.0101	This study

## RESULTS AND DISCUSSIONS

### *Aluminosilicate materials and several sources of excess barium (Ba(ex))*

The sediment of the study area is composed of large portions of terrigenous material and minor amounts of biogenic fractions. The terrigenous component is supplied directly from adjacent Japanese inland and from aeolian dust, and its variations in accumulation are related with climatic changes (Rea and Janecek, 1982; Dersch and Stein, 1994). The ratios of two typical terrigenous elements (Ti/Al) indicate narrow range of variations (Hyun *et al.*, 1998) except for several volcanic ash layers even though the slight lithological change is recognized at the lower part of the core (Ahagon, 1997). Because aluminum and titanium are considered as typical conservative terrigenous elements (Goldberg and Arrhenius, 1958; Spears and Kanris-Sotirios, 1976), the terrigenous materials supplied in study area are thought to be common origin (Hyun *et al.*, 1998). This fact is fundamental factor in calculating Ba(ex) concentration.

The various sources of barium are discussed in the open ocean (Deharis *et al.*, 1980). The barium concentration in hemipelagic sediment, however, is related with terrigenous aluminosilicate materials. Apart from the barite phase barium, aluminosilicate related barium and carbonate-bound barium may also contribute significantly to the total barium content, especially in the hemipelagic environment (Dymond, 1981). Thus, it is necessary to discriminate bio-, and carbonate-bound and/or absorbed barium from bulk barium for the accurate estimation of Ba(ex).

The selective leaching experiment is conducted to manifest the sedimentary minor element behavior including barium. This experiment is divided into three parts (Table 2). The first step is the results of

**Table 2.** Selective leaching results on a sample from the studied core

Elements	Untreated sample (ppm)	Carbonate-free (ppm)	Hydroxylamine-hydrochloride (ppm)
Ba	538.9	665.1	671.4
Nb	9.8	10.9	11.2
Ni	43.8	42.1	38.4
Pb	22.5	18.3	18.6
Rb	124.1	139.9	143.6
Sr	256.7	142.8	129.4
Th	11.4	12.7	13.5
Y	23.1	22.3	22.8
Zr	144.7	166.3	164.8

non-treated measurement of the powdered samples. The second step includes treatment by 4M acetic acid, and the samples were centrifuged in order to remove biogenic carbonate and carbonate-bound elements. In the last step, carbonate-free sediment is treated by hydroxylamine hydrochloride, and the result of this step is considered to reflect oxyhydroxide-associated minor element concentration (Fe, Mn oxide concentration). As shown in Table 2, in the case of Ba, Nb, Rb and Zr, the concentration is higher at the second and the last step. On the other hand, Sr concentration became low at the second step. This indicates the carbonate-free based barium is related to particulate barite, on the other hand, the strontium is believed to be carbonate-bound lattice. Thus, most amount of Sr is believed to be carbonate-bound form, and Ba probably indicates that a high amount of barium in bulk sediment exists in a form of carbonate-attached particle (not only in carbonate-bound form). Only slight increase of barium in the last step is recognized, suggesting that small amount of Fe and Mn related barium exist.

The scatter diagrams of carbonate-free barium with

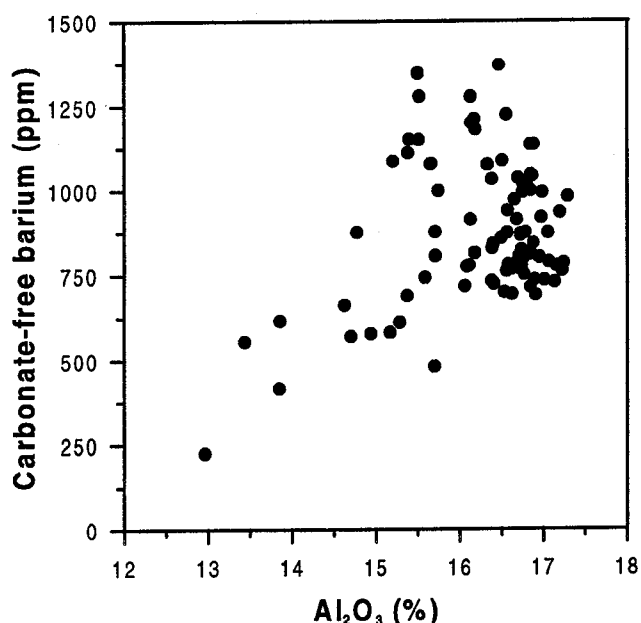


Fig. 2. Scatter diagrams of the aluminum to carbonate-free barium concentration. Large fluctuations of carbonate-free barium is recognized.

respect to Al content are illustrated in Fig 2. If we consider all aluminum and carbonate-free barium are originated from the terrigenous materials, the correlation between two factors should be strong. This higher correlation in both elements means that both elements came from the same terrigenous materials. However, the correlation between two factors shows faint or no correlation, which suggest that relatively large amount of barium is included in terrigenous aluminosilicate materials. Also this fact indicates that some part of carbonate-free barium is related with non-terrigenous aluminosilicate materials. Therefore, the source of carbonate-free barium is thought to be admixture of the terrigenous materials and other sources. The barium from other sources is what we want to know, and termed as excess barium (Ba(ex)) in this study.

Over 90% of barium in total sedimentary barium was considered as an aluminosilicate-related one in the Nazca plate (Dymond *et al.*, 1981). Most of barium is considered as a biogenic in the high productivity area (Goldberg and Arrhenius, 1958). In this study, it is impossible to determine how much of barium is related with aluminosilicate and with biogenic bound. However, we consider that about one third to one fourth of the total barium is originated from extraneously, that is not related with terrigenous aluminosilicate materials.

### Variations of excess barium (Ba(ex)) and diagenetic mobilization of Ba

The concentrations of the sedimentary carbonate-free barium for analyzed samples are highly variable (Fig. 2). The higher values are at the lower part of the core. Entire pattern of the carbonate-free barium concentration in the core shows a distinctive glacial decrease and interglacial increase. This is one of the strong evidences that the variation of carbonate-free barium is not only related to the supply of aluminosilicate materials but in part included in biogenic fraction such as bounded in carbonate materials and organic matters.

The sediment at high biological productivity area usually shows a high percentage of sedimentary barium concentration (Goldberg and Arrhenius, 1958). Ba(ex) concentrations, however, vary from 10 to 90 % in accordance with area where high productivity is high Ba(ex) concentration and vice versa. In this northwest Pacific Ocean sediment, the lithology of the core is composed of 60-70 % of siliceous materials and about 15% of aluminum content (Hyun, 1997). With a relatively large content of volcanic glass recognized by smear slide observation, terrigenous materials are accumulated through the time recorded in core. Relatively high sedimentation rate and low biogenic fractions at the core support this terrigenous input.

The results of the bulk barium and carbonate-free barium concentrations indicate coupled variation with a time and biogenic fraction. Also, the barium behaviour shows a specific conservation pattern; more than half of the bulk barium is believed to be coupled variations with aluminosilicate mineral in this study. But in equatorial area where more productivity than study area shows a rather distinctive behaviour, which is related with productivity directly (Gingele and Dahmke, 1994).

Because the sedimentary barium can be easily mobilized under some special environment such as anoxic sulfate reduction condition, it is also need to be assessed whether sedimentary barium indicates real or over growth one. Anoxic mobilization and hydrothermal activity are known to produce relatively high levels of barium which is not related to surface productivity (Torres *et al.*, 1996). However, the influence of hydrothermal activity is probably limited to ocean ridge sediment. Thus, to establish the barium as a proxy element at the hemipelagic setting, it is need to assess the influence of each sulfate reduction,

aluminosilicate and hydrothermal contribution in this study.

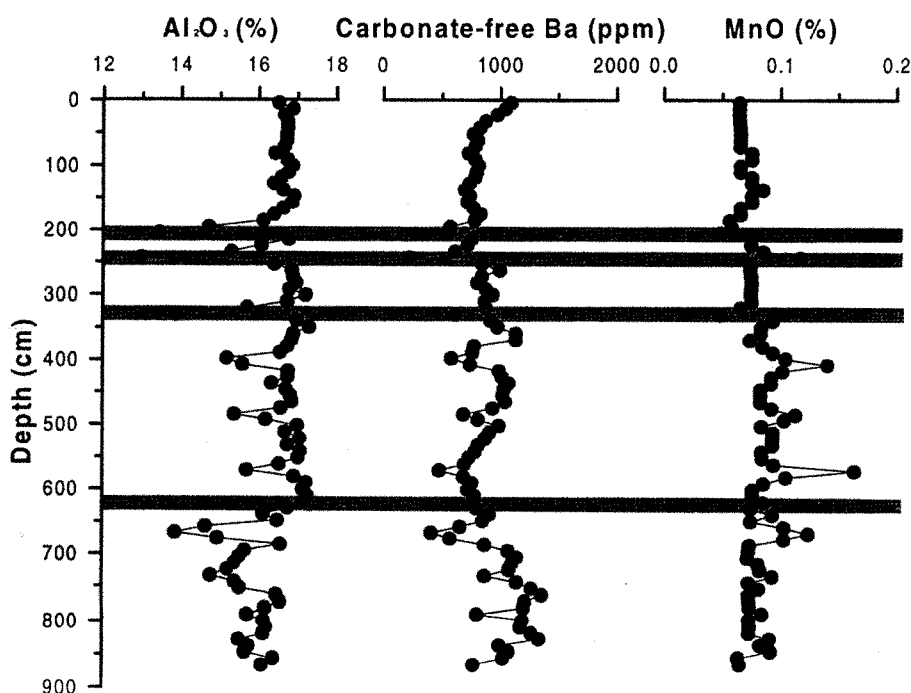
It is thought that mobilization of barium is controlled by the porewater sulfate barium concentration. Barite precipitation is thought to occur in sulfate rich sediment section, generally supplied by downward diffusion (Torres *et al.*, 1996). Especially, in anoxic sediment, the porewater sulfate concentration may decrease to low levels, thereby enhancing the dissolution of barite. A simple diagenetic model, but shown that large accumulation of barite cannot formed under steady-state condition of constant sedimentation rate (Torres *et al.*, 1996).

Unfortunately, we do not have pore water sulfate data, but we used bulk elements concentration profiles to evaluate the degree of diagenetic mobilization. Abrupt increase and decrease of several elements are checked in vertical concentration variation. One of the useful elements is sedimentary Mn which is usually cooperated with barium (von Breyman *et al.*, 1992). And this element is thought to be mobile in suboxic and anoxic sedimentary condition, and is considered as an indicator of initial signal of diagenetic processes (Froelich *et al.*, 1979). This geochemical characteristic implying that the concordant variation in both Ba and Mn might be interpreted as an initial signal of daigenesis. The vertical profile of aluminum, carbonate-free barium and that of MnO(%) at the core are illustrated in Fig. 3. Even though it seems that slight switching point of Mn concentration

occurred at around 40 ka, no significant coupled variation of two elements is recognized. These elements show a relatively constant downcore variation except for several volcanic ash layers. This result may indicate that the consistent steady-state sedimentary condition. The serious diagenetic mobilization is presented in the Japan Sea and Gulf of California (Torres *et al.*, 1996). The changing interstitial barium concentration is attributed to the consequences of diagenetic mobilization because interstitial sulfate ion shows extremely exhausted, and bottom sedimentary condition has been repeated between oxic and anoxic. Even though sulfate and barium ion in pore water is not examined in this study, we assume that mobilization and redistribution of barium did not take place, because no significant variation of MnO(%), and gradual variation of major and minor element concentration with depth are prevailing character of this sediments. Even if diagenetic barium is present, it might not affect on the bulk sedimentary barium concentration as well as total sediment composition. Thus, sulfate reduction is not likely established suggesting no serious diagenetic mobilization.

#### *Mass accumulation rate (MAR) of excess barium and dissolution proxy*

The MAR of Ba(ex) of the core shows strongly positive correlation with the MAR of biogenic carbonate and TOC. Especially, MAR of biogenic car-



**Fig. 3.** Vertical profiles of the content in aluminum, carbonate-free barium and MnO(%). Horizontal bars indicate volcanic ash and turbidite layers. Even though slight switching point is present at 40ka, carbonate-free barium and oxide manganese have no distinctive changes in concentration.

bonate has a strong positive correlation ( $r^2=0.85$ ) with MAR of Ba(ex). In conjunction with this carbonate excursion, Ba(ex) preserved in sediment shows a tight linkage with carbonate variation, and moderate to weak correlation with TOC and biogenic silica (Fig. 4). There is a tendency of better correlation between Ba(ex) and biogenic carbonate during the glacial periods. The variation in MAR of carbonate and that of Ba(ex) shows a coincident variation with a high amplitude. It also shows an increasing trend during the oxygen isotopic stage 2 (the last glacial maximum), and shows a decreasing trend at the other isotopic stages (Fig. 5). Thus, the variations of MAR of Ba(ex) are controlled by the MAR of carbonate.

Assuming that the proportional variation exist between the MAR of the Ba(ex) and carbonate during glacial and interglacial periods, the difference in correlation may indicate difference in dissolution rate because the particulate barite has a more refractory nature in dissolution than that of carbonate. Fig. 6 is schematic map of two potential factors (carbonate and barium). If line A is set sup based on strong correlation between carbonate and Ba(ex), when carbonate dissolution exceed barite dissolution line A moves toward B, and barite dissolution exceeds carbonate dissolution, it would move toward C. If one factor of the sediment has been more subject to dissolution, correlation between Ba(ex) and biogenic carbonate should become less pronounced. This observation also supports that the reduced dissolution during the glacial period. Overall, we suggests that the Ba(ex)/biogenic carbonate relationship is a useful indicator for the dissolution effect.

The correlation difference between glacial and interglacial periods indicates difference in dissolution. In Fig. 7, glacial and interglacial correlation is shown. The correlation coefficient during glacial period is clearly higher than that of interglacial. This phenomenon, thus is interpreted as difference in carbonate dissolution between the glacial and the interglacial periods. This observation clearly indicates that the carbonate dissolution is more outstanding during interglacial than glacial period. This difference in correlation coefficient is probably attributed to the change of water depth and oceanic chemistry during glacial and interglacial periods.

The variation of carbonate in the sediment can be interpreted as a consequence of change in calcareous production or dissolution change and/or dilution effect due to the terrigenous input. The overall trend of carbonate content shows an interglacial increase and gla-

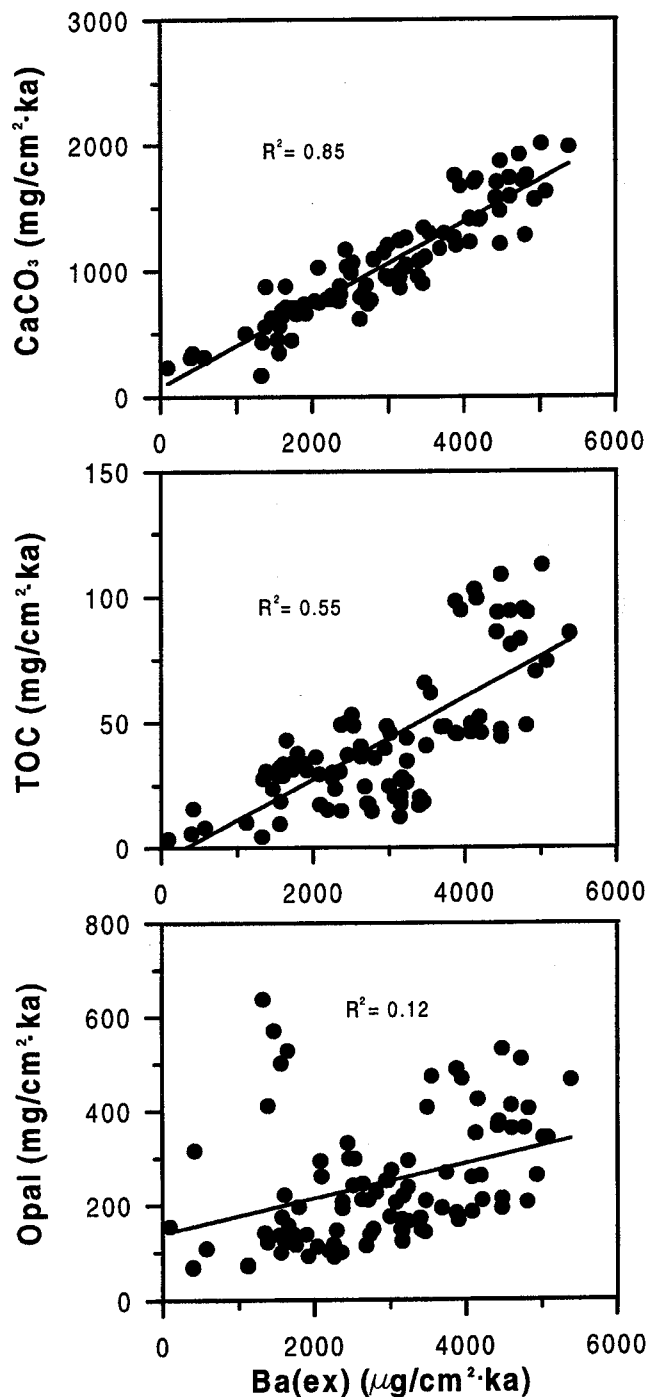


Fig. 4. Scatter diagrams of biogenic fractions to excess barium. Strong positive correlation between the MAR of carbonate and the MAR of excess barium suggesting excess barium is dependant of carbonate content.

cial decrease, and its MAR shows a glacial increase. Considering the typical Pacific type of carbonate record in the East China Sea as suggested by Thunell *et al.* (1992), carbonate excursion of this studied core sediment shows an intermediate excursion (Pacific type

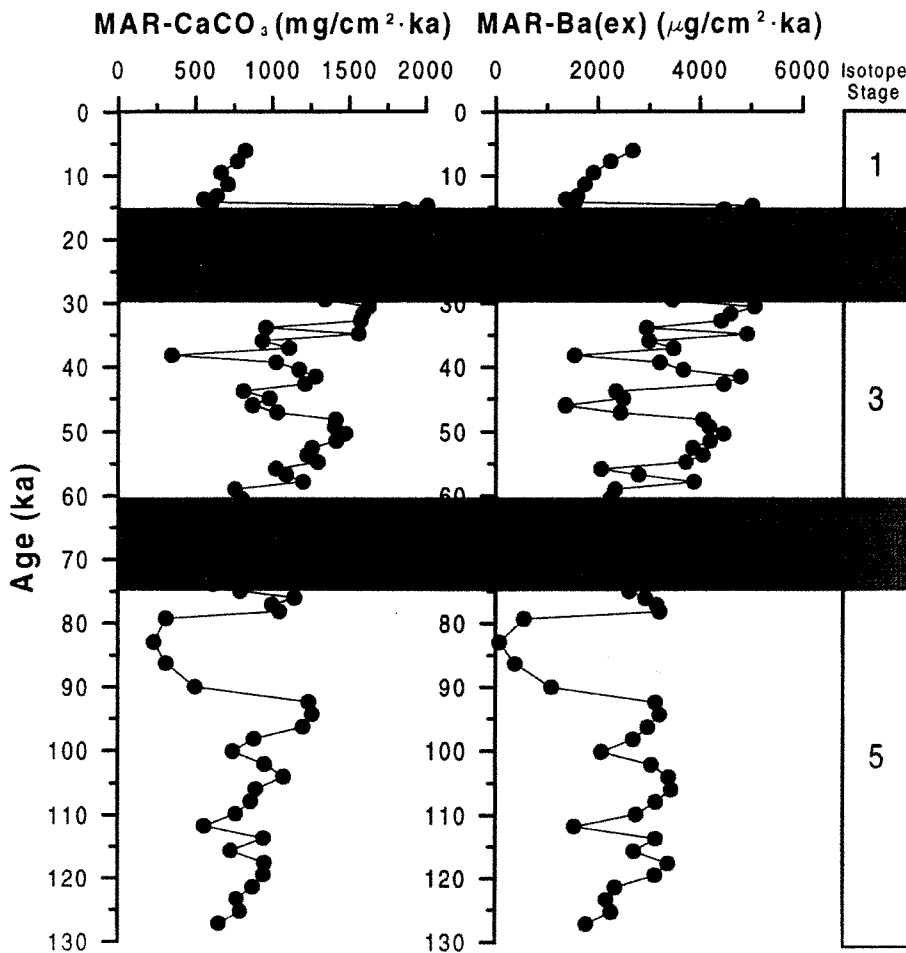


Fig. 5. Vertical profiles in mass accumulation rate of carbonate and excess barium. Gradual increase in both factors is recognized during isotope stage 2 with large fluctuation. Upper shade area indicates the last glacial maximum, and lower one is subglacial isotopic stage 4.

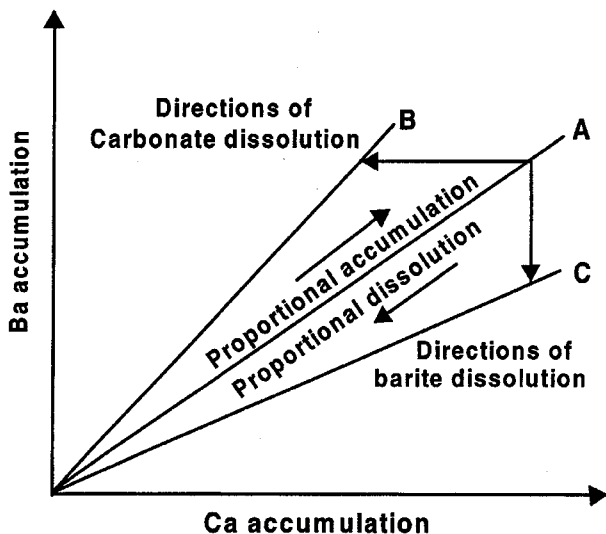
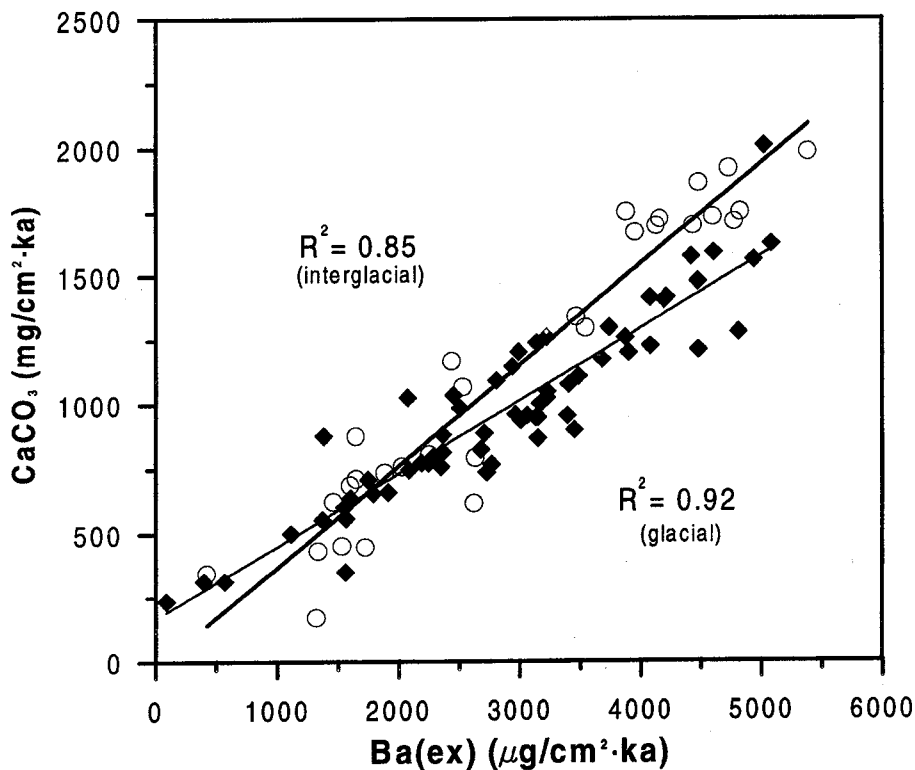


Fig. 6. Schematic map of the relationship between the barium and the carbonate accumulation. A line is build up on the base of proportional accumulation of barium and carbonate. When the carbonate dissolution exceed barium dissolution the A line would move to B, and when the barite dissolution exceed carbonate dissolution the A line would move to C.

but showing spatial carbonate preservation changes in terms of time and water depth). Thus, carbonate excursion from this study indicates rather specific excursion; basically following Pacific type with slight spatial variation.

The carbonate dissolution rate has been studied using direct counting of foraminiferal fraction using microscope and dissolution index based on visual observation (*e.g.*, Thompson, 1976; Matsuoka, 1989). It is well known that the carbonate dissolution at the Pacific Ocean shows a cyclic change; increasing dissolution during the interglacial and decreasing during the glacial periods (*e.g.*, Wu *et al.*, 1990; Thunell *et al.*, 1992). This kind of approach for testing carbonate dissolution rate of original surface carbonate production is not dealt in this study. However, it should be emphasized that how much of carbonate production in sediment has been remained from dissolution? Thus, we tried to evaluate the carbonate dissolution in order to evaluate the paleoceanographic change. It is thought that carbonate accumulation rate recorded in sediment is affected by various degrees





**Fig. 7.** Relationship between mass accumulation rate of carbonate and excess barium during the glacial and interglacial period. Open circles indicate interglacial and black circles indicate glacial values. Thin lines represent glacial correlation and thick line indicate interglacial correlation. High correlation during glacial period indicating less carbonate dissolution.

of dissolution even though water depth is shallower than CCD.

The carbonate contents in sediment show a fluctuated pattern between glacial and interglacial period as pointed out firstly by Arrhenius (1952), and this is interpreted as a variation of surface carbonate production at that time. However, carbonate dissolution is the most important factor in determining carbonate preservation (*e.g.*, Berger, 1973; Thompson, 1976). Moreover, carbonate dissolution during the glacial-interglacial shows different patterns between basin to basin (*e.g.*, Crowley, 1983). Until present, several parameters are considered in understanding the dissolution patterns such as percent of the carbonate content, percent of the coarse fraction, and percent of the whole planktonic and benthic foraminifera.

In order to evaluate the carbonate dissolution, we derived the Ca/Ba ratio as an index of carbonate dissolution assuming the proportional variation between the MAR of carbonate and the MAR of Ba(ex). As shown in Fig. 8, Ca/Ba ratio shows that carbonate dissolution has been varied slightly between the isotopic stage 2 and the other stages. Slight negative Ca/Ba peak is recognized at 75 ka with general negative during isotope states 1, 3 and 5. This fact suggests that at least two important oceanographic changes would have been occurred: high carbonate dissolution

during interglacial and high dissolution event at 75 ka. As known in previous study about the carbonate dissolution, the carbonate dissolution pattern shows a typical Pacific type, and a distinctive carbonate dissolution peak occurred at 75 ka is one of the important events (Matsuoka *et al.*, 1994). Unfortunately, the reason for this event is not studied. The local oceanographic change linked with climatic change is one of the possible causes. The other important fact derived from Ba(ex) and sedimentary Ca/Ba ratio are useful in evaluating of carbonate dissolution. The best match in this region is a good example. However further study about this is needed to evaluate the Ba(ex). Also this result is compared with other carbonate index which was conducted using fractured and well-preserved foraminiferal ratio, independently (Matsuoka, 1989) at more southward side of the three piston cores.

## CONCLUSIONS

The results of geochemical study on the sedimentary barium taken from the northwest Pacific Ocean sediment can be summarized as follows:

1. Most portion of sedimentary barium concentration is related with the aluminosilicate material. The accumulation rate of sedimentary excess barium has a strong to weak relationship with mass accumulation

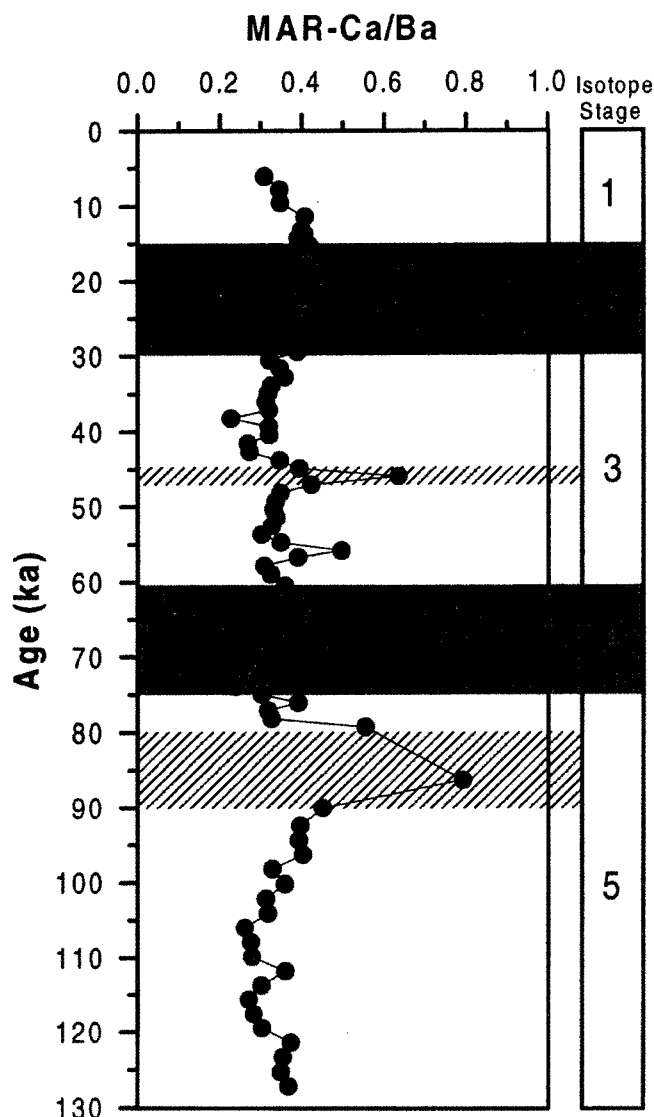


Fig. 8. Variations of Ca/Ba ratio. Higher values during the last glacial maximum (isotopic stage 2) suggests reduced carbonate dissolution in this period. Dashed areas indicate volcanic and turbidite layers. Shade areas indicate glacial period (isotopic stage and subglacial isotopic stage 4).

rate of biogenic fractions. This fact probably suggests that excess barium is originated from terrigenous aluminosilicate material and other extraneous source. Selective leaching may imply that two thirds of total barium is related with aluminosilicate material and the remaining portion is believed to be excess barium.

2. A strong correlation ( $r^2 = 0.85$ ) between mass accumulation rate of the excess barium and the biogenic carbonate at the core indicates that the preserved excess barium is related with sinking carbonate particles. This can be thought to be a mechanism of barite preservation in hemipelagic settings and possible proxy for reconstruction of carbonate production.

3. Assuming the proportional variations between the excess barium and biogenic carbonate, we developed a new index of the sedimentary Ca/Ba ratio as a proxy element for the record of the carbonate dissolution. Based on this new index, the pattern of carbonate dissolution follows a typical Pacific pattern; increased dissolution during the interglacial period and decreased dissolution during the glacial period. This fact is supported by previous work (*e.g.*, Farrell and Prell, 1989). However, the pattern seems to be affected by water depth.

4. A distinctive carbonate dissolution event occurred at 75 ka is identified by using the sedimentary Ca/Ba ratio. This distinctive event is strongly matched with the other foraminiferal dissolution index study in further southern part of the Pacific Ocean.

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