12. CARBON ISOTOPE RATIO OF TOTAL INORGANIC CARBON IN PORE WATERS ASSOCIATED WITH DIAGENESIS OF ORGANIC MATERIAL AT SITE 808, NANKAI TROUGH[1]

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ABSTRACT

The $\delta^{13}C$ values of total inorganic carbon (ΣCO_2) were measured for interstitial waters extracted from the turbidite and hemipelagic sediments of the Nankai Trough accretionary prism during ODP Leg 131. At 3.0 mbsf in the bacterial sulfate reduction zone, a significant low $\delta^{13}C$ of −29.8‰ (PDB) was found, suggesting oxidation of upward-migrated methane from the zone below. At 6.0 mbsf, below the sulfate reduction zone, the $\delta^{13}C$ value increases abruptly to a maximum value of +12.0‰, reflecting an enrichment of ^{13}C in residual ΣCO_2 from the bacterial reduction of some ΣCO_2 to ^{12}C-enriched CH_4. Below 80 mbsf, the ^{13}C values decrease almost linearly with depth to ~ −20‰ at 1000 mbsf, indicating that the fraction of ΣCO_2 derived from thermal degradation of organic material increases gradually with increasing in-situ temperature.

INTRODUCTION

That $\delta^{13}C$ of total inorganic carbon (ΣCO_2) in interstitial waters is a sensitive indicator of the degradation processes of organic matter has been demonstrated for various marine environments (e.g., Nissenbaum et al., 1972; Claypool and Kaplan, 1974; Irwin et al., 1977; Grossman, 1984; McCorkle et al., 1985; Berner et al., in press). In this study we measure variations of the carbon isotope ratio of interstitial waters, and interpret their geochemical implications with respect to organic matter diagenesis in rapidly deposited sediments of the Nankai Trough accretionary prism south of Japan.

ΣCO_2 and its carbon isotope composition ($\delta^{13}C$) in interstitial waters are controlled by anaerobic bacterial (sulfate reduction, fermentation, and methane generation) as well as thermocatalytic degradation processes of organic matter. As shown for example by Claypool and Kaplan (1974), at shallow burial depths just below the aerobic respiration zone, bacterial sulfate reduction (reaction 1) is the dominant process for decomposing organic matter (CH_2O):

$$2CH_2O + SO_4^{2-} \rightarrow 2CO_2 + S^{2-} + 2H_2O \quad (1)$$
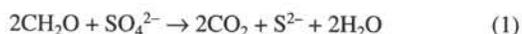
After SO_4 is completely consumed from interstitial waters, bacterial methane generation (CO_2 reduction) is considered to occur as shown in reaction 3, where fermentation-derived CO_2 (reaction 2) as well as the sulfate reduction CO_2 (reaction 1) is reduced to CH_4 (Whiticar et al., 1986).

$$2CH_2O + 2H_2O \rightarrow 2CO_2 + 4H_2 \quad (2)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O. \quad (3)$$
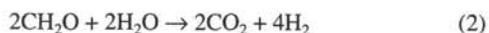
At high in-situ temperatures of greater than 50°C, thermocatalytic decarboxylation of organic acid functional groups also occurs:

$$R\text{-}CO_2H \rightarrow R\text{-}H + CO_2. \quad (4)$$
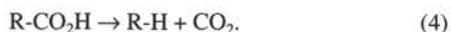
The carbon isotopic ratio ($^{13}C/^{12}C$) of the produced and remaining ΣCO_2 varies among the processes. Little carbon isotopic fractionation occurs between organic material and the CO_2 in reactions 1, 2, and 4

(e.g., Claypool and Kaplan, 1974; Irwin et al., 1977), while reaction 3 causes a significant enrichment in ^{13}C in the residual ΣCO_2, because $^{12}CO_2$ is removed at a rate about 7% faster than $^{13}CO_2$ during methane formation (Rosenfeld and Silverman, 1959). This is also documented through the high fractionation factors of 1.055–1.09 reported by Whiticar et al. (1986).

During the ODP Leg 131 cruise (March 30 to June 2, 1990), sediment core samples were taken from the following three holes at Site 808: Hole 808A, 32°21.116′N, 134°56.666′E, depth = 4676.0 mbsf; Hole 808B, 32°21.085′N, 134°56.613′E, depth = 4674.2 mbsf; and Hole 808C, 32°21.170′N, 134°56.657′E, depth = 4674.6 m, in the western Nankai Trough accretionary prism (see Fig. 1), as reported by Taira, Hill, Firth, et al. (1991). The total organic carbon, whose content varies within the range of 0.1 wt.% and 0.75 wt.%, shows an apparent decrease with depth (Taira, Hill, Firth et al., 1991). The depth profiles of $\delta^{13}C$ of dissolved ΣCO_2, of CH_4 and of kerogen as well as of SO_4^{2-} and titration alkalinity concentrations in the squeezed interstitial waters (or in the sediments), enabled us to trace each organic matter diagenetic process mentioned above.

EXPERIMENTAL METHODS

Interstitial waters were retrieved on board the ship by using stainless steel or titanium squeezers (Manheim and Sayles, 1974) immediately after the core samples were brought on deck. Samples of 1 to 5 mL were sealed for carbon isotope ratio analysis in glass ampules in vacuum and stored in darkness.

After the cruise, the ΣCO_2 in each sample was completely extracted by acidifying and bubbling an aliquot of the sample in CO_2-free helium flow or by acidifying the whole sample by breaking the glass ampule in an evacuated ball mill made of Pyrex glass (Kita et al., 1982). There was no systematic difference between the results of the two methods. Water vapor in the evolved CO_2 gas was removed by condensing it at dry-ice temperature, and the CO_2 was collected in a trap cooled by liquid nitrogen. Carbon isotope analysis was carried out at the Ocean Research Institute, University of Tokyo, with a Finnigan MAT 250 mass spectrometer modified for small sample analysis. Isotope results are expressed as per mil values relative to the PDB standard:

$$\delta^{13}C = \{(R_{sample}/R_{standard}) - 1\} \times 1,000,$$

where $R = {}^{13}C/{}^{12}C$. The $\delta^{13}C$ values were calibrated by using the NBS-16 and NBS-17 CO_2 standards (Coplen et al., 1983). The accuracy of $\delta^{13}C$ measurements is estimated to be ±0.1‰.

Figure 1. A bathymetric map showing the locations of Site 808 and nearby DSDP sites along the Nankai Trough as well as of the Shikoku Basin and the Shimanto Belt, an ancient accretionary prism (Taira, Hill, Firth, et al., 1991).

In addition to the interstitial water samples, nearby bottom seawater collected ~20 m above the seafloor at (32°23′N, 135°01′E) by the *Tansei Maru* (Ocean Research Institute, University of Tokyo) was analyzed using the same procedure for reference.

The diagenetic carbonate samples were also analyzed for $\delta^{13}C$ values at the Scripps Institution of Oceanography following the procedure of McCrea (1950). The $\delta^{13}C$ measurements for CH_4 and organic matter (kerogen) in the sediment samples were performed at the Federal Institute for Geosciences and Natural Resources (Berner and Faber, this volume; Berner and Koch, this volume).

RESULTS AND DISCUSSION

Figure 2 shows a general lithostratigraphy for Site 808 (Taira, Hill, Firth, et al., 1991). The sediments at Site 808 are roughly classified into two layers: trench turbidites (0–557 mbsf, Units I–IIc) and the Shikoku Basin hemipelagic sediments (619–1243 mbsf, Unit IVa–IVb). The rate of sediment accumulation for the upper layer is extremely rapid (787–1381 m/m.y.), while that for the lower layer is relatively slow (46–107 m/m.y) (Taira, Hill, Firth, et al., 1991). Pore-water chemistry of Site 808 is summarized in detail by Gieskes et al. (this volume).

Table 1 lists the results of $\delta^{13}C$ measurements for ΣCO_2 together with the data of titration alkalinity and SO_4^{2-} that were measured on board the ship (Taira, Hill, Firth et al., 1991). The values reported as 0 mbsf are those of the bottom seawater sample mentioned above.

Figure 3 shows the vertical profiles of $\delta^{13}C$ (ΣCO_2), SO_4^{2-}, and titration alkalinity over the depth interval of 0 to 30 mbsf. The SO_4^{2-} concentration decreases steeply from 28.9 mM to zero at 6.0 mbsf, which means that the sulfate reduction zone is restricted to a

very narrow zone, of the uppermost 6.0 m of the section. Indeed, only in the first two samples (Nos. 131-808A-1H-3 and -1H-4) was the distinct smell of hydrogen sulfide noticed (Taira, Hill, Firth et al., 1991). Titration alkalinity increases abruptly from 2.4 mM to 39.9 mM between 0 and 6.0 mbsf, reflecting the production of ΣCO_2 due to decomposition of organic matter by bacterial sulfate reduction.

In the sulfate reduction zone, $\delta^{13}C$ (ΣCO_2) values abruptly decrease from the bottom seawater value of +0.7‰ to −29.8‰ at 3.0 mbsf. It is worth noting that this single measured value is significantly lower than the value of the organic matter of −24‰ (Berner and Koch, this volume). Because the CO_2 production by sulfate reduction (reaction 1) causes little carbon isotope fractionation between the CO_2 and organic matter as described earlier, there must be another carbon source with a lower ^{13}C value than marine organic matter. The methane generation process below the SO_4 reduction zone that produces CH_4 with a much lower ^{13}C value than that of organic matter, is an obvious internal light carbon source. Therefore, CH_4 may diffuse upward into the sulfate reduction zone, where a portion of it is being oxidized to CO_2 (Whiticar and Faber, 1986). The overall reaction is:

$$CH_4 + SO_4^{2-} \rightarrow CO_2 + S^{2-} + 2H_2O \qquad (5)$$
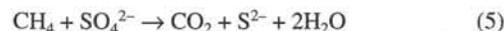
In fact, a minor amount of CH_4 (40 ng/g) was detected in the sediment sample at 2.95 mbsf (Berner and Faber, this volume). The unusually ^{13}C-poor ΣCO_2 ($\delta^{13}C = -35.2‰$) was also observed at 3 mbsf at Site 582 in the western Nankai Trough (see Fig. 1) during DSDP Leg 87 (Claypool et al., 1986).

At 6.0 mbsf, below the SO_4 reduction zone, the $\delta^{13}C$ (ΣCO_2) increases rapidly to 12.0‰, and keeps a constant value of 10‰–11‰
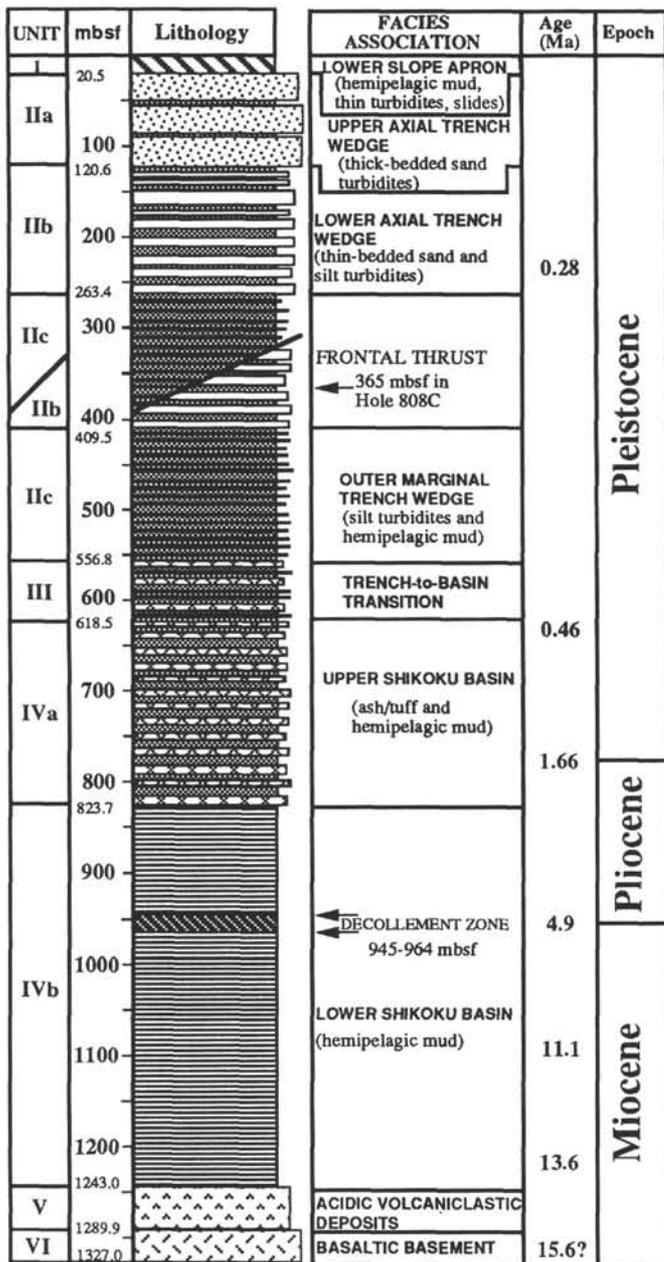
Figure 2. Summary of lithostratigraphy and age for Site 808 (Taira, Hill, Firth, et al., 1991).

Table 1. Interstitial water $\delta^{13}C(\Sigma CO_2)$, titration alkalinity (TA), and SO_4^{2-} concentrations, Site 808.

Hole	Core	Sec.	Int. (cm)	Depth (mbsf)	$\delta^{13}C$ (%)	TA (mM)	SO_4 (mM)
				0.0	0.7	2.40	28.9
808A	1H	3	0–10	3.0	−29.8	24.06	10.6
808A	1H	4	140–150	6.0	12.0	39.92	0.5
808A	2H	3	0–10	9.3	9.2	47.72	0.2
808A	2H	5	140–150	13.8	10.0	48.11	0.0
808A	3H	3	0–10	18.8	11.2	46.55	0.0
808A	4H	1	135–150	26.8	11.0	44.96	0.2
808A	7H	4	135–150	59.7	10.8	55.14	0.0
808A	8H	1	135–150	64.7	10.8	54.67	0.3
808A	10H	3	0–15	80.8	11.0	51.72	0.1
808A	13H	2	122–137	109.0	8.9	40.63	0.1
808B	5X	1	88–103	151.0	7.5	24.97	0.0
808B	10X	1	130–150	203.0	4.7	17.62	0.8
808B	11X	2	130–150	209.7	5.2	17.60	0.8
808B	13X	1	125–145	227.0	4.4	16.15	0.8
808B	17X	2	130–145	266.5	3.1	13.98	1.1
808B	23X	CC	5–10	317.0	2.8		0.5
808C	1R	1	133–150	299.9	1.3	16.04	1.3
808C	6R	3	108–118	350.7	0.9	15.08	1.6
808C	10R	2	130–150	388.1	0.7		2.7
808C	12R	1	130–150	406.0	0.5	16.42	3.6
808C	13R	2	135–150	417.2	0.6	16.88	2.5
808C	18R	3	130–150	466.8	−1.5	13.14	1.0
808C	20R	4	132–150	487.6	−4.1		1.7
808C	21R	1	120–144	492.6	−5.3	13.27	0.7
808C	29R	6	125–150	577.5	−5.8	4.87	0.9
808C	34R	2	125–150	619.4	−9.2	5.61	0.6
808C	35R	4	132–150	632.1	−8.0	5.02	0.5
808C	46R	2	125–150	734.4	−9.9		1.5
808C	60R	4	116–150	872.5	−14.0		2.8

between 6.0 and 80.8 mbsf as shown in Table 1 and Figure 3. The rapid increase of $\delta^{13}C$ (ΣCO_2) clearly indicates the initiation of methane generation by bacterial reduction of CO_2 (reaction 3) that causes a large carbon isotope fractionation between CO_2 and CH_4 as described earlier. Indeed, the measured $\delta^{13}C$ values of CH_4 are expectedly low, −71.7‰ at 19.02 mbsf and −65.4‰ at 55.25 mbsf (Berner and Faber, this volume). Such positive $\delta^{13}C$ (ΣCO_2) values due to CH_4 generation were also observed at the DSDP Sites 582 and 583 (Claypool et al., 1986). As this ^{13}C-enriched ΣCO_2 is thought to migrate upward into the sulfate reduction zone along with the CH_4, even more CH_4 oxidation is implied to maintain the low $\delta^{13}C$ (ΣCO_2) value in the sulfate reduction zone.

Below 80.8 mbsf, the $\delta^{13}C(\Sigma CO_2)$ decreases gradually and almost linearly with depth as shown in Figure 4, where $\delta^{13}C$ values for authigenic pure calcite recovered from the sediments at 910 and 1063 mbsf are also plotted as alternatives for the interstitial water data,

because little carbon isotope fractionation occurs between ΣCO_2 and authigenic calcium carbonate.

The decrease of $\delta^{13}C$ (ΣCO_2) with depth suggests that the addition of isotopically light CO_2 by fermentation (reaction 2) occurs at a faster rate than CO_2 removal by CH_4 generation (reaction 3). Also, below ~400 mbsf, the importance of thermal degradation of organic acid functional groups (reaction 4), which also produces isotopically light CO_2, increases with depth. The temperature profile estimated from the heat flow of 126–129 mW/m^2 (Taira, Hill, Firth et al., 1991) indicates that the in-situ temperature below 400 mbsf (50°C) is high enough to support thermal decomposition of organic matter (Hunt, 1979; Tissot and Welte, 1984). The existence of thermogenic hydrocarbons has been evidenced by the appearance of C_2H_6, C_3H_8, and C_4H_{10} at depths greater than 340–390 mbsf as well as the decrease of CH_4/C_2H_{6+} ratio with depth (Taira, Hill, Firth, et al., 1991). Higher content of thermal hydrocarbons at greater depth is also confirmed by the relationship between $\delta^{13}C(CH_4)$ and $C_1/(C_2 + C_3)$ ratio (Berner and Faber, this volume).

The $\delta^{13}C$ (ΣCO_2) at ~1000 mbsf is approximately −20‰, which is very close to the value of the organic matter of −24‰ (Berner and Koch, this volume) as shown in Figure 4. As bacterial activity should be extremely limited by a high temperature of ~90°C at this depth (Taira, Hill, Firth et al., 1991), bacterial processes (reactions 2 and 3) are unlikely. Most of the ΣCO_2 at ~1000 mbsf is therefore thought to be derived thermogenically.

CONCLUDING REMARKS

The origin of ΣCO_2 in the interstitial waters from the Nankai Trough accretionary sediments was deduced from its $\delta^{13}C$ value and interstitial water chemistry. ΣCO_2 within the bacterial SO_4-reducing zone in the uppermost 6 m of the sediment column is shown to be a mixture of ΣCO_2 formed by in-situ oxidation of sedimentary organic matter in this zone and of CH_4 that has migrated from the zone below. Just below the SO_4-reducing zone, bacterial fermentation accompa-
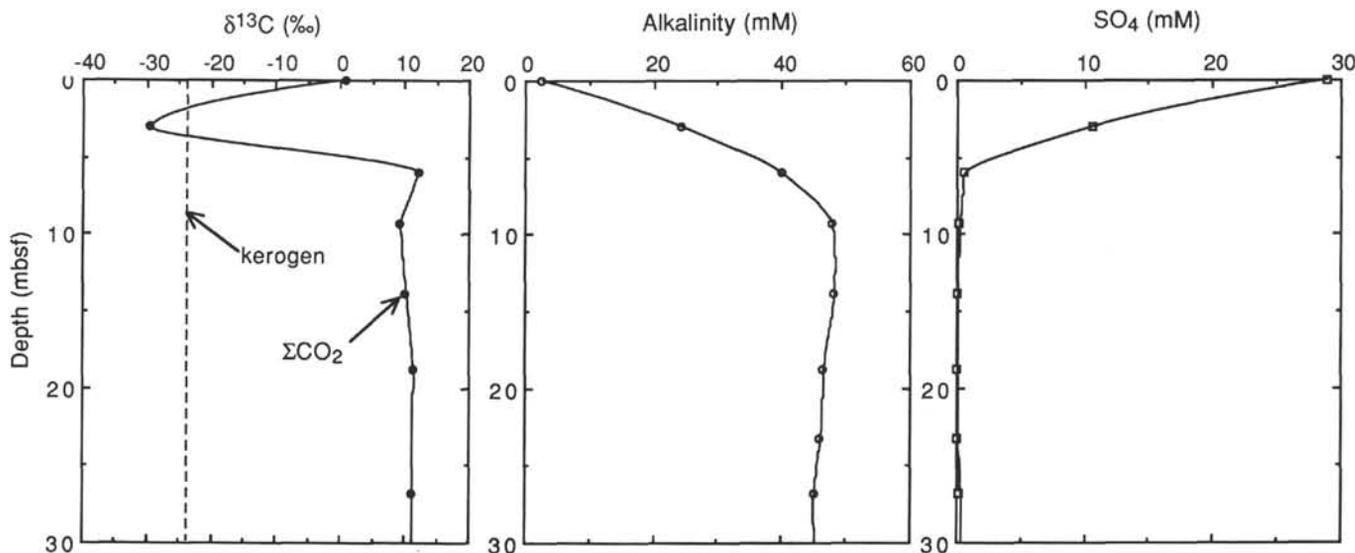
Figure 3. Depth profiles of $\delta^{13}C$ (ΣCO_2), titration alkalinity, and SO_4^{2-} concentrations, between 0 and 30 mbsf, Site 808. Kerogen $\delta^{13}C$ data is marked by a dashed line (Berner and Koch, this volume).
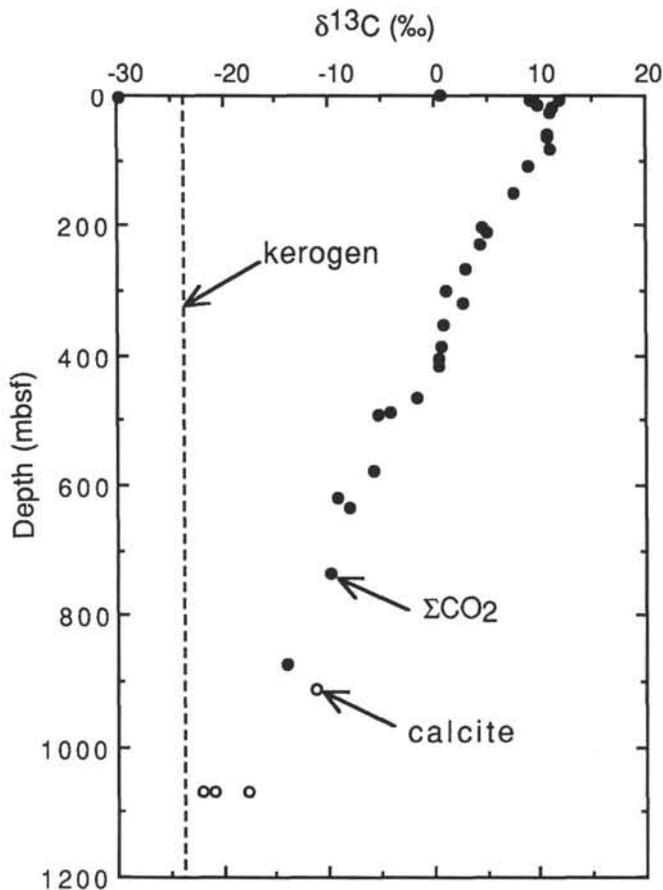
Figure 4. Vertical profile of $\delta^{13}C$ (ΣCO_2) over the depth interval of 0–1200 mbsf at Site 808. Solid circles are the interstitial water data, and open circles are the authigenic calcite data. The $\delta^{13}C$ values of the organic matter are indicated by a dashed line (Berner and Koch, this volume).

nied by methane generation plays a dominant role in producing ΣCO_2 with a high $\delta^{13}C$ value of 12‰. With increasing depth and higher temperature, the fraction of thermogenic ΣCO_2 increases as seen from the monotonous decrease of the $\delta^{13}C$ (ΣCO_2) values with depth as well as from the evolution of light hydrocarbons.

ACKNOWLEDGMENT

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