

31. ISOTOPIC COMPOSITION OF INTERSTITIAL FLUIDS IN SEDIMENT OF THE NANKAI TROUGH, DEEP SEA DRILLING PROJECT LEG 87¹

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ABSTRACT

The isotopic compositions of dissolved CO₂ and CH₄ in sediments of the Nankai Trough indicate that CH₄ is formed during early diagenesis by microbial reduction of CO₂. At the shallowest sampled depths, the CO₂ dissolved in the pore water is unusually enriched in ¹²C ($\delta^{13}\text{C} = -35.2\text{‰}$), indicating contribution of CO₂ from oxidation of CH₄. The most intense microbiological activity appears to be confined to the uppermost 50 m of sediment, based on relative lack of change in the isotopic compositions below this depth. Gas hydrate probably is not present at these localities (Sites 582, 583) because of CH₄ concentrations that are insufficient to saturate the pore water with respect to gas hydrate stability.

INTRODUCTION

Seismic reflection profiles of the inner slope of the Nankai Trough show an anomalous bottom-simulating reflector (BSR) that has been interpreted as the base of the zone in which gas hydrates occur (Yamano et al., 1982; Aoki et al., 1983). Drilling at Sites 582 and 583 on Leg 87 provided an opportunity to test, at least partly, this interpretation. Site 582 was drilled in undeformed sediment of the Trough floor (water depth = 4879 m), whereas Site 583 was located in deformed sediment at the toe of the landward slope adjacent to the Trough (water depth = 4618 m). At neither site was a BSR obvious on marine seismic profiles (Karig et al., 1983). Nevertheless, at more shallow water depths northwest of these sites, slope sediment of the Nankai Trough shows a well-developed BSR suggesting the presence of gas hydrates. As part of a continuing program to determine the geochemical and geologic factors controlling the generation and accumulation of methane and the occurrence of gas hydrates, gas and pore-water samples were obtained from Sites 582 and 583, where significant methane outgassing was observed.

Our main emphasis in previous work has been characterization of the ¹³C/¹²C ratios of CH₄ and CO₂ species dissolved in the pore waters of marine sediments (Claypool and Threlkeld, 1983). We are trying to use natural ¹³C-abundance as a tracer to interpret rates of organic matter decomposition, assuming that CH₄ and CO₂ have a kinetically controlled, product-precursor relationship. If rates can be inferred from ¹³C-fractionation and used in conjunction with other aspects of the depositional environment (including organic productivity, sedimentation rate, organic matter content, water

depth, tectonic setting), we may be able to develop predictive models for the occurrence of gas hydrates in deep-sea sediments.

SAMPLES AND METHODS

Sediment gas from Site 583 and interstitial water from Sites 582 and 583 were sampled according to standard DSDP procedures (Gealy and Dubois, 1971; Manheim, 1966). Gases were analyzed by the procedures of Claypool and others (1980), and water samples were analyzed by the techniques of Presley and Claypool (1971). ¹³C/¹²C was measured on CO₂ gas in a Finnigan-MAT 251 mass spectrometer, and the results expressed in the delta notation, relative to the Pee Dee belemnite (PDB) standard:

$$\delta (\text{‰}) = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) 10^3, \text{ where } R = \frac{^{13}\text{C}}{^{12}\text{C}}.$$

RESULTS

Total dissolved CO₂ concentration (ΣCO_2) and $\delta^{13}\text{C}$ for pore-water samples from Holes 582 and 583 are listed in Table 1, and the chemical and isotopic compositions of gas samples from Hole 583 are given in Table 2. Data from Tables 1 and 2 are plotted in Figure 1. The carbon isotopic composition of ΣCO_2 at Holes 582 and 583, and of CH₄ at Hole 583 show similar trends. The most ¹²C-enriched ΣCO_2 and CH₄ occurs at the shallowest depths (< 30 m). At greater depths, the $\delta^{13}\text{C}$ is relatively constant ($\pm 2\text{‰}$) with tendencies toward heavier CH₄ values and lighter ΣCO_2 values below about 100 m. The ΣCO_2 concentration profiles (Fig. 2) show a shallow (20-m) maximum in Hole 583 and a deep (191-m) maximum in Hole 582.

DISCUSSION

The $\delta^{13}\text{C}$ profiles for both CH₄ and ΣCO_2 at Sites 582 and 583 are similar, with most of the variation expressed at depths more shallow than about 30 m. The most shallow CH₄ sample in Hole 583, recovered from a depth of 15 m, has a carbon isotopic value of -73.5‰ . From a depth of 22 m down to 132 m, the $\delta^{13}\text{C}$ of CH₄ remains nearly constant at $-70 \pm 1\text{‰}$. Methane carbon isotopic compositions below 250 m depth in Hole 583F are slight-

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Table 1. Concentration and $\delta^{13}\text{C}$ of total dissolved carbonate, Sites 582 and 583.

Hole-Core-Section	Sub-bottom depth (m)	ΣCO_2 (mmol kg ⁻¹)	$\delta^{13}\text{C}$ of ΣCO_2 (‰)
582-1-3	3	12.9	-35.2
582-3-5	26	11.3	-5.0
582A-1-5	38	13.1	9.8
582A-2-5	45	15.5	10.9
582B-2-2	60	20.4	6.8
582B-14-5	181	34.9	6.3
582B-18-3	216	25.3	10.7
582B-30-5	235	15.5	1.6
582B-38-3	408	13.8	6.8
582B-50-3	522	17.1	5.9
582B-61-2	626	15.3	8.5
583-2-5	13	19.7	0.4
583A-5-1	20	25.0	8.3
583-3-5	22	19.2	7.3
583-4-2	29	16.6	13.0
583-5-4	40	18.0	12.6
583-7-3	50	17.9	12.7
583-17-2	110	20.3	12.4
583-23-3	140	12.0	11.2
583F-6-2	202	18.0	11.5
583F-12-1	258	15.0	11.8
583F-17-1	306	11.2	-0.2
583F-20-1	335	9.6	9.7

Table 2. CH_4 and CO_2 content (air-free) and $\delta^{13}\text{C}$ of CH_4 in gas samples, Site 583.

Hole-Core-Section	Sub-bottom depth (m)	CH_4 content (%)	CO_2 (air-free) (%)	CH_4 $\delta^{13}\text{C}$ (‰)
583-2-7	15	99.94	0.06	-73.5
583-3-6	22	99.05	0.95	-69.8
583-4-6	31	99.08	0.92	-71.1
583-5-5	39	98.02	1.98	-70.9
583-7-4	51	98.94	1.06	-70.7
583-8-1	56	98.90	1.10	-70.7
583-10-1	68	98.79	1.21	-71.1
583-22-2	132	99.46	0.44	-69.4
583F-6-6	208	99.38	0.62	-68.4
583F-12-1	257	99.72	0.28	-66.8
583F-16-1	296	99.70	0.30	-67.8
583F-27-1	402	99.61	0.39	-66.7
583F-29-1	421	99.69	0.31	-68.1

ly heavier (-66.7 to -68.1‰). The most shallow ΣCO_2 sample came from 3 m depth in Hole 582 and has $\delta^{13}\text{C}$ value of -35.2‰, which is unusually light for ΣCO_2 in pore waters of marine sediments. Such a negative value undoubtedly reflects some contribution of CO_2 from the oxidation of CH_4 . With increasing depth of burial at both Sites 582 and 583, the $\delta^{13}\text{C}$ of CO_2 rapidly reaches positive values (around +10‰) and generally ranges from +6 to +13‰. These positive $\delta^{13}\text{C}$ values are interpreted as kinetic ^{13}C -enrichment in the ΣCO_2 reservoir, resulting from CH_4 generation by CO_2 reduction (Claypool and Threlkeld, 1983).

The $\delta^{13}\text{C}$ profiles for CH_4 and ΣCO_2 in the Nankai Trough sediment can be interpreted as indicating that active, microbiologically mediated, diagenetic processes are largely confined to the uppermost 30 m or so at these sites. The sediments probably are anoxic at relatively shallow depths, about 1 m. The zone in which sul-

fate reduction is the dominant process of anaerobic bacterial respiration probably extends to a depth of about 4 m, and below this depth CH_4 generation is the dominant process.

Based on findings at Sites 582, 583, and the nearby DSDP Site 298 (Ingle et al., 1975), the rate of sediment accumulation during the period from the Pleistocene to the present has been extremely rapid (770 to 900 m/Ma) and the organic carbon content is relatively low (0.4 to 0.6%). The development of anoxic conditions at shallow depths may be due more to the lack of replenishment of oxygen by diffusion (because of the rapid burial of the sediments) than to consumption of oxygen by rapid bacterial oxidation of organic matter. Continued biological activity at depth may be limited by the concentration of metabolizable organic matter, which must be low if total organic carbon is only about 0.5%.

There is no evidence for the presence of gas hydrates in these Leg 87 sediments, either physical presence in the cores or indirect evidence such as low-salinity pore waters (Hesse and Harrison, 1981). The water depth at Sites 582 and 583 is quite deep (4879 to 4678 m, respectively). Pore-water CH_4 concentrations in excess of some minimum value are required to stabilize CH_4 hydrate in deep-sea sediments. Given the low organic matter concentrations in Nankai Trough sediments and the apparent cessation of CH_4 generation below depths of 30 to 50 m, it seems unlikely that this minimum concentration of CH_4 accumulated in the pore waters, and it is unlikely that CH_4 hydrate is present. This conclusion supports the observation that BSRs attributable to gas hydrates are not observed on marine seismic records at these sites (Karig et al., 1983).

The chances of observing gas hydrates in the sediments of the Nankai Trough would be improved considerably by drilling at more shallow depths on the trench slope, where lower pressures decrease the CH_4 concentration requirement for hydrate formation and possibly higher organic matter contents would support more rapid and sustained CH_4 generation. The occurrence of a well-developed BSR in seismic profiles of these slope sediments (Aoki et al., 1983) suggests that the presence of gas hydrates could be confirmed by drilling.

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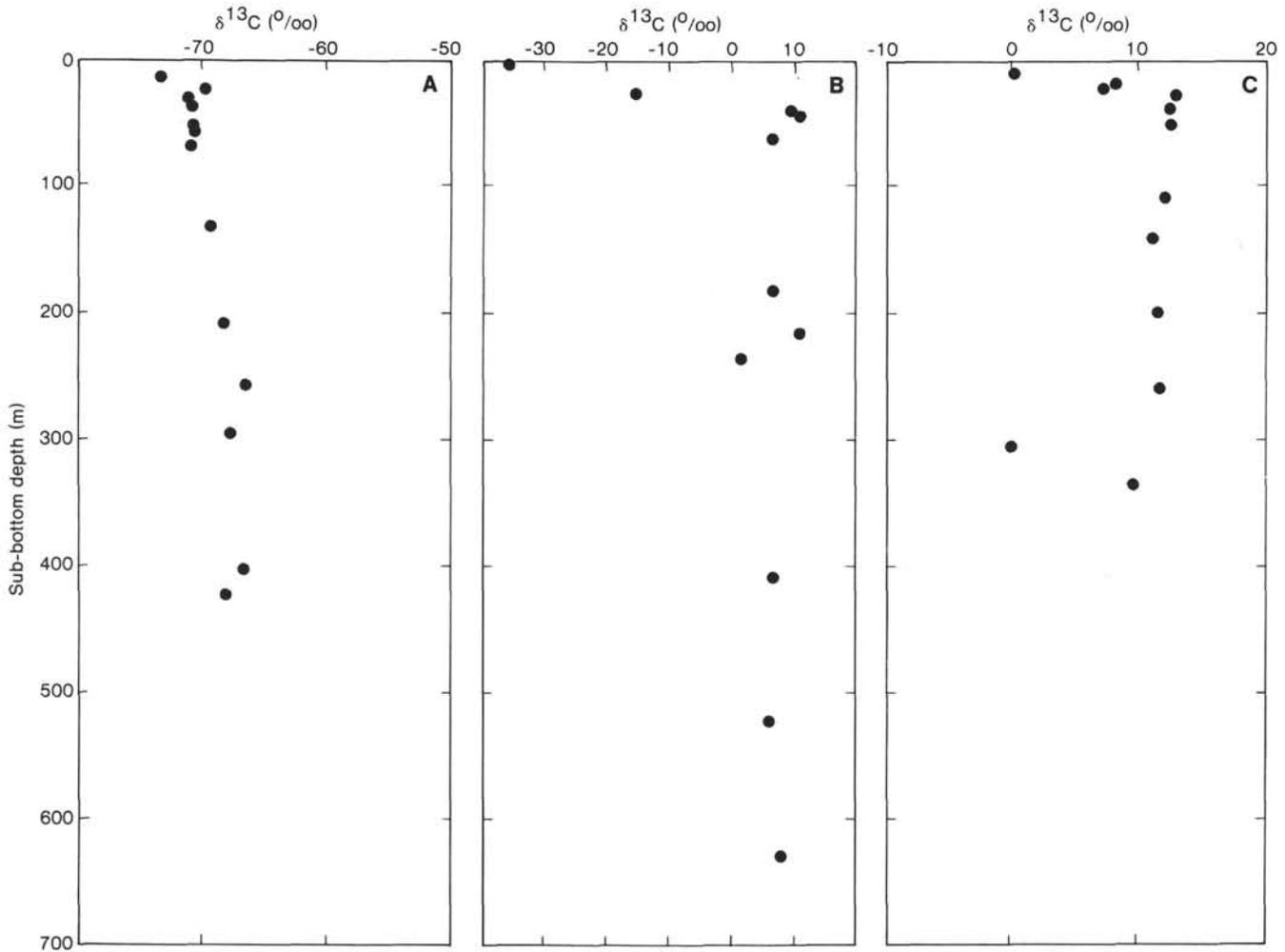


Figure 1. Plots of carbon isotope ratios of methane and total dissolved carbon dioxide from vacuiner gas and interstitial water samples versus sub-bottom burial depth in Nankai Trough sediments, Leg 87. A, Site 583, CH_4 ; B, Site 582, ΣCO_2 ; C, Site 583, ΣCO_2 . $\delta^{13}\text{C}$ in ‰ versus PDB standard.

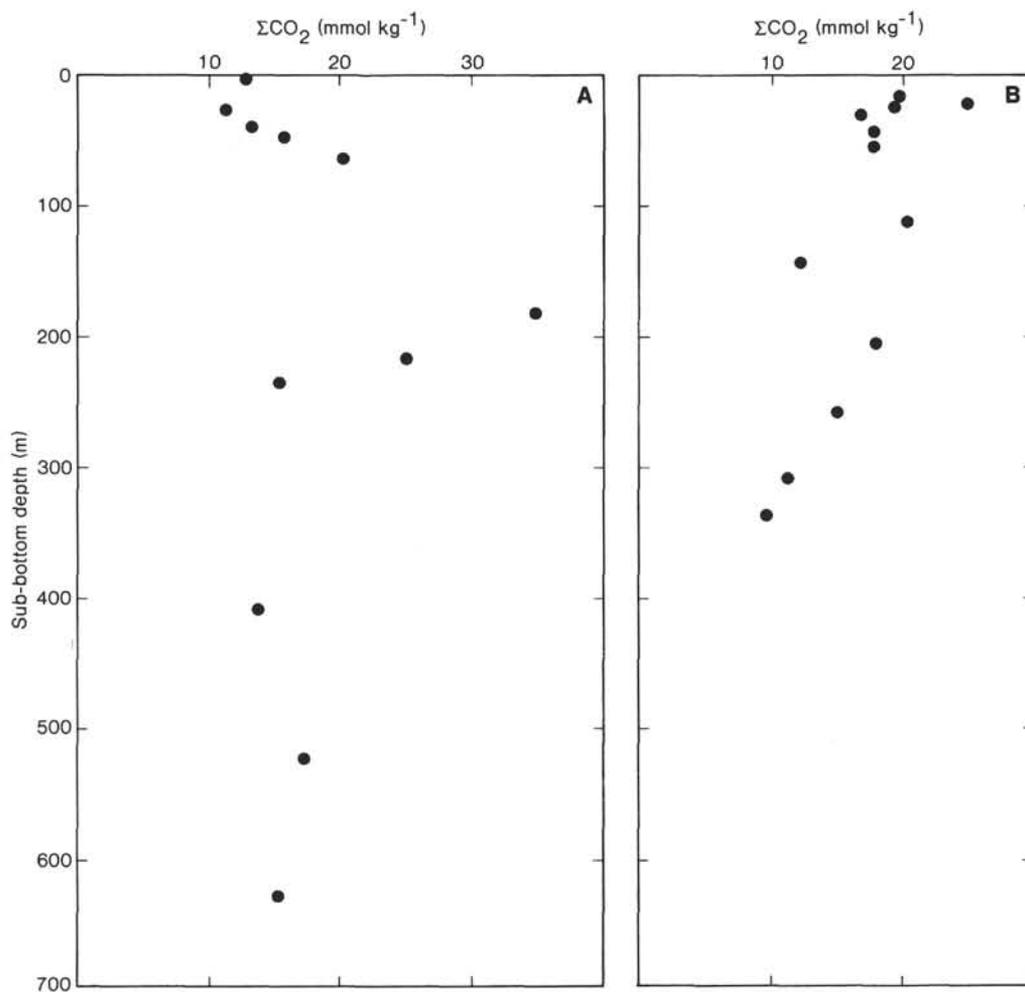


Figure 2. Plots of interstitial total carbon dioxide concentrations versus sub-bottom burial depth in Nankai Trough sediments, Leg 87. A, Site 582; B, Site 583.