31. ISOTOPIC COMPOSITION OF INTERSTITIAL FLUIDS IN SEDIMENT OF THE NANKAI TROUGH, DEEP SEA DRILLING PROJECT LEG 87

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ABSTRACT

The isotopic compositions of dissolved CO\textsubscript{2} and CH\textsubscript{4} in sediments of the Nankai Trough indicate that CH\textsubscript{4} is formed during early diagenesis by microbial reduction of CO\textsubscript{2}. At the shallowest sampled depths, the CO\textsubscript{2} dissolved in the pore water is unusually enriched in $^{13}$\textsubscript{C} ($\delta^{13}$\textsubscript{C} = -35.2‰), indicating contribution of CO\textsubscript{2} from oxidation of CH\textsubscript{4}. 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 CH\textsubscript{4} 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 $^{13}$\textsubscript{C}/$^{12}$\textsubscript{C} ratios of CH\textsubscript{4} and CO\textsubscript{2} species dissolved in the pore waters of marine sediments (Claypool and Threlkeld, 1983). We are trying to use natural $^{13}$\textsubscript{C}-abundance as a tracer to interpret rates of organic matter decomposition, assuming that CH\textsubscript{4} and CO\textsubscript{2} have a kinetically controlled, product-precursor relationship. If rates can be inferred from $^{13}$\textsubscript{C}-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 (Geary 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). $^{13}$\textsubscript{C}/$^{12}$\textsubscript{C} was measured on CO\textsubscript{2} gas in a Finnigan-MAT 251 mass spectrometer, and the results expressed in the delta notation, relative to the Peedee belemnite (PDB) standard:

$$\delta (\%o) = ([R_{sample}/R_{standard}-1] \times 10^3)$$

where $R = ^{13}$\textsubscript{C}/$^{12}$\textsubscript{C}.

RESULTS

Total dissolved CO\textsubscript{2} concentration ($$\Sigma$$CO\textsubscript{2}) and $\delta^{13}$\textsubscript{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 $\Sigma$CO\textsubscript{2} at Holes 582 and 583, and of CH\textsubscript{4} at Hole 583 show similar trends. The most $^{12}$\textsubscript{C}-enriched $\Sigma$CO\textsubscript{2} and CH\textsubscript{4} occurs at the shallowest depths (<30 m). At greater depths, the $\delta^{13}$\textsubscript{C} is relatively constant (± 2‰) with tendencies toward heavier CH\textsubscript{4} and CO\textsubscript{2} values below about 100 m. The $\Sigma$CO\textsubscript{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 $\delta^{13}$\textsubscript{C} profiles for both CH\textsubscript{4} and $\Sigma$CO\textsubscript{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 CH\textsubscript{4} 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 $\delta^{13}$\textsubscript{C} of CH\textsubscript{4} remains nearly constant at -70 ± 1‰. Methane carbon isotopic compositions below 250 m depth in Hole 583F are slight-
ly heavier (-66.7 to -68.1‰). The most shallow \( \Sigma CO_2 \) sample came from 3 m depth in Hole 582 and has \( \delta ^{13}C \) value of -35.2‰, which is unusually light for 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 \( \delta ^{13}C \) of \( CO_2 \) rapidly reaches positive values (around +10‰) and generally ranges from +6 to +13‰. These positive \( \delta ^{13}C \) values are interpreted as kinetic \( ^{13}C \)-enrichment in the \( CO_2 \) reservoir, resulting from \( CH_4 \) generation by \( CO_2 \) reduction (Claypool and Threlkeld, 1983).

The \( \delta ^{13}C \) profiles for \( CH_4 \) and \( \Sigma CO_2 \) 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 sulfate 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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REFERENCES


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Figure 1. Plots of carbon isotope ratios of methane and total dissolved carbon dioxide from vacutainer gas and interstitial water samples versus sub-bottom burial depth in Nankai Trough sediments, Leg 87. A, Site 583, CH₄; B, Site 582, ECO₂; C, Site 583, ECO₂. δ¹³C 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.