24. ISOTOPIC COMPOSITION OF INTERSTITIAL FLUIDS AND ORIGIN OF METHANE IN SLOPE SEDIMENT OF THE MIDDLE AMERICA TRENCH, DEEP SEA DRILLING PROJECT LEG 84[1]

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ABSTRACT

CH_4 and CO_2 species in pore fluids from slope sediments off Guatemala show extreme ^{13}C-enrichment ($\delta^{13}C$ of -41 and $+38‰$, respectively) compared with the typical degree of ^{13}C-enrichment in pore fluids of DSDP sediments ($\delta^{13}C$ of -60 and $+10‰$). These unusual isotopic compositions are believed to result from microbial decomposition of organic matter, and possibly from additional isotopic fractionation associated with the formation of gas hydrates. In addition to the isotopic fractionation displayed by CH_4 and CO_2, the pore water exhibits a systematic increase in $\delta^{18}O$ with decrease in chlorinity. As against seawater $\delta^{18}O$ values of 0 and chlorinity of 19‰, the water collected from decomposed gas hydrate from Hole 570 had a $\delta^{18}O$ of $+3.0‰$ and chlorinity of 9.5‰. The isotopic compositions of pore-fluid constituents change gradually with depth in Hole 568 and discontinuously with depth in Hole 570.

INTRODUCTION

Previous drilling on DSDP Legs 66 and 67 demonstrated the presence of gas-charged sediments and gas hydrates on the continental slope of Middle America. The sampling and analytical programs on these earlier legs, however, were not specifically designed for the study of gassy sediments. In addition, the presence of gas hydrate and the possibility of free gas beneath the gas hydrate zone prevented achievement of some of the drilling objectives. Subsequently, Leg 84 was scheduled to drill in the same area as Leg 67. Drilling objectives for Leg 84 were selected in areas where gas hydrates were believed not to be a problem, or where they could be reached at depths shallower than the base of the gas hydrate zone. In addition, one site was selected for the specific study of gas hydrates, with specialized equipment to be deployed. This is the second site selected for intensive study of gas hydrates, the first being Site 533 on Leg 76 (Kvenvolden and Barnard, 1983).

On Leg 84, Site 568 was selected for intensive study of gas hydrates. Interstitial fluid samples were collected at closely spaced depth intervals. The pressure core barrel was used in an attempt to sample gas hydrates. Readily observable gas hydrate was recovered in Hole 568, and an unexpected layer of relatively pure gas hydrate, 3 to 4 m thick, was cored in Hole 570, with about 1 m of gas hydrate recovered. Minor gas hydrate occurrences were also observed in Holes 565, and possibly in Holes 566 and 569 (Kvenvolden and McDonald, this volume).

In this chapter, we present the results of chemical and isotopic analyses of the interstitial fluids (gas and water) from selected Holes on Leg 84. Also, we discuss the diagenetic processes responsible for the gas and possible effects of gas hydrate stability and occurrence on the operation of these diagenetic processes.

SAMPLES AND METHODS

Sediment gas and interstitial water were sampled according to standard DSDP procedures (Gealy and Dubois, 1971; Manheim, 1966). Gases were analyzed by the procedures of Claypool et al. (1980) and Schoell (1980), with modifications. Water samples were analyzed by the techniques of Presley and Claypool (1971) and Epstein and Mayeda (1953). $^{13}C/^{12}C$, $^{18}O/^{16}O$, and D/H were measured by standard techniques on CO_2 and H_2 gas; the results are expressed in the delta notation (δ, ‰ $= \{[R_{sample}/R_{standard}] - 1\}10^3$, where $R = {}^{13}C/^{12}C$, $^{18}O/^{16}O$, D/H) relative to the standards PeeDee belemnite (PDB) for carbon and standard mean ocean water (SMOW) for hydrogen and oxygen.

RESULTS

Pore-water samples from three holes (565, 568, 570) are listed by depth of burial in Table 1. The concentration and $\delta^{13}C$ of total dissolved carbonate (ΣCO_2) and the $\delta^{18}O$ of the water are reported, along with the shipboard determinations of chlorinity and titration alkalinity.

The chemical and isotopic compositions of gas samples from Holes 565, 568, and 570 are given by depth of burial in Table 2. The $\delta^{13}C$ of CH_4 is given for each sample. On about half of the samples, δD of the CH_4 was measured, and for fewer samples, $\delta^{13}C$ of the CO_2 was also measured.

Selected data from Tables 1 and 2 are plotted in Figure 1. The carbon isotopic compositions of CH_4 and total dissolved CO_2 (ΣCO_2) in the interstitial water show similar trends at each of the three sites, but with signifi-

Table 1. Concentration and $\delta^{13}C$ of total dissolved carbonate, and $\delta^{18}O$ of interstitial waters, with chlorinity and alkalinity, Sites 565, 568, and 670, DSDP Leg 84.

Hole-Core-Section	Sub-bottom depth (m)	ΣCO_2 (mmol kg^{-1})	$\delta^{13}C$ (‰)	$\delta^{18}O$ (‰)	Chlorinity[a] (‰)	Titration alkalinity[a] (meq L^{-1})
565-1-5	7.4	3.1	−11.8	—[b]	19.1	4.7
565-2-5	17.9	7.4	−25.8	+0.47	19.0	11.2
565-3-5	27.4	11.6	−28.1	—	18.6	19.5
565-5-5	46.4	—	+7.5	—	17.3	29.9
565-6-4	54.4	19.8	+9.5	+0.47	17.0	28.5
565-8-4	73.4	27.6	+13.6	+0.51	16.5	38.4
565-11-1	97.4	25.9	+14.4	—	15.2	34.7
565-13-5	122.4	19.8	+15.1	—	14.4	37.2
565-17-1	154.4	20.0	+16.6	−0.16	14.2	27.8
565-19-3	176.4	16.1	+16.8	—	14.0	23.4
565-23-1	211.4	11.0	+15.7	—	13.8	15.1
565-27-5	255.4	6.3	+13.9	—	15.3	9.3
565-29-6	275.9	7.2	—	—	13.9	10.3
568-1-1	1.4	11.2	−14.8	+2.85	—	—
568-1-2	3.0	27.5	−13.5	+0.28	19.1	41.5
568-2-3	7.9	26.9	−16.4	+0.34	—	—
568-3-4	19.0	69.0	+12.7	+0.37	18.6	85.3
568-4-3	27.2	75.0	+15.1	+0.37	18.2	88.2
568-5-4	38.3	88.5	+16.2	+0.61	18.1	97.1
568-6-4	48.0	99.7	+17.4	+1.05	17.1	118.5
568-8-5	68.1	90.9	+18.3	—	16.1	115.8
568-10-3	84.6	70.5	+18.9	+0.71	16.0	93.4
568-12-3	103.3	64.3	+19.8	—	14.5	84.5
568-14-4	123.8	47.2	+20.3	+1.18	13.6	64.9
568-18-4	162.5	19.1	+23.4	+1.64	12.5	25.7
568-24-4	220.7	7.3	+25.9	—	13.3	11.5
568-32-5	299.4	6.3	+23.1	+2.20	12.0	9.8
568-36-4	336.9	7.4	+26.9	+2.48	11.4	10.6
568-43-2	401.7	14.8	+35.7	+3.02	9.5	20.5
570-1-3	4.5	26.1	−24.5	+0.26	19.5	36.8
570-4-3	31.7	38.7	+7.7	—	19.5	51.0
570-6-5	53.9	36.4	+9.9	+0.51	19.0	52.9
570-10-1	86.6	51.3	+10.2	—	19.0	63.1
570-16-5	150.5	39.7	+14.0	+0.08	18.2	51.9
570-20-1	183.3	27.8	+15.3	+0.13	18.8	41.3
570-27 (hydrate)	249.0	—	—	+3.72	0.7	—
570-25-3	234.2	16.6	+21.2	—	18.5	27.4
570-30-3	279.5	13.0	+37.5	—	14.3	18.1
570-36-1	337.1	2.2	+27.1	+1.74	8.9	3.7

[a] Shipboard analyses.
[b] — = no analysis.

cantly more ^{13}C-enrichment at greater depths in Holes 568 and 570, compared with Hole 565.

The ΣCO_2 and titration alkalinity profiles with depth are also quite different at the three drill sites. In Hole 565, ΣCO_2 and alkalinity maxima of about 30 mmol/kg and 40 meq/L, respectively, are observed at depths of about 70 to 100 m, and decrease regularly with increasing depth, approaching seawater values at depths below about 256 m. In Hole 458, maxima of 100 mmol/kg and 118 meq/L occur at about 50 m depth, and decrease to about 7 mmol/kg and 10 meq/L below 200 m. In Hole 570, ΣCO_2 and titration alkalinity increase to 51 mmol/kg and 63 meq/L at about 90 m, then decrease regularly to seawater values below 300 m.

Where the $\delta^{13}C$ of CO_2 in gas samples has been measured, the estimated difference between the coexisting CO_2 gas and ΣCO_2 is about 11 to 14‰, the CO_2 gas being lighter in all cases.

The δD–$\delta^{13}C$ crossplot (Fig. 2) for CH_4 shows different trends in Holes 568 and 570. Significantly more D-enrichment in CH_4 occurs at depth in Hole 568.

The $\delta^{18}O$ of the pore water is plotted against chlorinity in Figure 3. The same general trend of increasing $\delta^{18}O$ with decreasing chlorinity is observed in the Leg 84 data as was previously observed in this same area on Leg 67 (Harrison et al., 1982).

DISCUSSION

Hole 565 was drilled in 3111 m of water on the landward slope of the Middle America Trench off Costa Rica. Gas hydrate was recovered from a sandstone at a depth of about 278 m in Core 565-30. Isotopic composition of the major pore-fluid constituents in Hole 565 is fairly typical of other DSDP sites. Holes 568 and 570 were drilled in 2300 and 1700 m of water, respectively, off Guatemala. In comparison with Hole 565, the pore-fluid chemistry of Holes 568 and 570 is unusual and is the focus of the following discussion.

The interstitial-fluid chemistry of DSDP Leg 84 sediments is unique in at least three respects. First, extremely ^{13}C-enriched ΣCO_2 occurs in Holes 568 and 570. Second, samples of gas hydrate were recovered in both Hole

Table 2. Isotopic composition of CH$_4$ and CO$_2$ in gas samples from void-spaces in cores, Sites 565, 568, and 570, DSDP Leg 84.

Hole-Core-Section	Sub-bottom depth (m)	CH$_4$ $\delta^{13}C_{PDB}$ (‰)	CH$_4$ δD_{SMOW} (‰)	CO$_2$ $\delta^{13}C_{PDB}$ (‰)
565-6-6	58	−73.3	—[a]	—
565-19-4	177	−66.3	—	—
565-24-3	223	−64.7	—	—
565-29-2	270	−61.8	—	—
565-33,CC	319	−62.2	—	—
565-34-1	320	−63.6	—	—
568-4-4	28	−70.8	−196	—
568-5-5	39	−68.0	—	—
568-6-4	47	−67.3	−194	+3.4
568-7-3	56	−66.3	—	—
568-8-5	68	−65.8	−192	+6.3
568-9-4	76	−65.6	—	—
568-10-4	85	−65.3	−196	+5.6
568-12-4	104	−63.9	—	—
568-13-4	114	−63.4	−194	+9.8
568-14-6	126	−63.0	—	—
568-15-6	135	−62.3	−193	—
568-16-4	137	−61.2	−198	—
568-17-4	153	−59.8	—	—
568-18-3	160	−57.4	−191	—
568-19-7	176	(−39.8)[b]	(−120)	—
568-20-6	184	−54.6	—	—
568-22-5	202	−51.5	−180	—
568-23-2	207	−50.1	−177	—
568-24-4	220	−49.5	—	—
568-25-6	232	−48.8	−171	—
568-27-3	247	−47.6	—	—
568-28-4	259	−47.1	−171	—
568-29-5	270	−46.7	—	—
568-30-6	281	−46.4	−166	—
568-32-6	300	−46.5	—	—
568-33-6	310	−46.3	−164	+0.2
568-35-4	327	−46.0	—	—
568-34-6	320	−45.9	−162	—
568-36-6	339	−45.4	−161	—
568-37-4	346	−44.3	—	—
568-38-6	359	−45.0	−164	—
568-39-3	363	−45.5	—	—
568-40-3	373	−44.2	−161	—
568-41-5	386	−44.3	—	—
568-42-6	398	−41.2	−145	—
568-43-4	404	−42.9, −44.3	—	—
568-44-4	414	−43.2	—	—
570-2-5	11.4	−83.4	−208	—
570-4-2	30	−77.4	—	—
570-6-5	53	−73.8	—	—
570-7-4	61	−71.6	−193	−2.0
570-8-3	69	−70.5	−191	+0.3
570-9-2	78	−69.4	—	—
570-10-2	88	−70.3	−193	−0.4
570-11-1	96	−69.2	—	—
570-14-5	130	−68.6	−193	−0.2
570-15-2	136	−68.9	—	—
570-16-6	151	−68.2	−191	+0.3
570-17-3	157	−67.5	—	—
570-18-1	164	−67.3	−190	−0.2
570-19-3	176	−66.1	—	—
570-20-1	183	−65.1	−191	+1.2
570-21-2	193	−63.1	—	—
570-22-3	205	−62.0	−191	+4.0
570-23-2	213	−60.3	—	—
570-24-3	224	−58.0	−185	—
570-25-4	234	−56.4	—	—
570-26-4	245	−54.4	−189	—
570-27-1	250	−43.6	−178	—
570-27-1	250	−40.3	−163	—
570-28	265	−39.6	−183	—
570-28-6	267	−43.4	—	—
570-29	270	−38.7	−188	—
570-29-4	274	−43.0	−185	+15.6
570-30-4	284	−42.9	−188	+15.2
570-31-1	289	−42.8	—	—
570-32-4	302	−42.7	−196	—
570-34-1	318	−42.2	−187	—
570-35-2	329	−42.0	−188	—
570-36-1	336	−41.7	−185	—
570-37-1	347	−41.0	—	—
570-41-2	386	−41.9	—	—

[a] — = no analysis.
[b] Values in parentheses are suspect because of deviation from trends.

568 and Hole 570 at about the depths at which the greatest ^{13}C-enrichment in CH$_4$ and CO$_2$ occurs. And third, low-chlorinity and ^{18}O-enriched pore water was present in Holes 568 and 570, confirming earlier observations from Leg 67 (Harrison et al., 1982). These unusual aspects of pore-fluid chemistry are undoubtedly related to the presence of gas hydrate, but the nature of the relationship is unclear. We know from observations on samples from Hole 533 (Claypool and Threlkeld, 1983) and Hole 565 (this chapter) that gas hydrate occurrence is not always accompanied by such degrees of ^{13}C-enrichment in CH$_4$ and CO$_2$. This suggests that the isotope effects are somehow related to the unusually organic-carbon–rich nature of these upper-rise and slope sediments off Guatemala. For example, is the extreme ^{13}C-enrichment in CH$_4$ and ΣCO$_2$ due to an isotope effect associated with more extensive gas hydrate formation? Or do unusually rapid rates of CH$_4$ generation occur at certain depths, leading to (1) extreme ^{13}C-enrichment in dissolved CH$_4$ and CO$_2$ (because of kinetic ^{12}C-depletion or diminished fractionation at more rapid rates) and (2) localized high concentrations of CH$_4$ and consequent localized gas hydrate formation?

Abundant CH$_4$ is required for the formation of gas hydrates. This CH$_4$ could be supplied to the sediments in two ways: first, by microbiological degradation of organic matter buried with the sediments; and second, by upward migration of natural gas generated by thermal degradation of organic matter in deeper, hotter sediments. Biogenic and thermogenic CH$_4$ occurrences are usually distinguished on the basis of isotopic and chemical compositions (Fuex, 1977; Schoell, 1983). Biogenic CH$_4$ generally has δ^{13}C more negative than −60 to −55‰, and is associated with very low contents (<0.1%) of C$_{2+}$ hydrocarbons. Thermogenic CH$_4$ usually has δ^{13}C of −45 to −30‰, and is accompanied by 1% or more of C$_{2+}$ hydrocarbons (except for CH$_4$ originating at very high temperatures). The δ^{13}C of CH$_4$ is more negative than −60‰ in sediments at all depths in Hole 565, and in sediments at depths shallower than about 150 m in Hole 568, or shallower than 200 m in Hole 570 (Fig. 1). However, CH$_4$ with δ^{13}C of −45‰ or heavier occurs in Hole 568 sediments below 350 m, and in Hole 570 sediments below 250 m. Thus, the δ^{13}C evidence alone could be interpreted to indicate the presence of biogenic gas in Hole 565 and the presence of both biogenic and thermogenic gas in Holes 568 and 570. The C$_{2+}$ contents are very low (<0.05%) in all cases, but this does not necessarily eliminate the possibility of a thermogenic origin for the isotopically heavy CH$_4$, because gases can become depleted in C$_{2+}$ hydrocarbons as a result of extensive migration (Coleman et al., 1977; Schoell, 1983).

The main evidence against significant amounts of upward-migrating thermogenic CH$_4$ in Guatemala slope sediments at shallow depths is the relationship between the δ^{13}C of coexisting CH$_4$ and CO$_2$ (Fig. 1). In Holes 568 and 570, the δ^{13}C of CH$_4$ is −41‰ (which is unusually positive for biogenic gas in marine sediments) near depths where the δ^{13}C of coexisting ΣCO$_2$ is +36 to +38‰ (a value which makes this residual pore-water
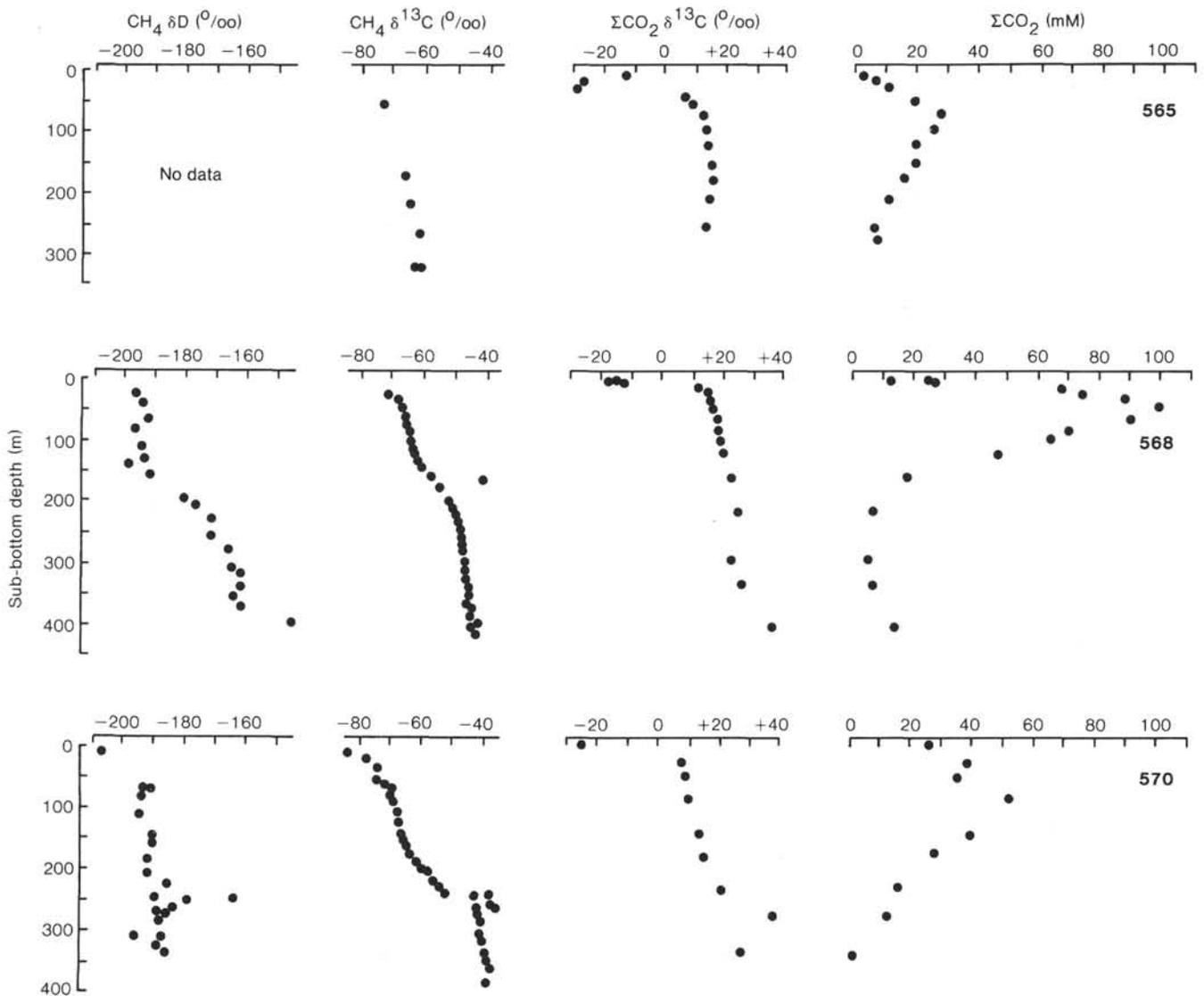
Figure 1. Isotopic composition (δD and δ^{13}C) of CH_4 in gas, and isotopic composition (δ^{13}C) and concentration of total dissolved CO_2 in pore-water samples from DSDP Sites 565, 568, and 570.

CO_2 among the most ^{13}C-enriched naturally occurring substances observed on Earth).

The 77‰ δ^{13}C difference between CH_4 (-41‰) and ΣCO_2 ($+36$‰) is essentially the same as the δ^{13}C difference in DSDP cores from other sites where CH_4 with δ^{13}C as negative as -90‰ has been observed (e.g., Hole 533, Leg 76; Claypool and Threlkeld, 1983). The observed δ^{13}C difference between coexisting CH_4 and ΣCO_2 is interpreted as resulting from a kinetic isotope effect associated with bacterial CO_2 reduction (Rosenfeld and Silverman, 1959). CO_2 reduction is the main process by which CH_4 originates in marine sediments during early diagenesis (Claypool and Kvenvolden, 1983). When CH_4 is generated in sediments, the ΣCO_2 reservoir becomes depleted in ^{12}C because of the preferential removal of ^{12}C-enriched CO_2 to form CH_4. In Figure 1, this is shown by the rapid increase in δ^{13}C of ΣCO_2 from negative to positive values just beneath the shallowest depth of significant CH_4 occurrence in the cores from Holes 565, 568,

and 570. The δ^{13}C of the ΣCO_2 reservoir undergoing CH_4 generation usually levels off at some positive value around $+10$ to $+15$‰. A possible explanation for this tendency of the ΣCO_2 reservoir to reach a constant δ^{13}C value during CH_4 generation is that additional CO_2 with δ^{13}C of about -25‰ is continually added by fermentation and decarboxylation processes, which establishes an isotopic balance between carbon added and carbon removed.

Kinetic Carbon-Isotope Effects

A more quantitative interpretation of kinetic isotope effects involved with early diagenetic CH_4 generation was given in connection with Leg 76, Hole 533 pore-fluid data (Claypool and Threlkeld, 1983). This treatment uses the open-system Rayleigh equations developed by Wigley et al. (1978) to model the concentration and δ^{13}C change of dissolved CO_2 reservoirs with depth (or time). The equations of Wigley et al. (1978) were extended for
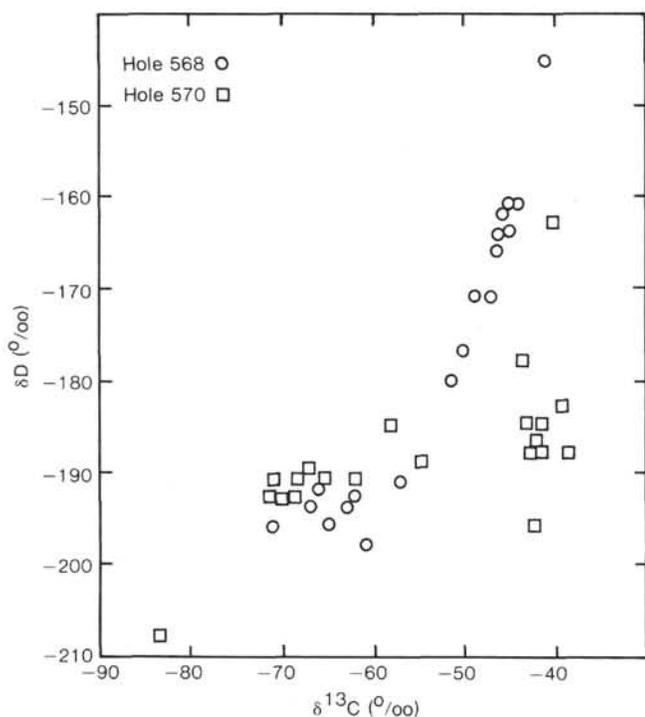
Figure 2. Crossplot of δD and $\delta^{13}C$ in CH_4 from DSDP Sites 568 and 570.
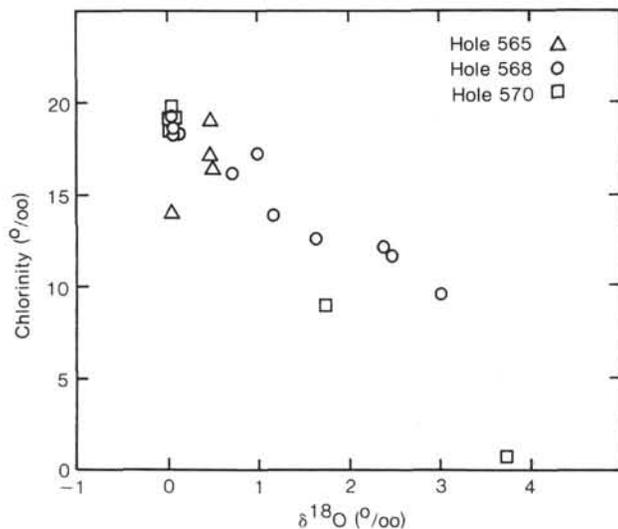
Figure 3. Crossplot of chlorinity and $\delta^{18}O$ of pore water at DSDP Sites 565, 568, and 570.

the Hole 533 data to give the $\delta^{13}C$ and amount of cumulative CH_4 production. The other parameters required are the CO_2-input:total-output rate ratio and the CH_4-output:CO_3-output rate ratio. Trial-and-error combinations of these rate ratios can produce acceptable agreement between observed and calculated $\delta^{13}C$ values and ΣCO_2 concentrations. Results of such calculations for the Leg 84 data are summarized in Table 3.

The profiles of ΣCO_2 concentration and $\delta^{13}C$, and $\delta^{13}C$ of CH_4 for Holes 565, 568, and 570 were modeled

over the depth intervals where CH_4 production was the dominant diagenetic process and the CO_2–depth relationship approximated a regular, monotonic function. A general pattern emerges from these input–output kinetic calculations. The initial stages of CH_4 generation (typically from the onset to the first maxima in the ΣCO_2 concentration–depth profile) can be modeled by a single-input (CO_2 with $\delta^{13}C$ of -25‰):single-output (CH_4 with 70‰ kinetic ^{12}C-enrichment) mechanism. Duplication of the ΣCO_2 increase during the initial stages of CH_4 generation requires that input:output rate ratios be greater than one. Later stages of CH_4 generation, at depths where CO_2 concentration is decreasing, usually cannot be adequately modeled by the one-input:one-output mechanism, because a given decrease in ΣCO_2 is accompanied by a much larger degree of ^{13}C-enrichment than is observed in DSDP pore waters. A one-input: two-output (CH_4 generation and CO_3 precipitation) mechanism usually will duplicate the observed concentration and $\delta^{13}C$ changes. The decreasing ΣCO_2 concentration requires that the input:output rate ratio be less than one. The CO_2 concentration decrease can be balanced with the appropriate $\delta^{13}C$ increases for ΣCO_2 and CH_4 by adjusting the CO_3:CH_4 output rate ratio.

The purpose of these kinetic models is to show that several combinations of concentration and $\delta^{13}C$ trends are possible in marine sediments. Variation in the relative rates of processes that are known to occur in anoxic marine sediments can produce the different ΣCO_2 and $\delta^{13}C$ gradients. The three main processes are CO_2 generation via anaerobic respiration/oxidation of organic matter, CO_2 reduction to CH_4 (utilizing H_2/electrons generated by oxidation), and carbonate precipitation (usually dolomite, ankerite, or siderite) that is promoted by pH increase resulting from CO_2-reduction. The observation of ^{13}C-enrichment with increasing concentration of ΣCO_2 is not necessarily incompatible with CH_4 production by CO_2 reduction, as has been stated by other investigators (Friedman and Murata, 1979; Carothers and Kharaka, 1980).

Equilibrium Carbon-Isotope Effects

If chemical species such as CO_2(gas), HCO_3^-, and CO_3^{2-} are exchanging atoms by reversible equilibrium reactions, then the carbon and oxygen of coexisting species should be in isotopic equilibrium. Equilibrium $^{13}C/$ ^{12}C fractionation between CO_2(g) and HCO_3^- is given by the following equation (from the data of Mook et al., 1974):

$$10^3 \ln \alpha = 9.55(10^3 T^{-1}) - 24.10$$

where T is temperature in K, and

$$\alpha = \frac{(^{13}C/^{12}C)_{HCO_3^-}}{(^{13}C/^{12}C)_{CO_2}}$$

is the fractionation factor between HCO_3^- and CO_2.

The $\delta^{13}C$ differences between HCO_3^- (as ΣCO_2) and CO_2(g) were estimated from the trends for Holes 568

Table 3. Parameters of input–output carbon-isotope and mass-balance equations (Wigley et al., 1978) that satisfactorily reproduce concentration and $\delta^{13}C$ of dissolved CO_2 in interstitial water of Holes 568 and 570.

Hole	Sub-bottom depth interval (m)	Initial HCO_3^- (mmol kg^{-1})	$\delta^{13}C$ (‰)	No. of inputs, outputs	Input-to-output ratio	Carbonate-to-methane output ratio
568	10–25	27	-16	1, 1	1.65	0
	25–50	75	$+15$	1, 1	1.62	0
	50–100	100	$+17$	1, 2	0.90	3
	100–300	70	$+20$	1, 2	0.90	12
	300–400	7	$+25$	1, 1	1.20	0
570	20–25	40	-25	1, 1	0.84	0
	55–87	36	$+10$	1, 1	2.0	0
	87–280	51	$+10$	1, 2	0.80	1.5
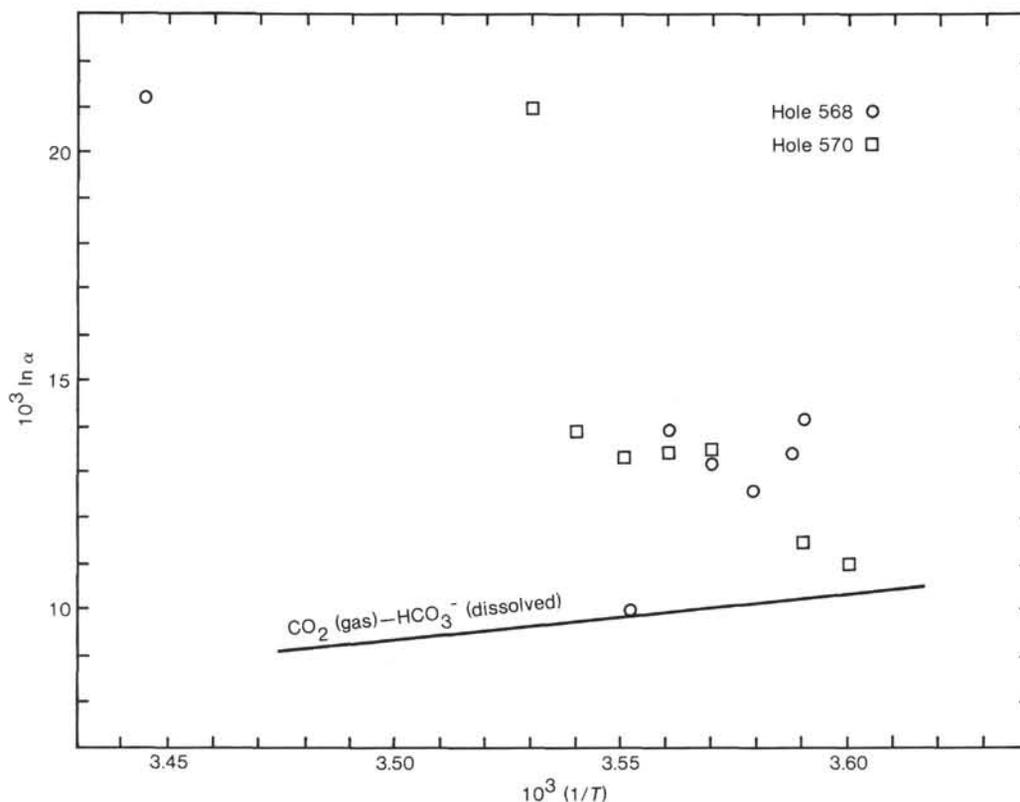
Figure 4. Observed $\delta^{13}C$ differences between coexisting CO_2 gas and dissolved ΣCO_2 (calculated as $10^3 \ln \alpha$; see text), plotted against estimated subsurface Kelvin temperature (as $10^3 \, T^{-1}$). The points are calculated from the difference between the inferred trends with depth because gas and water sample pairs from the same depth are usually not available. The line shown for comparison is the theoretical CO_2–HCO_3^- fractionation determined by Mook et al. (1974), as reported by Friedman and O'Neil (1977).

and 570 in Figure 1, and are plotted in Figure 4 as α_{eq} versus temperature. The temperature at any given depth was estimated from the bottom-water temperature and the thermal gradient (Kvenvolden and McDonald, this volume). The estimates of $\delta^{13}C$ differences were made near the depths where $\delta^{13}C$ of CO_2 measurements were available from gas analyses. The agreement is not good between the equilibrium fractionation factors (α_{eq}) calculated from the Leg 84 observations and those given by controlled lab experiments (the line from the preceding equation). A majority of the points (9 of 15), however, fall in a band that is parallel to the equilibrium line but offset by $(3.5 \pm 1) \times 10^3 \ln \alpha$. These points span the depth intervals from 50 to 100 m in Hole 568, and from 150 to 240 m in Hole 570. In both holes, these are the depth intervals where the ΣCO_2 and alkalinity concentrations show the greatest decrease, after reaching concentration maxima (Fig. 1). It can be assumed that the dissolved CO_2-species are in isotopic equilibrium under *in situ* conditions in the Guatemala slope sediments.

Therefore, the disagreement shown in Figure 4 must be due to various imperfections in the sampling and analytical procedures.

In contrast to isotopic equilibrium among species of the carbonate system, the assumption of carbon isotopic equilibrium between CH_4 and CO_2 in low-temperature sedimentary systems is not easily justified. Sackett and Chung (1979) observed no carbon-isotope exchange between CH_4 and CO_2 at 500°C for 10.5 days in the presence of mineral catalysts. Giggenbach (1982) reviews the relevant experimental data and suggests that any equilibration would be exceedingly slow ($> 10^{11}$ yrs.) at temperatures below 200°C. Despite the lack of experimental support for low-temperature carbon isotopic equilibration of sedimentary CH_4 and CO_2, some geochemists still favor the interpretation of temperature-dependent equilibrium fractionation in the formation of these gases (Gould and Smith, 1979; Friedman and Murata, 1979; Carothers and Kharaka, 1980). The $\delta^{13}C$ difference between CH_4 and CO_2 for Leg 84 pore fluids can be used to test the applicability of the equilibrium assumption. The calculations of Bottinga (1969, as plotted by Friedman and O'Niel, 1977) for the $^{13}C/^{12}C$ equilibrium fractionation between CH_4 and CO_2 gases for the tempera-

ture range 0 to 100°C can be summarized (for the temperature range 0 to 20°C) by the equation

$$10^3 \ln \alpha = 27.05(10^3 T^{-1}) - 4.80$$

where T is temperature in K, and

$$\alpha = \frac{(^{13}C/^{12}C)_{CO_2}}{(^{13}C/^{12}C)_{CH_4}}$$

Combining this equation with the equation given earlier for the $CO_2(g)$–HCO_3^- equilibrium fractionation, we can derive an equation for the CH_4–HCO_3^- fractionation which is

$$10^3 \ln \alpha = 36.6(10^3 T^{-1}) - 28.9$$

The $\delta^{13}C$ differences between the trends in Figure 1 for CH_4 and ΣCO_2 were plotted in Figure 5 as α_{eq} versus temperature, which was estimated in the manner already indicated. The lines shown are given by the equation for theoretical CH_4–HCO_3^- equilibrium (upper line) and CH_4–CO_2 equilibrium (lower line). The α values calculated from the trends in Figure 1 deviate from the CH_4–
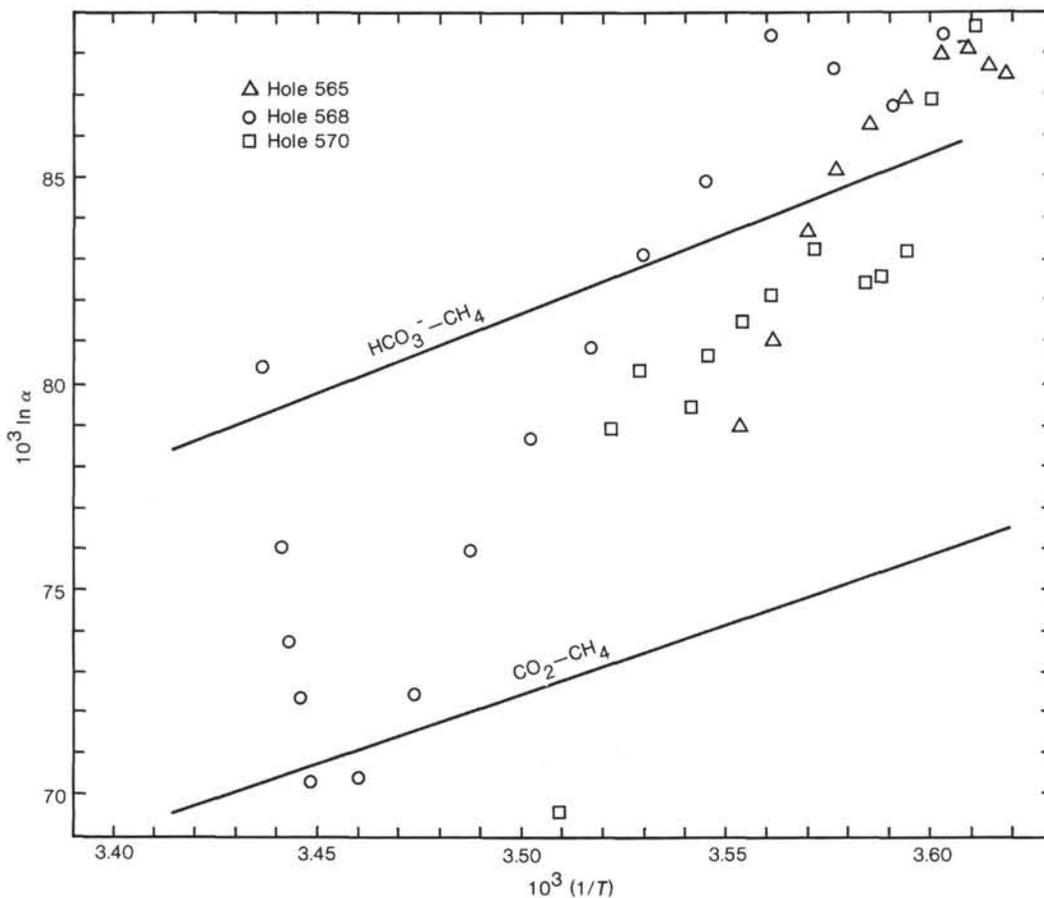
Figure 5. Observed $\delta^{13}C$ differences between coexisting CH_4 gas and dissolved ΣCO_2 (calculated as $10^3 \ln \alpha$), plotted against estimated subsurface Kelvin temperature (as $10^3 T^{-1}$). The points are regularly spaced depths along the inferred trends. The upper line is for theoretical HCO_3^-–CH_4 fractionation, derived from the combined data of Bottinga (1969) and Mook et al. (1974). The lower line is CO_2–CH_4 fractionation as calculated by Bottinga (1969) and reported by Friedman and O'Neil (1977).

HCO_3^- equilibrium line by about $+4$ to $-20‰$. Moreover, the detailed trends in the $\delta^{13}C$ difference with increasing depth are significantly different from that predicted by temperature-dependent equilibrium. The calculated values are in only general agreement with what is predicted by equilibrium considerations. The kinetic approach to interpreting CH_4-CO_2 $\delta^{13}C$ differences is more useful because it incorporates consideration of amounts of reactants and products, and the relative rates of the biological processes.

Gas-Hydrate Isotope Effects

The correlation between increasing $\delta^{18}O$ and decreasing chlorinity or salinity of pore water in sediments on the continental slope off Guatemala was first observed on Leg 67 (Harrison et al., 1982; Hesse and Harrison, 1981). The pore-water $\delta^{18}O$ analyses reported in Table 1 and shown in Figure 3 for samples from Holes 568 and 570 confirm the Leg 67 observations. The water molecules that form the solid clathrate hydrate are known to exclude salts and concentrate ^{18}O, relative to the coexisting liquid water (Davidson et al., 1983). The fractionation factor, $\alpha = (^{18}O/^{16}O)_{solid}/(^{18}O/^{16}O)_{liquid}$, is believed to be about the same as that for the ice–water equilibrium (O'Neil, 1968), or about 1.003. As shown in Table 1, pore-water samples with normal chlorinities have $\delta^{18}O$ values in the range of 0.3 to 0.5‰, whereas water collected from decomposed gas hydrate from Core 27 of Hole 570 has $\delta^{18}O$ of 3.72‰. If 0.5 and 3.7‰ are taken as the $\delta^{18}O$ values of the liquid and solid H_2O, a value of $\alpha = 1.0032$ is obtained.

The question of what happens to the salts and ^{18}O-depleted H_2O excluded during gas hydrate formation has not been resolved, but loss to overlying seawater or adjacent sediments seems to be required. An earlier interpretation (Hesse and Harrison, 1981) was that the gas hydrate probably is in contact with pore water of normal salinity and $\delta^{18}O$. In this view, the observed "freshening" and ^{18}O-enrichment is due to decomposition of gas hydrates during sampling and dilution of the pore water with water from the hydrate. The jagged depth-profiles for $\delta^{18}O$ and chlorinity at Site 533 of Leg 76 support this interpretation (Jenden and Geiskes, 1983). However, results obtained with the *in situ* pore-water sampler in Hole 568 do not support this interpretation for the Guatemala slope sediments. The chlorinities of the *in situ* pore-water samples showed about the same Cl^--depletion as squeezed pore-water samples from similar depths. It should also be noted that pore water in Hole 570 does not show the regular changes in chlorinity and $\delta^{18}O$ with depth. Only the water from decomposed gas hydrate at 249 m and the deepest samples (at 280 and 337 m) shows significant departure from seawater/pore-water chlorinity and $\delta^{18}O$.

Is the ^{18}O-enrichment in H_2O of gas hydrates accompanied by similar ^{13}C- and D-enrichment in the CH_4 of gas hydrate? There is reason to expect that there would be some isotopic effect (Trofimuk et al., 1974), but the possible magnitude of such an effect is difficult to evaluate. CH_4 hydrate is not easy to study experimentally, and the conditions required for its formation in the laboratory (vigorous stirring) make meaningful observation

of possible isotopic effects difficult. No obvious isotopic effect has been observed during controlled decomposition of CH_4 hydrate. Indirect evidence that gas hydrates are not the major cause of ^{13}C-fractionation is provided by the fact that similar patterns of $\delta^{13}C$ change with depth are observed in regions where gas hydrates are not stable, such as the Cariaco Trench (Claypool and Kaplan, 1974).

SUMMARY AND CONCLUSIONS

The pore-fluid samples from sediments in Holes 568 and 570 have extremely ^{13}C-enriched early diagenetic CH_4 and CO_2 (-41 and $+38‰$, respectively). The sediments also have very high contents of organic matter (3–4% organic carbon), and the best-developed marine gas-hydrate occurrences observed to date. The abundant organic matter should have supported prolonged and vigorous microbiological CH_4 generation, with consequent extreme ^{13}C-depletion in the ΣCO_2 reservoir from which the CH_4 was formed, and more extensive development of gas hydrates. Alternatively, methane generation could have resulted in the degree of ^{12}C-enrichment that is typical for deep-sea sediments, and the development of gas hydrate may have superimposed additional fractionation and resulted in the observed extreme ^{13}C-enrichment. Resolution of these alternative interpretations will have to await an improved understanding of the relevant diagenetic processes.

Isotopic compositions of other pore-fluid constituents (δD of CH_4, $\delta^{18}O$ of H_2O) in continental-rise sediments of the Guatemala margin also exhibit systematic trends. The trends of isotopic composition with depth at the two sites differ significantly where gas hydrates either are massively developed at intermediate depths (Hole 570), or are disseminated and sufficiently developed to permit recovery only in the deepest part of the section penetrated (Hole 568). These different isotope–depth gradients may represent two different diagenetic styles or situations: one (Hole 570) in which the gradients are predominantly diffusion-controlled and gas hydrate development is concentrated at some preferred zone (e.g., beneath an unconformity), and another (Hole 568) in which there is progressive development of gas hydrate with increasing depth, and the gradients are predominantly those of steady-state diagenesis.

The pore-fluid data from DSDP Leg 84 provide abundant material for developing hypotheses regarding early diagenetic processes of the decomposition of organic matter in continental-margin sediments. Geochemical investigations to test these hypotheses should play a major role in planning for future deep-sea drilling.

REFERENCES

Bottinga, Y., 1969. Calculated fractionation factors for carbon and hydrogen isotope exchange in the system calcite–CO_2–graphite-methane-hydrogen and water vapor. *Geochim. Cosmochim. Acta*, 33:49–64.

Carothers, W. W., and Kharaka, Y. K., 1980. Stable carbon isotopes of HCO_3^- in oil-field waters—implications for the origin of CO_2. *Geochim. Cosmochim. Acta*, 44:323–332.

Claypool, G. E., and Kaplan, I. R., 1974. The origin and distribution of methane in marine sediments. *In* Kaplan, I. R. (Ed.), *Natural Gases in Marine Sediments:* New York (Plenum), pp. 94–129.

Claypool, G. E., and Kvenvolden, K. A., 1983. Methane and other hydrocarbon gases in marine sediment. *Ann. Rev. Earth Planet. Sci.*, 11:299–328.

Claypool, G. E., and Threlkeld, C. N., 1983. Anoxic diagenesis and methane generation in sediments of the Blake Outer Ridge, Deep Sea Drilling Project Site 533, Leg 76. *In* Sheridan, R. E., Gradstein, F. M., et al., *Init. Repts. DSDP*, 76: Washington (U.S. Govt. Printing Office), 391–402.

Claypool, G. E., Threlkeld, C. N., and Magoon, L. B., 1980. Biogenic and thermogenic origins of natural gas in Cook Inlet Basin, Alaska. *Am. Assoc. Pet. Geol. Bull.*, 64:1131–1139.

Coleman, D. D., Lin, C., and Keogh, R. A., 1977. Isotopic identification of leakage gas from underground storage reservoirs—a progress report: *Ill. State Geol. Surv. Ill. Petrol.*, 111:1–10.

Davidson, D. W., Leaist, D. G., and Hesse, R., 1983. Oxygen-18 enrichment in the water of a clathrate hydrate. *Geochim. Cosmochim. Acta*, 47:2293–2295.

Epstein, S., and Mayeda, T., 1953. Variation of oxygen-18 content of waters from natural sources. *Geochim. Cosmochim. Acta*, 4: 213–224.

Friedman, I., and Murata, K. J., 1979. Origin of dolomite in Miocene Monterey Shale and related formations in the Temblor Range, California. *Geochim. Cosmochim. Acta*, 43:1357–1365.

Friedman, I., and O'Neil, J. R., 1977. Compilation of stable isotope fractionation factors of geochemical interest. *Data of Geochemistry* (6th ed.), Geol. Surv. Prof. Pap. U.S., 440-KK:1–12.

Fuex, A. N., 1977. The use of stable carbon isotopes in hydrocarbon exploration. *J. Geochem. Explor.*, 7:155–188.

Gealy, E. L., and Dubois, R., 1971. Shipboard geochemical analysis, Leg 7, *Glomar Challenger. In* Winterer, E. L., Riedel, W. R., et al., *Init. Repts. DSDP*, 7, Pt. 2: Washington (U.S. Govt. Printing Office), 863–870.

Giggenbach, W. F., 1982. Carbon-13 exchange between CO_2 and CH_4 under geothermal conditions. *Geochim. Cosmochim. Acta*, 46: 159–165.

Gould, K. W., and Smith, J. W., 1979. The genesis and isotopic composition of carbonates associated with some Permian Australian coals. *Chem. Geol.*, 24:137–150.

Harrison, W. E., Hesse, R., and Geiskes, J. M., 1982. Relationship between sedimentary facies and interstitial water chemistry of slope, trench, and Cocos Plate sites from the Middle America Trench transect, active margin off Guatemala, DSDP Leg 67. *In* Aubouin, J., von Huene, R., et al., *Init. Repts. DSDP*, 67: Washington (U.S. Govt. Printing Office), 603–614.

Hesse, R., and Harrison, W. E., 1981. Gas hydrates (clathrates) causing pore-water freshening and oxygen isotope fractionation in deepwater sedimentary sections of terrigenous continental margins. *Earth Planet. Sci. Lett.*, 55:453–462.

Jenden, P. D., and Geiskes, J. M., 1983. Chemical and isotopic composition of interstitial water from Deep Sea Drilling Project Sites 533 and 534. *In* Sheridan, R. E., Gradstein, F. M., et al., *Init. Repts. DSDP*, 76: Washington (U.S. Govt. Printing Office), 453–462.

Kvenvolden, K. A., and Barnard, L. A., 1983. Gas hydrates of the Blake Outer Ridge, Site 533, Deep Sea Drilling Project Leg 76. *In* Sheridan, R. E., Gradstein, F. M., et al., *Init. Repts. DSDP*, 76: Washington (U.S. Govt. Printing Office) 353–366.

Manheim, F. T., 1966. A hydraulic squeezer for obtaining interstitial water from consolidated and unconsolidated sediments. *Geol. Surv. Prof. Pap.* U.S., 550-C:256–261.

Mook, W. G., Bommerson, J. C., and Staverman, W. H., 1974. Carbon isotope fractionation between dissolved bicarbonate and gaseous carbon dioxide. *Earth Planet. Sci. Lett.*, 22:169–176.

O'Neil, J. R., 1968. Hydrogen and oxygen isotope fractionation between ice and water. *J. Phys. Chem.*, 72:3683–3684.

Presley, B. J., and Claypool, G. E., 1971. Techniques for analyzing interstitial water samples. Part II: Determination of total carbonate and carbon isotope ratios. *In* Winterer, E. L., Riedel, W. R., et al., *Init. Repts. DSDP*, 7, Pt. 2: Washington (U.S. Govt. Printing Office), 1756–1757.

Rosenfeld, W. D., and Silverman, S. R., 1959. Carbon isotope fractionation in bacterial production of methane. *Science*, 130:1658.

Sackett, W. M., and Chung, H. M., 1979. Experimental confirmation of the lack of carbon isotope exchange between methane and carbon oxides at high temperatures. *Geochim. Cosmochim. Acta*, 43: 273–276.

Schoell, M., 1980. The hydrogen and carbon isotopic composition of methane from natural gases of various origins. *Geochim. Cosmochim. Acta*, 44:649–661.

_____, 1983. Genetic characterization of natural gases. *Am. Assoc. Pet. Geol. Bull.*, 67:2225–2238.

Trofimuk, A. A., Cherskiy, N. V. and Tsarev, V. P., 1974. Mechanisms for fractionation of isotopes of water and gas in crustal zones of hydrate formation. *Dokl. Akad. Nauk SSSR*, 215:1226–1229.

Wigley, T. M. L., Plummer, L. N., and Pearson, F. J., Jr., 1978. Mass transfer and carbon-isotope evolution in natural water systems. *Geochim. Cosmochim. Acta*, 42:1117–1140.