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Decadal- to centennial-scale variability of sedimentary biogeochemical parameters in Kagoshima Bay, Japan, associated with climate and watershed changes

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Abstract

In order to detect responses of primary productivity in Japanese coastal embayments to climate and watershed changes for the last 500 years, we unraveled sedimentary records of $\delta^{13}C$, $\delta^{15}N$, TOC, TN, and C/N ratio in the north basin of Kagoshima Bay (KB). Based on principal component analysis of these geochemical data, primary component (PC) 1 that explains 65% of the total variance within all the geochemical parameters was identified. The records of $\delta^{13}C$, $\delta^{15}N$, TOC, and TN having high loadings on the PC1 axis showed centennial-scale variations (low levels during AD 1595–1725 and high levels during AD 1725–1860) and a shift (AD 1725). A comparison between our records and previous studies on the biogeochemical processes suggests that the factor responsible for fluctuations in $\delta^{13}C$, $\delta^{15}N$, TOC, and TN is likely to be the changes in primary productivity in the north basin of KB rather than other factors. C/N values, which have high loadings on PC2, are possibly related to input of C_3 land plants to the north basin of KB, suggesting changes in the surrounding forest environments.

The centennial-scale decrease in primary productivity that is represented by the TOC record is coincident with a temperature decrease associated with the Little Ice Age, suggesting that the primary productivity in the north basin of KB might have been influenced by global or Northern Hemispheric-scale climate changes.

Keywords: stable carbon and nitrogen isotope; C/N ratio; primary productivity; climate and watershed changes; Little Ice Age; Kagoshima Bay

1. Introduction

Sedimentary records in estuaries and coastal embayments have demonstrated that marine environments and productivity have been significantly influenced not only by human impacts over the last decade to centuries (e.g., Zimmerman and Canuel, 2002; Bratton et al., 2003; Smittenberg et al., 2005) but also by climate changes on decadal to centennial timescales (Willard et al., 2003; Sepúlveda et al., 2005; Kuwae et al., 2006a). These studies have highlighted the fact that the long-term variability of the marine environment and productivity in estuaries and coastal embayments is closely related to human impacts and climate changes. However, these studies are still restricted to some regions, and further case studies in different marine settings are necessary for a general understanding of processes driving the long-term variability of coastal environments and productivity.

In Japanese coastal embayments, there has been only one paleoceanographic study of the response of marine environments and productivity to climate changes on decadal timescales. This study of the Bungo Channel demonstrated the response of diatom productivity to oceanic dynamics in the

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Kuroshio front region associated with the Pacific Decadal Oscillations (Kuwae et al., 2006a). This study emphasized the importance of decadal-scale ocean climate variability of the Kuroshio region in the long-term variability of primary productivity in Japanese coastal embayments. However, it is still unclear how primary productivity responds to the century-scale variability of climate, as detected from the $\delta^{13}C$ in the tree rings of a giant 2000 yr old Japanese cedar growing on Yakushima Island, southern Japan (Kitagawa and Matsumoto, 1995).

In order to detect changes in the estuary and embayment environment and productivity, the biogeochemistry of stable isotopes ($\delta^{13}C$ and $\delta^{15}N$), total organic carbon (TOC), total nitrogen (TN), and C/N ratio has been previously employed (e.g., Zimmerman and Canuel, 2002; Bratton et al., 2003). In coastal embayments in Japan, downcore records of biogeochemistry are scarce (Nakai et al., 1982) and the lack of studies on paleoceanographic processes is evident.

In this study, we attempt to reconstruct long-term records of $\delta^{13}C$, $\delta^{15}N$, TOC, TN, and C/N ratio of the core samples collected from the north basin of Kagoshima Bay (KB), which is one of the largest bays of Japan. Furthermore, we discuss the factors controlling variations of the biogeochemical parameters and examine the relationship between the primary production or biogeochemical processes in the north basin of KB and centennial-scale climate changes or watershed changes.

2. Regional settings

Kagoshima Bay, located in southern Kyushu, Japan, opens southward with a length of approximately 75 km and a width of approximately 25 km (Fig. 1). The bay consists of three basins: bay mouth, central basin, and north basin. The north basin, our study area, is connected to the central basin by a narrow passage which forms a 50 m deep sill. Two main rivers, Amori and Beppu, flow into the north basin; their drainage areas are 401 and 181 km^2, respectively. The north basin is rather flat-floored and mostly about 140 m deep, with a small area in the eastern part where water depth is up to 200 m. During the three years 1975–1977, water temperature varied 15–28 °C at depths of 0–10 m, but below 150 m was more stable 14–18 °C (Oki, 1989). Salinity at depths <25 m shows a wide seasonal fluctuation; the range is 23.3 to 32.7‰ in summer, 33.0 to 34.3‰ in winter. The lower salinity values reflect run-off from seasonal summer rainfall (Oki, 1989). However, the salinity below 150 m is almost stable, ranging from 33.5 to 34.3‰. The dissolved oxygen concentrations at the bottom of the depressed basin in the eastern part of the north basin of KB are low (minimum value: 0.28 mL/L), except during the coldest season (maximum value: 3.7 mL/L) (Oki, 1989). The higher coldest season values are due to overturn of the water mass. The mean annual, mean summer (July and August), and mean winter (January and February) temperatures around the bay during the interval 1900–1999 are 17.1 °C, 23.3 °C, and 7.4 °C, respectively (Kagoshima; Japan Meteorological Agency, 1999). The annual, summer (May to October), and winter (December to March) precipitations are in the approximate ranges 1610–4020, 760–3260, and 200–750 mm, respectively (Kagoshima; Japan Meteorological Agency, 1999).

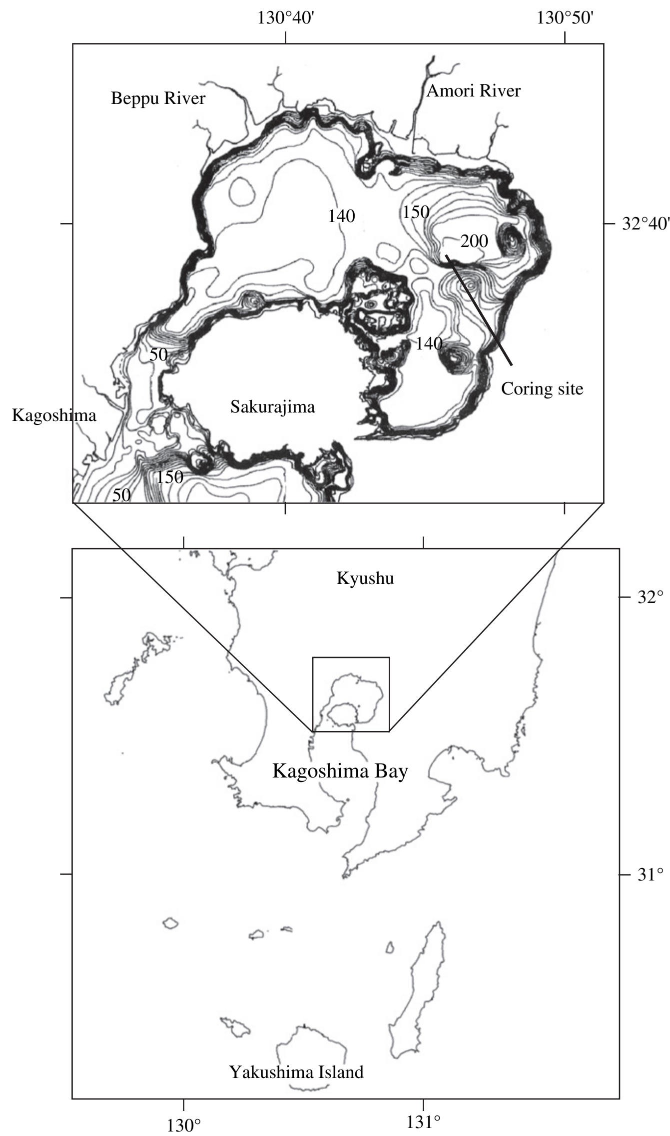

Fig. 1. Study area in Kagoshima Bay, which is located in southern Kyushu, Japan.

3. Methods

Sediment cores were collected in March 2004 at the depressed area in the north basin of KB at a water depth of 200 m (lat. 31°39.91′ N, long. 130°45.59′ E; Fig. 1). The cores were collected using a 4-m piston corer during a cruise of R/V Hakuho-Maru. Sediment core Kg 1 recovered the total length of 332 cm.

The Kg 1 sediment consisted mainly of pale gray or greenish pale gray silty clay or silt (Fig. 2). The sediment was intercalated by seven tephra layers at a depth of 3–18 cm, at 26–40 cm, at 44–55 cm, at 63–67 cm, at 117–120 cm, at 158.5–166.5 cm, and at 219–221.5 cm. These tephra layers

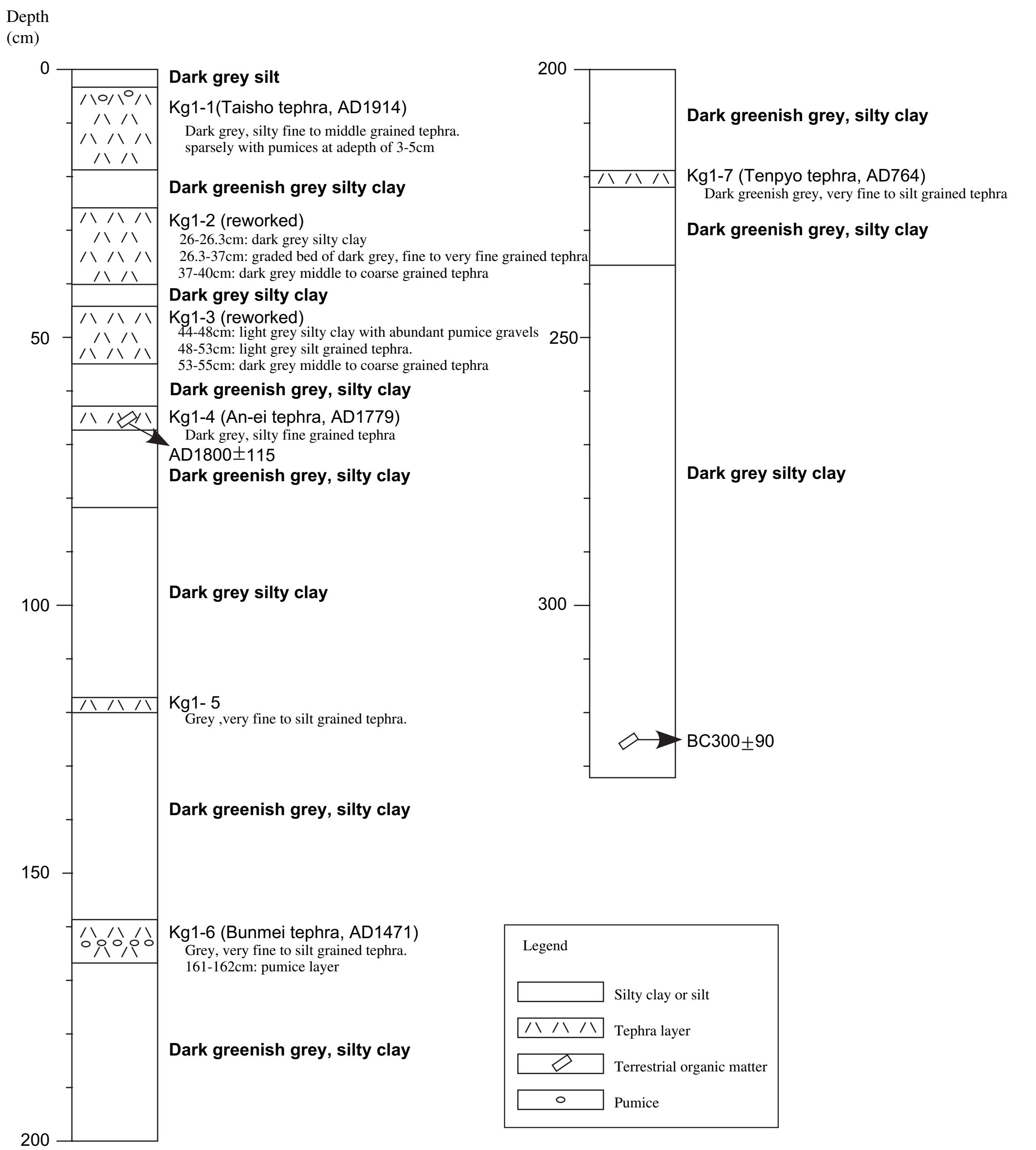

Fig. 2. Lithology of the Kg 1 piston core. The figure shows tephra layers labeled from Kg1−1 to Kg1−7 and ^{14}C dating data indicated by arrows.

were labeled from Kg1−1 to Kg1−7, respectively. Fragments of pumice were found in Kg1−1 and Kg1−6. The silty clay sediments of Kg 1 core did not show any seasonally formed lamination despite the low DO values at the bottom of the depressed area of the north basin during most of the year.

The core samples were sliced vertically at intervals of 0.5 cm; samples at intervals of 2 cm (except for the tephra and reworked layers) were employed. All the samples were then frozen at −20 °C, subsequently thawed and dried at 60 °C, and ground to a fine powder. They were then acidified with 1 M HCl solution for a day to eliminate any carbonates, dried again, and homogenized.

In order to examine the isotopic values and the C/N ratios of the end members (phytoplankton, zooplankton, secondary consumer, and macrobenthos) of sedimentary organic materials, living organisms were collected from KB. Particulate organic matter (POM) (0.7−100 μm) that was collected at a water depth of 5 m by a pump was substituted for the phytoplankton. The POMs were filtered onto precombusted GF/F filters after being sieved with a 100-μm mesh sieve. We also sampled zooplanktons in the layer corresponding to the depth range 0−150 m by the vertical haul of a 330-μm mesh plankton net (Norpack); macrobenthos was sampled using a grab sampler. A species of copepod, *Sagitta* spp., and *Polychaeta* sp. (macrobenthos) were picked up immediately after the samples were collected and then frozen at −20 °C. According to the procedures of Takai et al. (2002), samples were dried at 60 °C and ground to a fine powder and lipids were removed with chloroform/methanol (2:1) solution. The samples were exposed to the vapor of concentrated 12 N HCl for a day to eliminate any carbonates and were then dried on a hot plate.

The stable isotope ratios of carbon ($\delta^{13}C$) or nitrogen ($\delta^{15}N$), TOC, and TN in the bulk core samples, POMs, and living organism samples were measured using a mass spectrometer (ANCA-SL, PDZ Europa Ltd) at the Center for Marine Environmental Studies, Ehime University, Japan. The isotope ratios of carbon and nitrogen were expressed in per mil deviations from the standard by the following equation.

$$\delta^{13}C,\ \delta^{15}N = \left(R_{\text{sample}}/R_{\text{standard}} - 1\right) \times 1000$$

where $R = {}^{13}C/{}^{12}C$ or ${}^{15}N/{}^{14}N$. Pee Dee Belemnite (PDB) limestone carbonate and atmospheric nitrogen (N_2) were used as standards for the carbon and nitrogen isotopic ratios, respectively. The analytical precision was better than $\pm 0.01‰$ and $\pm 0.19‰$ for $\delta^{13}C$ and $\delta^{15}N$, respectively. L-histidine ($\delta^{15}N = -7.81‰$) was used as the reference material.

4. Age determination

AMS ^{14}C dating on terrestrial organic materials (small branches) was conducted by the Institute of Accelerator Analysis Ltd., Japan. The radiocarbon ages (Table 1) were reported using the Libby half-life of 5568 yr, following the conventions defined by Stuiver and Polach (1977), and were converted into calendar ages using INTCAL98 calibration data (Stuiver et al., 1998). The maximum and minimum calibrated age ranges (2 sigma) obtained from the ^{14}C calibration data set are shown as age errors in Table 1.

Some of the tephra layers have potential use in chronostratigraphic correlation, especially the two layers with pumice fragments. According to Aramaki (1975), the sediments in the north basin of KB are intercalated by two pumice layers at 5–15 cm and 135–165 cm. They were identified as the Taisho pumice layer (AD 1914) and the Bunmei pumice layer (AD 1471), respectively, which have their origin from Sakurajima volcano (Fig. 1). In core Kg1, an upper layer occurs at 3–5 cm and a lower layer at 161–162 cm (Fig. 2). The two tephra layers with pumice fragments in core Kg1, Kg1–1 (3–18 cm) and Kg1–6 (158.5–166.5 cm), were lithologically and chronologically correlated with the two pumice layers reported by Aramaki (1975) (Table 1; Fig. 2).

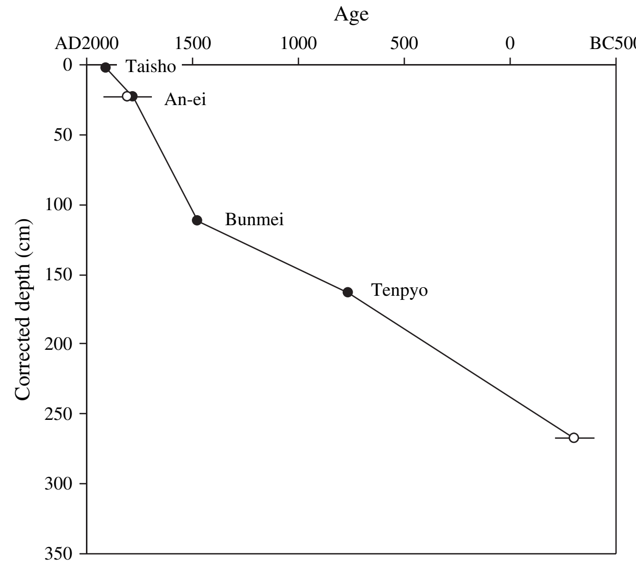

Fig. 3. Age model of the Kg 1 core. Solid circles indicate the dates and the depths of the tephra layers, which were formed by historical volcanic eruptions of Sakurajima Volcano. Open circles indicate plots of the AMS ^{14}C dating of the terrestrial organic materials. Horizontal bars indicate the standard error (2 sigma).

There are additional time markers in the Kg 1 core. The ^{14}C age of the sample in Kg1–4 was shown to be AD 1800 ± 115 (Table 1; Fig. 2), which is consistent with the inference that Kg1–4 is An-ei tephra (AD 1779). An-ei eruption was the famous major volcanic eruption that occurred between the Bunmei and Taisho. Furthermore, Kg1–7 possibly corresponds to the layer formed during the Tenpyo eruption of AD764. This interpolation is based on the time controls of the Bunmei tephra, AD1471, and the ^{14}C age of BC300 ± 90 at a core depth of 325 cm in Fig. 3. We assumed that Kg1–2 and Kg1–3 were reworked layers because they had layers with graded structures, which may have been formed by turbidity currents from the western adjacent slope (Fig. 2) when local earthquakes and so on occurred. This interpretation is supported by no historical record of major volcanic activities of Sakurajima and the other volcanoes around the north basin of

Table 1
Depths and ages of the tephra layers identified as historical Sakurajima eruptions and the AMS ^{14}C dating data of terrestrial organic materials (small branches). Radiocarbon ages were reported using the Libby half-life of 5568 yr and converted into calendar ages using the INTCAL98 calibration data (Stuiver et al., 1998). The maximum and minimum calibrated age ranges (2 sigma) obtained from the ^{14}C calibration data set are shown as age errors

Tephra layers and ^{14}C dating	Historical volcanic eruption	Depth in the core (cm)	Thickness (cm)	Corrected depth (cm)	Age
Kg1–1	Taisho	3.0–18.0	15.0	3.0	AD 1914
Kg1–2	Reworked	26.0–40.0	14.0	11.0	
Kg1–3	Reworked	44.0–55.0	11.0	15.0	
Kg1–4	An-ei	63.0–67.0	4.0	23.0	AD 1779
Kg1–5	Unknown eruption	117.0–120.0	3.0	73.0	
Kg1–6	Bummei	158.5–166.5	8.0	111.5	AD 1471
Kg1–7	Tenpyo	219.0–221.5	2.5	164.0	AD 764
^{14}C		63.0–67.0		23.0	AD 1800 ± 115
^{14}C		325		267.5	BC 300 ± 90

the KB during the period between An-ei (AD 1779) and Taisho (AD 1914) volcanic eruption.

Based on these time markers and ^{14}C dating (Table 1), the age model of the Kg 1 core is shown in Fig. 3. In this model, tephra and reworked layers were excluded from the core depth, and Kg1–4 (AD 1779) was employed as the time control instead of the ^{14}C age (AD 1800 ± 115) of Kg1–4 because of the large error in the latter. The sedimentation rates of sediments in the layers Kg1–1 (Taisho tephra) to Kg1–4 (An-ei Tephra), and Kg1–4 to Kg1–6 (Bunmei tephra) showed 0.15, and 0.29 cm yr^{-1}, respectively. The time resolution of the geochemical records corresponds to 7–13 years except at depths of 24–43 cm (35 years).

5. Results

5.1. Biogeochemical records

Fig. 4 shows the records of δ^{13}C, δ^{15}N, TOC, TN, and atomic C/N ratios during the interval AD 1550–1925. The δ^{13}C record showed variations from −24 to −21.6‰; values higher than −22.7‰ were revealed during the intervals AD 1550–1595, 1725–1860, and 1910, while those lower than −22.7‰ corresponded to AD 1595–1725, 1860–1890, and 1925. The δ^{15}N record showed variations in the range 0.9–5.4‰; values lower than 3.5‰ were revealed the most during AD 1595–1725, and those higher than 4.1‰ after AD 1725 except for AD 1760 (there is no data during AD 1550–1580 because of a shortage of samples. Further, there are no pertaining to nitrogen concentration and C/N ratio). The TOC ranged from 0.5 to 2.4 and showed values lower than 1.4 during AD 1595–1725; it showed values higher than 1.4 during AD 1550–1595 and after AD 1725. The TN ranged from 0.06 to 0.22% and showed values lower than 0.10% during AD 1595–1725; it showed values higher than 0.10% for 1594 and after AD 1725. The C/N ratio ranged from 10.3 to 14.8, showing values higher than 14 during AD 1860–1890 and 1925 and values lower than 14 during AD 1594–1860 and 1890–1915.

In order to detect the factors responsible for the fluctuating variations of these biogeochemical parameters and to conduct zonation of the biogeochemical records, we performed principal component (PC) analysis of the temporal variations in these data during the interval AD 1594–1925 (Fig. 5). The results captured two main patterns of variability in most of the data. PC1 explained 65% of the total variance within all the geochemical parameters; together with PC2, this value rose to 91%. The loadings of TOC, TN, δ^{13}C, and δ^{15}N on the PC1 axis were high (0.96, 0.97, 0.79, and 0.85, respectively), but that of C/N ratio was low (0.18). In contrast, the loadings of C/N ratio and δ^{13}C on the PC2 axis were high (0.97 and −0.55, respectively), but those of δ^{15}N, TOC, and TN showed low values (0.23, 0.14, and −0.06, respectively). On the basis of the distribution of sample PC scores on the first and second PC axes, three sectors were identified (Fig. 5). Sector a (1725–1860, 1890–1915) is characterized by high PC1 (0.5–1.5) and low PC2 (<1.1) values, Sector b (1595–1725) by low PC1 values (< − 0.3), and Sector c by high PC1 (>0) and high PC2 (>2.2) values. Although the sample of AD 1594 is plotted between Sectors a and b, it possibly belongs to Sector a according to the observation that the values of TOC and δ^{13}C of the samples before AD 1595 (Fig. 4a,c) are apparently higher than those of the samples of Sector b (1595–1725) and similar to those of Sector a (1725–1860, 1890–1915). On the basis of these categories, the geochemical records are characterized by 6 stages: 1550–1595, 1595–1725, 1725–1860, 1860–1890, 1890–1915, and 1925 (Fig. 4).

5.2. End members of bulk organic materials

In order to examine δ^{13}C, δ^{15}N and C/N ratios of the end members of bulk organic materials in the core samples, we measured these parameters for the primary producers (POMs), primary consumers (copepod species), secondary consumers (*Sagitta* spp.), and macrobenthos (*Polychaeta* sp.) (Table 2). δ^{13}C, δ^{15}N, and C/N ratios of the POMs in KB had the values −21.6 to −21.0‰, 6.8–7.6‰, and 6.5–8.0, respectively. The values of δ^{13}C, δ^{15}N, and C/N in the copepod species in KB showed −18.4‰, 10.1‰, and 4.1, respectively; the values in *Sagitta* spp., −16.6‰, 12.7‰, and 3.8; and those in *Polychaeta* sp., −18.6‰, 9.2‰, and 4.0.

Fig. 6 shows plots of δ^{13}C and δ^{15}N of the end members and those previously reported (Takai et al., 2002; Okuda et al., 2004). According to the theory of food-chain-related fractionation (DeNiro and Epstein, 1978; Minagawa and Wada, 1984), the values of POMs in KB, which represent the values of primary producers, are inconsistent with the values of primary and secondary consumers and macrobenthos (possibly POM-derived seston feeder) if it is assumed that they fed the POMs. In other words, according to the stepwise trophic level enrichment in δ^{13}C and δ^{15}N (1‰ and 3.4‰, respectively; DeNiro and Epstein, 1978; Minagawa and Wada, 1984), the stable isotopic position of the primary producer in the food chain relating to *Sagitta* spp., copepod species, and *Polychaeta* sp. should be located at the position corresponding to approximately −19‰ of δ^{13}C and 6‰ of δ^{15}N (thin circle in Fig. 6). However, the position is different from the observed values (POMs) by 2–3‰ in δ^{13}C. The difference between the hypothetical values of POMs and the observed values may reflect the large temporal variability of the δ^{13}C values (e.g., Takai et al., 2002; Okuda et al., 2004) and the anomalous values of samples in a limited part of the waters (Cloern et al., 2002). In other words, the values of the observed POMs might be different from those of the POMs that consumers had been preying before the sampling; alternatively, unknown δ^{13}C values of POMs in deep layers, which are the mainly preyed layers, might be different from those of the surface POMs in this study. In lakes, since the δ^{13}C values of phytoplankton largely vary temporally and spatially, δ^{13}C values of zooplanktons, which represent temporally/spatially averaged values, have been employed in order to estimate base line values of δ^{13}C in food chains in individual lakes (e.g., Vander Zanden and Rasmussen, 1999).

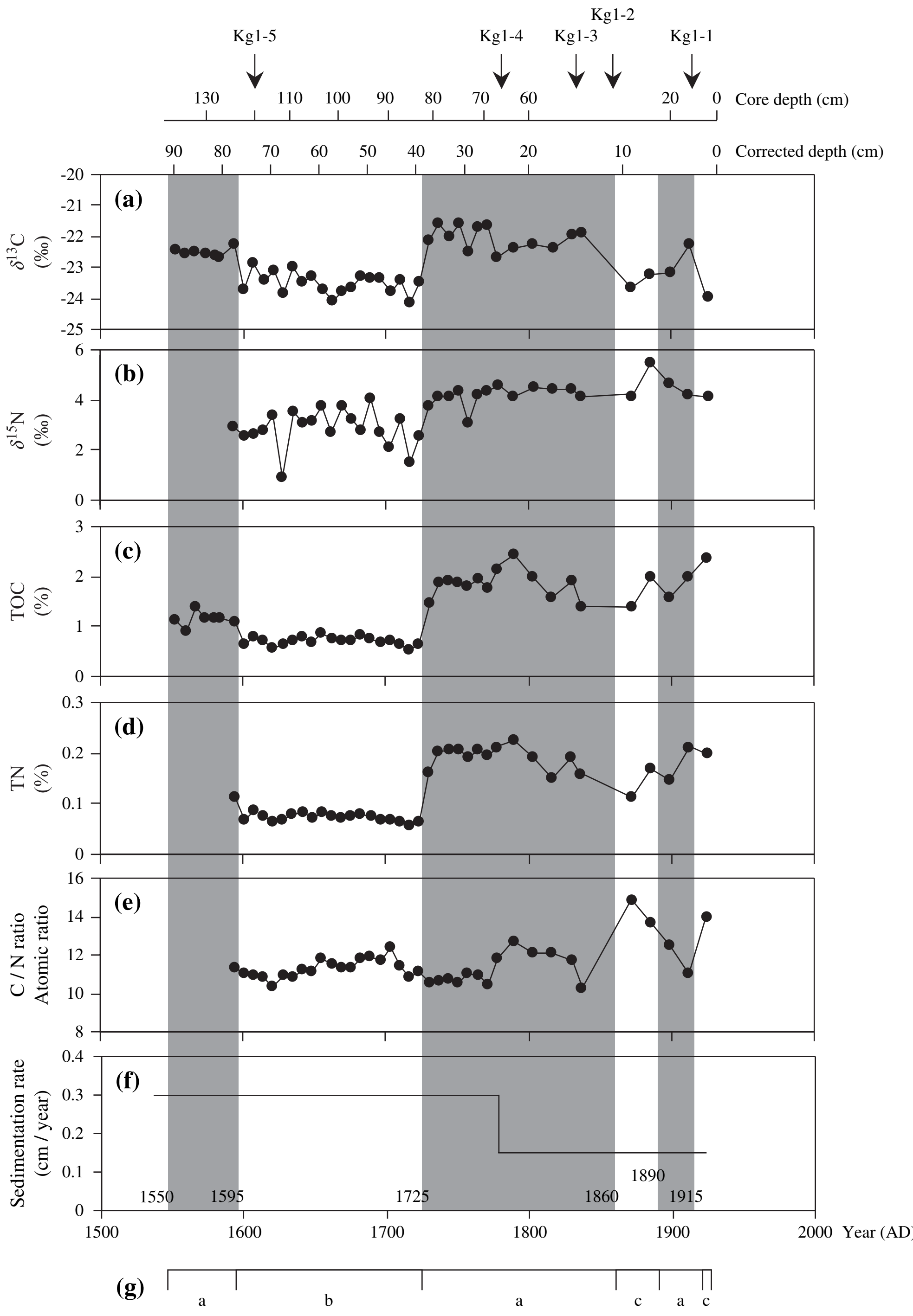

Fig. 4. The biogeochemical records of the Kg 1 core over the past 500 years. The figure shows $\delta^{13}C$ (a); $\delta^{15}N$ (b); TOC (c); TN (d); atomic C/N ratio (e); and sedimentation rate (f). Arrows in the top of figure indicate the tephra layers or reworked layers. Corrected depth is denoted by those except the tephra and reworked layers. In order to detect the factors responsible for the fluctuating variations of the biogeochemical parameters and to conduct zonation, principal component (PC) analysis was performed using all the biogeochemical parameters. Zonation (g) was determined based on biplots of the sediment sample scores for PC1 and PC2 (see Fig. 5).

Nevertheless, by including the both hypothetical and observed $\delta^{13}C$ values of the POMs in KB, the $\delta^{13}C$ values of phytoplankton in KB are within values of -22 to $-19‰$ (Fig. 6). These values are consistent with the values of POMs in the enclosed seas of Japan (Fig. 6 (+): Ariake Sound, Kyushu, Yokoyama et al., 2005; Hiroshima Bay, Seto Inland Sea, Takai et al., 2002; Uwa Sea, Shikoku, Okuda et al., 2004) and the general trend in waters ($-22 \pm 3‰$; Frans, 1995). The $\delta^{15}N$ values of POMs in KB are lower than those in the other enclosed seas of Japan; this fact might reflect the effect of anthropogenic

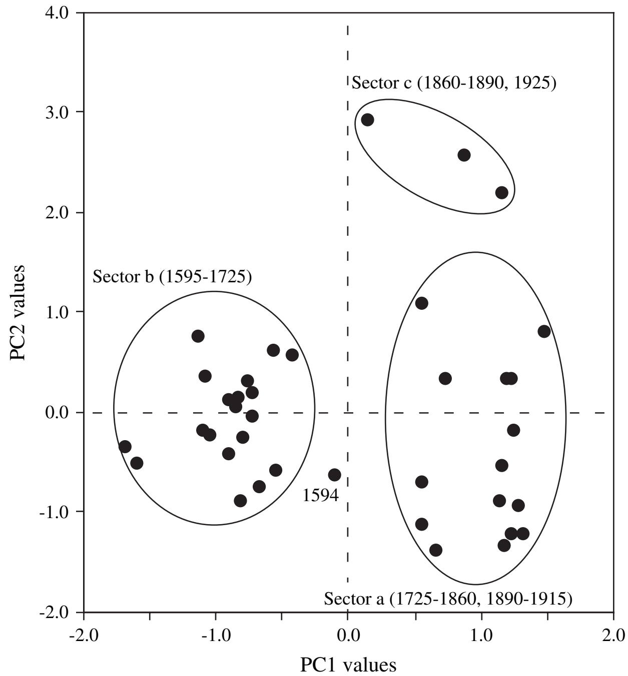

Fig. 5. Biplots of the sediment sample scores for PC1 and PC2. Three sectors were identified from the biplots of the data.

nutrient inputs, which leads to an increase in δ^{15}N (Cabana and Rasmussen, 1996).

While there is no data for δ^{13}C and δ^{15}N in terrestrial organic materials around the KB watershed, in Ariake Sound, northwestern Kyushu, detrital terrestrial plant materials with -26.7 ± 3‰ of δ^{13}C and 1.7 ± 1‰ of δ^{15}N are found. These values are consistent with the general trend that is within −35 to −25‰ of δ^{13}C (Meyers, 1994; Cloern et al., 2002) and 0 to 4‰ of δ^{15}N (Wada, 1986; Peterson and Howarth, 1987).

6. Discussion

On the basis of the distribution of sample scores on the PC axes, three sectors were identified (Fig. 5). According to this classification, the biogeochemical records of the Kg 1 core were divided into six zones (Fig. 4). In particular, in the records of δ^{13}C, TOC, and TN, there were stable regimes that persisted over 100 years (low-value regime during 1595–1725; high-value regime during 1725–1860), and shifts between these regimes were observed. It is improbable that these centennial patterns are accidental and due to bioturbations. If bioturbations influence these records, the shifts should be invisible due to the vertical mixing of sediments. However, the shifts are identified in the records of δ^{13}C, TOC, and TN. These shifts occur within 2 cm, indicating that the mixing is within only a 2-cm layer that corresponds to 7 years, even if there is an effect of bioturbation.

6.1. Main factor driving the biogeochemical variations

The centennial pattern is apparent in the record of δ^{13}C, δ^{15}N, TOC, and TN values (Fig. 4). Since TOC, TN, δ^{13}C, and δ^{15}N have high loadings on PC1, a factor driving all these parameters should exist.

In previous studies on bulk δ^{13}C and δ^{15}N values, there are some possible factors that may drive changes in both the values. In many cases, the mixing of marine and terrestrial particulate organic materials (factor 1) is one of the factors driving changes in δ^{13}C and δ^{15}N values (e.g., Thornton and McManus, 1994; Andrews et al., 1998; Owen and Lee, 2004; Usui et al., 2006; Kuwae et al., 2007). The combined effect of HCO_3^- assimilation by phytoplankton resulting from dissolved CO_2 limitation due to high productivity (Fogel et al., 1992), and the resulting oxygen depletion in waters (Lehmann et al., 2002) might also be one of the factors (factor 2). Additionally, the sedimentation rate might cause changes in δ^{13}C and δ^{15}N values through organic matter preservation associated with the sediment burial rate (factor 3).

With respect to factor (2), under oxic conditions, microbial decomposition leads to a decrease in δ^{13}C and increase in δ^{15}N (Lehmann et al., 2002); in contrast, high productivity leads to increase in δ^{13}C (Fogel et al., 1992), and resulting anaerobic decomposition causes decrease in δ^{15}N (Lehmann et al., 2002). If these processes play an important role in changes in δ^{13}C and δ^{15}N of bulk organic matters, δ^{13}C and δ^{15}N records should show the opposite trends. However, such a pattern was not identified in our records, indicating that changes in productivity and oxygen condition do not significantly contribute to the δ^{13}C and δ^{15}N signals.

Table 2
δ^{13}C, δ^{15}N, and atomic C/N ratios of POMs, zooplanktons, macrobenthos, and detrital terrestrial materials

Sampling site	Sample	Taxon	*n*	Water depth (m)	δ^{13}C (‰)	δ^{15}N (‰)	Atomic C/N	Reference
North basin	POM		1	5	−21.0	7.6	8.0	This study
of Kagoshima Bay	Zooplankton	Copepod species	1	0–150	−18.4	10.1	4.1	This study
	Macrobenthos	*Polychaeta* sp.	1	200	−18.6	9.2	4.0	This study
Central basin	POM		1	5	−21.6	6.8	6.5	This study
of Kagoshima Bay	Zooplankton	*Sagitta* spp.	1	0–150	−16.6	12.7	3.8	This study
Uwa sea	POM				−19.5	8.8		Okuda et al. (2004)
Hiroshima Bay	POM				−21.9	8.9		Takai et al. (2002)
	POM				−20.1	8.3		
Ariake Sound	POM				−19.0	7.3		Yokoyama et al. (2005)
	Detrital terrestrial plant material				−26.7	1.7		

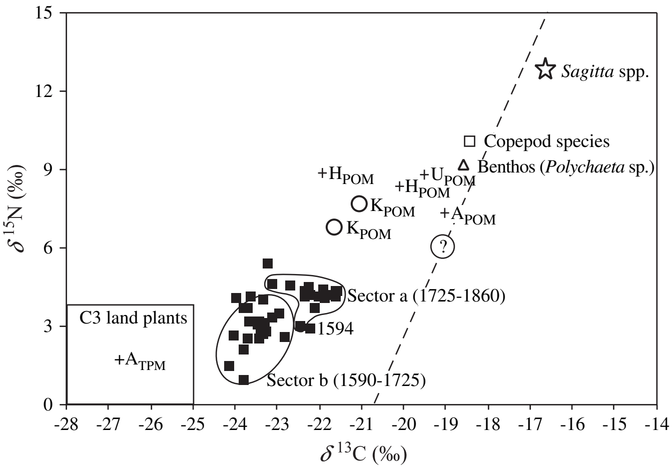

Fig. 6. $\delta^{13}C$ and $\delta^{15}N$ values of the core samples (solid squares). The figure also shows the $\delta^{13}C$ and $\delta^{15}N$ values of the surface POMs (small open circles), the copepod species (open square), the macrobenthos, *Polychaeta* sp. (open triangle), and *Sagitta* spp. (open star) collected from Kagoshima Bay. Previously reported data—the POMs from Hiroshima Bay (H_{POM}; Takai et al., 2002), Ariake Sound (A_{POM}; Yokoyama et al., 2005), and Uwa Sea (U_{POM}; Okuda et al., 2004) and the detrital terrestrial plant material from Ariake Sound (A_{TPM})—are also shown by the crosses. The dashed lines indicate the hypothetical pathways of the consumers in the food chains, where consumers become enriched in ^{13}C and ^{15}N relative to those of their foods by 1‰ and 3.4‰, respectively (DeNiro and Epstein, 1978; Minagawa and Wada, 1984). According to the hypothetical pathway, the stable isotopic position of the primary producer in the food chain relating to *Sagitta* spp., copepod species, and *Polychaeta* sp. would be located at the position corresponding to approximately −19‰ (^{13}C) and 6‰ (^{15}N) (large open circle).

If the sedimentation rate had varied greatly over time, not only $\delta^{13}C$ and $\delta^{15}N$ but also TOC and TN should have been influenced by the sedimentation rates. However, the timing of changes in $\delta^{13}C$, $\delta^{15}N$, TOC, and TN (AD 1725) does not coincide with that in the sedimentation rates (AD 1779) (Fig. 4). Furthermore, although a decreased aerobic decomposition that is expected from the high sedimentation (high burial rate) during the interval 1595–1725 would lead to an increase in TOC, TN and $\delta^{13}C$ and a decrease in $\delta^{15}N$, the former three records show the opposite trends. These observations indicate that the effect of sedimentation rate does not dominate these biogeochemical signals.

The shifts in $\delta^{13}C$ and $\delta^{15}N$ values between those of Sector a and those of Sector b are most likely due to factor (1) on the basis of the downcore data and source materials of $\delta^{13}C$ and $\delta^{15}N$ values. Since the downcore data in Fig. 6 are plotted between the two end members—terrestrial organic matter (−35 to −25‰ of $\delta^{13}C$ and 0 to 4‰ of $\delta^{15}N$) and marine POMs (−22 to −19‰ of $\delta^{13}C$ and 6 to 8‰ of $\delta^{15}N$) (Fig. 6), the shift can be explained by changes in the mixing of the two end members.

Marine POM is the more dominant member that influences the variations in $\delta^{13}C$ and $\delta^{15}N$ values as well as in TOC and TN for the following reasons. If there are large changes in the input of terrestrial materials in the KB watershed, this would be associated with changes in rainfall and resulting sedimentation rates. However, all these biogeochemical records did not show patterns similar to the sedimentation rates as described above. Therefore, the effect of production of marine phytoplankton-derived organic matters rather than the input of terrestrial organic matters is dominant in the $\delta^{13}C$, $\delta^{15}N$, TOC, and TN records. The centennial-scale pattern and shifts recognized in these records possibly represent changes in the primary productivity.

6.2. Factors associated with variations of C/N ratio

The maximum C/N ratios occur in Sector c during the periods 1860–1890 and 1925, which are also accompanied by low $\delta^{13}C$ values (Fig. 4). Fig. 7 shows the core sample plots and potential end members in a plot of C/N ratio against $\delta^{13}C$. The plots of the core samples are distributed between the locations of marine POMs (C/N is in the range 6.5–8.0; $\delta^{13}C$ ranges from −22 to −19‰; see Table 2 for the C/N ratios and the above description for $\delta^{13}C$ of the POMs of KB) and terrestrial C_3 plant materials (C/N range is 12–70 (mode: 16–36), $\delta^{13}C$ ranges from −22 to −35‰ (mode: −25 to −30‰); combined data from Meyers, 1994; Cloern et al., 2002). The C/N ratios and $\delta^{13}C$ values of C_4 plant materials (C/N >40, $\delta^{13}C$ is between −18 and −10‰; Meyers, 1994; Cloern et al., 2002) are plotted at a distance from the spatial pattern of the marine POMs, terrestrial C_3 plant materials and the core samples. This spatial pattern among the sample plots and the locations of three end members suggests that variations in C/N ratios and $\delta^{13}C$ in the core samples can be explained only by a mixture of phytoplankton-derived organic matters and C_3 terrestrial plant materials. According to this observation, the maximum C/N values during AD 1860–1890 and 1925 are due to an increased influx of C_3

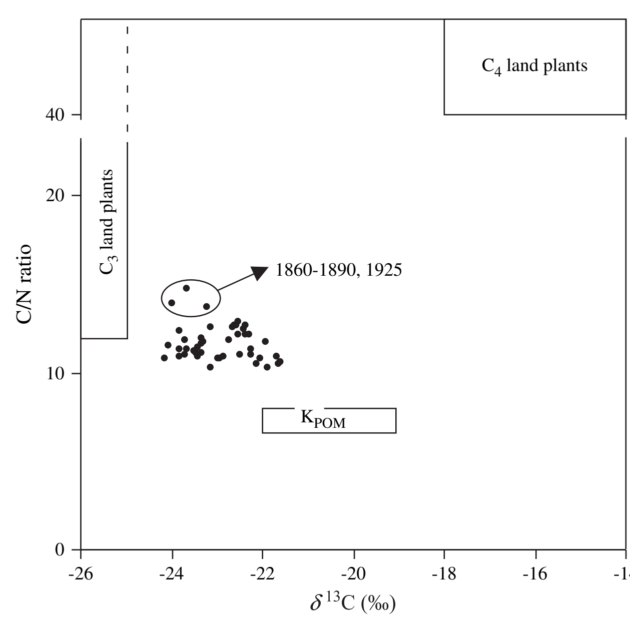

Fig. 7. $\delta^{13}C$ and C/N ratio values of the core sediment samples (solid circles), C_3 and C_4 terrestrial plants previously reported by Meyers (1994) and Cloern et al. (2002), and the POMs from Kagoshima Bay (K_{POM}). The thin oval indicates the samples of Sector c with high C/N ratios and low $\delta^{13}C$ values during AD 1860–1890 and 1925.

terrestrial plant materials into the north basin of KB. In fact, small tree-derived fragments are extremely abundant in coarse-size fractions that are sieved by a 180-μm mesh for Sector c samples. The increased influx of the fragments into KB is not possibly due to increased rainfall levels because the observed meteorological data at Kagoshima (Japan Meteorological Agency, 1999) do not show increased rainfall levels during AD 1860–1890 and 1925. At this point, the cause for the abundance of small tree-derived fragments is unclear; however, the possible cause might be either the human-induced clearance of forests—which leads to an enhancement in mobile detrital plant materials—or forest fire-induced influx of plant materials through air into the north basin of KB. Nevertheless, variations of C/N and δ^{13}C values might reflect the changes in the surrounding forest environments.

6.3. Factors controlling primary productivity in KB

The long-term record of TOC suggests a centennial-scale variability of primary productivity in the north basin of KB. Primary productivity is likely to be influenced by three factors: (1) light availability; (2) nutrient input from watersheds; and (3) uplift of deep-water nutrients by convection or wind-driven mixing. Factor (2) is not the main cause driving primary productivity. If there is an obvious linkage between primary productivity and nutrient input, the sedimentation rate which is strongly influenced by rainfall and runoff should reveal a similar centennial pattern in TOC record which indicates primary productivity. However, there is no similar trend between both the records (Fig. 4). Factor (1) is associated with variations in the amount of solar radiation, wind velocity, and air temperature. The amount of solar radiation directly influences light availability for phytoplankton. The air temperature and wind velocity influence a particular thickness of the mixing layer through convection and turbulence. Thicker mixing layers cause less light availability, resulting in reducing phytoplankton growth because of diffusion of phytoplankton biomass toward deeper layers (Sugimoto, 2003). Mixing also influences factor (3), that is, the uplift of deep-water nutrients to the surface layer, and leads to enhanced primary productivity. All these factors would influence the primary productivity in the north basin of KB. However, we cannot examine which of these is the major factor because we only have long-term data of air temperature. In this paper, we compare TOC as a primary productivity index with the air temperature reconstructed from the δ^{13}C in the tree ring of a giant Japanese cedar of Yakushima Island, near KB (Kitagawa and Matsumoto, 1995).

The record of TOC showed a centennial-scale regime of low primary productivity during AD 1595–1725. This centennial pattern is identified in the tree-ring derived temperature record in Yakushima Island (Fig. 8), indicating that primary productivity in the north basin of KB may be related to the decrease in temperature during this period. Kitagawa and Matsumoto (1995) reported that the cold period in South Japan can be correlated with the Little Ice Age (LIA; Grove, 1988). LIA is not a monotonously cold period, and there is evidence of lack of synchronicity among different locations around the world. However, many reconstructions of global or Northern Hemisphere averaged temperature (Jones et al., 1998; Mann et al., 1999; Crowley, 2000; Briffa et al., 2001; Esper et al., 2002; Mann and Jones, 2003; Huang, 2004; Moberg et al., 2005) showed that the period around AD 1595–1725 was coldest within the LIA. This indicates that this coldest period identified from the tree ring record in Yakushima Island represents global or Northern Hemispheric-scale climate. According to these observations, it is possible that primary productivity in the north basin of KB has been influenced by the decreased temperature related to the LIA. If so, primary productivity in the north basin of KB might have been influenced by factor (1), decrease in light availability, induced by strong convection due to sea-surface cooling or windy conditions associated with intensified winter monsoons. There are many unclear points such as the relation of seasons to phytoplankton responses and the extent to which the tree-ring based 2 °C decrease of temperature influences primary productivity in the north basin of KB. Nevertheless, the coincidence of

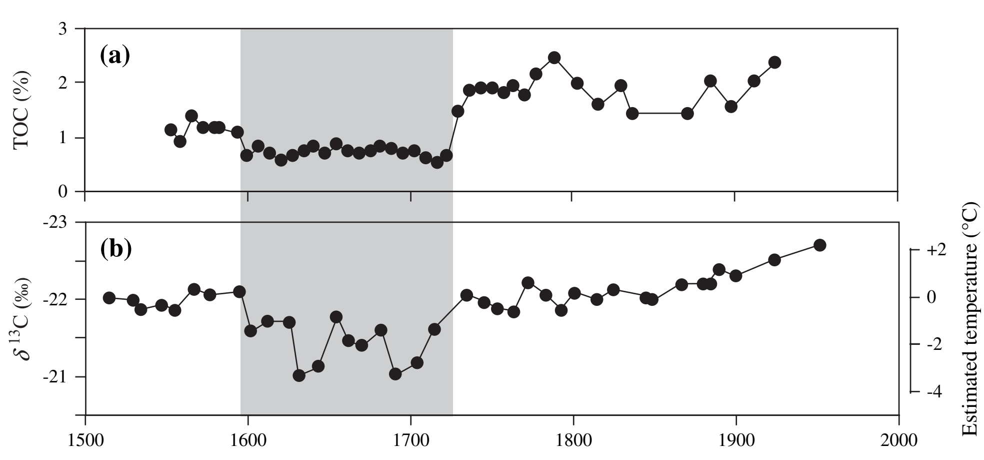

Fig. 8. Comparison of the record of the TOC (a); and the air-temperature record during the last 500 years based on the tree ring δ^{13}C of a giant Japanese cedar from Yakushima Island, south of Kagoshima Bay (b).

the centennial-scale decrease of TOC and temperature suggests that global or Northern Hemisphere-scale climate changes might be an important factor controlling the dynamics of primary productivity in Japanese coastal embayments.

7. Conclusion

In order to detect responses of primary productivity and marine sedimentary biogeochemical processes in Japanese coastal embayments to climate and watershed changes, we unraveled sedimentary records of $\delta^{13}C$, $\delta^{15}N$, TOC, TN, and C/N ratio in the north basin of KB. In the results of principal component analysis of these geochemical data, the major component PC1 explained 65% of the total variance within all the geochemical parameters. The records of $\delta^{13}C$, $\delta^{15}N$, TOC, and TN having high loadings on the PC1 axis showed centennial-scale variations (low levels during AD 1595−1725 and high levels during AD 1725−1860) and a shift (AD 1725). A comparison between our records and previous studies on organic geochemical processes suggests that the factor leading to mutually similar fluctuations in $\delta^{13}C$, $\delta^{15}N$, TOC, and TN is likely to be changes in primary productivity rather than other factors such as post-depositional diagenesis, input of terrestrial materials, or sedimentation rates. It can be concluded that the centennial-scale variations of $\delta^{13}C$, $\delta^{15}N$, TOC, TN, and C/N ratio possibly represent primary productivity in the north basin of KB.

High values of C/N which has high loadings on PC2 are observed during the periods 1860−1890 and 1925. The variations of C/N ratio are related to the input of C_3 land plants to the north basin of KB; this fact is supported by the high abundance of small tree-derived fragments in the samples corresponding to high C/N ratio. The C/N variations might reflect the changes in the surrounding forest environments.

The centennial-scale decrease in primary productivity is coincident with the decreased temperature associated with the LIA, suggesting that primary productivity in the north basin of KB might have been influenced by global or Northern Hemisphere-scale climate changes.

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