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24. VARIATIONS IN ORGANIC CARBON ISOTOPIC COMPOSITION IN SEDIMENTS AT SITE 1017 DURING THE LAST 25 K.Y.[1]

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ABSTRACT

A high-resolution analysis of Hole 1017E revealed that total organic carbon (TOC) concentrations (24.8 ± 2.9 mg/g) and $\delta^{13}C$ of TOC (–21.3 ± 0.2‰) in Holocene sections are higher than those in glacial sediments (14.2 ± 4.8 mg/g and –22.1‰ ± 0.1‰, respectively). The 306- to 280-cm section has high total sulfur concentrations, which may correspond to anoxia Event 1 (1 of the warm interstadials of GISP2) in the Santa Barbara Basin.

INTRODUCTION

Previous studies have demonstrated that sediments in the Santa Barbara Basin on the eastern margin of the North Pacific Ocean preserve well the records of short-term climatic events, such as Dansgaard-Oeschger Events and related oceanographic changes (e.g., Behl and Kennett, 1996; Kennett and Ingram, 1995; Thunell and Mortyn, 1995). However, our knowledge is still insufficient to understand oceanographic system and environmental changes in this region and their relation to the global climatic events.

We report the results of total organic carbon (TOC) and total nitrogen studies as well as their carbon isotope composition preserved in California margin sediments (Ocean Drilling Program [ODP] Site 1017) over the last 25 k.y. This study was performed as a part of an organic geochemical study of global climatic changes in the Northern Hemisphere.

MATERIALS AND METHODS

Sediments for Hole 1017E were taken from Site 1017 (water depth, 967 m). The sampling location is 34°32.009′N, 121°6.430′W. This paper reports the analytical results of the uppermost core (1H) of Hole 1017E. The approximate age of the bottom of Core 167-1017E-1H is estimated to be 26.3 ka (calendar age; R. Tada, pers. comm., 1998).

Organic Carbon, Total Nitrogen, and Sulfur Analyses

Organic carbon, total nitrogen, and sulfur were determined for a powdered HCl-treated sediment sample (~100 mg) by a dry combustion method using a Fisons Instruments NA1500NCS elemental analyzer. Wet sediment samples were treated with 6-M HCl for carbonate removal, washed with distilled water until pH > ~4, and freeze dried. The combustion furnace was operated at 1000°C, and the reduction oven was operated at 650°C.

Stable Carbon Isotope Analysis

Stable carbon isotopic compositions for TOC in sediment samples were measured with a Finnigan/MAT delta-S mass spectrometer on CO_2 converted from TOC. A powdered HCl-treated sediment (40–350 mg) was placed in a thin quartz tube (6 mm o.d. × 70 mm). Powdered CuO (2 g) was added to it. This quartz tube was placed in another large quartz tube (9 mm o.d. × 300 mm) that had 1 g of Cu placed in the bottom, and then a small amount of thin Ag film was added to cover the top of the thin quartz tube. After evacuation, the outer quartz tube was sealed. TOC was oxidized completely into CO_2 by heating the tube first at 500°C for 30 min and then at 850°C for 2 hr. The CO_2 that was produced was purified cryogenically using both a dry ice–ethanol trap and a liquid nitrogen trap. The $\delta^{13}C$ is reported vs. the Chicago Peedee belemnite standard. Analytical precision for the isotope analysis was within 0.2‰.

RESULTS AND DISCUSSION

Table 1 and Figure 1 provide vertical profiles for total organic carbon (TOC) and C/N ratios (TOC/total nitrogen, expressed by weight), total sulfur (total S), and $\delta^{13}C$ of TOC in the sediment samples of Core 167-1017E-1H. TOC concentrations in Hole 1017E range from 4 to 31 mg/g (dry sediments). The C/N ratios range from 7.1 to 10.2. Significant differences in TOC concentrations, C/N values, and $\delta^{13}C$ of organic matter (OM) are seen between the Holocene (sections above 222.7 cm in depth; <10.1 ka) and glacial period (sections below 222.7 cm in depth), as summarized in Table 2. TOC and total N concentrations in Holocene sections are roughly 1.8–1.9 times higher than those in glacial sections. C/N values for the former (8.7) resemble those for the latter (9.2). TOCs in Holocene sections are isotopically slightly heavier than those in glacial ones.

Source of Organic Matter in Sediments

C/N ratios for OM of marine origin generally range from 6 to 9 because of the high protein content of lower organisms such as phytoplankton and zooplankton (e.g., Müller, 1977). Higher plant–derived OM gives higher C/N values than that of marine origin because it has a high percentage of nonprotein materials (e.g., 20–546; Meyers and Ishiwatari, 1993). Thus, the present results of C/N for Hole 1017E may indicate that OM is of marine origin. $\delta^{13}C$ of TOC ($\delta^{13}C_{TOC}$) supports this conclusion because the $\delta^{13}C_{TOC}$ values for Core 167-1017E-1H range from –21.0‰ to –22.8 ‰, which are common to the organic matter of marine origin. A similar conclusion was reached by Gardner et al. (1997), who found $\delta^{13}C_{TOC}$ in the sediment cores from a similar region (35°N, 121°W) roughly –22‰ over the last 60 k.y. It is noteworthy that $\delta^{13}C_{TOC}$ values in the Holocene are ~0.8‰ higher than those in glacial sections, and $\delta^{13}C_{TOC}$ values in glacial are relatively constant. The invariability of $\delta^{13}C_{TOC}$ values in glacial contrasts with the synchronous fluctuations in TOC, C/N, and

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Table 1. Analytical results of total organic carbon (TOC), total nitrogen, total sulfur, and carbon isotopic composition of TOC for Hole 1017E from California margin sediments.

Sample number	Hole	Core	Section	Corrected depth (cmbsf)	TOC (mg/g)	Total N (mg/g)	Total S (mg/g)	C/N weight ratio	δ^{13}C of TOC
1	1017E	1H	1	1.4	31.4	3.75	2.46	8.36	–21.6
2	1017E	1H	1	4.3	29.3	3.47	3.45	8.45	–21.4
3	1017E	1H	1	7.2	30.5	3.56	3.80	8.55	–21.5
4	1017E	1H	1	10.1	28.7	3.40	4.35	8.45	–21.3
5	1017E	1H	1	12.9	31.5	3.67	5.34	8.57	–21.3
6	1017E	1H	1	15.8	32.1	3.77	7.37	8.52	–21.1
7	1017E	1H	1	18.7	26.7	3.10	4.76	8.62	–21.3
8	1017E	1H	1	21.6	24.1	2.82	4.85	8.53	–21.3
9	1017E	1H	1	24.4	25.0	2.86	5.82	8.72	–21.2
10	1017E	1H	1	27.3	25.1	2.89	5.65	8.66	–21.3

This is a sample of the table that appears on the volume CD-ROM.

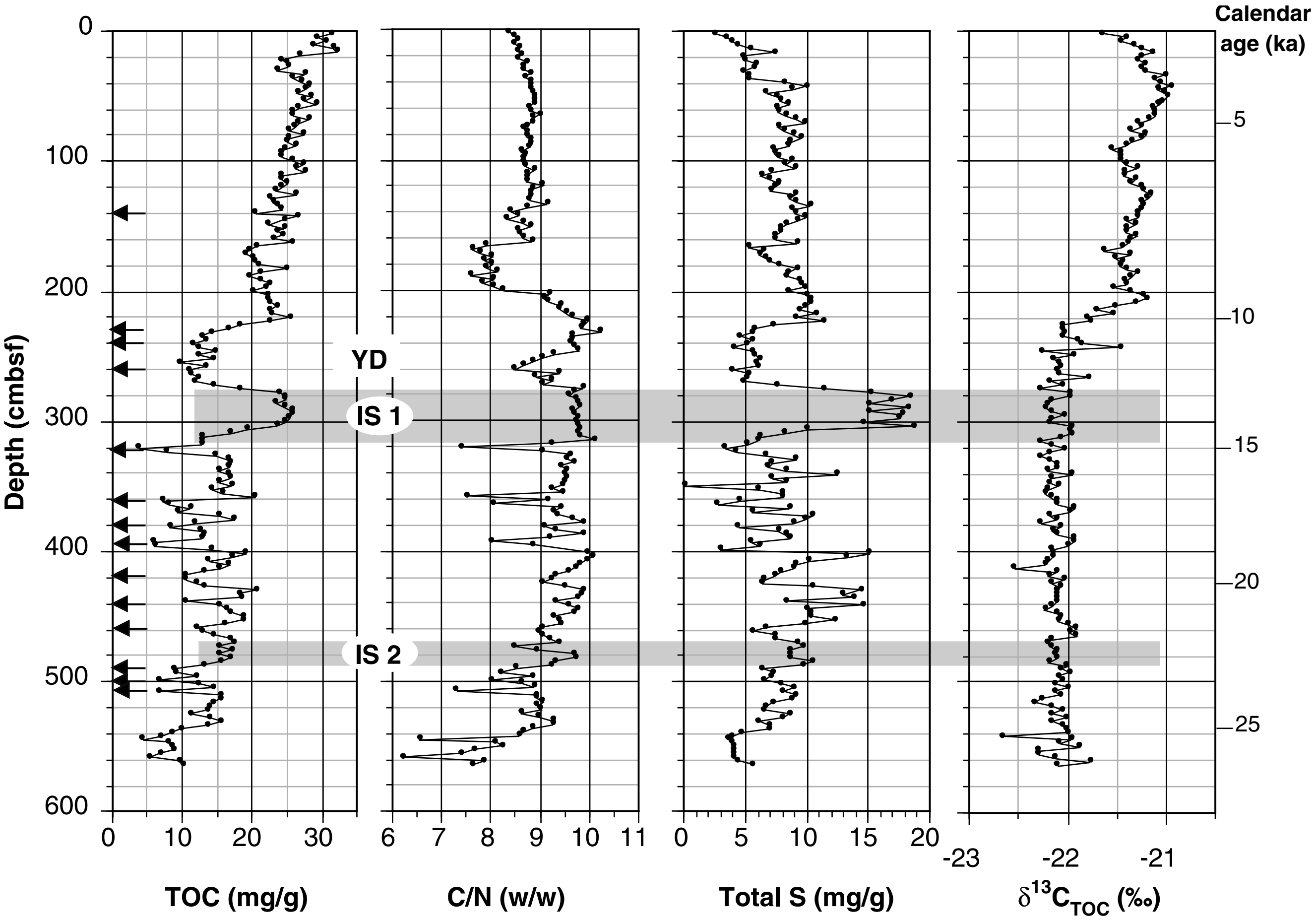

Figure 1. Vertical profiles of TOC, C/N (TOC/TN weight ratio), total sulfur, and carbon isotopic composition of TOC in the upper part of Hole 1017E. TOC = total organic carbon, YD = Younger Dryas, IS 1 = interstadial Event 1, IS 2 = interstadial Event 2, cmbsf = centimeters below seafloor. Arrows indicate a sandy layer. Shaded areas depict IS 1 and IS 2?.

total S. Most of the sections with low TOC concentrations, C/N, and total S concentrations in glacial are sandy (fine or coarse grained) deposits (~320, ~360, ~380, ~395, ~420, ~440, ~460, ~490, and ~507 cm in depth, respectively; Fig. 1). The stratigraphy of the sediment core is given by Tada et al. (Chap. 25, this volume). These sections are probably well oxygenated, which coincides with low total S contents. Low C/N ratios in the sandy sections may be produced as a result of contribution of inorganic ammonium sorbed by clays to total nitrogen, which often becomes important in TOC-poor sediment (Müller, 1977). A marked positive shift in $\delta^{13}C_{TOC}$ values around 10 ka can be explained as follows. Carbon isotopic composition of TOC in sediment is generally controlled by the following three factors: the nature of source material (terrestrial higher plants vs. marine phytoplankton), temperatures of the photosynthetic fixation of CO_2, and rate of photosynthesis (if we assume that TOC in sediment is derived from marine phytoplankton alone). Following Schoell et al. (1994), the relationship among the three factors can be expressed as

$$\delta^{13}C_i = \delta^{13}C_{DIC} - \varepsilon_p, \tag{1}$$

where $\delta^{13}C_i$ is the carbon isotopic composition of TOC in sediment, obtained after correction for a shift in $\delta^{13}C$ resulting from early di-

Table 2. Summary of analytical results of bulk organic matter and its carbon isotopic composition for Hole 1017E from California margin sediments.

	Holocene	Glacial
Sample number:	1-78	79-197
Depth (cm):*	0-222.7	225.6-563.7
Calendar age (ka):*	0-10.11	10.22-26.27
Number of samples:	78	119
TOC (mg/g-ds):	24.8 ± 2.9	14.2 ± 4.8
Total N (mg/g-ds):	2.86 ± 0.32	1.51 ± 0.50
C/N (weight ratio):	8.7 ± 0.4	9.2 ± 0.7
δ^{13}C of TOC (‰):	–21.3 ± 0.2	–22.1 ± 0.1

Notes: *= corrected depths and ages were provided by R. Tada (pers. comm., 1998). ds = dry sediment, TOC = total organic carbon.

agenesis in sediments (Hayes et al., 1983); $\delta^{13}C_{DIC}$ is the isotopic composition of the dissolved CO_2; and ε_p is the fractionation between dissolved CO_2 and primary photosynthate, as shown above. ε_p is written as

$$\varepsilon_p = a + (b - a)\frac{[CO_2]_i}{[CO_2]_{aq}}, \tag{2}$$

where *a* and *b* are the fractionations associated with diffusion of CO_2 into the phytoplankton (0.7‰) and fixation of CO_2 with the phytoplankton (27.0‰; Yoshioka, 1997). $[CO_2]_i$ is intracellular CO_2 concentration, and $[CO_2]_{aq}$ is extracellular concentration. The ratio $[CO_2]_i/[CO_2]_{aq}$ is assumed to be photosynthetic carbon demand and should be related to the phytoplankton growth rate when transport of CO_2 into the cell is controlled by diffusion, which is common in marine systems (Shemesh et al., 1993; Laws et al., 1995). $\delta^{13}C_{DIC}$ can be estimated from δ^{13}C of carbonate tests of planktonic foraminifers and paleo-sea-surface temperatures (paleo-SSTs) by using the following empirical equation (Jasper et al., 1994):

$$\delta^{13}C_{DIC} = \delta_t + 14.07 - 7050/T, \tag{3}$$

where δ_t presents the isotopic composition of foraminifera calcite and T is paleo-SST (in Kelvin).

The difference in δ^{13}C for sedimentary TOC at two different times ($\Delta^{13}C_i$) can be roughly expressed as

$$\Delta^{13}C_i = \Delta^{13}C_{DIC} - \Delta\varepsilon_p, \tag{4}$$

where $\Delta^{13}C_{DIC}$ is the difference in δ^{13}C of dissolved CO_2 in seawater, which is estimated from the difference in δ^{13}C of carbonate tests of planktonic foraminifers deposited at the different times with correction of paleo-SST.

The term $\Delta\varepsilon_p$, which is related to the difference in photosynthetic carbon demand at different times, can be calculated from Equation 4. The term $\Delta\varepsilon_p$ was named as a parameter related to comparative growth rate (PCGR; Ishiwatari et al., 1999). A high PCGR at a particular time indicates a low photosynthetic carbon demand (i.e., growth rate of phytoplankton would be low) relative to that at the reference time.

According to Cannariato (pers. comm., 1998), δ^{13}C of inorganic carbon (IC) of planktonic foraminifera (*Globigerina bulloides*) tests ranges roughly from –1.4‰ to 0.6‰ in 280–160 cm in depth (13–7 ka) and shows no marked trend. Sea-surface temperature (SST) estimated from alkenone analysis indicates a rapid increase from ~12°C at 230 cm in depth (10.5 ka) to ~15°C at ~210 cm in depth (9.5 ka; R. Ishiwatari et al., unpubl. data. In addition, δ^{13}C values of IC of planktonic foraminifera tests fluctuate around –1‰ and show no significant difference before and after 10 ka. Thus, δ^{13}C of the dissolved CO_2 is estimated to become higher by ~0.3‰ ($\Delta^{13}C_{DIC}$ = ~0.3‰) at the SST transition at ~10 ka. Consequently, $\Delta\varepsilon_p$ equals ~–0.7‰. This means that the increase in growth rate of phytoplankton, which may correspond closely to planktonic primary productivity, might be responsible for the ~0.5‰ positive shift in δ^{13}C values of sedimentary TOC at ~10 ka, although a substantial range of possibilities must be considered.

Another factor that can cause a part of the positive shift in $\delta^{13}C_{TOC}$ values around 10 ka is a drop in input of terrestrial higher plant–derived OM, which is suggested by lignin analysis (R. Ishiwatari et al., unpubl. data) of the sediment core. The lignin analysis indicates that TOC-normalized concentrations of lignin phenols in Holocene sediments are one-half to one-quarter times lower than those in glacial. However, we cannot evaluate at present how the drop in input of terrestrial higher plant–derived OM contributes to the positive shift in the $\delta^{13}C_{TOC}$ value.

Vertical Profile of Total Sulfur in Sediments

Sulfur concentrations are high in sections in the 306–280 cm range (25.3–13.1 ka), which matches excellently with anoxia Event 1, corresponding to the number 1 (Bølling/Allerød) of warm interstadials (15.5–12.7 ka; Behl and Kennett, 1996). Behl and Kennett (1996) evaluated the degree of oxygenation of sediments in the central Santa Barbara Basin (ODP Hole 893A: 34°17.25′N, 120°2.2′W: 576.5 m water depth), which is close to Site 1017, using the bioturbation index. An oxygenation level for the anoxia event indicates anaerobic/dysaerobic boundary conditions allowing only micro- to meiofaunal bioturbation sufficient to diffuse but not destroy primary laminations (~0.1 mL O_2/L; Behl and Kennett, 1996). The marked correlation of the high sulfur section to anoxia Event 1 suggests that the same factor (the presence of relatively old bottom waters) played a role for both events. This result seems to support the idea of Behl and Kennett (1996) on the bottom-water system in the California margin.

The section corresponding to anoxia Event 2 at 23.7–22.8 ka reported by Behl and Kennett (1996) does not show high sulfur content, probably because the oxygenation level (>0.3 mL O_2/L dysaerobic to aerobic) is not enough for producing high-sulfur sediments.

High-sulfur contents are observed for other sections (400 cm and 455–430 cm in depth). But the corresponding low benthic oxygenation was not seen in the Santa Barbara Basin (Behl and Kennett, 1996). These results suggest that short-term changes in the oxygenation level occur locally during glacial periods.

SUMMARY AND CONCLUDING REMARKS

An analysis of Hole 1017E revealed the following:

1. TOC concentrations (24.8 ± 2.9 mg/g) in Holocene sections are higher than those in glacial sediments (14.2 ± 4.8 mg/g). The δ^{13}C of TOC (–21.3‰ ± 0.2‰) in the Holocene sections are higher than those in glacial sediments (–22.1‰ ± 0.1‰).
2. The positive shift by 0.8‰ in δ^{13}C of sedimentary TOC at ~10 ka might be explained by a positive shift in δ^{13}C of the dissolved CO_2 (~0.3‰) because of the increase in SST, a positive shift by 0.5‰ resulting from increase in growth rate of phytoplankton (probably planktonic primary productivity), and (partly) resulting from a drop in input of terrestrial higher plant–derived OM.
3. Sulfur concentrations are high in sections corresponding to anoxia Event 1 of warm interstadials (Behl and Kennett, 1996). The marked coincidence suggests that the same factor (the presence of relatively old bottom waters) played a role for both events. However, another anoxia event (Event 2 at 23.7–22.8 ka) does not correlate with high sulfur contents, and higher sulfur contents are not found in other sections. These results may indicate that short-term changes in oxygenation level oc-

cur rapidly and locally and are controlled by a complicated water current system in this region during glacial periods.

A detailed organic geochemical study at molecular level is in progress to gain further insight into the relation between oceanographic and terrestrial processes and global climatic events.

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