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国立環境研究所加速器分析施設（NIES-TERRA）レポートの第３巻をお届けします。施設の完成式典を行った平成8年9月から５年余りがたちました。その間、Annual Reportと銘打ちながらなかなか次が出せず、ようやく３巻目の発刊にたどり着いたところです。

環境の世紀とも言われる２１世紀の始まりとともに、当研究所も独立行政法人化され、研究環境にもいろいろと変化がおきつつあります。そうした中、関連研究者の努力はもちろんのこと、関係各位のご理解、ご助力により、加速器質量分析法を用いた研究もようやく無事離陸し、成果を報告できるようになりました。詳しくは以下の各研究者による報告、並びに巻末の論文等の発表リストをご覧いただきたいと思いますが、過去の環境変化の解析のための年代測定という枠にとどまらず、環境中の物質動態、炭素循環、さらには個々の環境中化学物質の追跡にまでいたる様々な研究が展開され始めています。

加速器質量分析法の主な対象は放射性炭素^{14}Cを初めとする宇宙線起源の長寿命放射性核種ですが、これらはいわば自然が与えてくれた天然のトレーサーです。これらのトレーサーをうまく活用することで、自然の営み、環境の姿とそれらへの人為的な影響を詳しく解析することができます。本巻から加速器質量分析法の大きな潜在的能力、多様な環境研究への適用可能性を読みとっていただけることを願っています。

日本の加速器質量分析研究の推進と国際的な認知の高まりの中で、本年９月には名古屋において、アジア地域で初めての加速器質量分析国際会議AMS-9が開催されることとなりました。我々も国内ばかりでなく世界を対象とした情報発信を心がけたいと考えており、研究成果報告を中心とするこの第３巻は英語での執筆を多くの方にお願いしました。今後も毎年、英文主体の研究報告を出し続けていけるよう、関係者一同努力する所存です。

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This is the volume three of the Annual Report of NIES-TERRA, the Tandem Accelerator Facility at the National Institute for Environmental Studies. More than five years have passed since the Opening Ceremony of NIES-TERRA in September 1996. Although written as “Annual Report”, we have at last finished preparation of the third one.

At the beginning of the 21st century, in which Environment will be doubtlessly the key issue, our institute, National Institute for Environmental Studies, was reorganized to Independent Administrative Institution, and research environment has been changing. Fortunately the Accelerator Mass Spectrometry (AMS) research in our institute could take off and started to report interesting data due to the tremendous efforts of researchers/technicians involved in the related research and also the kind support and help of various people inside/outside of the institute. As shown in the articles in this report as well as others in the publication list, a variety of researches have been being conducted, including not only dating environmental samples for recognizing paleoenvironmental changes, but also elucidating environmental cycling of sea water, carbon, and even each particular compound.

Major research target in AMS is long-lived radio nuclei produced by cosmic ray, including radiocarbon or ^{14}C, which are expected to be very useful natural tracer for deeper understanding of natural processes and mechanisms of environment, and effects of human beings on them. We hope that the present report will show readers the enormous potential and vast application capability of AMS.

The 9th International Symposium on Accelerator Mass Spectrometry (AMS-9) will be held at Nagoya in September 2002. This is the first occasion of this important symposium held in Asian countries, thanks to the rapid progress of AMS researches in Japan and the International recognition of Japanese activities. As part of the efforts to present research activities and their outcomes internationally, we asked many of the contributors to write manuscript in English. We will do every effort to continue publication of the following English report year after year.

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Contents

Study on the applicability of ^{26}Al/^{10}Be method for dating of sediment core samples from Lake Baikal

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Abstract: Several partial dissolution methods were examined of their capability to selectively extract ^{26}Al and ^{10}Be from sediment core samples from Lake Baikal. Among the methods examined, the NH_2OH leaching method gave the most promising results of both the extraction efficiency of ^{10}Be and the suppression of Al dissolution from the bulk sediment. In addition, a decreasing trend of ^{26}Al could be observed along the first 100 m of the 200-m core of Lake Baikal sediments.

Key words: ^{26}Al/^{10}Be dating method, partial dissolution/leaching method, NH_2OH, AMS, Baikal Drilling Project (BDP)

Lake Baikal, located in the eastern part of Siberia, Russia, is the oldest, the largest in volume (2.3x10^4 km^3; area 3.15x10^4 km^2) and the deepest (1,643 m) lake in the world. The lake is located in the Baikal rift, which is the largest active rift system in Eurasia and is spreading at a rate of several mm/a [1]. A major moving force of this spreading apparently comes from the India-Eurasia collision [2] which started around 40 million years ago. Lake Baikal is expected to have stored more than 30 million years history, and its sediment should keep records of the environmental/climatic change in the inland area of the Eurasian continent of all that period. Therefore, the analysis of these sediments can provide us with valuable information for the understanding of the global environmental changes during this period. In the Baikal Drilling Project (BDP), a long sediment core covering up to ten million years was planned to be obtained from the bottom sediment [3,4]. The development/improvement of the dating methods covering ten million years is indispensable for this project.

Long-lived radio isotopes produced by cosmic ray have been used for the dating of long sediment core samples from lakes and oceans. Carbon-14 has been used extensively for dating sediment core samples in lakes, oceans and peat up to c.a. fifty thousands years, i.e. 10 time of the half life of ^{14}C. One needs a radio isotope having longer half life for the coverage of up to millions of years. Among various radio isotopes of cosmogenic origin, beryllium-10 and aluminum-26 seem to be suitable for such purposes due to their fairly long half lives, i.e., 1.5 and 0.7 million years, respectively [5]. An important difference is the lack of reference isotope in ^{10}Be. Cosmic-ray produced ^{14}C is mixed well with the stable isotope, ^{12}C, in the atmosphere before entering into the environmental cycle, and, as a first approximation, the original ^{14}C/^{12}C ratio is thought to be constant. Therefore one can date the sample by analyzing the ^{14}C/^{12}C ratios in the samples. On the other hand, there is no efficient mixing process of cosmic-ray produced ^{10}Be with the stable Be isotope, ^{9}Be, in the atmosphere, and ^{10}Be/^{9}Be ratios in the samples might have little, if not at all, practical meaning. In addition, there may be chances of large variation in sedimentation rate of ^{10}Be, due to geomagnetic field change and other environmental changes, during such a long term and for such element having no large reservoir (or buffer) before sedimentation. Therefore the dating of sediment samples by ^{10}Be analysis should be done in a different way. If the sedimentation rates of both ^{10}Be and whole sediments have been kept constant, ^{10}Be concentrations in the sediment core samples will show us an exponential decay curve along depth, and one can estimate the sedimentation age of a particular layer from this exponential curve and its known half life [5]. If either ^{10}Be sedimentation rate or the rate of whole sediments is kept constant, again one can estimate the sedimentation age by integrating all the ^{10}Be concentrations from the surface to the layer [6]. If both of them have varied during sedimentation, however, it is, in principle, not possible to determine the sedimentation age from the ^{10}Be analysis alone.

^{10}Be dating method has been used for dating marine sediment core samples, in which clear exponential depth profiles were observed occasionally, especially those taken far offshore places. Apparently a large volume of seawater is working as an efficient mixing device for ^{10}Be and ^{9}Be, and ^{10}Be data in manganese nodules [7] as well as in sediment core samples [8] supported the idea that cosmic ray –produced ^{10}Be is mixed well with ^{9}Be to have constant ^{10}Be/^{9}Be ratio before sedimentation in the middle of oceans. On the other hand, its applicability to lacustrine sediments is uncertain due to possible large variations of the hydrological and/or geological environment around the lake, and of the geomagnetic field and climatic conditions, all of which may affect the sedimentation rates of both ^{10}Be and whole sediments to the lake. In the present study, we focused on the possible application of ^{26}Al as a reference isotope to correct these variables for ^{10}Be dating. ^{26}Al is also produced by cosmic rays in the atmosphere, and it is expected that the produced ^{26}Al/^{10}Be ratio has been staying always constant although considerable variations in net production rate of each isotope might occur. Al has similar chemical properties to Be, and thus is expected to behave similarly to Be in the environment. Therefore, as a first approximation, it is expected that the original ^{26}Al/^{10}Be ratio at the surface of the sediments is constant, and that the change of this ratio is the indicator of passing times after the sedimentation, as in the case of ^{14}C/^{12}C ratios in radiocarbon dating.

Although the above idea of ^{26}Al/^{10}Be method was first proposed by Lal in 1962 [9], the application of the method to the real sediment samples has been rare. A major problem was the ^{26}Al analysis of samples having an extremely low abundance of ^{26}Al in comparison with the stable isotope, ^{27}Al. Both ^{10}Be and ^{26}Al are produced by spallation reaction, i.e., as fragments of destructed heavier nuclei by collision with high-energy cosmic rays, in the atmosphere. While ^{10}Be is produced from abundant elements, such as nitrogen and oxygen, the major source of ^{26}Al is argon, a minor gas in the atmosphere, and its production rate is much less than that of ^{10}Be. On the other hand, the stable isotope, ^{27}Al, is a major constituent of sediments, and it is estimated that ^{26}Al/^{27}Al is too low for AMS technology even in the surface where a highest value is expected [10].

This problem can be overcome if cosmogenic radio isotopes adsorbed on the surface of the sediment particles are selectively dissolved (leached) by some appropriate procedure without extracting the major Al in crystal lattice. Recently a NaOH-leaching method was developed for the analysis of ^{26}Al to ^{10}Be ratios in deep sea sediments [11]. In the present study, several partial dissolution/leaching methods were examined of their capability to selectively leach ^{26}Al and ^{10}Be from the Lake Baikal sediment core samples, and the feasibility and applicability of ^{26}Al/^{10}Be method was evaluated.

EXPERIMENTAL SECTION

A 200 m long sediment core sample, BDP96-1, was obtained from the bottom of Lake Baikal at a sampling site on the Academician Ridge (53° 41’49” N, 108° 21’06” E) [4]. The analysis of the palaeomagnetic record indicated that the core spans until 5 million years ago, and that the sedimentation rate seemed to be fairly constant with the average of 3.8 cm/ka, an exceptionally slow sedimentation rate for a lacustrine environment [3, 4, 12]. Al and Be analysis was conducted by an ICP/MS, PMS 2000 (Yokogawa Analytical). Mineral composition was analyzed by taking powder X-ray diffraction patterns with a Rigaku RINT X-ray diffractometer.

The rim portion of the sediment remained in each drilling pipe (c.a. 2 m long) was recovered and freeze-dried. It was powdered and mixed well by an agate mortar in a clean booth. Then a small portion, typically one gram, was weighed precisely, and was treated by one of the following partial dissolution methods (see Table 1). Extracted Be and Al, after adding carrier (1 mL of 1000 ppm Be standard solution for AAS; Wako Pure Chemicals) for Be, were precipitated by ammonia, dissolved again by 0.2 N HCl, and loaded on a cation exchange column (20 ml) packed with AG 50X-W8 resin. Then the Be and Al fractions were eluted from the column by HCl solution in a step-wise manner. Each fraction was neutralized with ammonia, and the precipitate was collected by centrifugation. The precipitate was put in a platinum cup and heated to 1000 C for 1 hr to be converted to BeO and Al_2O_3, respectively.

The oxide was weighed and mixed with silver powder (BeO:Ag = 1:4, Al_2O_3:Ag = 1:3, w/w), and mixed well in a mortar. The mixed powder was pressed in a Cu cathode target manually, and was analyzed by accelerator mass spectrometry (NIES-TERRA). The detector system for ^{26}Al analysis is basically the same as that used for ^{14}C analysis [13]. The Be analysis was conducted by a fast bouncing mode and putting a thin foil of graphite (50 μg/cm^2; Nilaco, Tokyo) after the analyzing magnet in order to strip the ions again and to separate ^{10}Be from the major fraction of the interfering ^{10}B [14]. Also the detector window was changed to a metal thin foil made of Harvar foil (6 μm thickness; Nilaco, Tokyo), and the detector gas was replaced with carbon tetrafluoride in order to prevent production of another beryllium isotope, ^{7}Be, which interferes ^{10}Be analysis (to prevent $^{10}B(p, a)^{7}Be$ reaction by removing proton-containing materials in the detector) [15]. The thickness of the foil and the gas pressure of the detector was set by calculating ranges by a simulation software, SRIM 2000 (made by Dr. J.F. Ziegler, IBM), and subsequent optimization by careful adjustment of the gas pressure.

RESULTS

Variety of step-wise dissolution or partial dissolution methods have been developed and applied to the sediment/soil samples in order to characterize the status of elements present in the environmental samples. The basic idea is to separate elements in soil fractions into 1) weak-bound fraction (by ion-exchange reaction), 2) fraction bound to carbonate minerals, 3) fraction bound to iron/manganese hydroxides, 4) fraction bound to organics, and 5) fraction in crystal lattice of minerals, by step-wise application of a series of solvents [16]. Cosmic-ray produced ^{10}Be and ^{26}Al are expected to be contained mainly in the fractions 1) to 4); therefore an appropriate leaching condition selectively dissolve Be and Al in these fractions are to be selected. Here these fractions are termed “secondary Be/Al fraction” to distinguish them from the elements included in the crystal lattice of the minerals.

The partial dissolution methods examined in the present study [17-19] are listed in Table 1, and the results of AMS and element analyses are summarized in Table 2. The three methods were applied to three set of samples, i.e., surface sediments (1-1), bottom of the core (97-2) and the middle of the core (49-1). Conc. HCl method is extracting elements without destroying the silicate lattice. This was used for the ^{10}Be analysis in a pond sediment [17]. Oxalate buffer method [18] and hydroxylamine hydrochloride method [19] have been used for the dissolution of iron and manganese oxides/hydroxides and the elements co-precipitated with them. The latter method was used for ^{10}Be analysis in marine sediments together with the total decomposition method [19]. The leaching method based on an NaOH treatment [11], on the other hand, is rather tedious and not so suitable for the analysis of many samples in the sediments. Furthermore, it was reported to attain only 3 to 10 times improvement in $^{26}Al/^{27}Al$ ratio [11]; hens this method was not examined carefully in the present study.

Among these methods, hot 8N hydrochloric acid treatment (HCl method) gave the highest recovery of ^{10}Be, which were almost identical to the total ^{10}Be contents obtained by total dissolution by hydrofluoric acid-containing acids mixture [20]. Major part of Al, however, was also extracted by the procedure, and the ^{26}Al/^{27}Al ratio at the surface seemed to be already too low to be analyzed by AMS. The time course of the extraction procedure (Figure 1) showed almost completion of total Be extraction during the first 2 hours while total Al extraction efficiencies also slowed down around 2 hours but not stopped. Several different HCl concentrations between 1N and 0.1N were tested to improve the selectivity, but no substantial improvement could be achieved. Figure 2 shows the X-ray diffraction patterns of a sample after 8N HCl treatment. Several peaks shown by bars, corresponding to clay minerals, disappeared after HCl treatment while they still remained after oxalate buffer treatment, suggesting that 8N HCl treatment is too strong for the selective leaching.

The other two methods showed more or less similar performance each other; ^{10}Be recovery was roughly half of the hot 8N HCl method, while extracted total Al concentration was about two orders lower than the HCl method. If ^{26}Al extraction efficiency is same as that of ^{10}Be, c.a. 50 times improvement in ^{26}Al/^{27}Al ratios will be obtained by these two methods compared with HCl method. Among the two methods, the hydroxylamine hydrochloride method (NH_2OH method) gave a slightly higher ^{10}Be extraction efficiency, higher ^{10}Be/^{9}Be ratios and a lower extracted Al concentration compared with the oxalic acid/ammonium oxalate method (oxalate method). In addition, NH_2OH method also gave a better time course profiles of the extraction (Figures 3 and 4); i.e., total Be extraction completed and Al extraction also slowed down considerably after 5.5 hours in NH_2OH treatment while both slowed down but continue to occur after the first 5 hours in oxalate method. Therefore NH_2OH method was selected, and further research was conducted to evaluate the feasibility of the analysis of ^{26}Al in the samples.

Further improvement of extraction condition is being pursued by changing concentration of NH_2OH and temperatures, etc, and analyzing both ^{10}Be/^{9}Be and ^{26}Al/^{27}Al in the sample extracts. Figure 5 shows NH_2OH concentration dependent profiles of extracted total Al and ^{26}Al/^{27}Al ratios. Extracted total Al concentrations (*) changed about five folds by changing NH_2OH concentration from 0.04 M to 1.0 M. However, ^{26}Al/^{27}Al ratios did not show concomitant decrease but rather an increasing tendency, in spite of the increase of total Al (= ^{27}Al). This suggests that cosmic ray-produced ^{26}Al is deposited in a thick surface layer together with stable Al deposition, and is fairly resistant against leaching procedures. From this result, 1.0 M NH_2OH was selected as a suitable solution for ^{26}Al leaching. Figure 6 shows depth profiles of Al concentrations extracted by 1.0 M and 0.04 M NH_2OH from the sediment core samples. Interestingly the extractable Al concentration tended to decrease in deeper layers, suggesting gradual progress of authigenic crystal formation, which is more resistant to leaching in sediments. This decreasing tendency is less clear in higher NH_2OH solution. This is another reason to select higher concentration solution (1.0 M) for the selective leaching.

Figure 7 shows the results obtained by 1 M NH_2OH leaching. For comparison, total ^{10}Be concentrations of the same set of samples obtained by total dissolution method by Horiuchi et al. [20] were also plotted in the figure. The vertical axis is plotted as logarithmic scale, and exponentially decaying curve is plotted as a straight line on the figure. As shown in the figure, the overall trends of ^{10}Be obtained by this partial dissolution method is basically similar to the total dissolution method, and a general decreasing trend of ^{10}Be in accordance with its half life was evident. The extractable ^{10}Be was nearly half of the total in each layer. We could also detect a decreasing trend of ^{26}Al in the sediment under this condition (note that the scales of the ^{10}Be axis and the ^{26}Al axis are different each other).

DISCUSSION

By the careful optimization of partial extraction condition, ^{26}Al in sediment samples in terrestrial environment could be detected. The ^{26}Al/^{27}Al ratio was 10^{-14} at the surface, and was decreased to less than 10^{-15} below 100m. The averaged slopes of the decrease of ^{26}Al/^{27}Al and ^{10}Be/^{9}Be are in good agreement with those expected from their decay rates and the sedimentation rate inferred from the palaeomagnetic record of the core (Figure 8; each line (-·-·-· for ^{10}Be and ·········· for ^{26}Al) was drawn based on the assumption that the bottom of the core corresponds to five million years old and that no significant change in sedimentation rate occurred during the period). Although the obtained results were in good agreement with the expected decay of ^{26}Al in the sediment, each data in the figure has a large statistical error (not shown) because of the lack of total counts of ^{26}Al even for an hour analysis. Clearly further improvements in selectivity and sensitivity are necessary to establish practically applicable method to real sediment samples from Lake Baikal and other lacustrine environment.

Bourles et al. [19] conducted careful examination of the presence of ^{10}Be in each fraction of marine sediment samples by the stepwise extraction technique. They found that ^{10}Be/^{9}Be ratios in the secondary fractions, i.e., those absorbed in $CaCO_3$ and in iron/manganese hydroxides/oxides, gave similar values each other while those in other fractions (including weakly bound form and organically bound form) were substantially different. Furthermore, ^{10}Be/^{9}Be ratios in the secondary fractions showed a clear exponential decay profile along depth. Based on these data, they concluded that the initial ^{10}Be/^{9}Be at the time of sedimentation has been kept constant for millions of years in marine environment, and that the secondary fraction obtained by partial dissolution technique is useful for dating marine sediment cores. As summarized in Figures 7 and 8, both total and leached ^{10}Be fractions in Lake Baikal sediments also showed, at first glance, a good correlation with the expected decay process. It was pointed out, however, that short term variations in total ^{10}Be was eminent in the recent 2.7 million years while more stable and consistent profile with theoretical line was observed between 2.7 million years and 5 million years ago. These variations are thought to reflect input of variable amounts of atmospheric dusts by the stronger winds in colder periods during recent ice age started c.a. 2.5 million years ago [20]. The extracted ^{10}Be also showed a quite similar profile to the total ^{10}Be (Figure 7). The ^{10}Be/^{9}Be data from Lake Baikal (Figure 8) also support a general view that ^{10}Be is fairly well mixed with ^{9}Be before deposition and that ^{10}Be/^{9}Be in secondary fraction will be useful as a proxy to estimate sedimentation age. ^{26}Al/^{27}Al ratios also showed a good correlation with the theoretical line (Figure 8), although large statistical uncertainties due to lack of total ^{26}Al counts practically hamper the application of this isotope.

As summarized in the introduction, ^{26}Al/^{10}Be method is based on the assumption that Al and Be show practically indistinguishable environmental behavior because of the similarity in their chemical properties. The above data seem to support this hypothesis in a general sense, but more detailed study will be necessary to answer this question properly. The present method is also based on the idea that cosmic ray produced ^{10}Be and ^{26}Al are included (not fixed tightly) in surface layer of soil particles (secondary fractions) by co-precipitation with iron/manganese hydroxides etc. In addition, authigenic minerals might glow on the surface during long term after sedimentation, in which these cosmogenic radio nuclei might be trapped. The major objective of the present study is to find a suitable extraction procedure to leach these secondary fractions efficiently and selectively without extracting elements fixed in the crystal lattice of sediment minerals themselves. Time course of the extraction procedure (Figures 1, 3, 4) show us that Be could be easily and rapidly extracted while Al extraction is harder and time-consuming in any of the three condition. Apparently nearly half of the total Be and 60% of total ^{10}Be could be extracted selectively by 0.04M NH_2OH treatment after 6 hrs. This seems to be the target fraction, i.e., secondary Be fraction. The extraction performance of oxalate method against Be was found to be a bit inferior to the NH_2OH method. The time courses (Figures 3 and 4) could be interpreted that NH_2OH could extract secondary Be completely while oxalate method could extract them incompletely within a limited time. On the other hand, secondary Al, a hypothetical fraction containing cosmic ray produced ^{26}Al precipitated on the surface of soil particles during or after sedimentation, could not be extracted efficiently within a limited time by any of the methods examined in the present study. Time course of Al extraction did not show any clear sign of the completion of extraction for a particular Al fraction in the sediments. Both NH_2OH and oxalate methods showed shoulder or slow down of extraction speed at around 6 hrs in accordance with the completion of Be extraction. However, the concentrations of extracted Al at the shoulder are considerably different each other. Thus no clear evidence could be obtained to support the presence of chemically definable Al sub-fraction in the sediments. Furthermore, ^{10}Al/^{9}Al ratios in the extract increased in accordance with the increase of NH_2OH concentration, suggesting that secondary Al, if present, needs stronger extraction condition compared with that for secondary Be.

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Table 1 Partial Dissolution Methods Examined in the Present Study

1) **Hot-8N-HCl method** [17]

Experimental Condition; 1g dry sample was put in a polypropylene bottle with 30ml 8N HCl, and kept at 90 C for 0.5 to 5.2 hrs. Extraction under different HCl concentrations (1 N, 0.3 N, and 0.1 N) were also investigated.

2) **Oxalic acid-Ammonium oxalate method (oxalate method)** [18]

Experimental condition; 1g dry sample was put in a polypropylene bottle with 40ml 0.175M ammonium oxalate-0.1M oxalic acid and kept at room temperature under dark for 2 to 16.2hrs.

3) **Hydroxylamine hydrochloride method (NH_2OH method)** [19]

Experimental Condition; 1g dry sample was put in a polypropylene bottle with 20ml 0.04M hydroxylamine hydrochloride in 25% acetic acid and kept at 90 C for 2 to 16.3 hrs.

Table 2 Results of Partial Dissolution Treatments

Samples	Depth (m)	Methods	Total Conc.(mg/kg dry) Be	Al	$^{10}Be/^{9}Be$ ratio	^{10}Be/g dry sample
					x 10^{-9}	x10^{8}
1-1	0 – 1.8	HCl	1.44	106,000	7.7	7.4
		Oxalate	0.49	2,540	9.6	3.2
		NH_2OH	0.64	1,400	10.7	4.6
49-1	95.2 – 97.2	HCl	1.84	140,000	2.7	3.3
		Oxalate	0.57	2,000	-	-
		NH_2OH	0.81	1,200	-	-
97-2	190.5 – 191.3	HCl	1.65	120,000	1.2	1.3
		Oxalate	0.68	1,350	-	-
		NH_2OH	0.67	540	1.2	0.53

-: not analyzed.

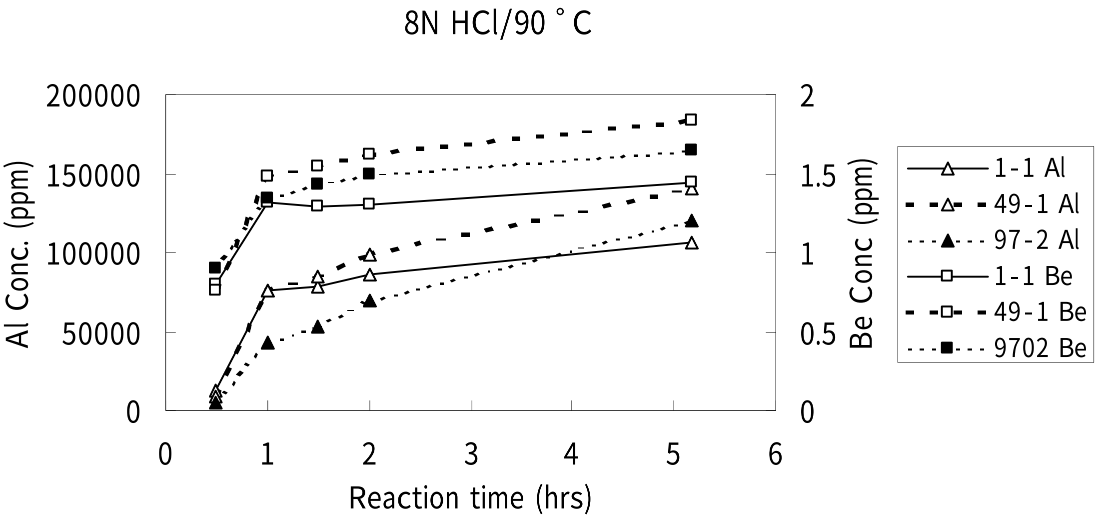

Figure 1 Time course of total Be and Al extracted by HCl method

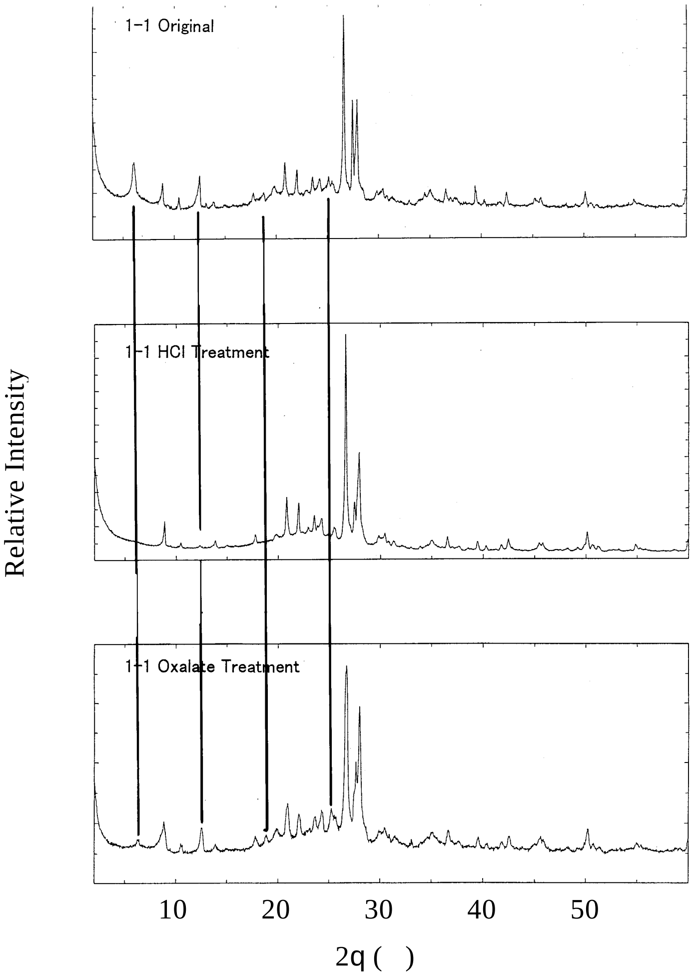

Figure 2 X-ray diffraction patterns of sediment sample before (top) and after extraction (middle: HCl treatment, bottom: oxalate treatment)

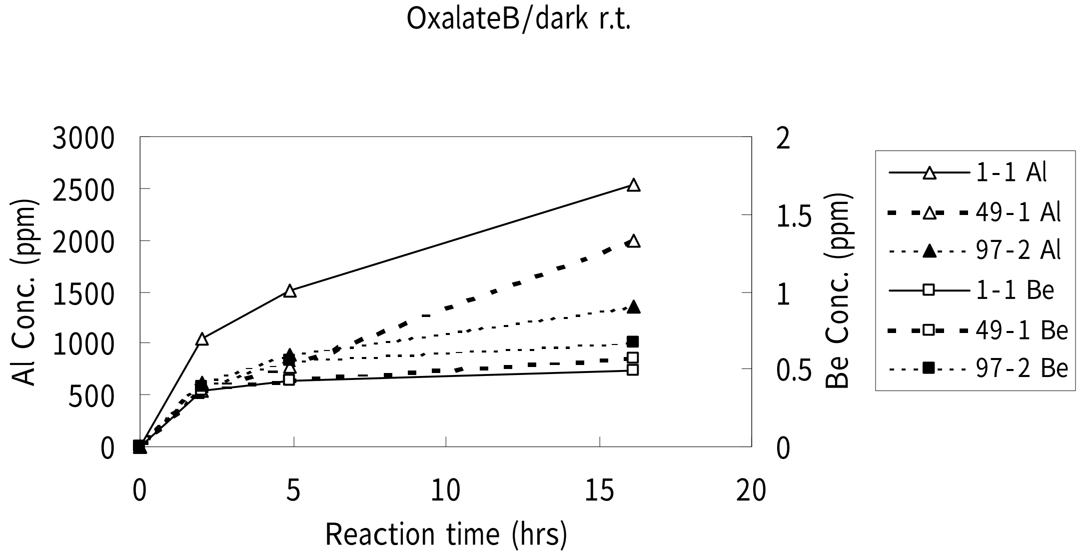

Figure 3 Time course of total Be and Al extracted by oxalate method

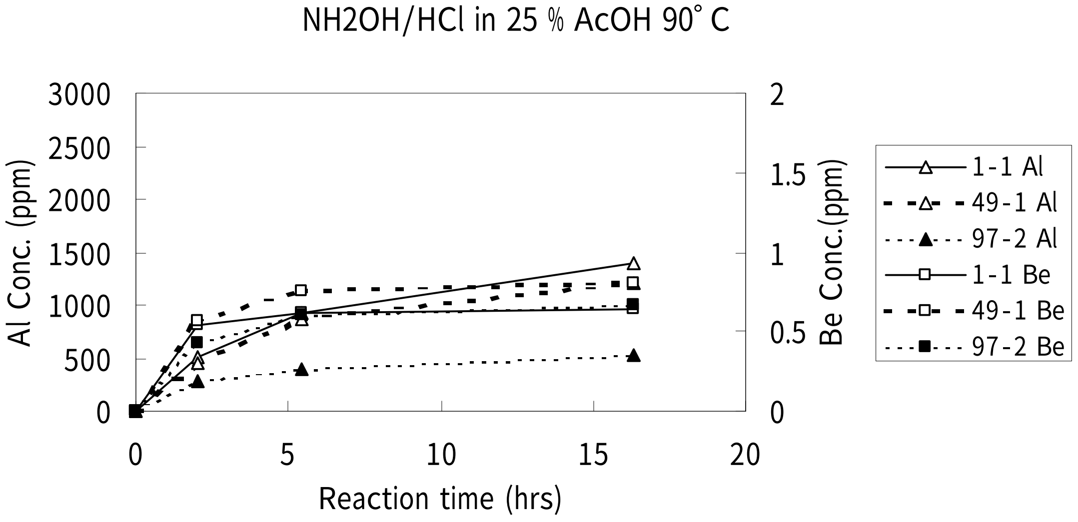

Figure 4 Time course of total Be and Al extracted by NH_2OH method

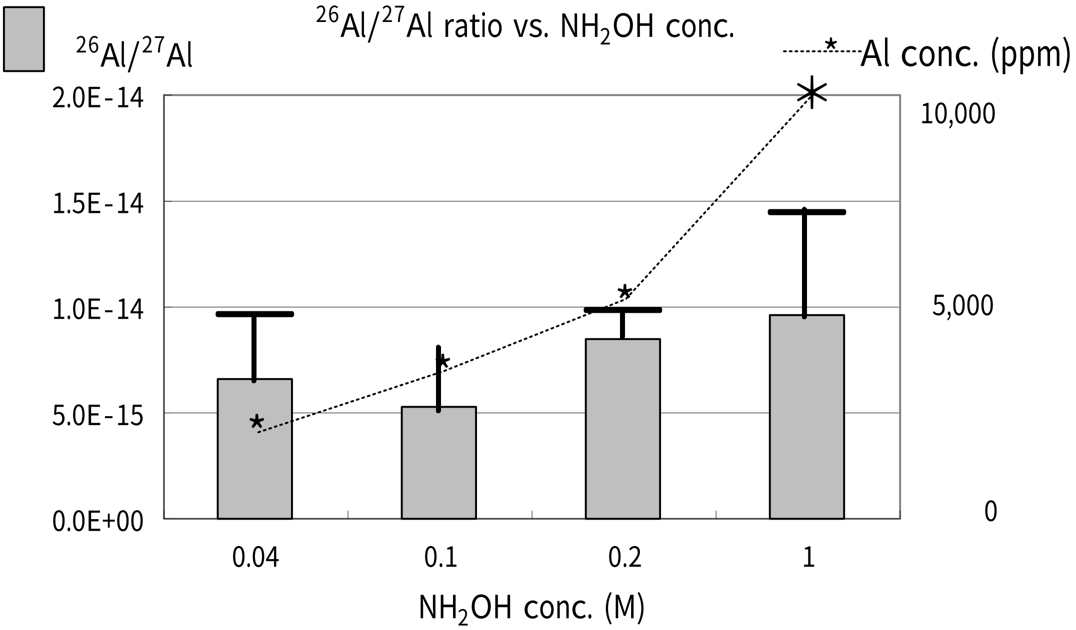

Figure 5　Total Al and ^{26}Al/^{27}Al ratios as a function of NH_2OH concentration

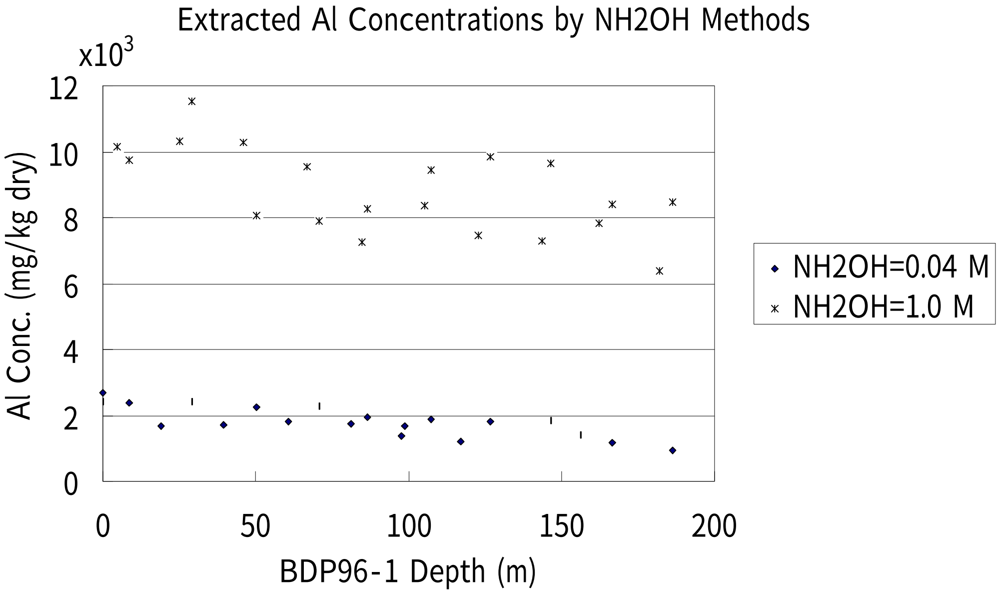

Figure 6　Extracted total Al concentrations by 1 M and 0.04 M NH_2OH

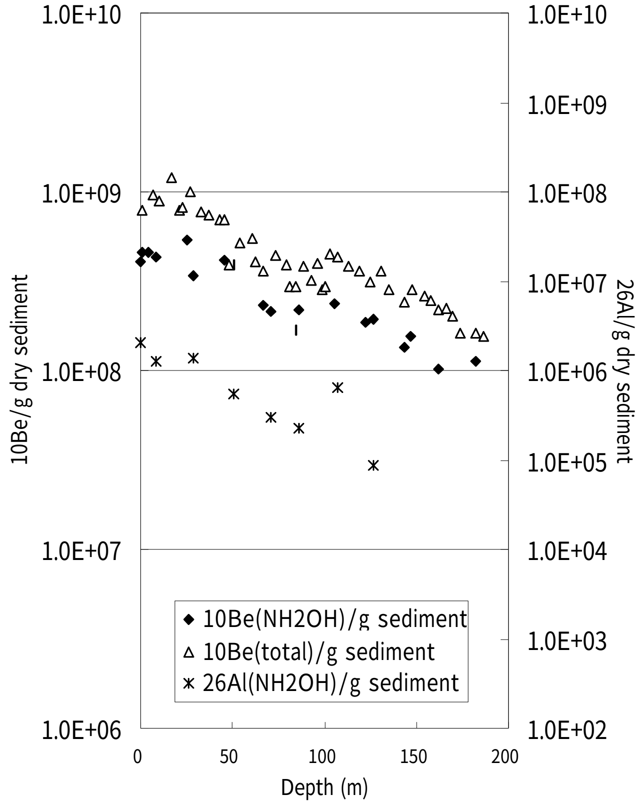

Figure 7 Depth profiles of NH_2OH-extracted ^{10}Be and ^{26}Al

Δ indicates total ^{10}Be concentrations (Horiuchi et al., [16])

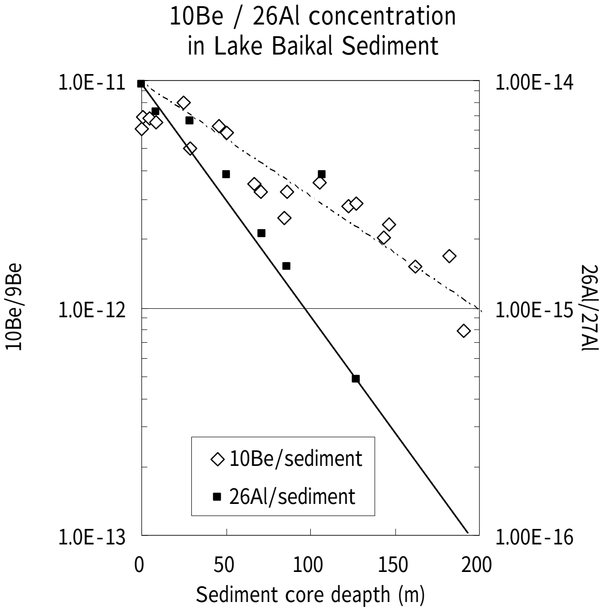

Figure 8 ^{10}Be/^{9}Be and ^{26}Al/^{27}Al depth profiles in the sediment core sample

The lines show expected decay curves based on their half lives as well as estimated sedimentation age from palaeomagnetic record.

Vertical Distributions of Photosynthetic Pigments and Other Biological Indicators in the Sediment Core from the Southern Basin of Lake Baikal As a Record for the Last 30,000 Years*

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Abstract: Depth profiles of carotenoids, chlorophyll derivatives and other biogenic indicators, such as biogenic silica (BGS), total organic carbon (TOC) and nitrogen (TON), and perylene were measured in AMS ^{14}C dated sediment cores (< 2m) collected from the southern basin of Lake Baikal. The photosynthetic pigments, BGS and TOC (TON) accumulated in the upper part (above 80 cm) of the core (12,000-13,000 y BP), whereas higher concentration of biogenic perylene was observed in the lower part (below 80 cm). BGS in the upper part showed a negative correlation with total carotenoids and no significant positive correlation with TOC and total chlorophyll a. This indicates that high BGS represents the lake in a well-mixed oxic condition stimulating aerobic decomposition of organic compounds, especially carotenoids, in the water column and the surficial sediment. Association of high perylene concentration in the lower part with low lacustrine productivity suggests presence of specific precursor or formation process.

INTRODUCTION

Depth profile of photosynthetic pigments such as carotenoids and chlorophylls in the sediment are potentially useful records on the change in the algal population relating to, e.g., the development of eutrophy in lakes. Soma et al. previously reported the distribution of photosynthetic pigments and biogenic perylene in sediments of Lake Baikal for two short (ca. 40 cm length) core samples from near-coast site (water depth 112 m and 130 m) of the southern basin [1]. The photosynthetic pigments mainly of algal origin included chlorophylls as well as their decomposition and/or diagenic products, and carotenoids. As the composition of carotenoids is more or less specific in the level of classes of phytoplanktons (algae) [2], the pigment residues in sediment possibly tell historical changes in dominant algae in Lake Baikal, while we should note also that photosynthetic pigments in general and especially carotenoids are susceptible to decomposition [3]. As the two cores were not dated and only limited information for sedimentation rate in the southern basin is available currently, a study on dated longer sediments from the same area is necessary to see how long the pigments can be preserved in the sediment. This report has addressed on this point based on the analysis of a 173 cm gravity core and a 28 cm box core samples obtained from the same site as the St. 13 sample in the previous report [1] and studied relation among the pigments (chlorophylls and their degradation/diagenetic products, and carotenoids), and other indicators of algal and/or biological activities, including total organic carbon(TOC), total organic nitrogen (TON), biogenic silica (BGS) and perylene.

MATERIALS AND METHODS

Study sites and sampling

Two sediment cores, a gravity and a box cores, collected at sites near the southern shore of the southern basin of Lake Baikal on 7 September 1996, were used for analysis. The core lengths of the gravity (96-St10GC-1) (sampling site; 51°30’10”N, 104°18’32”E, water depth 285 m) and box (96-St10BC)(sampling site; 51°29’57”N, 104°18’31”E, water depth 280 m) cores were 173 cm and 28 cm, respectively. The core samples were sliced into 2-5 cm sections immediately after the sampling and each slice was transferred to a plastic bag. The sliced sediment samples were stored at -80°C until analysis. The 96-St10GC-1 gravity core obviously lacked a top (surficial) sediment layer during sampling. By comparing depth profiles of water contents, particle size distributions, TOC(TON) and BGS in the 96-St10BC box core sediment with those in the upper part of the 96-St10GC-1 gravity core sediment comprehensively, we estimated the length of the top sediment layer lacked to be 15 cm. Thus the data corresponding to 0-28 cm and 29-188 cm depths were from the 96-St10BC box and 96-St10GC-1 gravity cores, respectively, and this depth assignment was used throughout in this report.

Analytical methods

(1) Photosynthetic pigments and perylene by HPLC-PDA

Photosynthetic pigments and perylene in the sediment samples were analyzed by the method described earlier[1] using a Shimadzu LC-10 liquid chromatography system with photodiode array (PDA) absorbance detection. Concentration of SCEs (streyl chlorin esters) transformed from chlorophyll a [4-7] was determined as the sum of the pheophytin derivatives eluted after pyropheophytin a in the HPLC analysis by assuming their absorption coefficents at 400 nm were the same to that of pheophytin a. The presence of SCEs in Lake Baikal sediment has been briefly reported[8].

(2) Biogenic silica (BGS) and total organic carbon and nitrogen (TOC, TON)

BGS was extracted by 2 M Na_2CO_3 solutions at 85°C for 5 h after treatment in 10% H_2O_2 for 30 min and 2 M HCl for 30 min of the oven dried samples[9]. The concentration of dissolved Si was determined by an atomic absorption spectrometer

(Perkin-Elmer AAS 3300) with an N_2O-acetylene high-temperature burner system. Total organic carbon (TOC) and nitrogen (TON) were determined by an element analyzer (Fisons Instruments, EA1108) after treatment in 2 M HCl overnight followed by three-times washing with pure water.

(3) AMS ^{14}C measurement

Sediment samples were treated with 6 M HCl at 80°C until dryness to remove inorganic carbon. The acid-pretreated samples containing about 0.4 mg of organic carbon were heated with 900°C for 8 h with 0.5 g of Cu, 1g of CuO and a small piece (ca. 0.5 mm x 5 mm x 0.01 mm) of Ag foil in a sealed quartz tube to convert organic carbon to CO_2. The CO_2 thus produced was purified cryogenically using liquid N_2 and a mixture of CH_3OH and dry ice in a vacuum line and then converted to graphite on iron powder catalyst (1 mg) by reducing with H_2 at 470°C for 2 h. An accelerator mass spectrometer at National Institute for Environmental Studies (NIES-TERRA) [10-12] was used for the determination of ^{14}C contents.

RESULTS AND DISCUSSION

Vertical distributions of biological indicators in the sediment core

Depth profiles of total chlorophyll a, total carotenoids, perylene and other principal indicators (TOC, TOC/TON, water content, BGS and AMS ^{14}C date) are shown in Figure 1. Total chlorophyll a represents the sum of concentration of chlorophyll a, pheophytin a, pyropheophytin a, pheophorbide a and SCEs. There was a dip at depths between 51.5 ± 1.5 and 54.5 ± 1.5 cm common in the profiles of biological indicators. Analysis of particle size distribution showed sediment of this layer had a high content of coarse sand fraction as compared to the other layers. This and the paucity of biogenic substances indicate that the layer is turbidite. The average values of biogenic indicators in the upper (above 80 cm except for the turbidite layers) and lower (below 80 cm) parts were listed in Table 1. The concentrations of these indicators were generally high in the upper part of sediment and low in the lower part. The average concentrations in the upper 80 cm were 4.7, 3.4, 27 and more than 9.6 times higher for BGS, TOC, total chlorophyll a and total carotenoids, respectively, than those in the lower part (below 80 cm).

The extrapolation of ^{14}C data for the two layers (1187 ± 97 and 9715 ± 140 y BP at depths of 0.5 ± 0.5 and 60.5 ± 1.5 cm, respectively) in the upper part of sediment (Figure 1h) showed the transition (depth at 80 cm) occurred at about 12000 y BP. The similar transition in depth profiles of the biological indicators at about 12000 y BP was also observed in a core sediment collected at a site (52°05'N, 150°50'E; water depth 200 m) south west to the Selenga delta[13]. Then the relative high concentration of various biological indicators, except for perylene, in the upper part of the core represents high biological activity in Holocene, which has been recognized for sediment cores of Lake Baikal, notably in distribution of biogenic silica [14, 15].

Two ^{14}C date are available for the lower part of the core. One was 30478 ± 333 y BP and the other 31479 ± 384 y BP at 140 ± 2.5 cm and 190 ± 2.5 cm, respectively. If near constant rate of sedimentation can be assumed, the latter value might have been affected by the contamination from the upper part of sediment, younger and more organic [16, 17]. If, on the other hand, the two data represent the real ages, then an episodic input of thick layer of sediment should be assumed. A few observations concerning nature of this lower part of the core should be mentioned. Firstly, this part was silty and a larger proportion of sandy coarser particles as in the turbiditic layer observed in the upper part of core was not observed. Composition of detrital elements in the sediment did not suggest a discrepancy between the upper and lower part of the sediment. Secondly, the water content of the sediment correlated with BGS [18], whereas the plot of water content versus logarithm of BGS exhibited a smooth line (R^2 = 0.9417) for whole lengths of the sediment. Finally, we note the distribution of SCEs. SCEs represent the algal production, predation of algae [7] and thus the sediment under a lacustrine environment. SCEs existed through the lower part of core and its proportion in total chlorophylls slightly increased with the depth of the core. We accordingly considered the sediment in the lower part was continuous lacustrine sediment spanning down to 30 ky BP.

Relation of photosynthetic pigments with other biological indicators and factor deciding their preservation in the sediment of Lake Baikal

Major carotenoids detected in the upper part of the core were diatoxanthin, lutein, zeaxanthin, -carotene, canthaxanthin and alloxanthin. It was thus demonstrated that such carotenoids as well as chlorophyll derivatives could be preserved in the sediment of Lake Baikal as long as 10 ky BP (Figure 1). Lutein is a marker carotenoid of green algae and higher plants [19, 20]. Diatoxanthin is contained in diatoms with fucoxanthin and converted from diadinoxanthin in oxygen or light defect (Xanthophyll cycle)[21, 22]. Alloxanthin is characteristic of Cryptophyceae [2]. Zeaxanthin is a marker carotenoid of cyanobacteria including picocyanobacteria and is observed to be a main carotenoid in *Synecocystis* spp. in Lake Baikal [23, 24]. Canthaxanthin is observed in some cyanobacteria, such as *Anabena* spp. or *Nostec* spp [25]. Thus the presence of green algae, diatoms, cyanobacteria and Cryptophyceae and picocyanobacteria were deduced from carotenoids observed.

As the variability in TOC/TON ratio (Figure 1e) was small and within the range reported by Qiu et al.[14], as described to essentially autochthonous production, we presume that allochthonous input for TOC of the sediment did not vary in a large portion and that chlorophyll and carotenoid residues in the sediment were of essentially autochthonous.

Figure 2 shows the relationship of the concentrations of BGS and total carotenoids in the upper part of the sediment core. Note that a negative correlation was observed (R = -0.622, n = 28). The negative correlation between BGS and total carotenoids preserved was also reported in the surficial sediment throughout Lake Baikal [25]. In addition, total carotenoids exhibited a trend to increase with the depth in the sediment, while total chlorophyll a showed an opposite trend to decrease with depth in the upper part of sediment. As the amount of total carotenoids was small in the surficial sediment, the trend is not attributable to diagenesis after burial in the sediment but rather should be to degradation in the water column and sediment surface. Determination of manganese in the reducible hydrous oxide form, extracted by 0.1 M $NH_2OH•HCl$ (25% CH_3COOH) solution (90°C for 6 h) [26, 27], showed that concentration of Mn in this form increased towards the surface of sediment from the layers below. Therefore, an oxic condition prevailed in the sediment surface in which condition carotenoids were more susceptible to decomposition than chlorophyll. These considerations lead us to relate the high diatom productivity to the enhancement of degradation of organic compounds, especially carotenoids. Effective circulation of lake water may make both possible. It would supply nutrients to the photic zone from the deeper parts of water column to ensure the growth of diatoms (and other algae) in one hand, and at the same time supply oxygen to deep water and sediment to promote aerobic degradation of organic compounds. Then the portion of carotenoids remained in sediment critically depended on the redox condition during their deposition [28] and was very low under oxidizing conditions [29] which was compatible with a high diatom growth in the lake.

Table 2 shows the correlation among carotenoids in the upper part of the core. Lutein, zeaxanthin and diatoxanthin have good correlation with each others, being in essential agreement with the previous results. Alloxanthin and canthaxanthin showed somewhat different profiles. Cryptophyceae (alloxanthin) and cyanobacteria (canthaxanthin) hence may have population histories different from the other classes of algae, green algae (lutein), picocyanobacteria (zeaxanthin) and diatoms (diadinoxanthin). Relative amounts of alloxanthin and canthaxanthin were higher at the period between 4 ky BP and 10 ky BP, suggesting that populations of Cryptophyceae and soma cyanobacteria were relatively higher during this period.

Perylene and the other biological indicators in the lower part of sediment

Provided that the sediment was of essentially continuous deposition through the core as described above, the lower concentrations of indicators such as TOC, BGS and chlorophylls indicate the low biological productivity before Holocene. TOC/TON ratio of the lower part changed little from that of the upper part indicating relative contribution of autochthonous and allochthonous organic sources also stayed similar for the both part of sediment.

The inverse profile of perylene, as compared with other indicators related to the biological productivity of the lake, suggests that perylene is not a direct indicator of the amount of source material but rather a indicator of diagenetic process leading to its formation, as pointed out by Sillimann et al. [30]. The concentration of perylene in the lower part of the core was as high as those of photosynthetic pigments in the upper part. It, however, constituted only small fraction of TOC. Accordingly, the possibility that perylene was derived from the autochthonous organic material can not be excluded. As was suggested by the partial profiles of total chlorophyll a and perylene both in the upper part and in the lower part of the core (Figure 1a and c), respectively, a significant correlation existed between total chlorophyll a and perylene, R = 0.708 for 28 cm to 80 cm (n = 15), and R = 0.826 for 95 cm to 188 cm (n = 19) of the sediment. Thus algal products are still possibly source material for diagenetic formation of perylene.

It is generally accepted that perylene found in sediments deposited before modern anthropogenic influence became significant is biogenic and was formed through certain precursor under anoxic condition [30], but the agreement has not been established as to how perylene is formed in the sedimentary environments. The observed high concentration of perylene with low concentrations of the indicators for lacustrine biological activities would suggest that there should be certain specific precursor(s) or biological process(es) leading to the formation of perylene.

ACKNOWLEDGMENT

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Table 1 Average values of biogenic indicators in the upper (0-80 cm) and lower (80 – 188 cm) parts of the sediment cores

Indicators	Upper[a]	Lower	Ratio[b]
BGS (%)	15	3.1	4.7
TOC (%)	1.7	0.51	3.4
TON (%)	0.15	0.05	3
TOC/TON (wt/wt)	11.9	10.2	1.16
Total chlorophyll a (μg/g)	1.5	0.056	27
Total carotenoids (μg/g)	0.96	< 0.1	> 9
Perylene (μg/g)	0.33	1.2	0.28

[a] Data for the turbidite layers (51.5 ± 1.5 and 54.5 ± 1.5cm) were excluded.

[b] Ratio of the values in the upper part relative to those in the lower part.

Table 2 Correlation factors among carotenoids (n = 22) in the sediment core in Lake Baikal[a].

	Alloxanthin	Diatoxanthin	Lutein	Zeaxanthin	Canthaxanthin	b-carotene
Alloxanthin	1.000					
Diatoxanthin	0.428	1.000				
Lutein	0.514	0.916	1.000			
Zeaxanthin	0.587	0.941	0.969	1.000		
Canthaxanthin	0.743	0.306	0.360	0.427	1.000	
b-carotene	0.699	0.851	0.941	0.958	0.515	1.000

[a] Data for the layers, where no carotenoids was detected, were excluded.

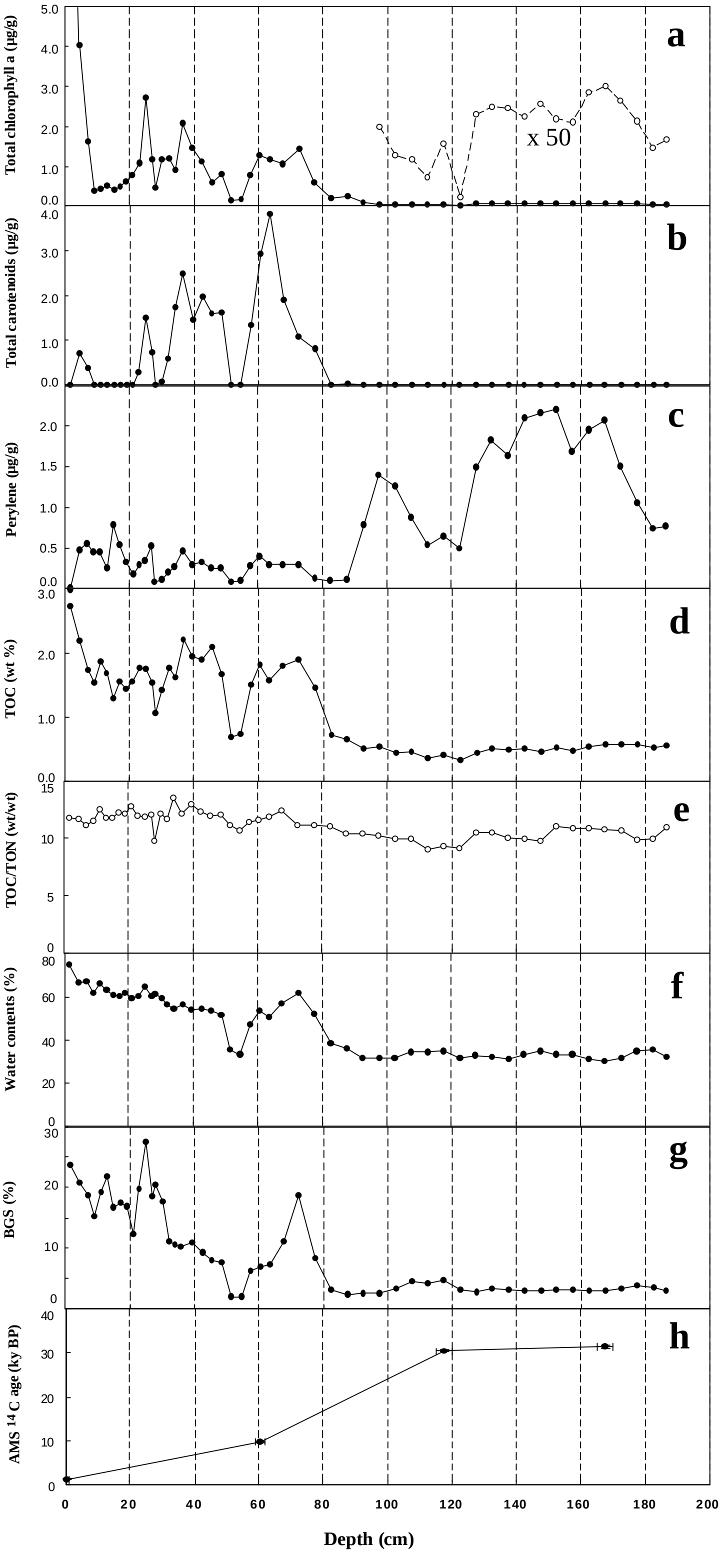

Figure 1 Depth profiles of biogeochemical parameters in the sediment. *a* total chlorophyll a representing the sum of concentration of chlorophyll a and its degradation/diagenetic derivatives; *b* total carotenoids representing the sum of concentration of carotenoids; *c* perylene; *d* TOC; *e* TOC/TON; *f* water content; *g* biogenic silica; *h* ^{14}C age determined by accelerator mass spectrometry (AMS).

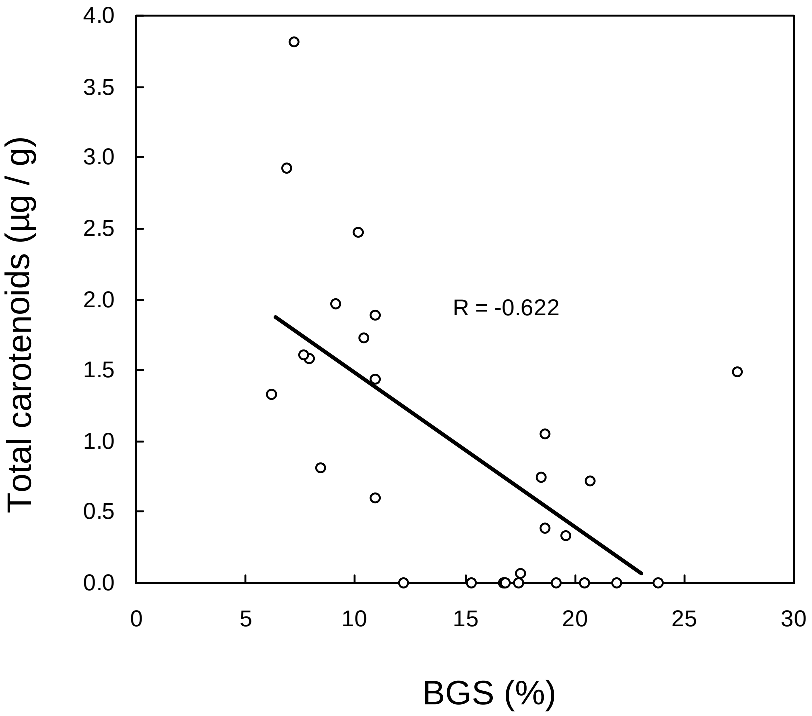

Figure 2 Relation between total carotenoid and biogenic silica content in the upper part of the core (0 - 80 cm, n = 28). Data for the turbidite layers (51.5 ± 1.5 and 54.5 ± 1.5 cm) were excluded.

Oceanic Radiocarbon in the Japan Sea

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Abstract: Increase of radiocarbon in the bottom water of the Japan Sea for the last 16 years (1979-1995) was observed by means of AMS radiocarbon measurement. This increment is due to penetration of surface bomb radiocarbon, which obviously suggests a rapid turnover of the bottom water of the Japan Sea. The turnover time is estimated to be ca. 100 years which coincides with results obtained by other chemical tracers.

KEYWORDS: Radiocarbon, Japan Sea, AMS

INTRODUCTION

The Japan Sea is a marginal sea of the western Pacific and is constituted by the Japan, Yamato, and Tsushima Basins (Figure 1). The water depth of the Japan Basin is about 3500 m and deeper than the other two basins (about 3000 m). The Japan Sea is connected to the North Pacific Ocean and the Okhotsk Sea via the straits of Tsushima, Tsugaru, Soya, and Tatarskiy (Mamiya). Because these straits are shallower than 150 m, the Japan Sea is isolated below that depth, which suggests the deep water of Japan Sea is formed somewhere in the Japan Sea itself. The deep water of the Japan Sea is colder and richer in dissolved oxygen than the deep water of the adjacent Pacific Ocean, which implies its formation in the northern part of the sea in winter season and rapid turnover time of the deep water [1-5]. The turnover time of the deep water have been investigated by chemical tracers. Gamo and Horibe [4] found high value of $\Delta^{14}C$ in the bottom water (below about 2000 m depth). They estimated the turnover time of the bottom water of the Japan Sea as ca. 300 years. Distributions of tritium and other chemical tracers, however, give shorter turnover times of the deep water as ca. 100 years [6-7]. The objective of the present study is to investigate penetration of surface bomb radiocarbon into the deep and bottom water of the Japan Sea by radiocarbon measurements in the Japan Sea in the past decades.

METHODS

The observation in the Japan Sea was carried out during a joint cruise of Japan and Russia on board of R/V Akademik M. A. Lavrentyev in the period 18 November - 7 December, 1995. Figure 1 shows the sampling locations (R1-R10). The seawater samples for radiocarbon measurement were poisoned with $HgCl_2$ on board. In our laboratory, the CO_2 was extracted from 500 ml of the seawater sample by pure nitrogen and separated from H_2O cryogenically using a vacuum system which was designed according to the WOCE Operations Manual [8]. The extraction efficiency for one hour stripping was more than 99% of the concentration of total dissolved inorganic carbon which was measured by a coulometer (Carbon Dioxide Coulometer Model 5012 UIC Inc.). The extracted CO_2 samples and the NIST oxalic acid II standard (HOxII), which was oxidized to CO_2 by a combustion method, were reduced to graphite catalystically on iron powder as described by Kitagawa et al. [9]. The yield of graphite and carbon fractionation during the graphite process were more than 85 % and ca. -0.6 ‰ for δ^{13}C, respectively, which is negligible for the AMS radiocarbon measurement. Radiocarbon measurement was carried out at NIES-TERRA (Tandem accelerator for Environmental Research and Radiocarbon Analysis at National Institute for Environmental Studies) which consists of a 5 MV horizontal accelerator (Pelletron Accelerator 15SDH-2, National Electrostatics Corp.) and a rare isotope beam analyzing line. During 10 minutes measurement, 3   4 mg of the mixture of graphite and iron (C:Fe = 1:1) yielded about 40,000 counts of $^{14}C^{+4}$ which were clearly identified by the ΔE-E analyzing. The final precision for seawater sample was estimated to be 0.8 %, approximately. Further information about NIES-TERRA was described by Shibata et al. [10] and Kume et al. [11].

RESULTS

Figure 2 shows Δ^{14}C transect from station R1 to station R10. Above 200 m depth, we can find a boundary between station 3 and 4 which corresponds with the subarctic front of the Japan Sea around 40^{o}N. The high Δ^{14}C water in the southern area is the Tsushima Warm Current which is a branch of the Kuroshio Current. The highest Δ^{14}C value at station R3 coincide with the recent Δ^{14}C in seawater of the Kuroshio Current [12]. Below 200 m depth, Δ^{14}C distribution is difference between Japan and Yamato Basin. Figure 3 shows vertical profiles of Δ^{14}C and potential temperature at stations R2 in Yamato Basin and R5 in Japan Basin. Δ^{14}C from 200 m to 1500 m depth at station R2 are lower than those at station R5. The potential temperature at station R2 decreases exponentially from 1000 m to 1500 m depth and from 1500 m to 2100 m depth, and is almost uniform below 2100 m depth, approximately. The profile of potential temperature at station R5 is similar with that at station R2 and the transition layers are found at 1300 m, 1700 m, and 2500 m depth. In this paper waters between the first and the second transition layers, between the second and the third transition layers, and below the third transition layer are referred to as the Japan Sea Upper Deep Water, the Lower Deep Water, and the Bottom Water, respectively. Applying a one dimensional diffusion advection model to the potential temperature in the Lower Deep Water, where a linear relationship between potential temperature and salinity was found, gives smaller K/w (the ratio of the vertical eddy diffusion coefficient to the upward advection velocity) value at station R2. If the K value of the Deep Water is constant in the Japan Sea, the upward advection velocity in the Deep Water at station R2 in Yamato Basin is larger than that at station R5 in the Japan Basin, which might cause the lower Δ^{14}C from 200 m to 1500 m depth at station R2.

DISCUSSION

In the past decades, Δ^{14}C in the Japan Sea was measured by Gamo and Horibe [4] and Watanabe et al. [13]. They measured ^{14}C by beta-counting method while the values in 1995 (this study) were obtained by AMS. Recently, AMS ^{14}C measurement was compared with the traditional counting method and a good agreement between the two methods was found [14]. Additionally, all the Δ^{14}C values were calculated by international agreements [15]. Thus we believe that there is no systematic shift between our Δ^{14}C data and the previous ones in the Japan Sea. Figure 3 also shows the past Δ^{14}C data in the Japan Sea. Gamo and Horibe [4] reported that Δ^{14}C in the surface seawater in the northern part of the Japan Sea was ca. 110 ‰ in the late 1970s (stations AL2 in September, 1977 and AL1 in June, 1979 as shown in Figure 1). It is, however, uncertain that surface Δ^{14}C decreased from 110 ‰ in the late 1970s to 74 ‰ in 1995 in the northern Japan Sea because of seasonal variety of surface Δ^{14}C which depends on seasonal variation of mixed layer thickness. Watanabe et al. [13] found low Δ^{14}C (ca. 30 ‰) in the surface seawater in the Yamato Basin (40°N, 138°E, a star in Figure 1) in late spring, 1987. The low surface Δ^{14}C of 30~40 ‰ suggests that there was no influence of the Tsushima Warm Current at their station. The seasonal variability of the mixed layer thickness could not explain this low surface Δ^{14}C because the value was observed in late spring. A possible explanation is coastal upwelling of the ^{14}C-poor deep water. As mentioned above, the large upward advection velocity was found at station R2 which locates in the south of Watanabe and his coworker's station. Topographically it is probable that a similar upwelling occurred at their station. Comparing the Δ^{14}C in the Deep Water at the both stations, Δ^{14}C increase of ca. 30 ‰ during the past 8 years (1987-1995) is apparent. In order to discuss the inventory of ^{14}C in the Yamato Basin, however, difference of the upwelling rate at the both stations should be considered.

In contrast to the surface and the Deep Water, we can directly compare our Δ^{14}C values in the Bottom Water and that obtained by Gamo and Horibe [4] in the late 1970s because the Japan Sea Bottom Water is quite uniform, which is certified by remarkable constant values of TCO_2 [16] as well as potential temperature. The averaged value of Δ^{14}C in the Bottom Water in the late 1970s was ca. -74 ‰4) while that in 1995 was -49 ‰ which is referred from data at station R5. Increase of Δ^{14}C from -74 ‰ to -49 ‰ for the past 16 years in the Japan Basin is clearly explained by the addition of the bomb radiocarbon. A two components model [4] is applied to the Bottom Water and the surface water in the northern Japan Sea where the Bottom Water is formed in order to obtain the turnover time of the Bottom Water. The calculated turnover time during the past 16 years ranged from 75 to 120 years approximately, which is almost consistent with the values estimated by tritium [6], other chemical tracers [7], and excess CO_2 [16]. On the other hand, Gamo and Horibe [4] estimated the turnover time of the Bottom Water to be ca. 300 years using their ^{14}C data and a box model. This disagreement is solved if the lower value of the pre-bomb surface $\Delta^{14}C$, ca. -90 ‰ is substituted for –40~–60 ‰ in their box model, which almost corresponds with a recalculation of Gamo and Horibe's model by Chen et al. [16].

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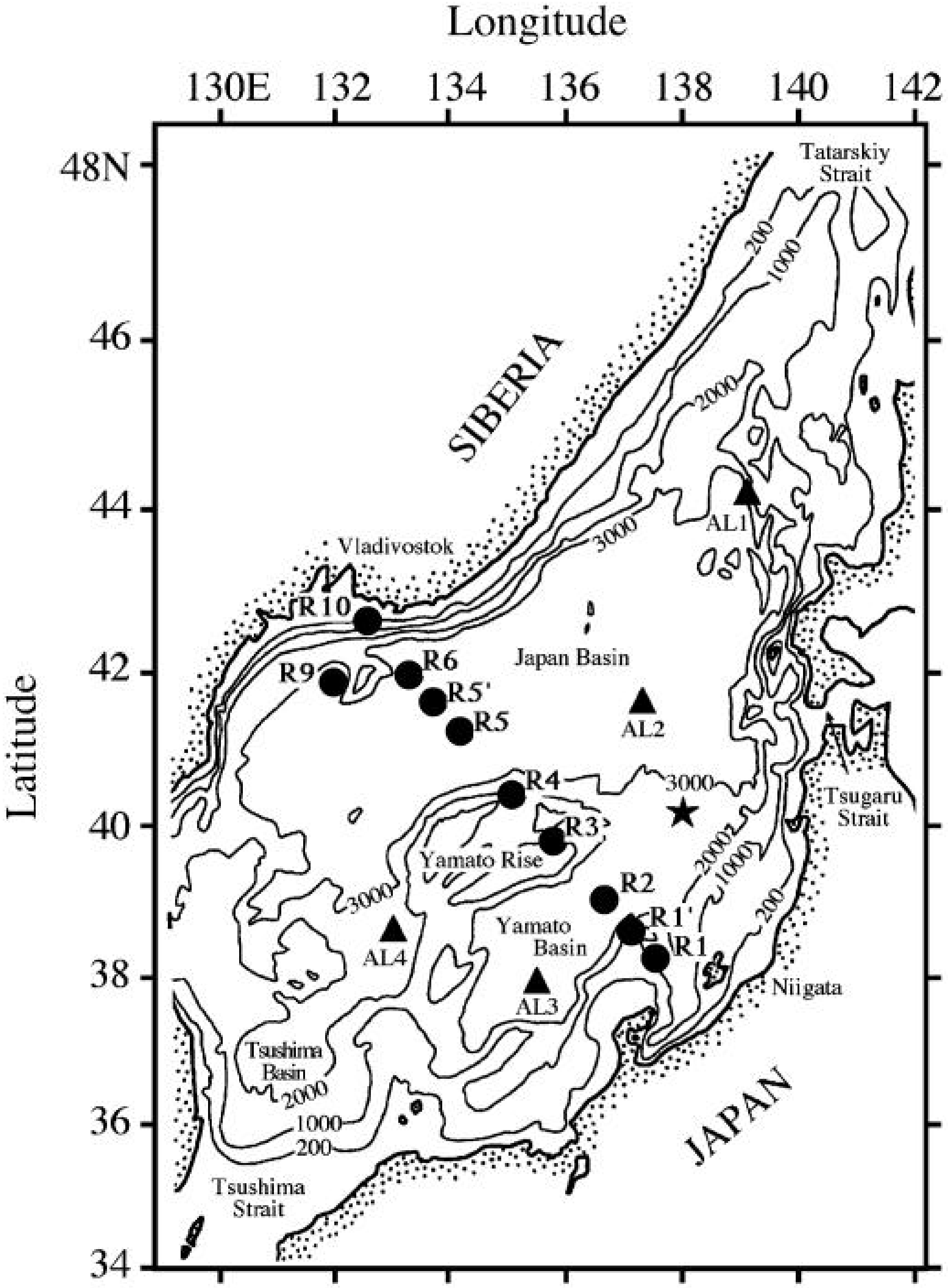

Figure 1 Sampling locations in the Japan Sea. Circles denote sampling stations during a joint cruise of Japan and Russia, 1995 (R1 R10). Stations in previous works are also shown in the figure: triangles (AL1 AL4) and a star denote stations of Gamo and Horibe4) and Watanabe et al.13), respectively.

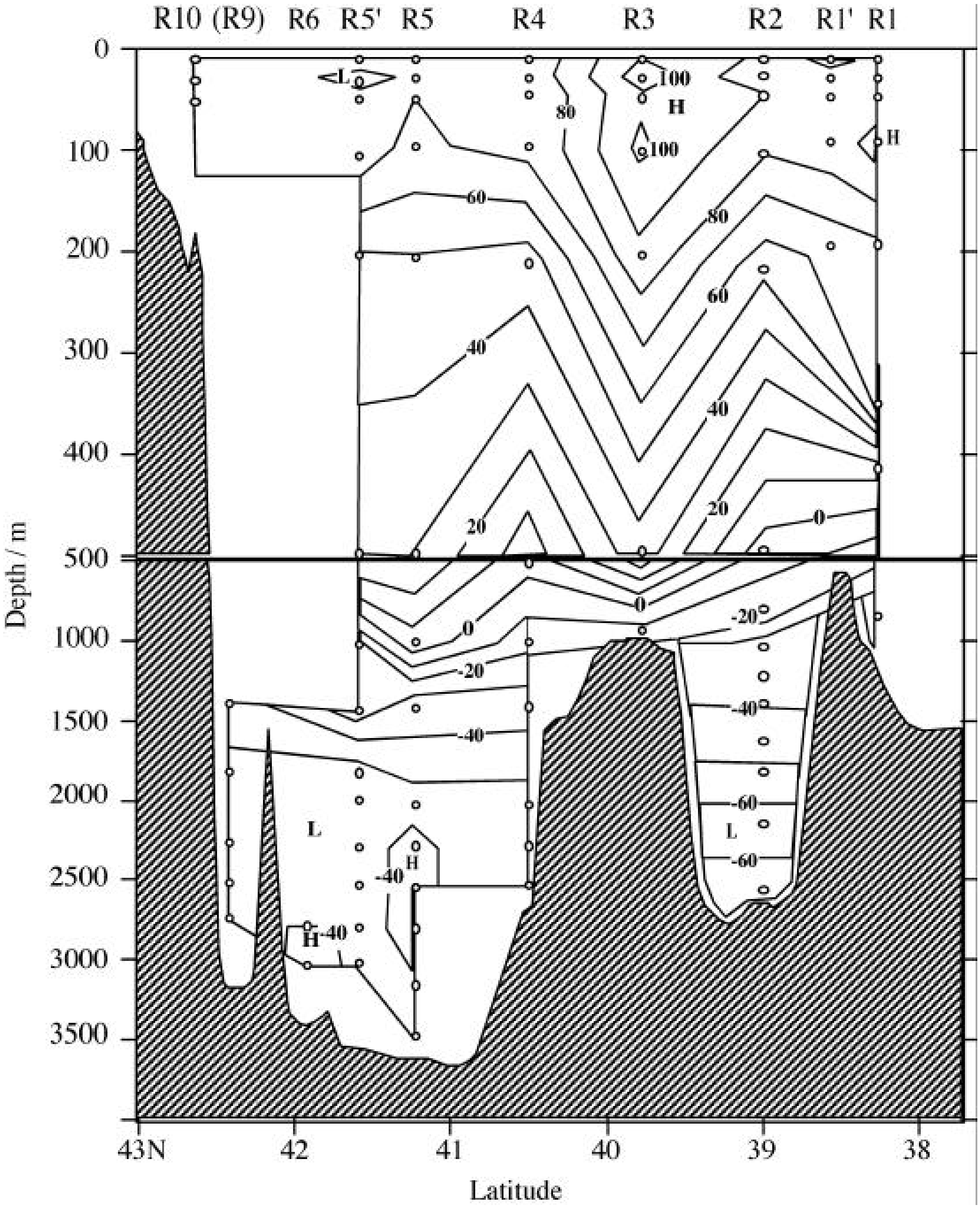

Figure 2 Δ^{14}C (‰) transect from station R1 to station R10.

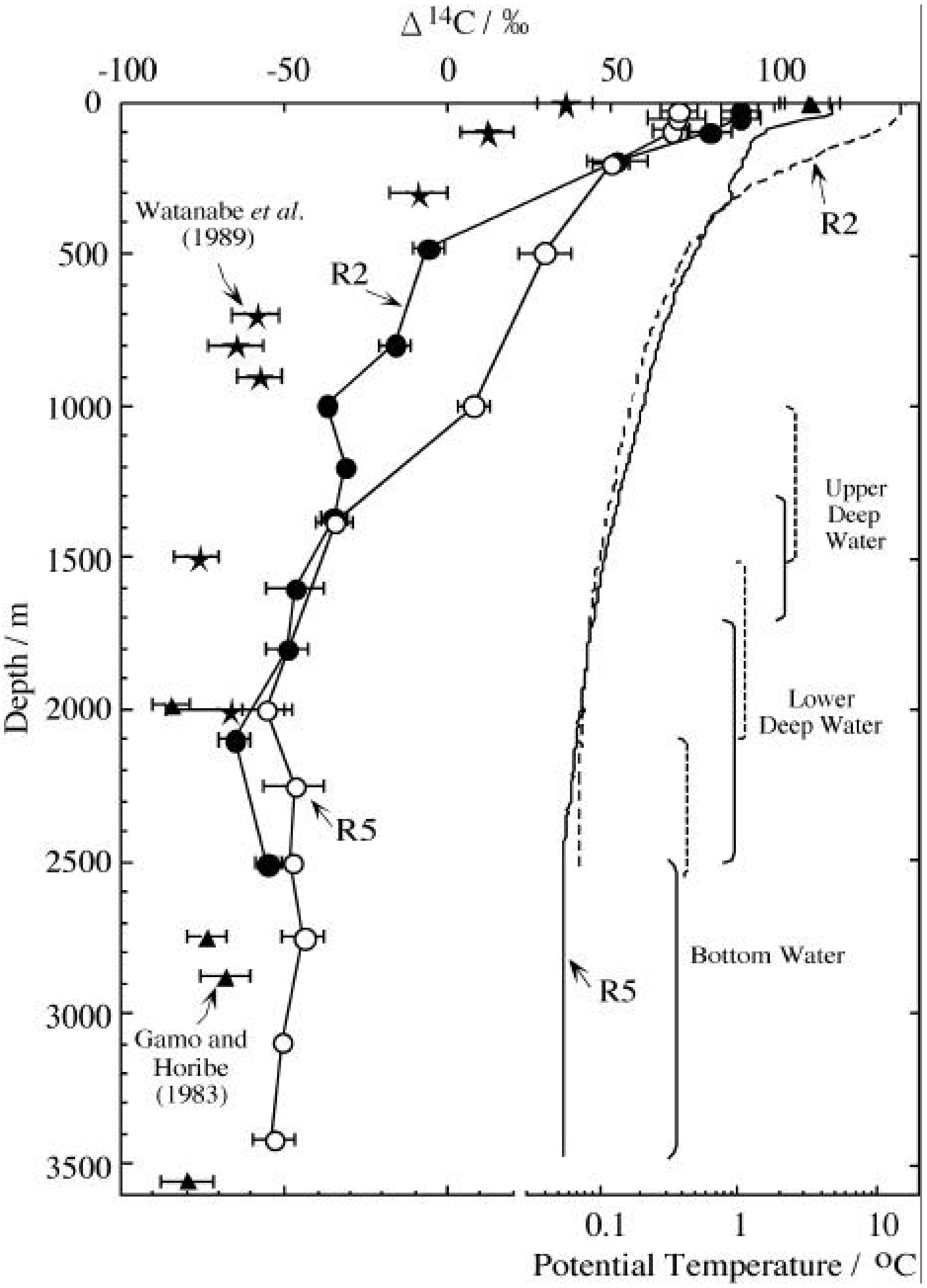

Figure 3 Vertical profiles of Δ^{14}C and potential temperature at stations R2 and R5. Solid (R2) and open (R5) circles show the averaged Δ^{14}C of three measurements for each sample with standard deviation (1 sigma). Broken (R2) and solid (R5) lines are vertical profiles of potential temperature in log scale. Triangles and stars with error bars denote Δ^{14}C data in summer, the late 1970s [4] and in late spring, 1987 [13], respectively.

Radiocarbon ages of benthic foraminifera and planktic foraminifera in deep-sea sediments of the Shatsky Rise.

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ABSTRACT: ^{14}C ages were determined on samples of benthic and planktic foraminifera separated from core from the Shatsky Rise, northwestern Pacific. In paleoceanographic study, benthic–planktic foraminiferal age differences from same horizon have been sometimes used as a proxy for the ventilation age of deep water. Planktic foraminiferal ages for the core top 29 cm range from 2,597 to 14,731 yr BP, corresponding to Holocene–last glacial period. On the other hand, benthic foraminifera range from 8,690 to 15,013 yr BP. As a result, benthic–planktic foraminiferal age differences show large variance from 7,013 to 177 yr BP. The age differences (6,093-7,013 yr) in mixing layer are approximately 5,000 yr older than present ventilation age (2,000 yr), reflecting the upward mixing of old benthic foraminiferal specimens.

INTRODUCTION

In paleoceanographic study, benthic–planktic foraminiferal age differences from same horizon have been sometimes used as a proxy for the ventilation age of deep water [1-3]. However, so far there is no data of benthic–planktic age differences for low sedimentation rate core. The paleoclimatic information recorded in sediments would necessarily be degraded by sediment mixing resulting from bioturbation. We first evaluate benthic–planktic foraminiferal age differences from low sedimenattion core samples collected from the Shatsky Rise, in order to identify the effects of bioturbation on understanding of the paleoclimatic record in deep-sea sediments.

Paleoceanographic data from the middle-latitude northwestern Pacific are lacking, due to poor carbonate preservation on the abyssal plain. The Shatsky Rise, which is located in a central part of the northwestern Pacific (Figure 1 - Location Map) and has thick deposits of carbonate sediments, is an especially important area for understanding the Quaternary climate record.

SAMPLES AND METHODS

Gravity core NGC102 (32 19'N, 15751'E, water depth 2612 m) was collected from the Shatsky Rise during cruise NH95-2 of the RV Hakurei-maru (Figure 1). The core consisted mostly of homogeneous, yellowish-brown, calcareous ooze (Kawahata et al., 1999). Samples consisting of 2 cm thick slices were taken along the length of the core. The δ^{18}O values of the planktic foraminifera *Globorotalia inflata* were already obtained [4]. The core chronology for the top 300 cm was determined by correlation of *G. inflata* δ^{18}O to the SPECMAP δ^{18}O record [5]. The estimated average sedimentation rate was relatively low, at 1.1 cm/kyr. The sediment structure is entirely dominated by bioturbation.

Planktic foraminifera *Globorotalia inflata* and benthic foraminifera *Uvigerina peregrina* were picked from six layers of the top 29 cm for AMS dating. Each sample consists of approximately 400 planktic shells and 230 benthic shells of the given species hand picked from the bulk sediments. These specimens were cleaned ultrasonically in H_2O_2 (30%). Each sample was reacted with 100% phosphoric acid within evacuated glass vessels at the temperature of 25°C. Preparation of graphite targets was conducted according to batch preparation [6]. Radiocarbon analysis was made at AMS facility at National Institute for Environmental Studies (NIES-TERRA). The results are listed in Table 1.

RESULTS

In Figure 2 the data are plotted against depth in the core. Planktic foraminiferal ages for the core top 29 cm range from 2597 to 14,731 yr BP, corresponding to Holocene – last glacial period. On the other hand, benthic foraminiferal ages range from 8690 to 15,013 yr BP. It is clear that a mixed layer is present above 12 cm. The ^{14}C ages within this layer are indistinguishable for the first 12 cm. Below 12 cm the ^{14}C ages increase with increasing depth. Thus, we identified that the layer below 12 cm is historical layer. Figure 3 shows the vertical profile of the age difference between benthic foraminifera and planktic foraminifera. The benthic – planktic foraminiferal age differences in the mixing layer are from 6093 to 7013 yr BP. On the other hand, the age differences in the deglacial layer (23-25 cm and 27-29 cm) is 177 and 282 yr. The age difference in the middle depth (15-17 cm) shows intermediate value (2470 yr). The results show general trend that the age differences remarkably decrease from 6,093 to 282 yr with increasing depth.

Figure 4 shows the vertical profile of the linear sedimentation rate. The linear sedimentation rate (LSR) was calculated from the planktic foraminiferal data. If core top age is 400 yr (reservoir age), the LSR in the mixing layer is 5.4 cm/kyr. In the historical layer, LSR rapidly increases with increasing depth. LSR in 10-17 cm is 0.6 cm/kyr. LSR in 15-25 cm is 2.7cm/kyr. LSR in 23-29 cm is 5.3 cm/kyr. LSR in 10-17 cm is approximately 9 times greater than that in 23-29 cm.

DISCUSSION

Our results show simple trend that the age difference between benthic foraminifera and planktic foraminifera in mixing layer is abnormally large and the difference in deglacial layer is very small. This core is characterized by low sedimentation rate and homogeneous sediments due to bioturbation. In this area, the ventilation age of the present Pacific deep water is about 2000 yr. The age difference (about 7000 yr) in mixing layer is 5000 yr older than the present ventilation age (2000 yr) of deep water in the North Pacific. On the other hand, the age difference (about 180 - 280 yr) in deglacial layer is 1820 - 1720 yr younger than the present ventilation age. Thus, the age difference does not reflect the past ventilation age. The age difference would be greatly affected by sediment mixing. Considering δ^{18}O-based average sedimentation rate (1.1 cm/kyr) and reservoir age (400 yr), the planktic foraminiferal age (2255 - 2597 yr BP) in the mixing layer is relatively young and reasonable. The sediment was not lost from the core top during coring. However, benthic foraminiferal ages in the mixing layer are considerably old. The benthic foraminiferal ages reflect the upward mixing of old benthic foraminiferal specimens.

A simple model of the sediment mixing process is as follows. The burrowing activity of benthic organisms largely homogenizes the sediments in the mixing layer, which lies just below the seafloor. Most sediment particles come to rest once they become incorporated into the historical layer below the mixing layer. Although individual worm burrows occasionally penetrate as deep as 20-30 cm, the downward mixing of particles to depths below the mixing layer is a rare process, as indicated by the model results of Berger and Heath [7]. Conversely, older particles are successively distributed with decreasing frequency into overlying sediments as sediment mixing continues during normal sedimentation. According to Berger and Heath [7], it is possible that microfossils can be transported upward a distance equal to three times the thickness of the mixing layer. Since the mixing layer at the Shatsky Rise is approximately 10 cm, based on ^{14}C dating, then microfossils in the present core could have been transported approximately 30 cm upward. Thus, we can explain that benthic foraminiferal ages in the mixing layer show older age than estimated age for benthic foraminiferal specimens in the case of no sediment mixing. However, we have to explain the young ages of planktic foraminifera in the mixing layer.

A second factor in the mixing process consists of temporal changes in the abundance of foraminiferal species [8]. Relatively young planktic foraminiferal ages in the mixing layer indicate the low abundance of old planktic foraminiferal specimens. The results implicate the high supply rate of planktic foraminifera in the late Holocene or the low supply rate in the early Holocene.

In summary, we should call attention to the paleoceanographic interpretation of deep-water circulation based on benthic-planktic foraminifera age difference. The detailed mixing process of sediments will be discussed with additional data of oxygen isotope of individual benthic foraminifera and abundance changes in foraminiferal species in the future paper.

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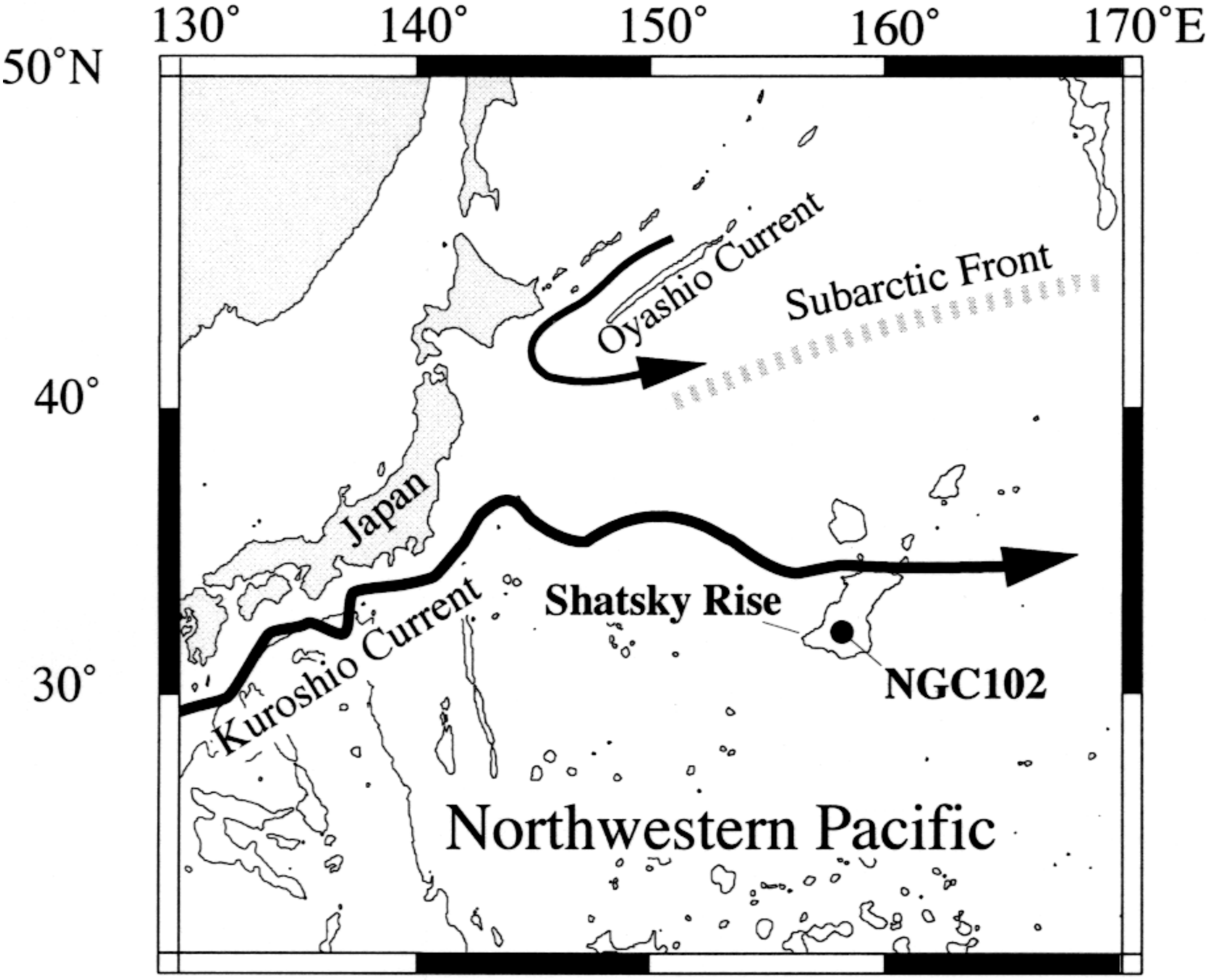

Figure 1 Location map of core NGC102 collected from the Shatsky Rise, northwestern Pacific Ocean.

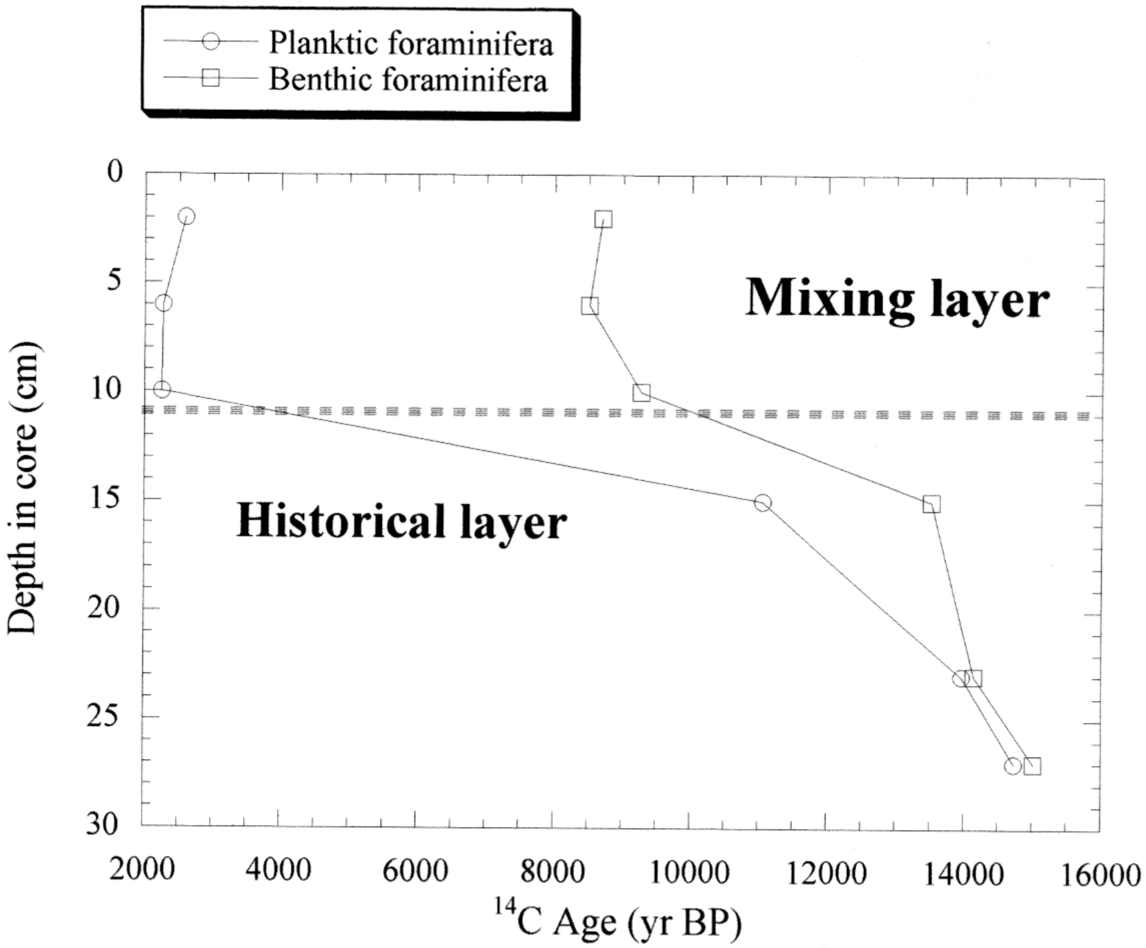

Figure 2 AMS ^{14}C ages of planktic foraminifera and benthic foraminifera vs depth obtained on core NGC102.

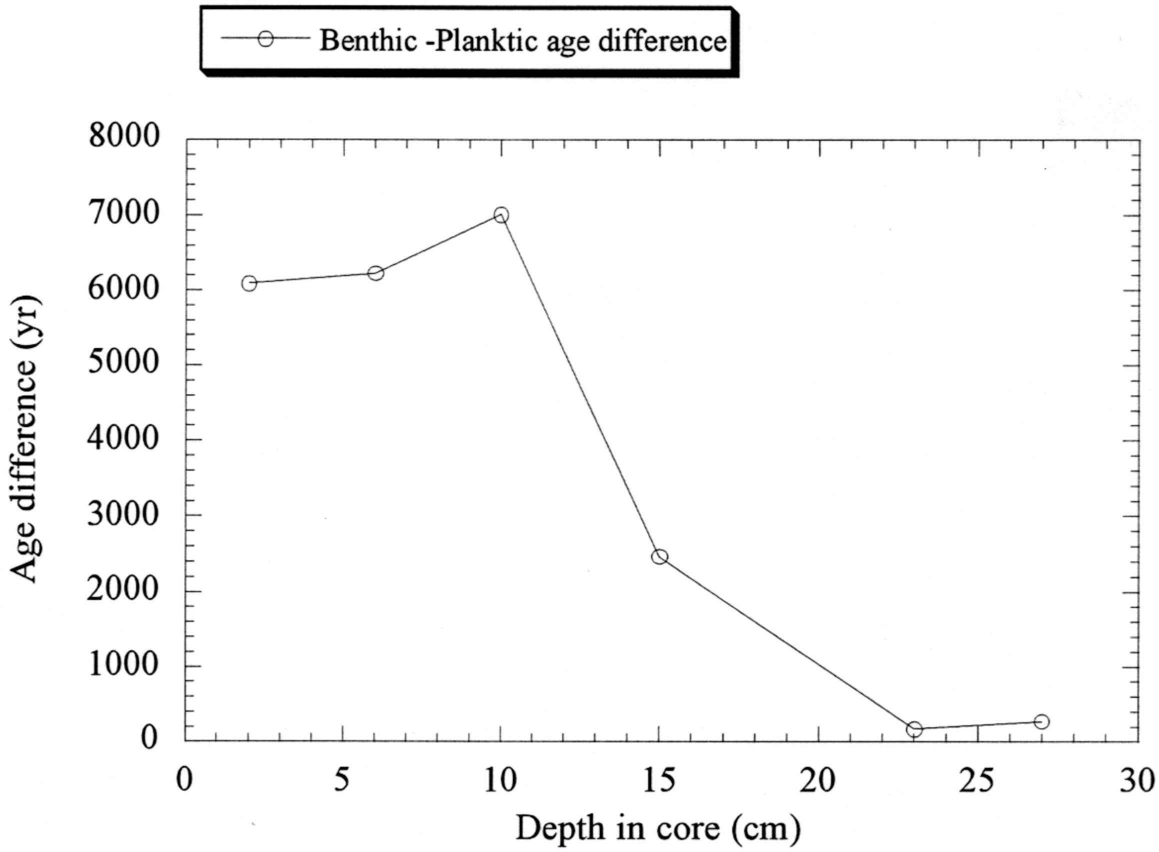

Figure 3 Depth plot of Benthic–planktic foraminiferal age differences in core NGC102.

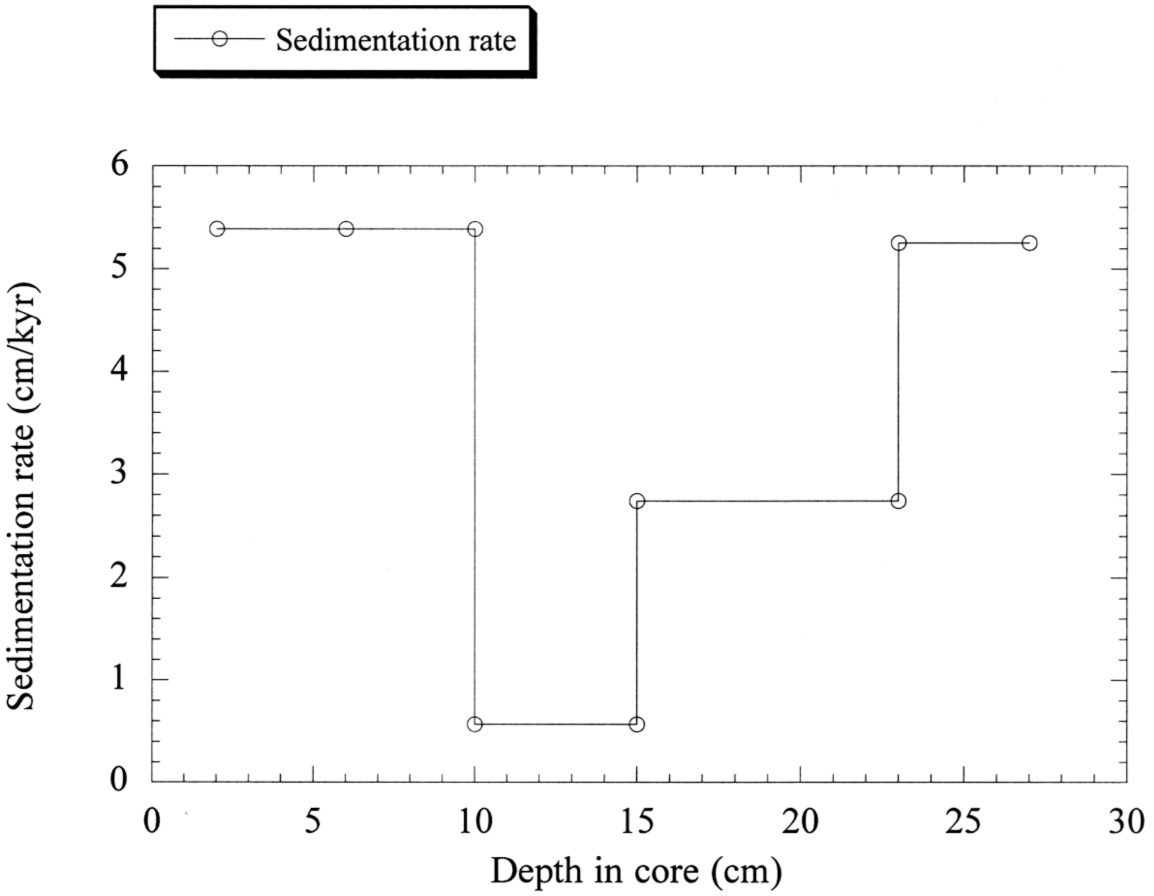

Figure 4 Depth plot of linear sedimentation rate estimated from planktic foraminiferal ages in core NGC102.

Compound specific radiocarbon and stable carbon isotope measurements of fatty acids in an aerosol sample and their geochemical significance

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Abstract: Compound-specific radiocarbon analysis of individual fatty acids was conducted for a semi-urban aerosol sample using preparative capillary gas chromatography (PCGC) system and accelerator mass spectrometry (AMS). The aerosol fatty acids (C_{16} to C_{34}) showed a typical bimodal distribution with two maxima at C_{16} and C_{26}. Their carbon isotopic compositions ranged from -30.3 ‰ (C_{26}) to -23.3 ‰ (C_{18}), suggesting that they are derived from terrestrial higher plants and marine sources. Radiocarbon measurements of C_{16}-C_{22} fatty acids showed modern ^{14}C ages, suggesting that the acids are emitted from living higher plants and possibly from marine organisms. On the other hand, C_{24}-C_{26} fatty acids that are characteristic to terrestrial plant waxes showed ^{14}C ages of 5860 (±200) years. This suggests that some portion of higher molecular weight fatty acids have been stored in geochemical reservoirs such as soils at least for hundreds to thousands of years and then emitted to the atmosphere. These aged fatty acids could be in part transported long distances from the Asian continent through the atmosphere. This new method would be varid and significant to discuss quantitative estimation of organic compounds for paleoceanographic and geochemical settings.

INTRODUCTION

Fatty acids are ubiquitous in environmental samples including aerosols [1], rain/snow [2], soils [3], and lake [4] and marine sediments [5]. They are biosynthesized by different types of organisms such as marine phytoplankton, terrestrial higher plants and bacteria [6] and have been frequently used as biomarkers in the fields of atmospheric chemistry and organic geochemistry. Previous studies of aerosols have shown that distribution of fatty acids are characterized by even carbon numbered predominance with two maxima at C_{16} and C_{24} or C_{26} [1,7]. Lower molecular weight fatty acids (C_{16}, C_{18}) are derived from marine organisms as well as terrestrial higher plants, whereas higher molecular weight fatty acids (>C_{20}) are more specific to terrestrial higher plant waxes [8]. Thus, fatty acids are useful for assessing the relative contribution from marine and terrestrial sources to the atmosphere [1, 7, 8] and to pelagic sediments [9].

In addition to the source information based on the organic molecular composition, we can extract additional information from their radiocarbon concentration, that is, the age of organic compounds after their photosynthetic production, by measuring ^{14}C concentration. Recently, compound specific radiocarbon analysis (CSRA) has become available in the field of environmental geochemistry [10]. Eglinton et al. [11] showed that sedimentary alkanes gave a diversity of ^{14}C ages even in a same layer of sediments. Uchida et al. [12] measured ^{14}C ages for individual fatty acids separated from the surface sediments of Tokyo Bay and reported that some higher molecular weight fatty acids such as C_{22} are old (up to 17 thousands years), although the most abundant fatty acid (C_{16}) was modern in age. These studies demonstrated that the diversity of ^{14}C ages for fatty acids may vary significantly in the same geochemical sample. Moreover, the diversity of ^{14}C ages in the same compound class may provide further information on the transport mechanism of organic matter from the source region to the sampling areas.

In this study, we undertook CSRA of fatty acids in continental aerosols collected from semi-urban area. We present here the ^{14}C ages of individual and/or groups of fatty acids and discuss the ^{14}C results in terms of transport processes and source regions. In addition, we argue the significances of this method to paleoceanography and geochemistry.

SAMPLE AND METHOD

An aerosol sample was collected using a pre-combusted quartz fiber filter (QFF 1969) on the roof of Institute of Low Temperature Science (15 m above the ground), Hokkaido University, from 18 June 1999 to 2 July 1999. Total air volume and the collected aerosol mass were 21470 m3 and 0.894 g, respectively. The aerosols were extracted with CH_2Cl_2/methanol (2:1, 100 ml, 3 times). The extracts were concentrated and saponified with 0.5M KOH/methanol (100 ml, 90 C, 1 h). After neutrals were removed, fatty acids were extracted at pH 1 with CH2Cl2. The acidic fraction was methylated with 14% BF3/methanol and then monocarboxylic (fatty) acid methyl esters were separated using silica-gel column chromatography. An aliquot of the methyl ester fraction was analyzed using a Carlo Erba 5160 mega series GC equipped with on-column injector and a HP-5 fused silica capillary column (30 m x 0.32 mm i.d. film thickness 0.25 μm). Hydrogen was used as carrier gas and the oven temperature was programmed from 70 to 120 C at 30 C min-1, to 320 C at 6 C min-1 and held at 320 C for 20 min.

In order to isolate sufficient quantities of individual fatty acids for ^{14}C age determination by AMS we employed a preparative capillary GC (PCGC) system equipped with automated cooled injector (CIS4, Gerstel, Germany), megabore column, zero-dead-volume effluent splitter, and cryogenic preparative fraction collector (PFC, Gerstel). The injection volume was 25µl and the CIS is programmed from 25 C (0.5 min) to 300 C at 12 C sec-1 and held at 300 C for 2 min. The GC oven temperature was programmed from 50 C (1 min) to 120 C at 30 C min-1, from 120 C to 310 C at 3 C min-1 and then held at 310 C for 20 min. Individual compounds were separated on a HP-5 fused silica megabore column (30 m x 0.53 mm i.d. film thickness 1.0 µm). Helium was used as carrier gas. A total of 60 consecutive PCGC runs were performed in order to isolate microgram quantities of the individual fatty acids.

GC chromatograms of fatty acid methyl esters before and after PCGC injection are shown in Figure 1a and Figure 1b-f, respectively. Purities of each fatty acid fraction were confirmed by GC to range from 98% to 100%, except for C_{28}-C_{32} fatty acids (94%). Because C_{20}-C_{32} fatty acids were not abundant enough to perform the AMS measurement for individuals, some target fatty acids are combined into the U tubes of the PFC as one fraction such as C_{20} plus C_{22}, C_{24} plus C_{26}, and C_{28}, C_{30} plus C_{32} (see Figure 1). After the PCGC separation, fatty acid methyl esters were purified on a silica-gel column to eliminate any methyl silicone contaminants derived from the GC column stationary phase. We confirmed that amounts of C_{16}, C_{18}-C_{22}, C_{24}-C_{26} and C_{28}-C_{32} fatty acid fractions were each more than 100 µg by GC analysis.

The isolated fatty acid methyl esters were combusted in the presence of CuO, Cu and Ag (800 C, 2 hrs) and the purified CO_2 was then converted to graphite carbon target. ^{14}C in the graphite target was measured using AMS facility (NIES-TERRA) at National Institute for Environmental Studies, Tsukuba, Japan [12]. To calculate Δ^{14}C values of fatty acids, we corrected the value of esters using a simple mass balance equation amongst Δ^{14}C values of fatty acid, methyl group of the derivative reagent (BF_3/methanol, Δ^{14}C = -998‰ and their methyl ester.

Stable carbon isotope ratios were determined using a Finnigan MAT delta-plus mass spectrometer interfaced to a HP 6890 GC and a combustion reactor. Individual fatty acid methyl esters were separated using a HP-5 fused silica capillary column (60 m x 0.32 mm i.d. film thickness 0.25 µm) with an on-column injector. The GC oven was programmed from 50 C to 120 C at 30 C min-1, then to 310 C at 3 C min-1 and held at 310 C for 20 min. The combustion reactor, CuO and Pt wires, was held at 850 C. 5α-cholestane, whose δ^{13}C value had been independently determined, was co-injected as internal isotopic standard. The δ^{13}C corrections from fatty acid methyl esters to fatty acids are calculated by a mass balance equation using δ^{13}C value (-46.32±0.14‰ of methanol).

RESULTS AND DISCUSSION

Table 1 gives abundances and δ^{13}C values of fatty acids in the aerosol sample. The fatty acids showed bimodal distribution with two maxima at C_{16} and C_{26}. This distribution pattern is typical for aerosol samples collected from continents and oceans [1, 7, 13]. Orders of the fatty acid concentrations in the aerosols from Sapporo are equal to those from Hong Kong [13].

The δ^{13}C values ranged from -30.3 ‰ (C_{26}) to -23.3 ‰ (C_{18}). These results suggest that C_{16}-C_{18} fatty acids (-24.3 to -23.3 ‰ may be derived mainly from marine organisms with lesser contribution from terrestrial plants, whereas C_{24}-C_{34} fatty acids (-27.9 to -30.3 ‰ are derived from terrestrial C_3 higher plants. These interpretations are consistent with the direct and indirect measurements of δ^{13}C samples for various biological sources. For example, δ^{13}C values for C_{16} and C_{18} fatty acids in marine algae range from -25.0 to -20.5 ‰ ($[CO_2]_{aq}$ up to 14.5 μM, which is typical concentration in the open ocean; [14]). δ^{13}C values for C_{16} and C_{18} fatty acids in terrestrial higher plants range from -36.0 to -35.1 ‰ [C_3 plants] [15]. Contributions of C_4 plants are inferred to be low because δ^{13}C values for C_{24} fatty acids in C_4 plants [e.g. -24.9 to -20.8 ‰ for C_{24}-C_{34} fatty acids of Zea Mays; Matsumoto et al., unpublished data] are significantly heavier than those of fatty acids in the aerosol sample studied here (-26.1 to -30.3 ‰).

Table 2 gives the purities of each fatty acid after the isolation by PCGC, and their Δ^{14}C values and ^{14}C ages for the aerosol sample. We report here, for the first time, ^{14}C ages of individual fatty acids in atmospheric aerosols. The results showed that ^{14}C ages of the fatty acids are extremely diverse, ranging from modern to ca. 5900 yrs BP. The ^{14}C ages of C_{16} fatty acid and the mixture of C_{18}, C_{20} and C_{22} fatty acids gave modern carbon values ($\Delta^{14}C>0$), suggesting that these acids are emitted from microlayers of seawater surfaces that contain abundant fatty acids of phytoplankton and bacterial origin [2]. However, the extremely high Δ^{14}C value of C_{16} fatty acid (Table 2) corresponds to Δ^{14}C of atmospheric CO_2 in the 1960s to 1970s [16]. This implies that the C_{16} fatty acid was photosynthesized in those periods by terrestrial plants. On the other hand, ^{14}C ages for the mixtures of C_{24} and C_{26} fatty acids and C_{28}, C_{30} and C_{32} fatty acids are 5900 and 270 years, respectively. These ^{14}C ages indicate that higher molecular weight fatty acids in the aerosols were not emitted directly from living terrestrial higher plants, but have been stored in certain reservoirs for hundreds to thousands years. The age difference between C_{24} and C_{26} fatty acids and C_{28}, C_{30} and C_{32} fatty acids might explain that fatty acids of terrestrial higher plant origin are derived from multiple sources ranging from modern to old carbon ages.

Although ^{14}C age of the total aerosol carbon was not measured, we analyzed the humic-like substances for ^{14}C, which were left in the acidified fraction of the CH_2Cl_2/methanol extracts of the aerosols after the fatty acids were removed. These humic-like substances were insoluble in acidified solution and non-extractable with CH_2Cl_2. They were isolated, converted to CO_2, and then subjected to AMS measurement as described above. The Δ^{14}C value of humic-like substances showed -470 ‰ (ca. 5000yrs.), being close to that of C_{24} and C_{26} fatty acids. This result again suggests that the aerosols studied contain fairly old carbons.

Soils are the most likely candidates as reservoirs for long chain fatty acids of leaf wax origin because they receive litter from trees and other higher plants and store them as soil organic matter for geological time. The soil organic matter that is exposed to the air can be emitted to the atmosphere as wind blown dusts. However, CSRA measurements of fatty acids isolated from the soils collected near the sampling site showed that the fatty acid carbons are all modern [Matsumoto et al., unpublished data]. This indicates that the aged fatty acids detected in the present aerosol sample are not supplied from the local soil sources.

Alternatively, it is likely that aged fatty acids can be transported from the Asian continent over the sampling site because Asian dusts are well known to be transported frequently over the Pacific during spring to early summer [8, 17]. Kawamura et al. [18] analyzed the arctic aerosols and reported that the concentrations of long chain dicarboxylic acids increased significantly between April and May. Their molecular distributions are characterized by relatively low even/odd ratios, which are different from those of fresh soils, but are similar to aged soils such as Chinese loess. The atmospheric transport of Chinese loess over Japan should be much more significant than over the Arctic. Thus, we consider that the atmospheric input of biogenic but old fatty acid carbon by wind blown dusts in Asian arid regions would be the likely source for the aged fatty acids in the aerosols collected over the Japanese Islands.
If continental aerosols which have all dead carbons (all ^{12}C) would be transported, the contribution of fatty acids from Asian continental in an aerosol sample in this study would be around 50%. Thus, we would calculate the portion of organic compounds in geochmical samples and would depict the geochemical carbon cycles using CSRA. Furthermore, we would illustrate the paleo-geochemical carbon cycles from the analysis of old sediment from the last 50,000 years. However,for the accurate quantification, we need to obtain the data of ^{14}C, ^{13}C and ^{12}C (molecular abundance) distributions in various geochmical end members such as soil, loess, higher plant, clude oil and algae. Further studies associated with ^{14}C would be awaited.

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Table 1. Concentrations and carbon isotopic compositions for individual fatty acids in a semi-urban aerosol sample.

Carbon number	concentration (ng/m^3)	$\delta^{13}C$ (‰)	1σ (‰)
16	22.3	-24.3	0.1
17	0.5	-24.5	0.6
18	10.2	-23.3	0.1
19	0.3	-25.8	0.2
20	4.1	-28.1	0.4
21	0.7	-27.9	0.8
22	5.6	-29	0.2
23	0.8	-28.9	0.5
24	7	-29.4	0.2
25	0.9	-28.4	0
26	7.6	-30.3	0.2
27	1.7	-29.7	0.7
28	5.1	-27.9	0.1
29	2.8	-26.1	1.2
30	2.4	-30.2	0.3
31	0.6	-32	2.6
32	3.2	-27.9	0.2
33	tr[a]	tr[a]	
34	1.7	-30.2	1.5

[a] trace.

Table 2. The ^{14}C data for individual fatty acids in semi-urban aerosol sample.

Fraction (Carbon number of fatty acid)	Purity (%)[a]	yield (μg C)[b]	$\Delta^{14}C$ (‰)	^{14}C Age (yrs. BP)	1σ (yrs.)
C_{16}	98	124	407	modern	98
$C_{18}+C_{20}+C_{22}$	99	175	44.1	modern	132
$C_{24}+C_{26}$	100	164	-518	5860	200
$C_{28}+C_{30}+C_{32}$	94	134	-33	271	120

[a] Purity was determined after the individual fatty acids were obtained by PCGC system.

[b] Yields calculated based on GC analyses of individual fatty acid fractions by PCGC analyses.

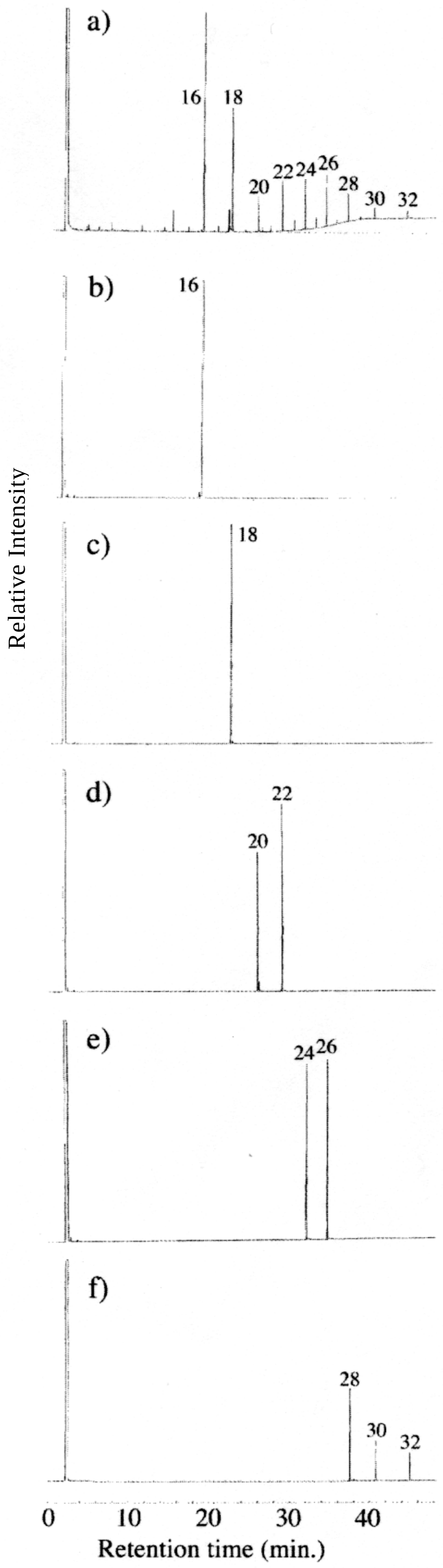

Figure 1
Capillary gas chromatograms of fatty acid methyl esters separated from semi-urban aerosols, (a) before PCGC analysis and (b-f) after purification using PCGC. The numbers superimposed on the chromatograms are carbon numbers of the fatty acids.

Compound-specific isolation technique using PCGC for AMS radiocarbon dating: A case study using marine sediment in the Western North Pacific

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ABSTRACT: We established a purification techniques of specific-organic molecules for specific compound radiocarbon analysis using PCGC system [1]. In this study, as application of this technique the marine surface sediment is used. In order to evaluate a possibility as one of proxies to elucidate marine organic matter cycle over paleo-time scale (~50,000 years BP), compound-specific radiocarbon analysis of five fatty acid biomarkers was conducted for the marine sediments collected from the western North Pacific. The fatty acids (C_{12} to C_{34}) showed a typical bimodal distribution pattern with two maxima at C_{16} and C_{26}. Their carbon isotopic compositions ranged from –25.1 ‰ (C_{16}) to –31.8 ‰ (C_{28}), suggesting that they derived from terrestrial higher plants and marine organisms. A large variations of ^{14}C ages was found among the fatty acids detected in the same sedimentary horizon of the core, ranging from 530 years BP (C_{18}) to 3250 years BP (C_{28}). The results of ^{14}C analysis of fatty acids could be divided into two groups, i.e., lower molecular weight (LMW) fatty acids (C_{16}, C_{18}) derived from marine organisms and higher molecular weight (HMW) fatty acids (C_{24}, C_{26}, C_{28}) derived from terrestrial higher plants. The HMW fatty acids showed older ages, ranging from 2550 years BP (C_{24}) to 3250 years BP (C_{28}), than LMW fatty acids (530 years BP (C_{18}) to 1820 years BP (C_{16})). On the other hand, bulk-phase total organic matter showed the age of 2,260 years BP between those of two groups, suggesting that it was likely mixtures of organic matter derived from marine and terrestrial sources. The compound specific ^{14}C ages and $\delta^{13}C$ data of sedimentary fatty acids presented here could provide an useful information to decipher the fate and transport process of terrestrial organic matter to marine sediments.

INTRODUCTION

It is important to elucidate glacial-interglacial changes in North Pacific circulation and hydrography because the Pacific Ocean is the end-member of the modern ocean circulation regime, and the circulation might be different during previous climate states [2]. Such records as deciphering the interaction between the ocean and the atmosphere during late quaternary environment have been collected from the analysis of sediment cores with higher sedimentation rate, which, in turn, need more accurate dating method for each sediment layers. Today we understand a foraminifera-based chronology as a single best one. However this method requires a good preservation condition of calcium carbonate in the sediments. In the North Pacific regions it is often difficult to get sufficient amount of planktonic foraminifera from sediment core for AMS analysis. Therefore, an alternative chronology tool is needed for sediment analysis in the Pacific Ocean.

Recently developed technique of compound-specific radiocarbon analysis (CSRA) has been expected as an alternative dating tool [3, 4]. This technique has been achieved using a preparative capillary gas chromatography (PCGC) system [1, 5] and microscale ^{14}C analysis [6]. The application of this technique to the marine sediments with varieties of different sedimentation conditions is in progress and is presenting some technical challenges [1, 7-10]. On the other hand, ^{14}C ages of total organic carbon (TOC) in the marine sediments have been considered to be less reliable for dating because of the reworking of organic material, such as humic detritus, and uncertainties of ratios of contribution from marine and terrestrial sources (eg. [11,12]). There are several reports showing that TOC in marine sediment could be derived from multiple sources and isotopically heterogeneous (eg., [1, 7, 13]). The development of the CSRA technique to the marine sediments, therefore, will enable us to construct compound-based sediment chronologies such as alkenones and other organic compounds as proxies, which are applicable to most oceanographic regions [3, 4]. Recently, Pearson et al. [9 ,10] reported that Δ^{14}C of some sterols derived from phytoplankton production in verve sediments were in good agreement with the Δ^{14}C of surface water dissolved inorganic carbon (DIC).

In this study, the CSRA was conducted on the fatty acids isolated from hemi-pelagic sediments in the western North Pacific. Fatty acids are synthesized as primary products through elogation of acetyl-CoA and are one of important and major components in living organisms (eg. [14,15]). They also play a variety of roles, such as membrane structure (phospholipids) and energy storage compounds (long-chain alkyl esters or wax esters and triacylglycerols) and are ubiquitous in marine sediments [16-18] (Parker, 1962, 1964; Volkman et al., 1980). The compound-specific ^{14}C data of fatty acids coupled to compound specific stable carbon isotope data are also discussed in terms of origins of organic matter and its transport process to marine sediments. It is also possible to interpret the occurrence in the sediment because molecular specific radiocarbon dating can elucidate the specific sources. As next stage of this techniques of specific compound radiocarbon analysis using PCGC system, we attempted to get noble acknowledgement on the marine organic matter cycle using real marine sediment sample. These information is useful to reconstract the palaeo-environment in glacial and interglacial ages, as well as sustaining the ancient human civilizations.

EXPERIMENTAL SECTION

The sediment sample was collected by a multiple core sampler at a water depth of 1536 m on the continental margin in the western North Pacific (Lat. 40 29'N, Long. 142 59'E, Figure 2) during MR00 -K01 cruise of JAMSTEC R/V *Mirai* [19]. The major lithology of sediment core is dark olive colored diatomaceous mud. The lengh is 26 cm. TOC contents ranged from approximately 2.5% in the top to 1.0 % in the bottom layers. The sedimentation rate was calculated as 2.8 cm/kyr from slope of ^{14}C ages of bulk-phase organic matter (Uchida et al., unpublished data).

Sediment section from 12 cm (1,700 years BP calculated based on the above sedimentation rate) to 15 cm (2,770 years BP), which corresponds to the time range of ca. 1,070 years, was used for CSRA. The content of individual fatty acids was also determined. A freeze-dried and homogenized sediment samples (300 g) for CSRA was extracted with a large Soxhlet apparatus with CH_2Cl_2/MeOH (99:1 v/v) [5]. Separation of fractions to several compounds types was conducted according to Kawamura et al. [20]. The total extracts were then saponified with 0.5M KOH/methanol for 2 hours under reflux. Neutral lipids were separated by an extraction with CH_2Cl_2/*n*-hexane (10:1), whereas acidic lipids were extracted with CH_2Cl_2 after the remaining solution was acidified to below pH 2. The neutral fraction was further separated into four subfractions on a silica gel column. The acidic lipids were derivatized to methyl esters with 14% BF_3/methanol. The methyl esters were separated into three subfractions on the silica gel column by stepwise elution. Fatty acid methyl esters (FAMEs) were eluted with *n*-hexane/CH_2Cl_2 (1:2). To determine the compound concentration and yield in a series of lipid extraction, 15-methyl hexadecanoic acid and 19-methyl octadecanoic acid were used as internal and external standards, respectively.

Each fraction of fatty acids preparatively isolated by PCGC was analyzed by GC-FID and GC/MS to determine their amounts and purities. Stable carbon isotope ratios of isolated compounds were determined by isotope ratio monitoring gas chromatography/mass spectrometer (GC/IRMS), consisted of an HP6890GC and a Finnigan MAT252 mass spectrometer. We also determined the carbon isotopic compositions of bulk phase organic matter by combustion in the sealed quartz tube with CuO/Ag, 850 °C for 4 hours. Stable carbon isotope ratios are calculated relative to the NBS-19.

The PCGC system (Figure 1) is composed of an HP 6890 GC with FID, a cooled injection system (CIS, Gerstel, Germany), a zero-dead-volume effluent splitter, and a cryogenic preparative collection device (PFC, Gerstel). The PFC device consists of eight port zero-dead-volume valve in a heated interface (320 °C) and six 10 μl glass traps and a 100 μl waste glass trap supported in cooled units (-5 °C) with circulation of ethyleneglycol cooled by an electric cooler.

The injection volume was approximately 10 μl in *n*-hexane per injection, which corresponds to the total amounts of 1-5 μg C. The injection port (CIS, Gerstel) was set at temperature programmed from 40 °C at a rate of 12.0 °C /min to 350 °C (hold time: 10 minutes) at a rate of 12.0 °C/min. Individual compounds were separated on a 60 m megabore (0.53 mm I. D.) fused silica capillary column coated with a cross-bonded methyl silicone phase (R_{TX-1}, RESTEK; film thickness 0.5 μm). The GC oven temperature was programmed from 50 °C (hold time: 1 min) to 120 °C at a rate of 10 °C /min and to 320 °C at a rate of 5 °C /min (hold time: 10 min.). Run time was about 60 min. Helium was used as carrier gas with a flow rate of 5 ml/min.

Prior to compound-specific ^{14}C analysis, we investigated repeated reproducibility of replicate injection and purity of target compounds on PCGC. The capirally gas chromatogram of FAMEs is also shown in Figure 3. Standard deviations of retention times for the target compounds from the 51 consecutive PCGC runs ranged from 0.02 minutes for $C_{15:0}$ fatty acid to 0.07 minutes for $C_{28:0}$ fatty acid. The reliability of isolation of target compounds by PCGC was checked using GC/MS. HRGC chromatograms of target compounds before and after isolations area also shown in Figure 3 and their isolations were successful. The yields of each compound after the PCGC runs were more than 90 %. Those also varied associated with trap temperature and parameter condition of CIS of PCGC system. The results of yields under various CIS conditions are described in other publication (Uchida et al., in preparation).

After PCGC isolation, the trapped components were recovered from the U-tubes by addition of CH_2Cl_2 (1ml) and transferred to a 2ml glass vial. An aliquot (50 μl) was used to determine the purity, yields, and stable carbon isotope analysis. For combustion, each trapped compounds were transferred to quartz tubes (10 cm, 6mm o.d.) using CH_2Cl_2 and the solvent was removed under a stream of high purity helium (99.999%). Then CuO, Ag, and Cu were added to the quartz tubes and combusted at 850 °C. As a precaution to remove the residual solvent from the quartz tubes, the tubes were evacuated to 10^{-6} Torr while immersed in a dry ice/EtOH. Preparation of graphite targets for 1 mg order samples was conducted according to the batch preparation method [21]. Graphitization of the small amount of carbon less than 100 μgC was made using technique modified in NIES-TERRA on the basis of the microscale ^{14}C analysis developed at NOSAMS [6] (Uchida et al., in preparation). Radiocarbon analysis was conducted at AMS facility (NIES-TERRA) at National Institute for Environmental Studies [22, 23].

Correction of $\Delta^{14}C$ ages by subtracting contribution from methyl group derivatized on fatty acids prior to chromatographic separation was made by using a simple isotopic mass balance equation by measuring $\Delta^{14}C_{MeOH}$ (-995 ‰) of the derivative reagent (BF_3/MeOH). The equation of isotopic mass balance is as follows,

$$Cn \cdot \Delta^{14}C_{free} = (Cn+1) \cdot \Delta^{14}C_{ester} \quad 1 \cdot \Delta^{14}C_{MeOH}$$

$\Delta^{14}C_{free}$ is real age and Cn represents carbon number of derivatived compounds.

RESULTS AND DISCUSSION

Table 1 gives the abundance of *n*-fatty acids in the sediment. Straight-chain saturated C_{12}-C_{34} fatty acids were detected and showed a bimodal pattern with maxima at C_{16} and C_{26} and a predominance of even-carbon number. Monounsaturated fatty acids ($C_{16:1}$, $C_{18:1}$, $C_{18:2}$) and branched-fatty acids ($C_{15:0}$), which originate from plankton and bacteria, respectively, are also detected in the sediments. The distribution pattern was similar to that of the samples collected from pelagic sediments in the Pacific Ocean [20, 24]. Moreover, similar distribution pattern has also been reported in the marine aerosol samples from the western Pacific Ocean [20], suggesting that substantial portions of HMW fatty acids are derived from air-to-sea deposition of aerosol particles. The abundance (7 μg/g-dry wt.) of C_{23}-C_{34} fatty acids in the sediments was, however, about twice higher than that of pelagic sediments [24]. This may suggest that contribution of organic matter derived from continental landmass nearby in our study site, ca. 100 km off the coast of Japanease Island, is also negligible.

Table 2 gives the $\delta^{13}C$ values of *n*-fatty acids and bulk-phase oraganic matter in the sediment. The $\delta^{13}C$ values of *n*-fatty acids ranged from -31.8 ‰ (C_{28}) to -25.1 ‰ (C_{16}). The $\delta^{13}C$ values of C_{16}-C_{18} fatty acids (-25.1 ‰ to -27.1 ‰) were also consitent with those of C_{16} and C_{18} fatty acids in marine algal lipids (-25.0 ‰ to –20.5 ‰) and in planktonic foraminifera lipids (-25.0 ‰ to –20.8 ‰) [25, 26].

The result of isotopically lighter C_{18} fatty acids compared to C_{16} fatty acids by 2.0 ‰ was significantly different from the other studies of plants, bacteria, mytilids and mussel (e.g. [27-30]), whose $\delta^{13}C$ values of fatty acids showed consistent enrichment in accordance with the increase of carbon number. On the other hand, $\delta^{13}C$ values for C_{16} and C_{18} fatty acids in terrestrial higher plants ranged from –36.0 ‰ to –35.1 ‰ [31]. The contribution of terrestrial source fatty acids to the LMW fatty acids fraction of the present sediments is thought to be low. The $\delta^{13}C$ values of C_{16}-C_{18} fatty acids were lighter than that of TOC (–20.9 ‰) which was consistent with those reported in previous studies on the marine sediments [32,33]. On the other hand, TOC had heavier $\delta^{13}C$ values than that of C_{24} -C_{28} fatty acids (-28.2 ‰ to -31.8 ‰) by 6 ‰ to 11 ‰. These results are consistent with the previous study in pelagic sediments in the western North Pacific, Japan [32]. The $\delta^{13}C$ values of C_{24} fatty acid of terrestrial higher plant was reported to be -33.8‰ [31]. Thus, the HMW fatty acids in the present sediments seem to be derived mainly from terrestrial higher plants.

Conventional ^{14}C ages and Δ^{14}C values of n-fatty acids as methyl ester (FAMEs) in the layers of 12 to 15 cm are also given in Table 2. The ^{14}C ages of bulk-phase organic matter and benthic foraminifera were also dated as 2260 years BP and 2520 years BP, respectively. Interestingly individual fatty acids showed large variances in ^{14}C ages, from ca 530 (C_{18}) to 3250 (C_{28}) years BP, even among the same sedimentary horizon. The results of CSRA are likely separated into two groups, i.e., LMW fatty acids (C_{16}, C_{18}) and HMW fatty acids (C_{24}, C_{26}, C_{28}). The age difference between the two groups may reflect differences of transport processes and their origins as inferred from compound specific stable isotope data.

HMW fatty acids (C_{24}, C_{26}, and C_{28}) derived from plant leaf waxes are dated from 2550 years BP (C_{24}) to 3250 years BP (C_{28}) with the average of 2890 years BP. The ages of HMW fatty acids showed tendencies to have older ages with an increase in carbon numbers. HMW fatty acids might experience the long residence time in reservoirs such as soil, river and lake sediments before reaching the sediments. The major transport processes of terrigenous organic matter to the marine sediments are likely both fall-out of aerosol particles and river runoff from the land (e.g., [20,34,35]). A recent study on the ^{14}C dating of particulate organic carbon (POC) in river discharging to the Ocean showed that the river is a source of predominantly old terrestrial POC to the Ocean [36,37]. The result of the present study seems to be consistent with these findings.

Bulk-phase organic carbon age in the same layer was dated as 2260 years BP and was between ages of the LMW and HMW fatty acids, supporting the idea that it was really mixture of organic matter derived from both marine and terrestrial sources.

On the other hand, the age of C_{18} fatty acids (530 years BP) was much younger than that of C_{16} (1830 years BP). Although δ^{13}C values of these fatty acids showed those of marine organisms as mentioned above, the cause of age difference between both fatty acids was unknown from small data sets on the present study. Influence of bioturbation might be not negligible because macro benthos such as starfish and molluscan extensively occupied the study site [38] and thick mixed layer (ca. 10cm) was recognized from the vertical profiles of bulk organic matter ^{14}C ages (Uchida et al., unpublished data). We should require a further study using other compounds derived from phytoplanktonic production such as alkenones molecules and dinosterol in the present sediments.

From compound-specific ^{14}C analysis, we found a significant age difference between LMW- and HMW-fatty acids in the same horizon in the marine sediment. These age differences of individual fatty acids may reflect the different sources (marine and terrestrial) of organic matter to the marine sediments, and CSRA together with compound specific stable carbon isotope data will be a powerful tool to study detailed transport, sedimentation process of organic materials in marine environment.

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Table 1. Concentrations of individual fatty acids in the western North Pacific sediments (Sediment layers of 12 to 15 cm).

Carbon number	μg/g -dry wt.)
12	
13	
14	
15	
16	
17	
18	
19	
20	
21	
22	
23	
24	
25	
26	
27	
28	
29	
30	
31	
32	
33	
34	

Table 2. AMS radiocarbon ages of fatty acids, foraminiferas and bulk-pahse OM in the western North Pacific Sediments layers of 12 to 15 cm)

Target compounds	Inferred source	$\delta^{13}C^{a}$ (‰)	yields^{b} (µgC)	$\Delta^{14}C^{c}$ (‰)	^{14}C age^{d} (years B.P.)	error (years B.P.)
C16:0	Marine	-25.1	265	-198	1828	128
C18:0	Marine	-27.1	220	-62	530	60
C24:0	Terrestrial	-30.6	158	-268	2550	70
C26:0	Terrestrial	-28.2	262	-296	2900	210
C28:0	Terrestrial	-31.8	233	-328	3250	370
Benthic foraminifera^{e}		-1.2			2520	40
Bulk-phase OM^{e}		-20.9			2260	70

a: Isotope ratio is relative to the PDB standard material and is corrected by measuring isotope ratio of derivative reagent (MeOH; -29.3‰): b: Determined after PCGC isolation. c: Radiocarbon concentration corrected for the presence of derivative carbon (MeOH; -995‰). d: Radiocarbon age (years B.P.) reported using the Libby half-life of 5568 years. e: Collected in the layer for compound-specific ^{14}C analysis.

Preparative capillary gas chromatography(PCGC)

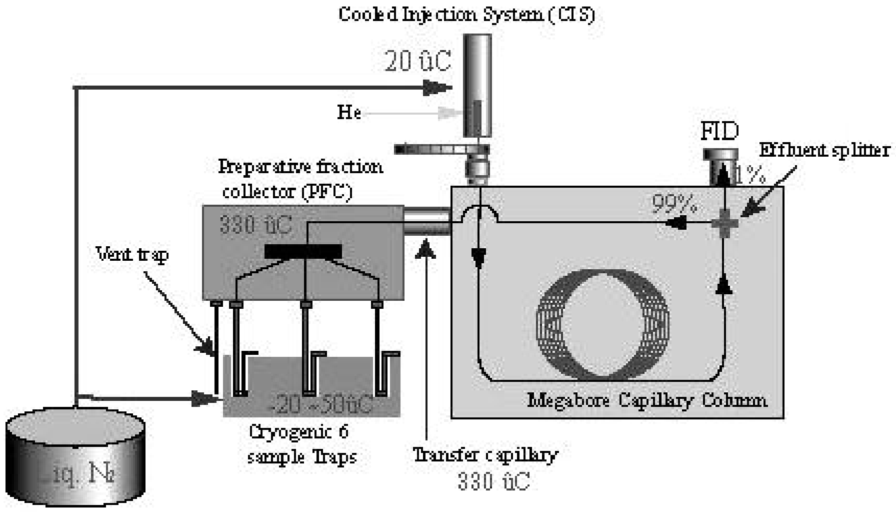

Figure 1 Preparative capillary gas chromatograph (PCGC) system.

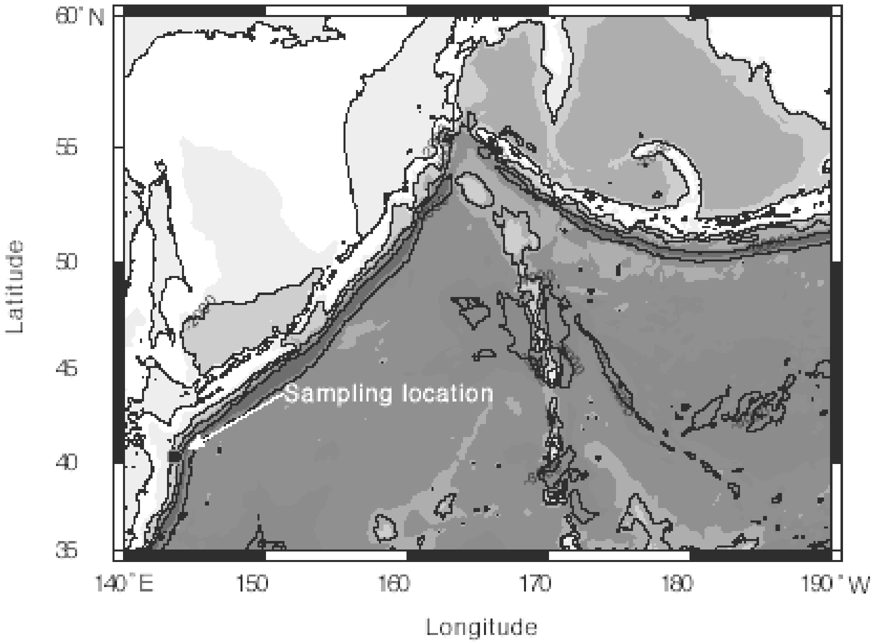

Figure 2 Sampling location of multiple core. Core sample was collected at the water depth of 1536 m on the continental margin in the western North Pacific.

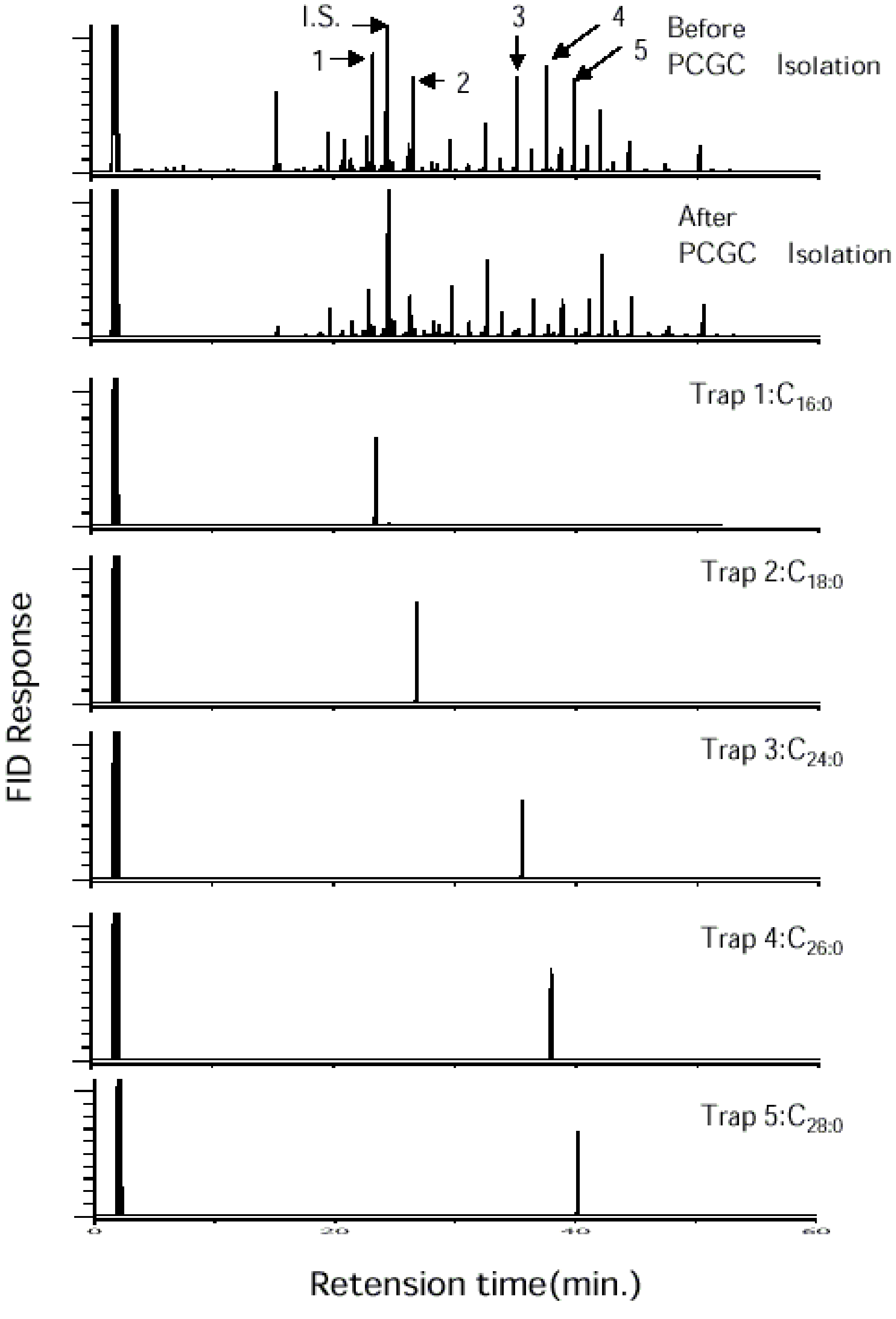

Figure 3 HRGC chromatograms of fatty acid methyl esters (FAMEs). Upper two chromatograms shows GC traces before and after PCGC isolations. Numbers of the peaks represent compounds isolated by PCGC; 1: $C_{16:0}$, 2: $C_{18:0}$, 3: $C_{24:0}$, 4: $C_{26:0}$, 5: $C_{28:0}$. Chromatograms of trapped compounds after PCGC separations show successful isolations of target compounds with enough purity.

Radiocarbon measurement of bone material at NIES-TERRA.

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Abstract: By using AMS technique, direct measurement of radiocarbon (^{14}C) dates on bones has been realized. Collagen extracted from bone samples could show not only ^{14}C ages but also ^{14}C levels in circumstance, which are useful information to understand palaeoenvironment.

INTRODUCTION

Because of recent development in the accelerator mass spectrometry (AMS), the availability of ^{14}C age determination has been expanded to many new academic fields. For example, the excavated bone materials can be dated by extracting the remaining protein, collagen, directly. It supposed much precise age determination for human and animal bones, especially for bones stored in museum collections, because it is usually difficult to find accompanied material such as charcoal in the case of museum specimens. ^{14}C measurement by AMS revealed not only the ^{14}C ages of animal remains, but also the information of environments where they had inhabited. In this paper, we report our procedure for collagen extraction and graphite pretreatment. Furthermore, some recent results on age determinations and investigation on palaeoenvironment using ^{14}C recorded in bone materials conducted at NIES-TERRA (National Institute for Environmental Studies, Tandem accelerator for Environmental Research and Radiocarbon Analyses) was also reviewed in this paper.

METHODS: Collagen Extraction and Graphite Production

Collagen is most common protein in vertebrate bodies. About 25% of fresh bone is composed of organic matters and collagen shares more than 90% of total organic matters. Although the inorganic apatite of bone sometimes suffers serious contamination from carbonates and/or soil organic matters in deposits because of it porous structure, collagen is relatively resist to the diagenetic process. Therefore, usually collagen or other kinds of biogenic organic matters have been employed to ^{14}C dating with bone samples today.

Collagen was extracted from bone by using improved method of Longin [1] and we referred the procedure reported by Nakai et al. [2]. At first, bone fragments of 1g were cleaned by brushing and ultrasonic cleaning. After removing humic acid and fluvic acid by soaking in 0.1 M NaOH overnight, bones were washed in pure water (Milli-Q^{TM} water). Cleaned and freeze-dried bone samples were crushed by SPEX freezer mill into fine powder. Hydrochloric acid was used to remove hydroxyapatite from powdered bone which were sealed in cellulose tubes. By using semipermeable membrane, reaction was moderated and fragments of decayed collagen with high-molecular weight (<12,000-14,000Daltons) would be trapped within tubes and could be collected as dissolved fraction. After overnight reaction, cellulose tubes were soaked in pure water overnight. Remaining material and solution in the tube were recovered and separated by centrifugation. Both remaining organic matters and supernatant were lyophilized. The former fraction was named extracted material and the latter was dissolved fraction. Usually we stock not only the extracted gelatin, but also aliquot of decalcified material, dissolved portion, and residue of geratinization for future analyses. Extracted organic matters were heated in pure water at the temperature of 90°C overnight in order to extract gelatin. After geratinization, dissolved gelatin and residue were separated by centrifugation. Both fractions were freeze-dried and stocked as gelatin and residue.

Usually the lyophilized gelatin was analyzed for carbon and nitrogen contents to investigate whether the extracted material was pure collagen or containing some amount of extraneous materials. Typically, 0.25mg of collagen was weighted in a tin cup at first. Carbon and nitrogen isotopes were measured automatically by using an elemental analyzer and isotope ratio mass spectrometer (EA-IRMS, consisted of Calro Erba NA1500^{TM} elemental analyzer, Finnigan MAT ConFlo II^{TM} interface and Finnigan MAT 252^{TM} mass spectrometer). The uncertainty with each measurement is estimated as 0.25‰ for δ^{15}N values and 0.10‰ for δ^{13}C values. Elemental analyzer supplied carbon and nitrogen contents at the same time. We monitored the C/N ratio to check the purity of extracted gelatin. When C/N ratios did not show a value between 2.9-3.6, the gelatin had got serious effect of diagenesis [3] and such material usually showed altered values in both stable isotopes and ^{14}C contents [4].

For the ^{14}C analysis, 2.5mg collagen, which contained about 1mg of carbon, was oxidized to CO_2 within evacuated tubes with copper dioxide at the temperature of 850°C, and then CO_2 was purified in a vacuum system cryogenically. At last, CO_2 was reduced to graphite with hydrogen and iron powder catalysis for accelerator mass spectrometry [5]. Amount of carbon was measured as the pressure of CO_2 in the volume-known portion of the vacuum line, and 2.2 times amount of hydrogen was put into a reaction tube with CO_2 and iron powder that was measured at 1mg in small inner tube (Figure 1). Reaction was succeeded at the temperature of 650°C overnight. Iron catalysis was usually pre-reacted with half atmospheric pressure of hydrogen at 450°C to refresh its surface. According to our experience, Aldrech's iron powder (-325 mesh, 97%: 20,930-9) had given the highest and most stable recovery rates in general. Produced graphite was weighted with an inner tube and iron, and recovery rate was calculated based on the amounts of raw material (gelatin), CO_2 and graphite. Typical recovery rate exceeded 90% and we repeated pretreatment for samples with worse rates.

Pretreatment of graphite and ^{14}C measurements were conducted at NIES-TERRA [6]. At least two kinds of standard materials were loaded with unknown samples contemporaneously to calibrate the ^{14}C contents. Usually we put the new oxalic acid (NBS RM-4990C) and IAEA-C6 ANU sucrose. In the case of archaeological material, a standard material which have corresponding level to samples, such as IEAE-C7 (5644 BP), was also measured. Almost half of a typical batch (40 cathodes in MS-SNICS^{TM}) was occupied by standards. One sequence of measurement continued for about 10 minutes (6000 cycles) and whole measurement of batch were repeated three or four times. In order to calculate the uncertainty of each measurement, standard error of mean with repeated measurements and statistical error with counting numbers were compared, and larger error was shown as one sigma error with each measurement. Modern standard materials showed errors less than 0.5 pMC typically. It corresponded to 40 ^{14}C yr as conventional ^{14}C age.

CASE STDY 1: Marine reservoir effect in western North Pacific observed in archaeological fauna

Conventional ^{14}C age should follow some rules to avoid confusion [7], but these rules sometimes cause bias on conventional ages. In order to calibrate ^{14}C age to calendar age, the calibration curves for atmosphere and marine material have been published [8], but more calibration factors are required for fractionation between carbon pools. These phenomena are known as the reservoir effects. In the case of marine materials, 400 ^{14}C yr difference from atmospheric ^{14}C age is known for the averaged surface water. Furthermore, attention should be paid for local variation by deep see water upwelling, addition of fresh water, hard water effect, and so on.

In this study, terrestrial mammal bones and marine mammals bones excavated from the same archaeological deposits were compared to evaluate the marine reservoir ages around the Hokkaido Island, Japan [9]. We would like to indicate the appropriate correction value for the marine materials in western part of North Pacific, because the appropriate correction for this region has not yet been established [10]. At the same time, historical fluctuation of reservoir ages in this region might reflect the past intensity of upwelling, which will be a direct monitor of global thermohaline circulation. In this study, precise age determinations on both terrestrial and marine animal bones are quite important. Because AMS technique make it possible to analyze multiple samples from the same assemblage, penetrated materials were recognized as outliers based on statistical consideration.

We collected archaeological samples excavated from the coastal area along the Volcano Bay (the Uchiura bay) on Hokkaido Island, Japan. In this region, archaeological shell mounds from prehistoric periods to recent time were frequently found and they contained both Japanese deer (*Cervus nippon*) and northern fur seal (*Callorhinus ursinus*) as dominant fauna. Analyzed samples were collected from five shell middens (Figure 2): the Kitakogane site (the Early Jomon period), Takasago site (the Latest Jomon period), the Minami Usu 6 site (the Zoku-Jomon period), the Minami Usu 7 site (the Satsumon period), and the Oyakotsu site (the Ainu cultural period). 101 animal bone samples were analyzed for ^{14}C measurements. The age differences between Japanese deer and northern fur seal showed the clear effect of old deep water upwelling in this region (Figure3), while most of layers showed some obvious outliers. Carbon and nitrogen ratios, as well as carbon and nitrogen contents measured with elemental analyzer, indicated diagnostic values for collagen. In the case of studied shell middens, it was likely that bone collagen was preserved very well and extraneous contamination seemed quite limited. Furthermore, results must be reflecting isotopic futures recorded *in vivo*. Clear age differences lager than surface ocean average were indicated at the periods from 4900 BP (Kitakogane) to 800 BP (Oyakotsu) (see Table 3). Kitakogane showed its ^{14}C age at 4913 ± 13 BP with deer bone, which agreed with previously reported duration period of Early Jomon culture (6100-4800 BP; [11] and ^{14}C age with charcoal, 4800 ± 140 BP (N-1094-2: [12]). Takasago site at ^{14}C age of 3900 BP also indicated good agreement with the duration (4050-3000 BP) of the Late Jomon period estimated by Keally and Mutou [11].

Table 1 shows pooled average and error of each data set, which was divided into several clusters based on the statistical method of Wilson and Ward [13]. The high percentage of outliers (36/101) at most archaeological deposits suggested that these shell middens were active spaces for inhabitant and deposits had much chance of disturbance. Therefore, it is quite suspicious to determine the age of shell midden site based on ^{14}C single measurement.

Five archaeological sites except for Takasago site indicated relatively similar age differences around 800 years. While Takasago site showed significantly smaller age difference of 583 ± 50 years, this layer contained a higher percentage of outliers and an alternative pair of clusters agreed with other sites. In order to interpret this exception, we require more data. Four values from Kitakogane, Minami Usu 6, Minami Usu 7 and Oyakotsu sites agreed with each other statistically and provided a pooled-averaged ΔR of 382 ±16 ^{14}C yr, based on Wilson and Ward [13]. At the moment, we concluded that 382 ^{14}C yr can be reasonable as a representative ΔR value in NW Pacific for further discussion. For more discussion, see Yoneda et al. [9].

CASE STUDY 2: ^{14}C age determination and dietary reconstruction on human remains excavated form the Satohama site, Miyagi, Japan

The Satohama shell midden is one of most popular and typical settlement of Jomon period in the Northern Japan (Figure 2). At the Satohama site, the first excavation was undertaken from 1918, and many archaeological and anthropological works, including morphology of Jomon inhabitants and settlement patterns, have been done up to now. Recently two points named the Nishihata point and HSO point were excavated and a series of human skeletons were recovered. We extracted collagen from these human bones not only for ^{14}C age determination but also for palaeo-dietary reconstruction based on nitrogen and carbon stable isotope ratios.

Three human remains form HSO point and Five human remains from No.10 Pit of Nishihata point in the Satohama site were analyzed for ^{14}C dating and dietary reconstruction (Table 2). Pretreatment was described in the previous section. In the case of four individuals recovered from Nishihata point, duplicate analysis was conducted on rib bones and limb bones. These limb bones were analyzed at University Erlängen in Germany in parallel. The preparation method at Erlängen is slightly different from ours but it also based on Longin [1,14]. Table 2 is also showing information on the quality of gelatin, such and C/N ratios, carbon and nitrogen contents. Nishihata-2, HSO-1 and HSO-2 showed larger values than normal distribution in modern collagen [3]. These three samples showed higher C/N ratios while recovery rate of gelatin, carbon contents and nitrogen contents seemed to be reduced. It might mean that these fringe C/N ratios did not originated from the contamination of extraneous organic matters, but from serious decomposition of collagen protein. Because such decayed samples showed strange values on stable carbon and nitrogen isotope ratios, it was difficult to discuss the antemortem dietary habits of these individuals. However, there was no clear evidence that extraneous organic matters have contaminated, ^{14}C result might be able to interpret carefully that they had kept their original information.

In the Table 3, conventional ^{14}C on human remains excavated form the Satohama site are shown. Regarding on the four samples from Nishihata point, comparison between skeletal parts and laboratories supposed good agreement with each other. Based on Wilson and Ward [13], pooled averages were calculated as 457 ± 39 BP, 441 ± 43 BP, 501 ± 33 BP, 490 ± 40 BP on Nishihata-2, 3, 4, and 5, respectively. While these were thought to belong to Yayoi period based on the archaeological context, it is highly possible that these four individuals were buried almost coevally in the Middle age of Japan.

HSO-2 and HSO-3 showed 2980 ± 50 BP and 2620 ± 50 BP, respectively, and these ages seems to agree with the observation that these burials accompanied with the Latest Jomon potteries. At the same time, Nishihata-1’s date of 340 ± 45 BP also showed a good agreement with archaeological supposition that the burial age had been the Edo era. However, the reconstructed dietary patterns indicated a high possibility that seafood contributed for their protein source strongly (Figure 4). As we saw in previous session, the ^{14}C level of marine organisms living in surface ocean in NW Pacific should be deplete by deep sea water upwelling. Therefore, the diet based on marine foods might introduce some amount of ^{14}C-reduced protein into human tissues. In the case of such samples, we have to consider the regional calibration for marine reservoir effect, while the local calibration values for Japan except for Hokkaido area has not yet been discussed. For the precise age determination on marine material, including fishing human populations, we have to study about present and past situation on the marine reservoir around Japan Archipelago. It will reveal not only archaeological information but also palaeoenvironmental condition recorded in archaeological and/or paleontlogical samples.

CONCLUSION

Since NEIS-TERRA was established as the third AMS facility in Japan in 1995, ^{14}C have been measured both for age determination and for tracing carbon dynamics in the environment. We have measured many kinds of material including charcoal, soil, peat, lake sediment, atmospheric methane, dissolved inorganic carbon in sea water, bathyal sediment, and bone. We have established routine procedure of collagen from bone samples extraction and hundreds of bone materials have been analyzed. A part of their results was shown in this paper and it was indicated that ancient bone materials were really useful material for not only dating but also palaeoenvironmental studies. For the next step, we are going to study bone samples from a more microscopic point of view. Individual amino acids should be investigated for further discussion, and compound-specific ^{14}C dating will be also powerful tool for bone chemistry.

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Table 1 Most reliable radiocarbon data sets on deer and fur seal from archaeological sites (Yoneda et al. n.d.). Regarding on the details in estimation of ΔR value, see Southon et al., 1995).

Site	Species	clustered sample	rejected sample	pooled average	age difference	ΔR
Kitakogane	Deer	20	10	4913 +/- 14	767 +/- 21	392 +/- 22
	fur seal	20	0	5680 +/- 15		
Takasago	Deer	3	1	3923 +/- 37	583 +/- 50	245 +/- 65
	fur seal	4	3	4297 +/- 33		
Minami Usu 6	Deer	2	1	2228 +/- 21	801 +/- 29	456 +/- 66
	fur seal	3	2	3029 +/- 20		
Minami Usu 7	Deer	7	3	794 +/- 19	740 +/- 24	357 +/- 26
	fur seal	7	3	1534 +/- 15		
Oyakotsu	Deer	2	1	882 +/- 47	767 +/- 53	370 +/- 80
	fur seal	7	2	1649 +/- 24		

Table 2 Result of elemental and stable isotopic analyses on the Satohama human remains.

Sample	Skeletal element	Organic matters (%)	C (%)	N (%)	C/N	Measured δ^{13}C (‰)	Measured δ^{15}N (‰)	dietary δ^{13}C (‰)	dietary δ^{15}N (‰)
HSO-1	Femur	0.7	32.6	5.7	*6.63*	-19.5	15.5	-	-
HSO-2	Costa	1.3	41.1	12.6	*3.80*	-16.1	14.9	-	-
HSO-3	Costa	6.2	46.2	16.6	3.25	-16.3	11.5	-20.8	8.0
Nishihata-2	Costa	6.6	42.0	13.1	*3.73*	-19.0	13.8	-	-
Nishihata-3	Costa	11.8	45.4	16.5	3.21	-18.1	13.0	-22.6	9.5
Nishihata-4	Costa	11.3	44.2	15.7	3.28	-17.7	13.1	-22.2	9.6
Nishihata-5	Costa	12.0	43.8	15.4	3.31	-18.5	13.6	-23.0	10.1
Nishihata-6	Costa	12.1	43.7	16.4	3.11	-19.3	11.1	-23.8	7.6

Table 3 Radiocarbon ages of Satohama human remains.

Sample	Lab number	element	Radiocarbon age(BP)
HSO-2	TERRA-030799a08	Costa	2980 +/- 50
HSO-3	TERRA-030799a09	Costa	2620 +/- 50
Nishihata-1	TERRA-052199a34	Costa	340 +/- 45
Nishihata-2	TERRA-030799a08	Costa	460 +/- 50
	TERRA-052199a26	Costa	535 +/- 110
	TERRA-032100a05	Humerus	430 +/- 115
	Erl-2641	Humerus	397 +/- 103
Nishihata-3	TERRA- 101698b20	Costa	390 +/- 50
	TERRA-032100a06	Femur	530 +/- 130
	Erl-2642	Femur	612 +/- 107
Nishihata-4	TERRA-030799a10	Costa	505 +/- 45
	TERRA-032100a04	Tibia	505 +/- 95
	Erl-2643	Tibia	492 +/- 56
Nishihata-5	TERRA-030799a15	Costa	440 +/- 50
	TERRA-032100a07	Humerus	515 +/- 125
	Erl-2645	Humerus	598 +/- 76

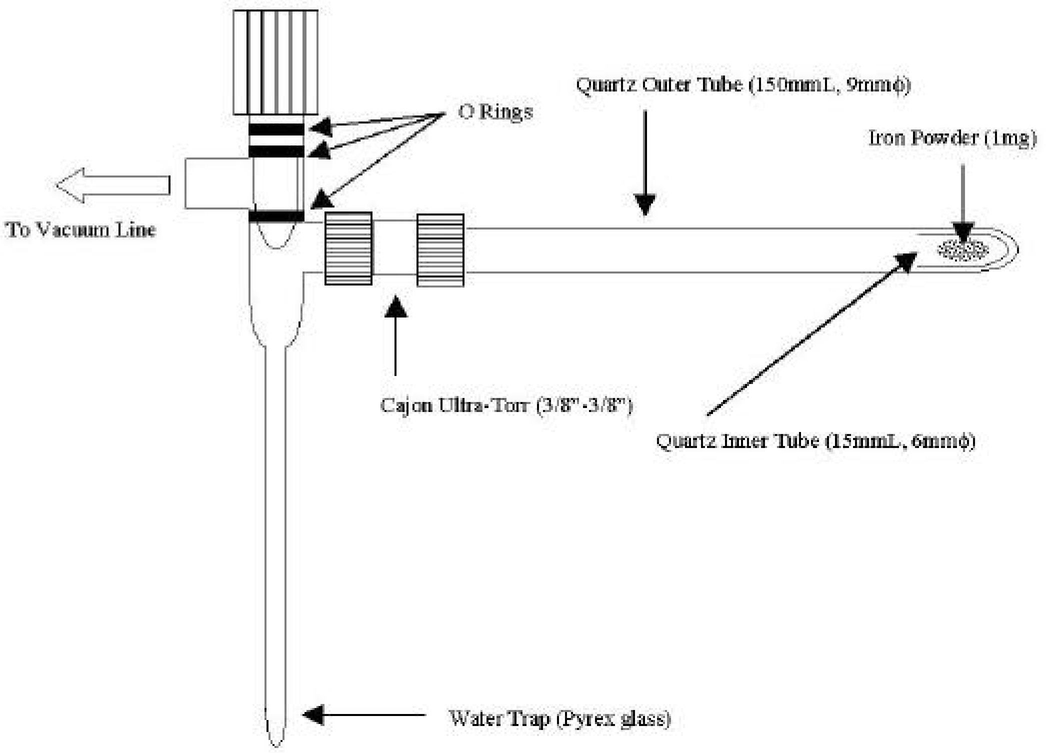

Figure 1 Reaction tube for graphite reduction. Outer reaction tube and inner tube are made from quartz glass.

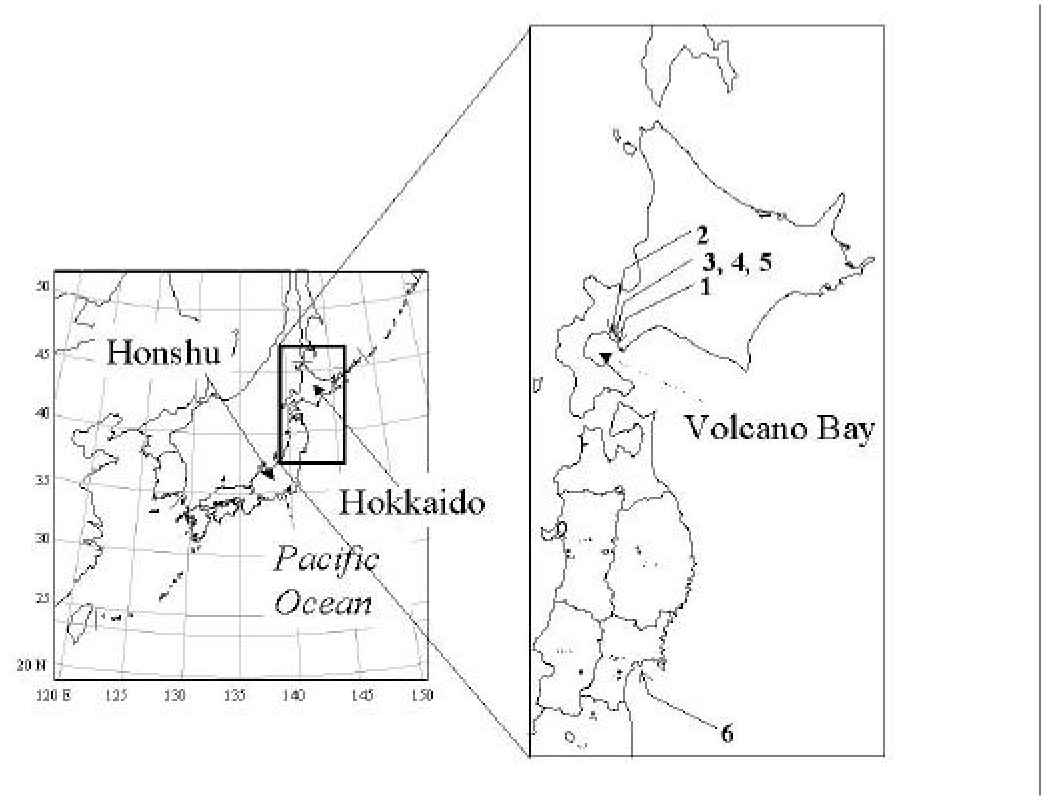

Figure 2 Location of archaeological sites (1: Kitakogane, 2: Takasago, 3: Minami Usu 6, 4: Minami Usu 7, 5: Oyakotsu, 6: Satohama).

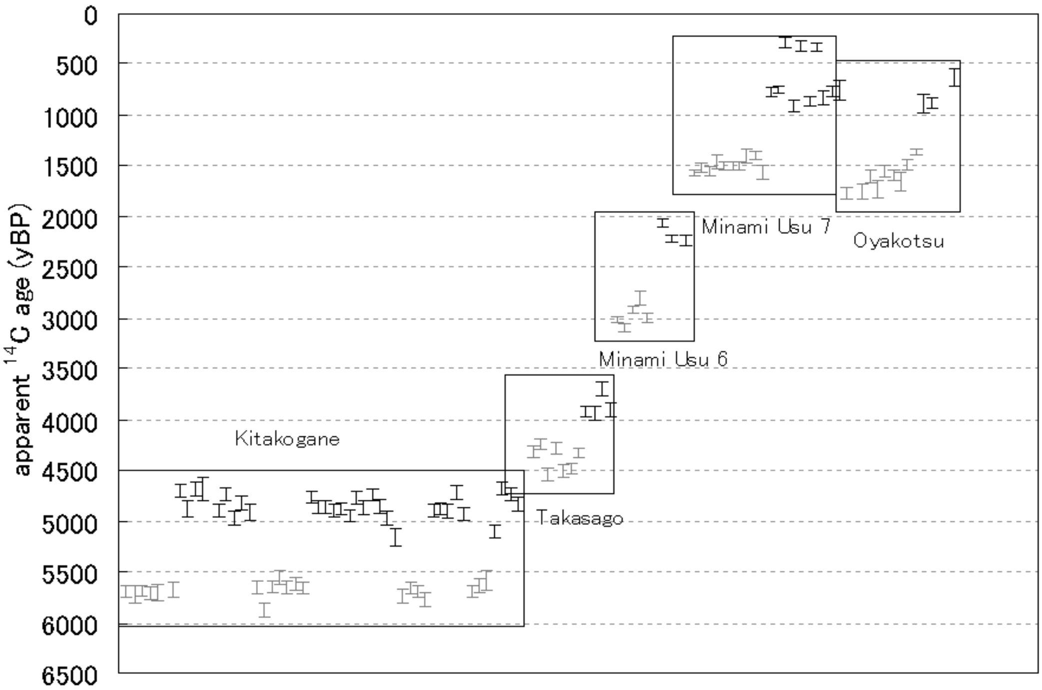

Figure3 Results of radiocarbon measurement of deer and fur seal bones. Deer bones are illustrated by black symbols and fur seal bones are gray symbols.

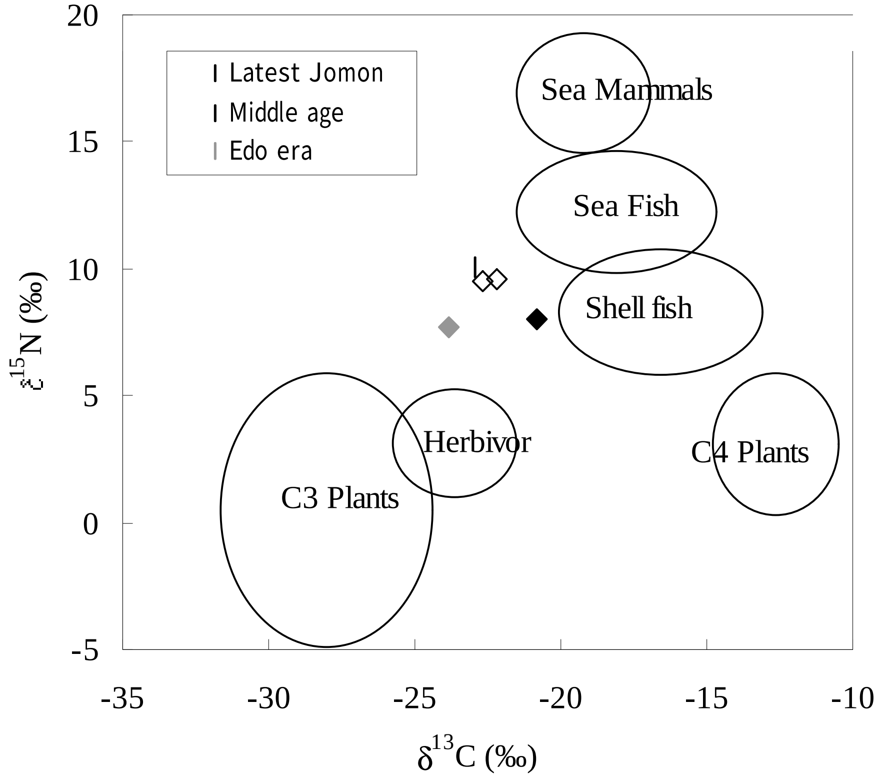

Figure 4 Reconstructed carbon and nitrogen isotope ratios in dietary protein of the Satohama population.

Ages of the Holocene former shoreline deduced from emerged erosional landforms along the southern coast of the Boso Peninsula, Central Japan

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Introduction

Holocene marine terraces are developed around the southern end of the Boso Peninsula, caused by seismic upheavals with great earthquakes occurred near the Sagami Trough. In order to study the detailed history of seismic crustal movements in this area, it is necessary to determine the past altitudes and ages of the emergence by measuring those of the strict evidences of the former shoreline, such as sea caves and notches. This study investigated the age of former shoreline based on AMS Radiocarbon (^{14}C) dating of *in situ* fossils from the retreat points in sea caves which are located on the southern coast of Tateyama Bay, southern end of the Boso Peninsula.

Investigation area

Holocene marine terraces along the coast of the south end of the Boso Peninsula have been studied in detail and classified into four levels; Numa I (age: 6150 years BP, 7150 calBP, altitude = 23.5 m), Numa II (4300 yBP, 4950 calBP, 17.5 m), Numa III (2850 yBP, 2950 calBP, 12～13.5 m) and Numa IV(247 yBP, AD1703, 5.5 m) from higher to lower [1, 2].

The investigated area in this study is Koyatsu area on the south coast of Tateyama Bay, Tateyama City (Figure 1). This hilly area was drowned like rias coast to form Paleo Koyatsu Bay during the maximum phase of the Holocene transgression stage (so called the “Jomon transgression”). In innermost part of the bay, famous “Numa coral bed” is located [3]. Sedimentation has not been active in this bay so that each terrace is not developed typically but erosional shoreline topographies are found frequently (Figure 2). Six fossil samples taken from one of sea caves (KO-3) and 8 coral samples from Numa coral bed and one from a wave-cut bench were measured for ^{14}C dates (Figure 3).

Results

At the result of detailed geomorphologic surveys and air-photo interpretation, the classification of Numa terraces are modified as follows; Numa II and III are subdivided into IIa, IIb, IIIa and IIIb, based on the existence of small cliffs. Consequently, the marine terraces in Koyatsu area are classified into six levels, which were named Koyatsu I, Koyatsu IIa, Koyatsu IIb, Koyatsu IIIa, Koyatsu IIIb and Koyatsu IV terraces.

Uplifted shoreline topographies indicating the former shoreline, such as sea erosion caves, were found at 25–26 m by the wave-cut bench about 5 m higher than the Koyatsu IIa bench. Five sea erosion caves were found in Paleo Koyatsu Bay at the same level of 25-26m above sea level, corresponding to Koyatsu I (Numa I). Erosional topographies such as notches or wave-cut benches were also found around the level of 21-22 m (Koyatsu IIa), 19 m (Koyatsu IIb) and 11 m a.s.l. (Koyatsu IIIa). On the surface of the erosional topographies, burrows of boring shells, marine molluskan shells and corals were observed (Figure 4).

One of the highest sea erosion caves (Koyatsu I), KO-3 cave is largest, whose size is10 m deep, 4 m wide, and 4.3 m high. The retreat point found in the innermost part of the cave is 25.3 m a.s.l. and small fossils such as coral (*Caryophyllia* sp.), molluskan shells (*Anomia* and boring shells) and tube worms were attached abundantly to the wall of hard tuffaceous mudstone. Those were concentrated into narrow zone of 80 cm above the retreat point, but only burrows of boring shells are distributed up to 27.3m. However, no fossils were found below the narrow fossil zone. The AMS measurements showed the ages between 5650 calBP and 5450 calBP for six fossil samples, KO-C1~6 (Figure 5) which were corals and molluskan shells taken from the retreat point in KO-3 cave (see Figure 4). In order to compare with ages of the KO-3, 8 samples (KO-N1 ~ 8) were collected from the Numa coral bed. Furthermore, one coral sample was collected from a wave-cut bench (KO-T1) on Koyatsu IIb located at 14.3 - 15.4 m a.s.l. in the inner part of the bay. The results shows the ages between 8100 calBP and 7600 calBP were for 7 coral samples and one molluskan shell (*Spondylus sp*.) taken from Numa coral bed, and 6455 ~ 6350 calBP for one coral sample (KO-T1) from a wave-cut bench of Koyatsu IIb.

Discussion and conclusion

Five upheaved erosion caves were found at the same level as the evidence of Holocene highest shoreline. One of them, KO-3 cave, was surveyed in detail. The results indicate that the Holocene highest shoreline was situated at 25.3 m a.s.l., and the age was 5650-5450 calBP by the AMS^{14}C dating of *in situ* fossil samples from the retreat point of the cave. This suggests that the emergence age of the highest shoreline was just after 5650-5450 calBP. The results of coral and molluskan shell samples collected from "Numa coral bed" show a time difference as large as 2000 ~ 2500 years between the formation of Numa coral bed ranging from 8100 to 7600 calBP and the emergence of the highest former shoreline(Koyatsu I). Matsushima [4] suggested that the water depth of the "Numa coral bed" was a few meters to 20 meters. Hence, it is possible that the sea level rose a few meters during the time from "Numa coral bed" to the highest former shoreline.

In the previous studies, Numa I terrace has been inferred to have been formed about 7150 calBP, being much older than Koyatsu I highest shoreline studied in this study. However, the ages reported in previous studies were not based on the direct evidences for the emergence. Many dating data in previous studies were derived from samples collected from the marine terrace deposit. However, the height of Numa I terraces in the area of Tateyama Bay and that of the former erosional shoreline at Koyatsu I showed nearly closed levels. This suggests strongly that the time of the emergence of Numa I terrace and the highest erosional shoreline of Koyatsu I were formed under the same highest sea level, and might be emerged at the same time. In conclusion, this study suggested the importance of precise measurements of altitudes and emergence ages on the uplifted erosional shoreline topographies in order to interpret the seismic crustal movements in this area.

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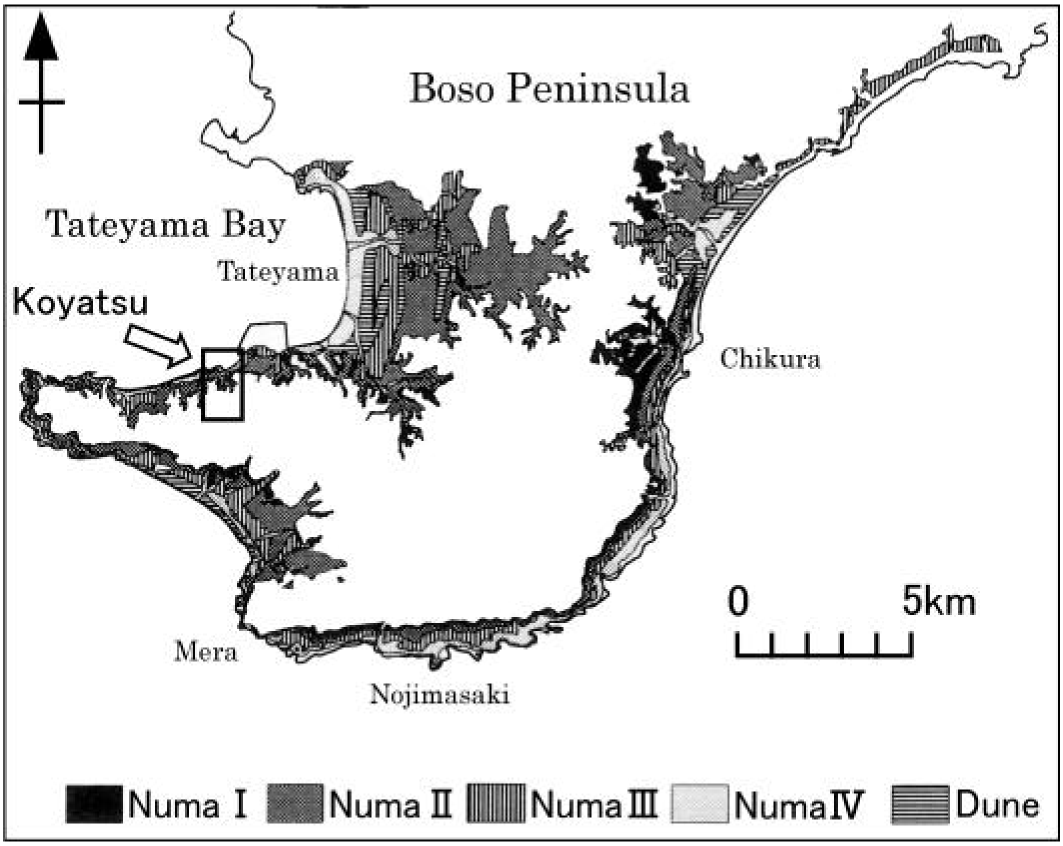

Figure 1 Location of the investigation area and distribution of Numa Terraces on the southern end of the Boso Penninsula (After Fujiwara et al. [5].

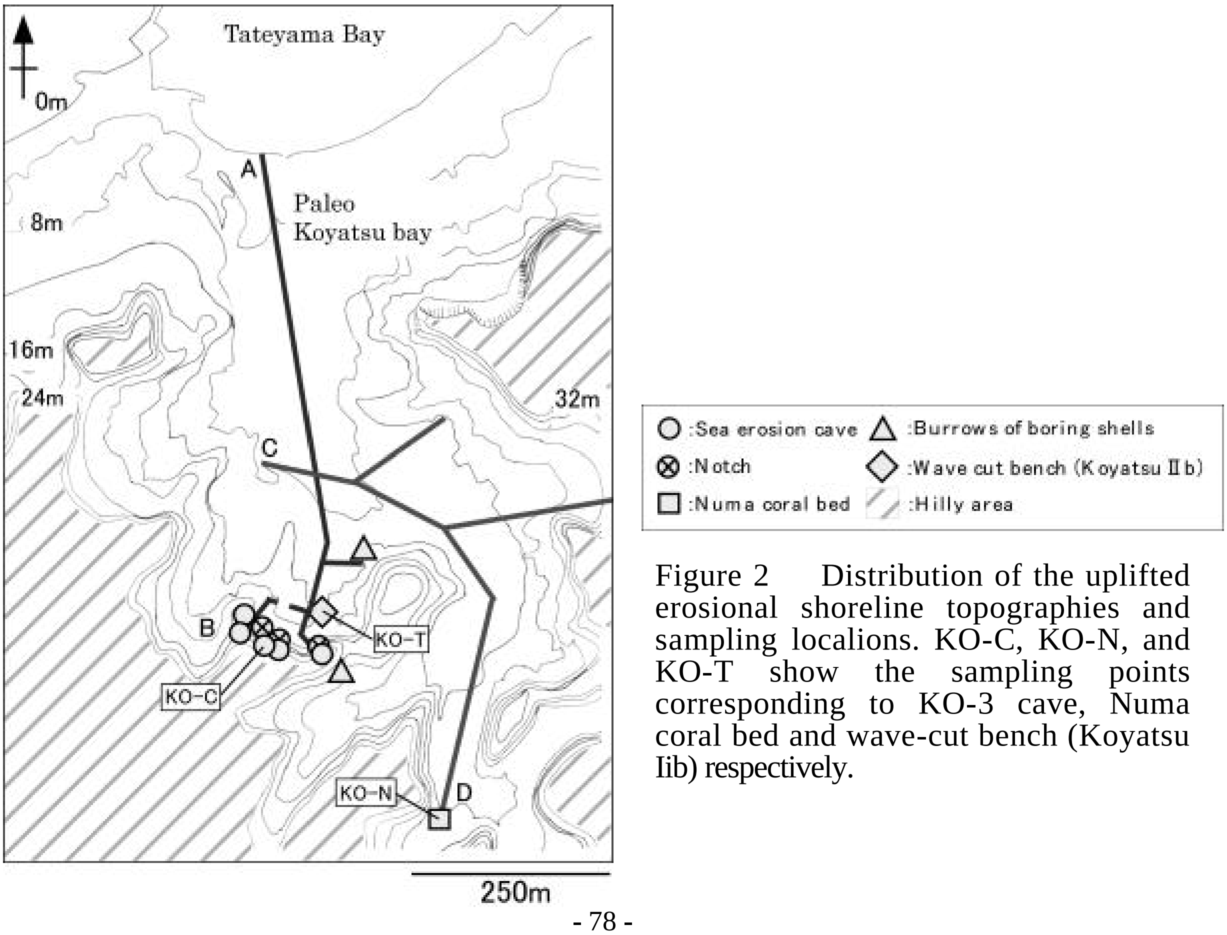

Figure 2 Distribution of the uplifted erosional shoreline topographies and sampling localions. KO-C, KO-N, and KO-T show the sampling points corresponding to KO-3 cave, Numa coral bed and wave-cut bench (Koyatsu Iib) respectively.

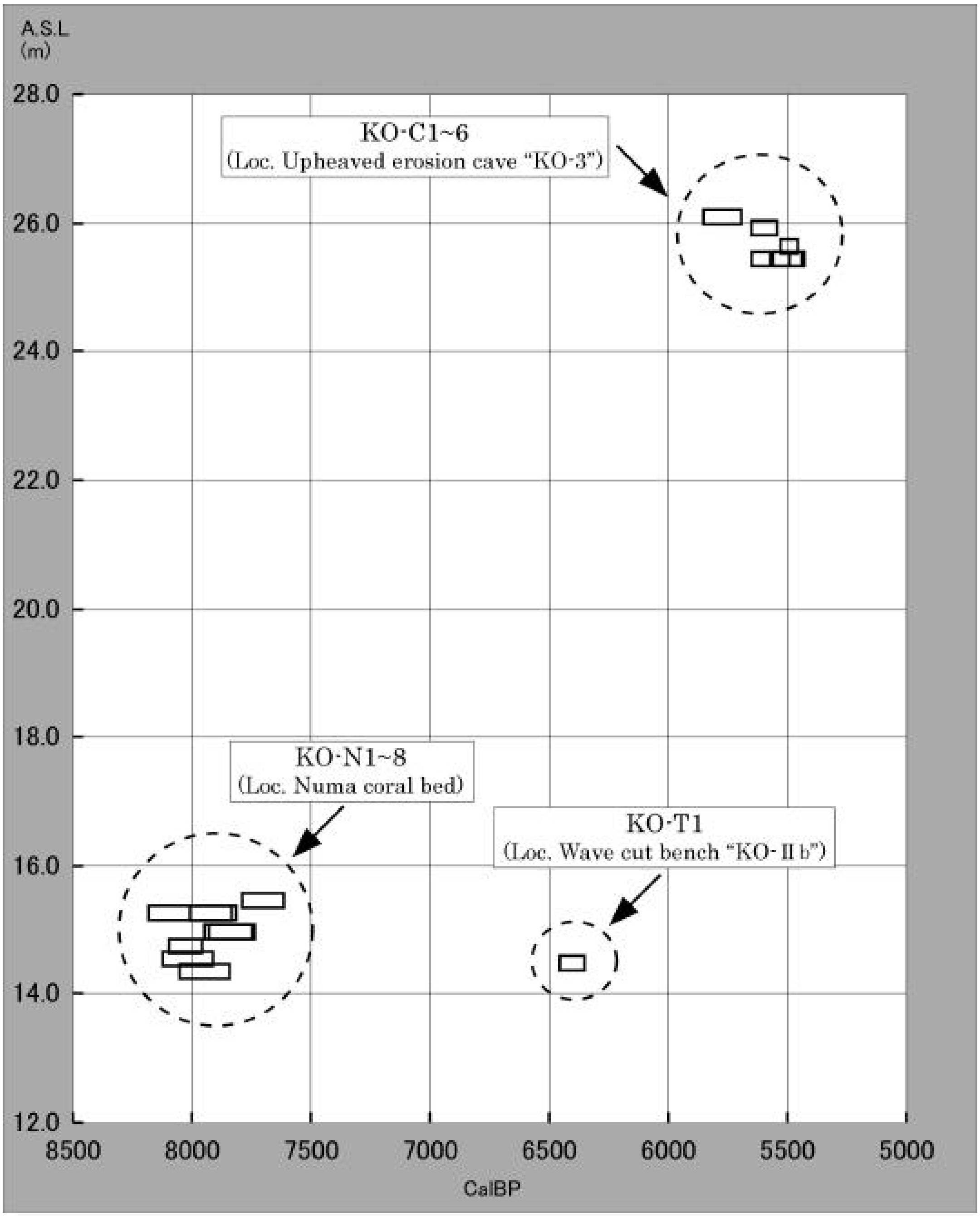

Figure 3 AMS Radiocarbon ages determined in this study.

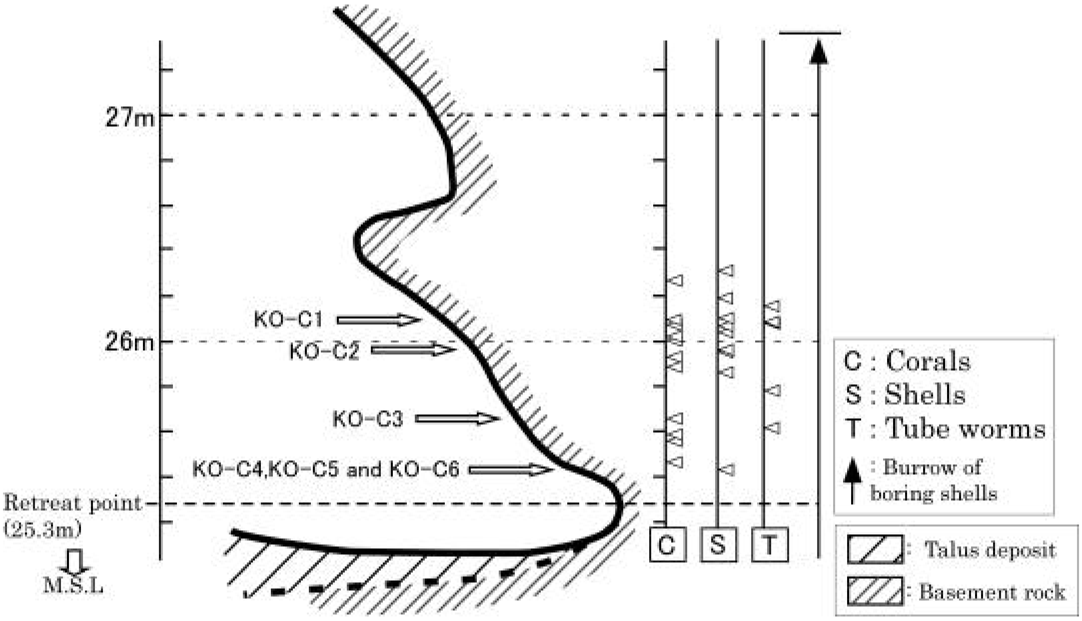

Figure 4 Geomorphic profiles of emerged erosional landforms and Koyatsu terraces, in Koyatsu area. Vertical distribution of the uplifted erosional shoreline topographies and fossils found in this study are shown by horizontal triangles on the right. Koyatsu terraces are classified into “IIa” to “IV” and “T” shows the Taisho 1923 raised bench.

Figure 5 Profile of the inner most part of the KO-3 cave, showing the retreat point. Horizontal arrows (KO-C1~6) show sampling points for AMS ^{14}C dating. Altitudinal distribution of fossils such as corals, shells and tube worms and the range of burrows of boring shells is shown .

NIES-TERRAの研究活動状況

＜関連学会、ワークショップ等開催＞

1. 1996年9月：加速器分析施設完成記念シンポジウム開催(国環研大山ホール)
2. 1997年7月：第10回「タンデム加速器及びその周辺技術の研究会」開催（国環研大山ホール）
3. 1999年1月：「加速器質量分析法の新展開に関する国際ワークショップ（International Workshop on Frontiers in Accelerator Mass Spectrometry）」開催（国環研大山ホール）

＜刊行物＞

1. Annual Report of NIES-TERRA Vol .1 (1998) F-112-‘98/NIES「国立環境研究所タンデム加速器分析施設完成記念シンポジウム『加速器質量分析法の展望』講演集」p.41
2. Annual Report of NIES-TERRA Vol. 2 (1998) F-113-‘98/NIES「第１０回タンデム加速器及びその周辺技術の研究会報告書」 p.134.
3. “Proceedings of the International Workshop on Frontiers in Accelerator Mass Spectrometry”, p. 265 (1999).

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