

## 11. ISOTOPIC COMPOSITION OF GASES AND INTERSTITIAL FLUIDS IN SEDIMENT OF THE VØRING PLATEAU, ODP LEG 104, SITE 644<sup>1</sup>

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### INTRODUCTION

Pleistocene- to middle Miocene-age sediment was drilled at Site 341 (67° 20.1'N, 6° 06.6'E) on the inner Vøring Plateau during Leg 38 of the Deep Sea Drilling Project (DSDP). In 1985, the Ocean Drilling Program (ODP) returned to the inner Vøring Plateau near Site 341 and drilled a new hole at Site 644<sup>3</sup> (66° 40.7'N, 4° 34.6'E) as part of a transect to study Norwegian Sea paleoenvironments. In Hole 341, gas expansion pockets formed in cores which were recovered from depths below 50 m. This gas was characterized as predominantly methane with  $\delta^{13}\text{C}$  values in the range of  $-87$  to  $-77$  ‰ (Morris, 1976). At Site 644, sediment gas and pore-water samples were obtained to study the geochemistry of methanogenesis. Of particular interest is the possibility that methane hydrate might be present in these sediments.

### SAMPLES AND METHODS

Sediment gases and interstitial waters from Site 644 were sampled using standard procedures (Gealy and Dubois, 1971; Manheim, 1966). Gas samples were withdrawn from expansion cracks in cored sediments and stored in Vacutainer<sub>TM</sub> tubes.<sup>4</sup> Pore-water samples were squeezed from sediments and collected in plastic syringes.

Ten gas samples and ten interstitial pore-water samples were analyzed to determine (a) chemical composition ( $\text{N}_2$ ,  $\text{CO}_2$ , and  $\text{C}_1$  through  $\text{C}_6$ ) and  $^{13}\text{C}/^{12}\text{C}$  measurement of methane ( $\delta^{13}\text{C}$   $\text{CH}_4$ ), and (b) both concentration ( $\text{mmol kg}^{-1}$ ) and  $^{13}\text{C}/^{12}\text{C}$  ( $\delta^{13}\text{C}$ ) of the carbonate species (mainly bicarbonate) and  $\text{CO}_2$  collectively as total dissolved  $\text{CO}_2$  ( $\Sigma\text{CO}_2$ ).

Composition of the gas collected in the Vacutainer tubes was determined by injecting an 18  $\text{cm}^3$  sample into an HP 5710A gas chromatograph (GC) equipped with a thermal conductivity (TC) detector and effluent peak withdrawal port. The methane peak was collected from the TC detector in a gas-tight syringe and combusted in a modified LECO Induction Furnace equipped with a closed-loop gas pumping system,  $\text{MnO}_2$  scrubber, an auxiliary CO conversion furnace, and  $\text{CO}_2$  cryogenic trap. Combustion at 1,000°C for 3 min in a recirculating, excess of purified oxygen (at +5 psi) within the furnace results in total conversion of methane to carbon dioxide and water. The carbon dioxide formed was collected in a liquid oxygen cold trap permitting recirculation of oxygen within the system. Further purification and dehydration of the gas was achieved by cryogenic distillation under vacuum. The volume of  $\text{CO}_2$  produced was measured via a calibrated manometer, and collected for isotopic determination on a Finnigan MAT 251, 90° sector isotope ratio mass spectrometer.

The volume and the carbon isotopic composition of the dissolved  $\text{CO}_2$  in interstitial pore waters were determined by acidifying the pore-water samples under vacuum prior to the collection and measurement of the liberated product on the mass spectrometer. A specific volume of pore water, required to generate sufficient  $\text{CO}_2$  gas for isotopic measurement, based on its alkalinity, was transferred to a sample reaction vessel

fitted with a rotating side arm containing 2 N HCl for acidification and generation of carbon dioxide gas. Atmospheric contamination of  $\text{CO}_2$  within the reaction vessels was minimized by sweeping the apparatus with a stream of purified, dry  $\text{N}_2$ . The evolved  $\text{CO}_2$  was dehydrated and purified, and the volume was measured following the techniques described above. The acidified water was then preserved for subsequent analysis of dissolved sulfate including measurement of  $\delta^{34}\text{S}$ . Remaining unacidified water was preserved for hydrogen/deuterium ratio measurement.

Isotopic compositions were compared with a carbon dioxide working reference standard prepared from NBS-19 calcite. Values are reported in the standard delta notation in units of per mil (‰) relative to the Pee Dee belemnite standard (PDB):

$$\delta^{13}\text{C} \text{ ‰} = [(R_{\text{sample}}/R_{\text{PDB}}) - 1] \times 10^3, \text{ where} \\ R = ^{13}\text{C}/^{12}\text{C}$$

Routinely repeated isotopic analyses are performed on random samples as well as on standards. Isotopic results are reproducible within  $\pm 0.5$ ‰. Chemical compositions reported are reproducible within  $\pm 5$ %.

### RESULTS

$\text{CH}_4$  and  $\text{CO}_2$  contents and isotopic compositions of gas samples from Site 644 are listed in Table 1. Both the concentration ( $\text{mmol kg}^{-1}$ ) and  $\delta^{13}\text{C}$  of  $\Sigma\text{CO}_2$  for pore-water samples are reported in Table 2. (Total dissolved  $\text{CO}_2$  is usually referred to as dissolved bicarbonate in the discussion that follows). The relations with depth (meters below the sea floor [mbsf]) and the carbon isotopic composition of both  $\text{CH}_4$  and  $\Sigma\text{CO}_2$  at Site 644 are depicted in Figure 1A and 1B, respectively. Also shown in Figure 1A are the  $\delta^{13}\text{C}$  values of methane in gas samples collected on DSDP Leg 38, as analyzed and reported by Morris (1977). Figure 2 illustrates the relation between concentrations of  $\Sigma\text{CO}_2$ ,  $\text{SO}_4^{2-}$  and alkalinity with respect to depth. Concentrations of  $\Sigma\text{CO}_2$  and alkalinity display relations with depth that are inverse to  $\text{SO}_4^{2-}$ .

### DISCUSSION

Sulfate reduction and methanogenesis control the pore-fluid chemistry of sediments cored at Site 644. The sediments appar-

Table 1. % $\text{CH}_4$  and % $\text{CO}_2$  (air-free) and  $\delta^{13}\text{C}$  of  $\text{CH}_4$  in gas samples, Site 644, ODP Leg 104.

Sample (hole-core-section)	Meters below sea floor	$\text{CH}_4$ (%)	$\text{CO}_2$ (%)	$\delta^{13}\text{C}$ of $\text{CH}_4$ (‰)
644-10-1	83.0	98.9	0.6	-78.9
644B-11-3	93.4	97.0	2.8	-77.1
644A-11-4	96.8	99.5	0.4	-76.6
644B-13-3	110.1	98.8	1.2	-77.4
644B-14-1	111.6	99.2	0.8	-76.9
644B-14-3	114.8	99.2	0.7	-76.7
644A-14-2	122.4	99.3	0.7	-76.9
644A-15-5	136.2	98.7	1.3	-75.3
644A-16-2	141.4	99.0	0.7	-75.5
644A-17-1	150.3	97.5	1.9	-74.2

<sup>1</sup> Eldholm, O., Thiede, J., Taylor, E., et al., 1989. Proc. ODP, Sci. Results, 104: College Station, TX (Ocean Drilling Program).

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<sup>3</sup> Refer to the location figure in the introduction to this volume.

<sup>4</sup> Use of trade names in this paper does not constitute endorsement by the U.S. Geological Survey and is for descriptive purposes only.

**Table 2. Concentration and  $\delta^{13}\text{C}$  of total dissolved carbonate, ( $\Sigma\text{CO}_2$ ), in interstitial pore-water samples, Hole 644A, ODP Leg 104.**

Sample (core-section)	Meters below seafloor	$\Sigma\text{CO}_2$ ( $\text{mmol kg}^{-1}$ )	$\delta^{13}\text{C}$ $\Sigma\text{CO}_2$ (‰)
1-4	5.9	6.7	-20.1
3-4	22.1	15.1	-31.8
5-3	39.6	14.1	-18.5
7-2	57.1	12.7	-11.2
10-4	88.6	11.7	-1.6
14-3	125	13.6	+0.6
16-4	146	14.3	-0.2
20-2	181	13.3	-4.2
25-2	209	9.6	+0.5
34-4	252	10.2	+0.1

ently are anoxic at a shallow (1 m) depth beneath the sea floor. Sulfate reduction is the dominant diagenetic process over the 0 to 25 mbsf depth interval, as shown by the depletion of sulfate (Fig. 2) accompanied by an increase in  $^{12}\text{C}$ -enriched total dissolved  $\text{CO}_2$  (Fig. 1B, extrapolated). Below a depth of about 25 mbsf, methane generation by  $\text{CO}_2$  reduction becomes the dominant anaerobic respiration process. Evidence for onset of methanogenesis includes (a) the reversal in the trend of  $\delta^{13}\text{C}$  of  $\Sigma\text{CO}_2$  with depth (Fig. 1B), and (b) the appearance of significant methane which was observed in the cores recovered below depths of about 40 mbsf. The unusually negative  $\delta^{13}\text{C}$  value of  $-31.8\text{‰}$  for the dissolved bicarbonate in the pore water at 22.1 mbsf indicates that methane is being oxidized at the base of the sulfate reduction zone.

In Figure 1A, the methane  $\delta^{13}\text{C}$  values measured by Morris (1976) on gas samples from nearby DSDP Site 341 are plotted and overlap with data from ODP Site 644. The trend of increasing methane  $\delta^{13}\text{C}$  with increasing depth at Site 644 is directly related to the subparallel trend of bicarbonate  $\delta^{13}\text{C}$  (Fig. 1B). The dissolved bicarbonate in pore water is the immediate carbon source for the formation of methane. The  $\delta^{13}\text{C}$  of dissolved bicarbonate reflects preferential removal of  $^{12}\text{C}$ -enriched  $\text{CO}_2$  as

$\text{CH}_4$ . The decrease in alkalinity after the onset of methanogenesis is in a range from about  $21 \text{ mmol kg}^{-1}$  at a depth of 22 mbsf to about  $16 \text{ mmol kg}^{-1}$  at about 90 mbsf (Fig. 2). Over this same depth interval, the isotopic  $\delta^{13}\text{C}$  enrichment of the dissolved bicarbonate changes from  $-31.8\text{‰}$  to about  $0\text{‰}$ , and the  $\delta^{13}\text{C}$  of methane changes from approximately  $-95\text{‰}$  (extrapolated) to about  $-75\text{‰}$ .

Similar trends in both the concentration and  $\delta^{13}\text{C}$  of the dissolved bicarbonate and methane  $\delta^{13}\text{C}$  were observed for samples from DSDP Hole 533 on the Blake Outer Ridge (Claypool and Threlkeld, 1983). At Hole 533, these pore fluids trends were modeled using open-system Rayleigh distillation equations (Wigley et al 1978), and carbon-isotope mass balance calculations. These calculations suggest that about  $17 \text{ mmol kg}^{-1}$  of methane were generated in Pleistocene sediment at a depth of 112 mbsf at DSDP Hole 533. By analogy with Hole 533, similar calculations indicate that about  $15 \text{ mmol kg}^{-1}$  of methane have been generated in Pleistocene sediment at a depth of 100 mbsf at ODP Site 644. The concentration of methane required to stabilize methane hydrate under the pressure and temperature conditions of Hole 644 is on the order of  $100 \text{ mmol kg}^{-1}$  (Claypool and Kvenvolden, 1983). Therefore, both the concentration and  $\delta^{13}\text{C}$  of  $\Sigma\text{CO}_2$  trends, along with the methane  $\delta^{13}\text{C}$  trend at Site 644, suggest that insufficient methane has been generated to stabilize methane hydrate in this Pleistocene sediment. Gas hydrates were specifically sought after in Hole 644B, but were not observed (Kvenvolden et al, this volume).

No consistent trends are shown in the methane and  $\Sigma\text{CO}_2$  isotopic compositions and  $\Sigma\text{CO}_2$  concentration over the depth interval from about 100 to 250 m in Hole 644. Methane  $\delta^{13}\text{C}$  values level off in the range of  $-76 \pm 3\text{‰}$  at both Site 644 and Site 341 (Morris, 1976). The  $\delta^{13}\text{C}$  of  $\Sigma\text{CO}_2$  is generally about  $0\text{‰}$  below 100 m. The  $\Sigma\text{CO}_2$  concentration increases from about  $2 \text{ mmol kg}^{-1}$  at the surface to about  $15 \text{ mmol kg}^{-1}$  at 22 m, then decreases to about  $12 \text{ mmol kg}^{-1}$  at 90 m, followed by an increase to about  $14 \text{ mmol kg}^{-1}$  at 150 m and another decrease to  $10 \text{ mmol kg}^{-1}$  at 250 m. Alkalinity is generally about  $1.4 \times \Sigma\text{CO}_2$ , except for the deepest sample at 252 mbsf, in which alka-

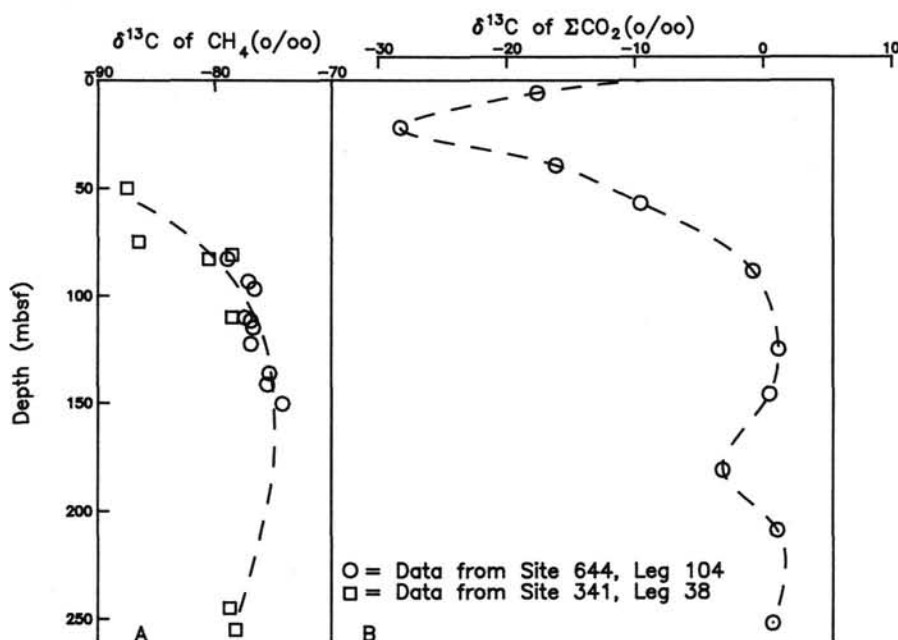


Figure 1. A. The  $\delta^{13}\text{C}$  values of  $\text{CH}_4$  in sediment cores from Site 644, Leg 104 compared to those from Site 341, Leg 38. B. The  $\delta^{13}\text{C}$  of dissolved  $\Sigma\text{CO}_2$  from interstitial pore-water samples, Site 644, Leg 104. Plotted lines are extrapolated to the seafloor.

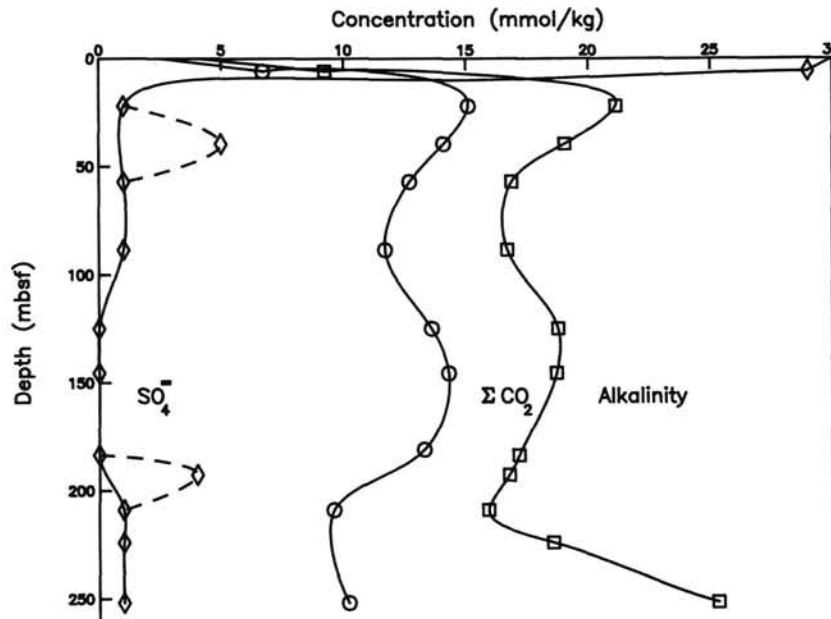


Figure 2. Concentration ( $\text{mmol kg}^{-1}$ ) of dissolved sulfate and titration alkalinity (from shipboard analyses), and  $\Sigma\text{CO}_2$  (this report) vs. depth (mbsf). Plotted lines are extrapolated to the seafloor.

linity is  $2.4 \times \Sigma\text{CO}_2$ . The lack of significant change in  $\delta^{13}\text{C}$  values of methane and  $\Sigma\text{CO}_2$  at depths below 100 mbsf may indicate (a) that methanogenesis has stopped or slowed below 100 mbsf, or (b) that steady-state  $\delta^{13}\text{C}$  values are reached with large degrees of reaction progress and constant input-output rate ratios (Wigley et al 1978).

In summary, sediments at ODP Site 644 are typical of hemipelagic sediments from many previous DSDP sites as observed by both the concentration and  $\delta^{13}\text{C}$  of dissolved  $\Sigma\text{CO}_2$  and the  $\delta^{13}\text{C}$  of dissolved methane in pore waters. The section penetrated is not unusually high in organic carbon content (0.4 to 1.0%), and the diagenetic processes have not resulted in unusually high concentrations of dissolved  $\Sigma\text{CO}_2$  (or extreme  $^{13}\text{C}$ -enrichment of methane and  $\Sigma\text{CO}_2$ ) that are characteristic of sediments in which gas hydrates are present.

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