23. GAS HYDRATES OF THE MIDDLE AMERICA TRENCH—DEEP SEA DRILLING PROJECT LEG 84[1]

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ABSTRACT

On DSDP Leg 84, gas hydrates were found at three sites (565, 568, and 570) and were inferred, on the basis of inorganic and organic geochemical evidence, to be present at two sites (566 and 569); no evidence for gas hydrates was observed at Site 567. Recovered gas hydrates appeared as solid pieces of white, icelike material occupying fractures in mudstone or as coarse-grained sediment in which the pore space exhibited rapid outgassing. Also a 1.05-m-long core of massive gas hydrate was obtained at Site 570. Downhole logging indicated that this hydrate was actually 3 to 4 m thick. Measurements of the amount of methane released during the decomposition of these recovered samples clearly showed that gas hydrates had been found. The distribution of evolved hydrocarbon gases indicated that Structure I gas hydrates were present because of the apparent inclusion of methane and ethane and exclusion of propane and higher molecular weight gases. The water composing the gas hydrates was fresh, having chlorinities ranging from 0.5 to 3.2‰. At Sites 565, 568, and 570, where gas hydrates were observed, the chlorinity of pore water squeezed from the sediment decreased with sediment depth. The chlorinity profiles may indicate that gas hydrates can often occur finely dispersed in sediments but that these gas hydrates are not recovered because they do not survive the drilling and recovery process. Methane in the gas hydrates found on Leg 84 was mainly derived *in situ* by biogenic processes, whereas the accompanying small amounts of ethane likely resulted from low-temperature diagenetic processes. Finding gas hydrates on Leg 84 expands observations made earlier on Leg 66 and particularly Leg 67. The results of all of these legs show that gas hydrates are common in landward slope sediments of the Middle American Trench from Mexico to Costa Rica.

INTRODUCTION

One of the objectives of DSDP Leg 84 was to learn more about gas hydrates in oceanic sediment in general and, in particular, to augment knowledge of the occurrence of gas hydrates in slope sediment of the Middle America Trench. Results from Leg 66 (Shipley and Didyk, 1982) and Leg 67 (Harrison and Curiale, 1982) clearly showed that gas hydrates are present in slope sediment of this Trench offshore Mexico and Guatemala. Leg 84 provided the opportunity to obtain additional information about gas hydrates in sediments offshore Guatemala and to determine if gas hydrates are also present in sediments offshore Costa Rica.

Natural gas hydrates are solids made of water molecules arranged in a cubic lattice framework that includes, and is stabilized by, molecules of natural gas (mainly methane) at appropriate pressure and temperature conditions. These conditions are met within continental margin sediments below water depths greater than ~ 500 m where the supply of methane is sufficient to stabilize the gas hydrate. Figure 1 shows the approximate pressure–temperature field in which gas hydrates are stable. Within the sediment, however, the geothermal gradient limits the depths at which the gas hydrates can occur. The fact that the temperature of the sediment increases with depth leads to conditions at which gas hydrates are no longer stable and will therefore decompose. The base of the zone of the gas hydrate stability follows a pressure–temperature surface that represents the maximum depth at which the gas hydrate of a given composition is stable.

The base of the gas hydrate stability zone often correlates with anomalous acoustic reflectors in marine seismic profiles obtained from a number of areas on outer continental margins (Shipley et al., 1979). The anomalous reflector approximately parallels the seafloor and therefore is commonly called a bottom-simulating reflector (BSR). The depths at which this reflector occurs can be predicted on the basis of considerations of the pressure–temperature stability field (Fig. 1) and the geothermal gradient. The reflector probably results from the velocity contrast between sediment cemented with gas hydrate and the underlying sediment where lower velocities occur because of the absence of gas hydrate and the possible presence of free gas.

Marine seismic surveys on the Mexican continental margin southwest of Acapulco showed BSRs that suggested the presence of gas hydrates in slope sediment of the Middle America Trench (Shipley et al., 1979). Drilling on DSDP Leg 66 confirmed that gas hydrates are indeed present here (Shipley and Didyk, 1982). Evidence for gas hydrates was collected at three drill sites. This evidence consisted of the recovery of icelike inclusions and of porous volcanic ash and fine sand cemented with icelike material. Two samples released 7 and 20 ml of gas, respectively, per ml of pore water. These large gas-release ratios indicated gas hydrates. The released gas was primarily methane ($>98\%$) accompanied by small amounts of CO_2, ethane, and higher molecular weight

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[1] von Huene, R., Aubouin, J., et al., *Init. Repts. DSDP*, 84: Washington (U.S. Govt. Printing Office).

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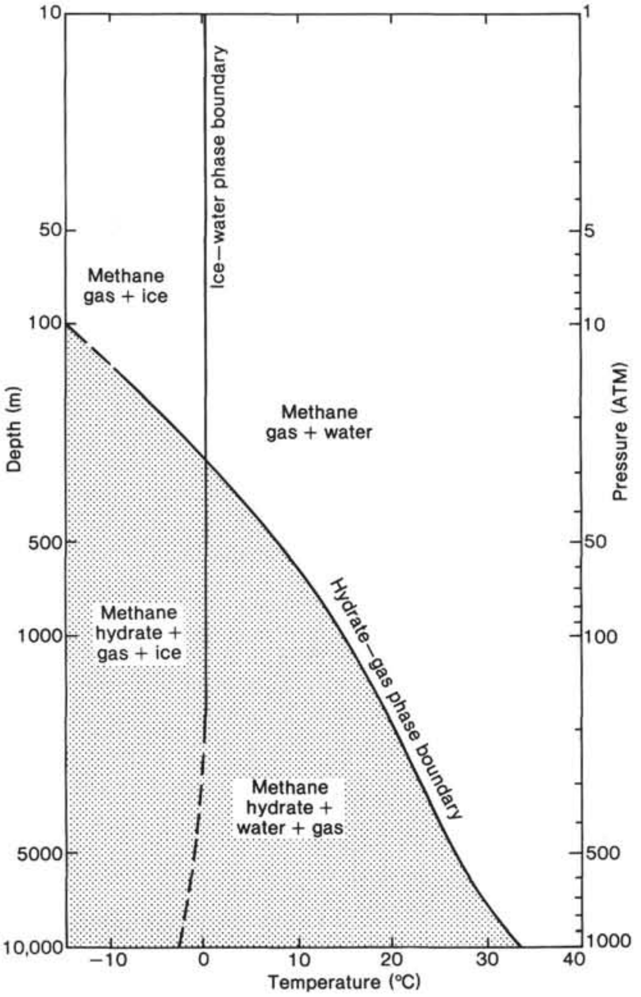

Figure 1. Phase boundary diagram showing in the stippled pattern the pressure (depth)–temperature region in which methane hydrate is stable. The hydrate–gas phase boundary is given for a pure water and pure methane system. Depth scale is an approximation based on the assumption that lithostatic and hydrostatic pressure gradients are both 0.1 atmosphere/m. Redrawn after Katz et al. (1959) and modified from Kvenvolden and McMenamin (1980).

hydrocarbons up through pentane. On the basis of the chemical composition of the gas, the methane was considered to be predominantly biogenic.

The presence of BSRs was not at first obvious on marine seismic records from surveys of the Guatemalan continental margin adjacent to the Middle America Trench. Thus, encountering gas hydrates at two sites on Leg 67 came as a surprise (Harrison and Curiale, 1982). Evidence of gas hydrates included the development of significant gas pressure within core liners, the observation of icelike solids and vitric sand cemented with icelike material, and the measurement of release of 50 to 80 ml of methane per ml of pore water in two experiments. Small amounts of CO_2, ethane, and propane were also found in the mixtures of released gases. The finding of gas hydrates on Leg 67 without supporting geophysical evidence from seismic surveys led to reprocessing of seismic records and a renewed search for BSRs (von Huene et al., 1982). BSRs were found to be present beneath much of the Guatemalan slope especially in areas of thick sediment accumulation. The new seismic evidence for gas hydrates coupled with the observations of Leg 67 showed that a detailed study of gas hydrate occurrence would be a reasonable primary objective for Leg 84.

METHODS

For the most part the analytical methods applied in this study were based on routine shipboard procedures. For gas analyses two techniques were used. In the first, which has been routine for DSDP legs since Leg 10 (Claypool et al., 1973), gases were recovered directly from the core liner as gas escaped from the sediment. Gases were sampled by means of a hollow punch with a valve to prevent immediate gas release. After the punch penetrated the core liner or end cap, gas was vented through the valve into standard 20-ml evacuated containers called vacutainers. The collected gases were analyzed by gas chromatography, and concentrations of C_1 through C_5 hydrocarbons were determined. The second technique involved extracting gases from sediment in a closed container and analyzing the gas in the headspace of the container. This technique was first used on samples from Leg 18 (McIver, 1973) and has been a nonroutine procedure on subsequent legs (McIver, 1975). The headspace analyses for Leg 84 followed modified procedures of Kvenvolden and Redden (1980). For each analysis, about 170 cm^3 of sediment were placed in a can (~ 0.5 L). The can was filled with helium-purged (degassed) water and a 100-cm^3 headspace established by removing water from the can. The can was sealed and the headspace was purged with helium through septa previously attached to the can. Gas from the sediment was equilibrated with the headspace gas by shaking the can on a high-speed shaker for ten min. Portions of the resulting headspace gas mixtures were analyzed by gas chromatography. Concentration of hydrocarbon gases C_1 through C_6 were measured.

Gas Chromatography

Methane and CO_2 were analyzed on a Carle Model 800 gas chromatograph (thermal conductivity detector) utilizing a ⅛ in. × 5 ft. column, packed with 8% Carbowax 1540 on 90–100 mesh Anachrom ABS, operated isothermally at 40°C. Sample size was 200 μl of gas recovered from vacutainers or the headspace of cans. Areas of peaks on the chromatograms were measured by a CSI Model 38 Integrator, and from these areas concentrations were calculated.

Hydrocarbons gases ethane through pentane were analyzed on a Hewlett-Packard 5711A gas chromatograph equipped with dual flame ionization detectors (Whelan, 1979). Analyses were carried out on a 18 in. × 4 ft. column, packed with 40–100 mesh Spherosil attached to a ⅛ in. × 12 ft. column packed with 20% OV 101 on 100-110 mesh Anakrom AS. Temperature of the columns was increased from 60 to 200°C at 8°C/min. A 5-ml gas sample, obtained from either a vacutainer or the headspace of a can, was introduced for chromatography through a septum into a chilled (~ 70°C ⅛ in. × 8 in. loop, packed with 60–80 mesh activated alumina (F-1), attached to an eight-port, two-way sampling valve through which helium flows. After a 2-min. delay, during which time methane and air were removed, the helium flow was interrupted, and the sample loop was heated for 1 min. in a water bath at ~90°C. Then the sampling valve was opened allowing the gas mixture to enter the gas chromatograph. Peak areas representing the various hydrocarbon gases were measured by a CSI Model 38 integrator, and concentrations were calculated from these integrated areas.

Pressure Measurements

Pressure developed during gas hydrate decomposition was measured in a pressure device (Parr Company) consisting of a 23-cm^3 sample holder, gauge block, gauge, and gas-sampling port with septum (Kvenvolden and Barnard, 1983). With this device the volume and composition of gas released could be calculated, and samples of gas could be removed for analyses.

Carbon Determination

Measurements of total carbon, carbonate carbon, and organic carbon were made utilizing routine shipboard procedures. Sediment samples were dried at about 40°C, pulverized in a mortar with a pestle, and weighed. One gram of sediment was acidified in a carbonate bomb to determine carbonate carbon. Total carbon was measured with a Hewlett-Packard 185 CHN analyzer on 20-mg sediment samples. Organic carbon was determined by the difference between total carbon and carbonate carbon. An assessment of the kind and maturity of carbon in the sediment was made utilizing the shipboard Rock-Eval instrument on 100 mg of sediment. Peak areas were estimated by measurement (peak height × peak width at half height) or by weighing the peaks cut from the recorder chart.

Interstitial Water Analyses

Methods used for pore-water analyses are based on routine shipboard methods described by Manheim and Sayles (1974). In addition the *in situ* pore-water sampler (Barnes et al., 1979; Moore and Gieskes, 1980) was successfully deployed. Chemical analyses followed methods of Gieskes (1974) and Gieskes and Lawrence (1976). Of the parameters measured, only chlorinity is discussed in this paper.

RESULTS

Distribution of Hydrocarbon Gases with Depth

The composition of hydrocarbon gases released from cores during core recovery was determined at each site. Details of the gas analyses and tabulations of results are given in the individual site reports. Gases were collected with vacutainers by sampling gas void spaces in the cores either through the core liner or through the end caps. In the measurement of composition of gases in these void spaces, the presence of air is always a problem. For example, the vacutainers have a residual background of air. Air can also be incorporated during sampling and during analyses. Although efforts were made to reduce the presence of air, and analyses were performed as consistently as possible, our results suggest that air is always a significant component of the gas analyzed. Figure 2 (A–E) shows the concentrations with depth of methane (C_1), ethane (C_2) and the sum of propane (C_3), *i*-butane and *n*-butane (*i*-C_4 and *n*-C_4), and *i*-pentane, *n*-pentane, and neopentane (*i*-C_5, *n*-C_5, and neo-C_5) at five of six sites. C_1 is the dominant hydrocarbon gas, and its concentration is plotted relative to the total gases in the void spaces. If there were no air contamination, then C_1 would likely compose almost 100% of the hydrocarbon gases present in each sample. The values of C_2 and C_{3+} have been normalized to C_1 equal to 100% to obtain a better estimate of the *in situ* trend of C_2 and C_{3+} concentrations with depth. This normalization process creates some apparent distributional artifacts, indicated by a question mark on Figures 2B, C, and D wherever very low C_1 values require large factors for calculating the normalized values of C_2 and C_{3+}.

Concentrations of C_1 in the void spaces of the cores is variable with depth as shown in Figure 2. At Sites 565, 568, and 570 most samples of gas contained more than 50% C_1, whereas at Sites 567 and 569, C_1 generally was <50% of the gas mixture. Normalized C_2 concentrations increase exponentially with depth at Sites 565, 568, 570, and possibly 567. This exponential increase in C_2 likely reflects the low-temperature diagenetic production of C_2 with depth (Claypool and Kvenvolden, 1983). In contrast, at Site 569 the amount of C_2 remains about the same with depth. The normalized concentrations of C_{3+} generally decrease with depth.

At Sites 565 and 568 gases were extracted from sediment samples by means of the headspace procedure, and the results are shown in Figure 3A and B. Here concentrations of gas recovered are related to the volume of sediment and thus provide an estimate of the relative *in situ* distribution of hydrocarbon gases. At both sites, C_1 concentrations are greatest in the upper 100 m of sediment and tend to decrease with depth. C_2 concentrations tend to increase with depth, whereas C_3 concentrations both increase and then decrease with depth.

Organic Carbon

Profiles with depth of organic carbon for each site are shown in Figure 4. The amount of organic carbon is variable. For example, at Site 565 organic carbon is <2%, ranging from 1.7 to 0.5%. The two samples examined at Site 566 had organic carbon contents of 3.4%. At Site 567 organic carbon decreased with depth from 2.5% at 196 m to 0.20% at 336 m. Organic carbon at Site 568 is >2.6% in the upper 180 m of sediment, reaching a maximum value of 4.2% at 66 m sub-bottom. Below 180 m the organic carbon decreases to 0.6% at 280 m then increases to 1.3% at 385 m. At Site 569 organic carbon generally decreases with depth, ranging from a maximum of 2.4% to a minimum of 0.4%. Organic carbon at Site 570 ranges between 1.1 and 3.2% in the first 275 m. Below this depth the organic carbon decreases rapidly.

Sediment samples were analyzed by Rock-Eval following the procedure outlined by Tissot and Welte (1978). The results were marginal, but a preliminary interpretation suggests that the organic carbon at most sites is terrestrial or a mixture of terrestrial and marine in source and is immature.

Chlorinity

Results of shipboard measurements of pore-water chemistry are summarized in each of the site chapters. Of particular interest are the depth profiles of chlorinity (Fig. 5) at each site. A common feature of Sites 565, 568, 569, and 570 is the decrease in chlorinity over the entire interval at each hole. This decreasing chlorinity of pore water with depth was observed previously at Sites 496 and 497 of Leg 67 (Hesse and Harrison, 1981; Harrison et al., 1982). Chlorinity values were also obtained on pore-water samples recovered by means of the *in situ* water sampler at Sites 565 and 568.

GAS HYDRATES

Six sites drilled on Leg 84 (Table 1) were located in slope sediment of the Middle America Trench. Site 565 samples slope sediment offshore from the Nicoya Peninsula of Costa Rica. The other sites (566, 567, 568, 569, and 570) were located offshore from Guatemala. Site 567 corresponded to Site 494, which was only partially drilled on Leg 67. Site 568 was positioned near Site 496 of Leg 67. Site 496 had been abandoned after gas of possible thermogenic origin was encountered and the presence of gas hydrate had been inferred (see Site 568 report, this volume). Although no BSR had been ob-

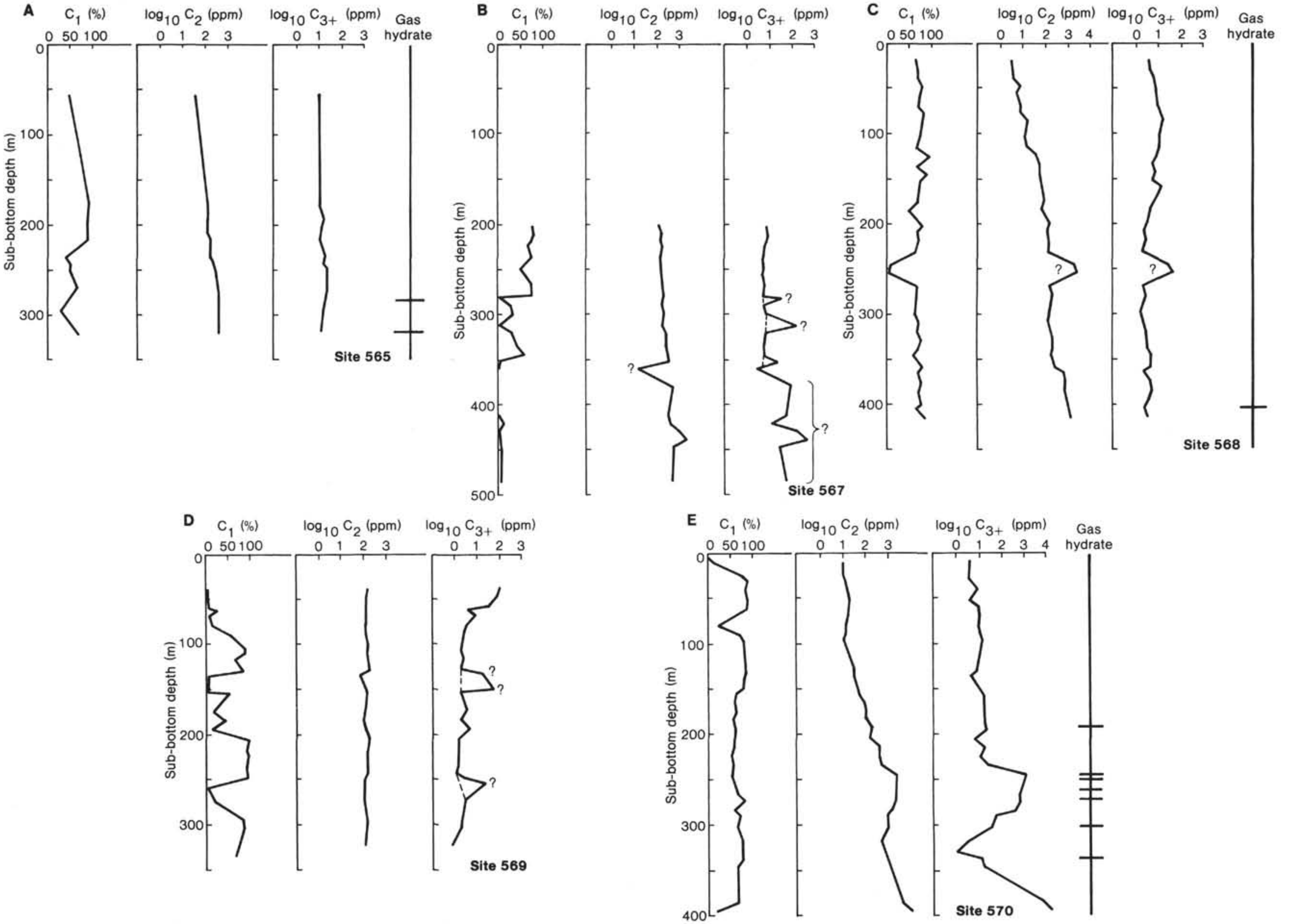

Figure 2. A–E. Graphs showing concentrations with depth of hydrocarbons in gas expelled from cores and collected in vacutainers at Sites 565(A), 567(B), 568(C), 569(D), and 570(E). C_1 is reported as the percentage of the total gas that contained not only hydrocarbons but also CO_2 and air. Concentrations of C_2 and C_{3+} (the sum of C_3, *i*-C_4, *n*-C_4, neo-C_5, i-C_5 and *n*-C_5) have been normalized to $C_1 = 100\%$ to obtain a more realistic estimate of the *in situ* trend of C_2 and C_{3+} concentrations with depth. Scale for concentration is given in $\log_{10}$. The question marks in B, C, and D indicate uncertainty in the normalized values because of large factors required for normalization of small concentrations. Depths at which gas hydrates were recovered are indicated.

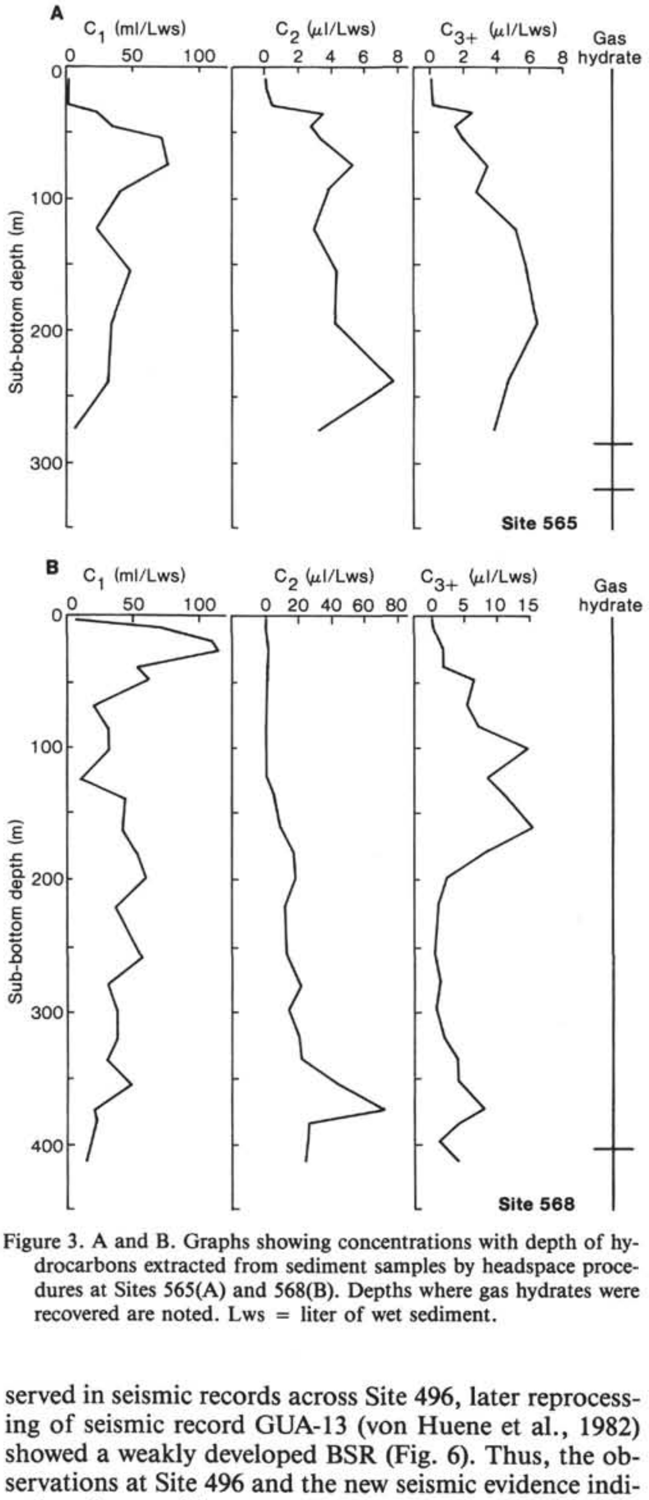

Figure 3. A and B. Graphs showing concentrations with depth of hydrocarbons extracted from sediment samples by headspace procedures at Sites 565(A) and 568(B). Depths where gas hydrates were recovered are noted. Lws = liter of wet sediment.

served in seismic records across Site 496, later reprocessing of seismic record GUA-13 (von Huene et al., 1982) showed a weakly developed BSR (Fig. 6). Thus, the observations at Site 496 and the new seismic evidence indicating the possible presence of gas hydrates led to the drilling of Site 568 where a primary objective was the detailed study of gas hydrates. BSRs were not observed in seismic records at the other Leg 84 sites.

All sites drilled on Leg 84 were located within the pressure (depth)–temperature field of gas hydrate stability (Fig. 7). This figure was constructed on the basis of information from Figure 1, water depths, bottom-water temperatures, hole depths, and measured or inferred geothermal gradients (see specific site reports, this volume, for details). Cores from all sites were carefully inspected for gas hydrates, which were recovered only at Sites 565, 568, and 570. Table 2 describes the appearance of these recoveries. Whenever possible, gas hydrates were placed in a pressure vessel and allowed to decompose. The volume of gas released was calculated from the pressure developed in the vessel, and the composition of the gas was determined by gas chromatography. Results are shown in Table 3.

Visual Observations and Initial Measurements

In drilling Site 565, gas hydrate was encountered at 285 and 319 m sub-bottom. The gas hydrate was first observed at 285 m through the core liner as pieces of white, icelike substances. The core catcher of Core 33 (319 m) expelled gas-releasing muddy sandstone that probably contained gas hydrate. At the top of the core catcher, a piece of white, icelike gas hydrate was found which was then analyzed (Table 3). Decomposition of this sample produced about 133 volumes of C_1 per volume of pore fluid that was very fresh, having a chlorinity of 0.51‰. The amount of C_1 released exceeds the methane solubility under the *in situ* pressure–temperature conditions of this sample by a factor of about 30. The C_1/C_2 ratio of this gas is about 2000; gas expelled from the core at 320 m sub-bottom has a C_1/C_2 ratio of 2500.

Gas hydrates were expected to be found at Site 568 because of observations of a BSR in a seismic record for this area. However, direct evidence for gas hydrate was not obtained until 404 m sub-bottom. At this depth white pieces of gas hydrate were recovered from fractures in a tuffaceous mudstone (Fig. 8A and Table 2). Two different samples were allowed to decompose in the pressure vessel. The first sample released 30 volumes of C_1 per volume of fluid. The second sample, which had partially decomposed in the laboratory while pressure measurements were being made on the first sample, only released 7 volumes of C_1 per volume of fluid. These results show that the amount of gas released from gas hydrates depends on how quickly measurements are made after recovery. The amount of C_1 released in both cases, however, exceeds the solubility of C_1, which is about 4 volumes of gas per volume of water at the *in situ* pressure–temperature conditions of this sample. The chlorinity of the water resulting from each decomposition was about 3‰.The C_1/C_2 ratio of the gas was 530; gas expelled from the core at 404 m had a C_1/C_2 ratio of 970. Coring at this site terminated at about 418 m sub-bottom, a distance of ~44 m above the BSR.

At Site 570 at least seven examples of gas hydrates were noted between 192 and 338 m sub-bottom (Table 2). The first evidence of gas hydrate at this site was in the form of ash laminated with gas hydrate. This sample outgassed only 4 volumes of C_1 per volume of water. The gas released had a C_1/C_2 ratio of 1100 compared to 5000 for gas expelled from the core at 193 m. A piece of white gas hydrate was next found at 246 m (Fig. 8B). The most spectacular occurrence of gas hydrate was found at 249 m sub-bottom where a 1.05-m core of massive gas hydrate was recovered (Fig. 8C). This gas hydrate was associated with fractured dolomite at its bot-

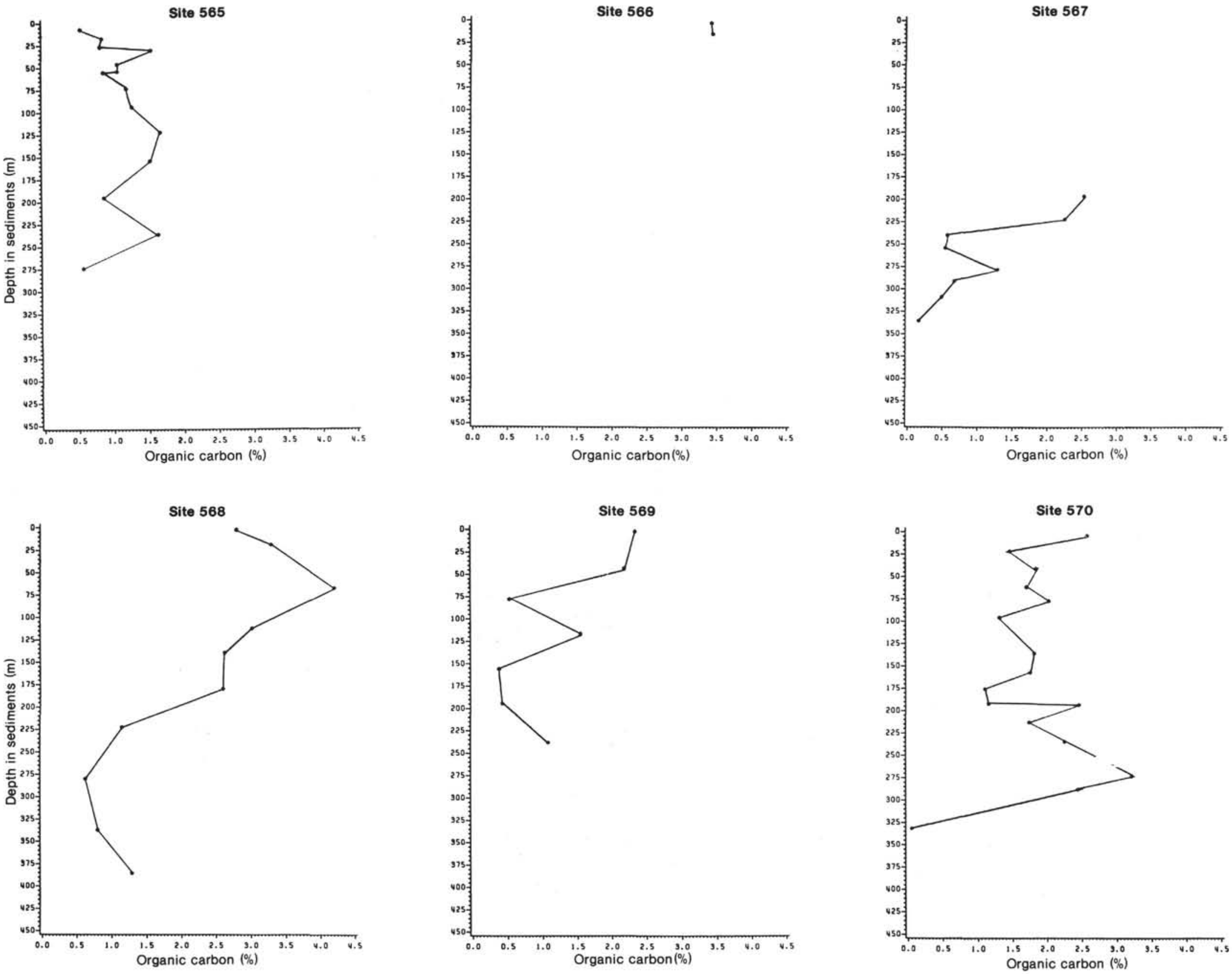

Figure 4. Profiles with depth of the organic carbon content of sediments at six Leg 84 sites.

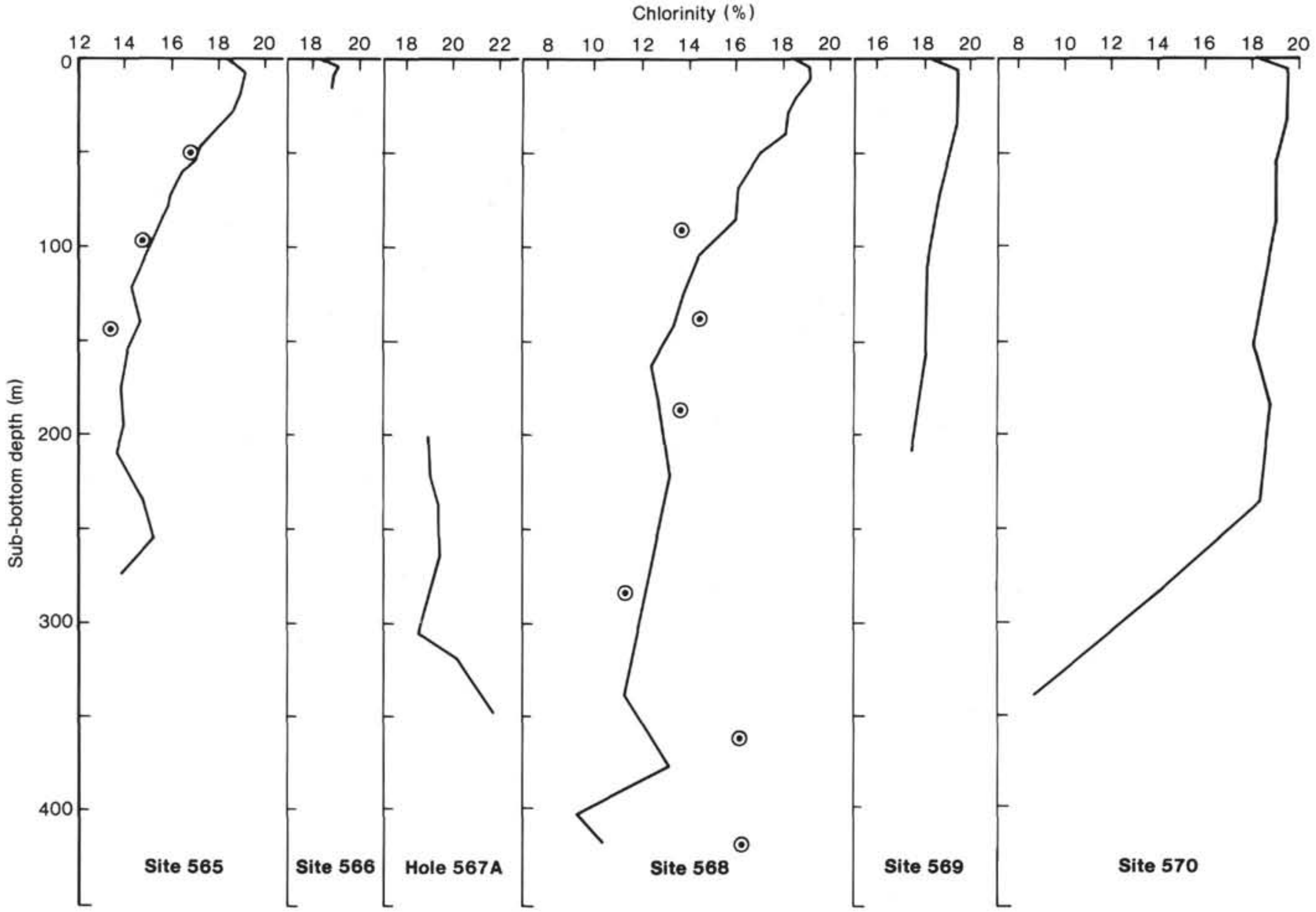

Figure 5. Profiles with depth of chlorinity in parts per thousand (‰) of pore water squeezed from sediment at six sites from Leg 84. ⊙ = chlorinity of waters recovered by means of an *in situ* sampler.

Table 1. Site locations, DSDP Leg 84.

Site	Latitude (N)	Longitude (W)	Water depth (m)	Hole	Hole sub-bottom depth (m)
565	09°43.7′	86°05.4′	3111	565	328
566	12°48.8′	90°41.5′	3673	566C	137
567	12°43.0′	90°56.0′	5529	567A	501
568	13°04.3′	90°48.0′	2031	568	418
569	12°56.3′	90°50.4′	2800	569A	365
570	13°17.1′	91°23.6′	1718	570	402

tom and was apparently located at the contact between upper Miocene and Pliocene sediments. A sample of this gas hydrate released about 29 volumes of C_1 per volume of water that had a chlorinity of 0.65‰. An average C_1/C_2 ratio of about 330 from experiments utilizing the pressure vessel contrasts with a ratio of 400 for gas expelled from the sediment core at 246 m. Downhole logging showed that this massive gas hydrate was 3–4 m thick at this location (Fig. 9). The log provides the first *in situ* measurements of the physical properties of a gas hydrate: sonic velocity = 3.3–3.8 km/s; density = 1.024–1.045 gm/cm^3; resistivity = ~200 ohm-m.

Below the massive gas hydrate other examples of gas hydrates were noted. For example, in Core 28 (259–268 m sub-bottom) a piece of gas hydrate occupied a fracture in mudstone. This sample degassed between 24 and 42 volumes of C_1 per volume of pore water. The average C_1/C_2 ratio was abut 730; gas expelled from sediments at 267 m had a C_1/C_2 ratio of 410. A piece of gas hydrate found at 273 m sub-bottom outgassed about 12 volumes of C_1 per volume of water. No other measurements were made on this sample. Other examples of gas hydrates were noted down to a sub-bottom depth of 338 m (Table 2).

Comparison of Hydrate Gas and Core Gas

To relate the distribution of hydrocarbon gases released from gas hydrates in the pressure vessel with the distribution of hydrocarbon gases expelled from cores and collected with vacutainers, the concentration of C_2 and C_{3+} can be normalized to C_1 equal to 100%, as done in Table 4. Here the gases from gas hydrates are compared with core gas obtained close to where the gas hydrates were found. With the exception of samples from site 570 (Core 28), the concentrations of C_2 in gas hydrates are larger than the concentration of C_2 in the core gas. Higher C_2 concentrations in gas hydrates than in core gas possibly results from the preferential inclusion of C_2 in the gas hydrate structure. Except for results at

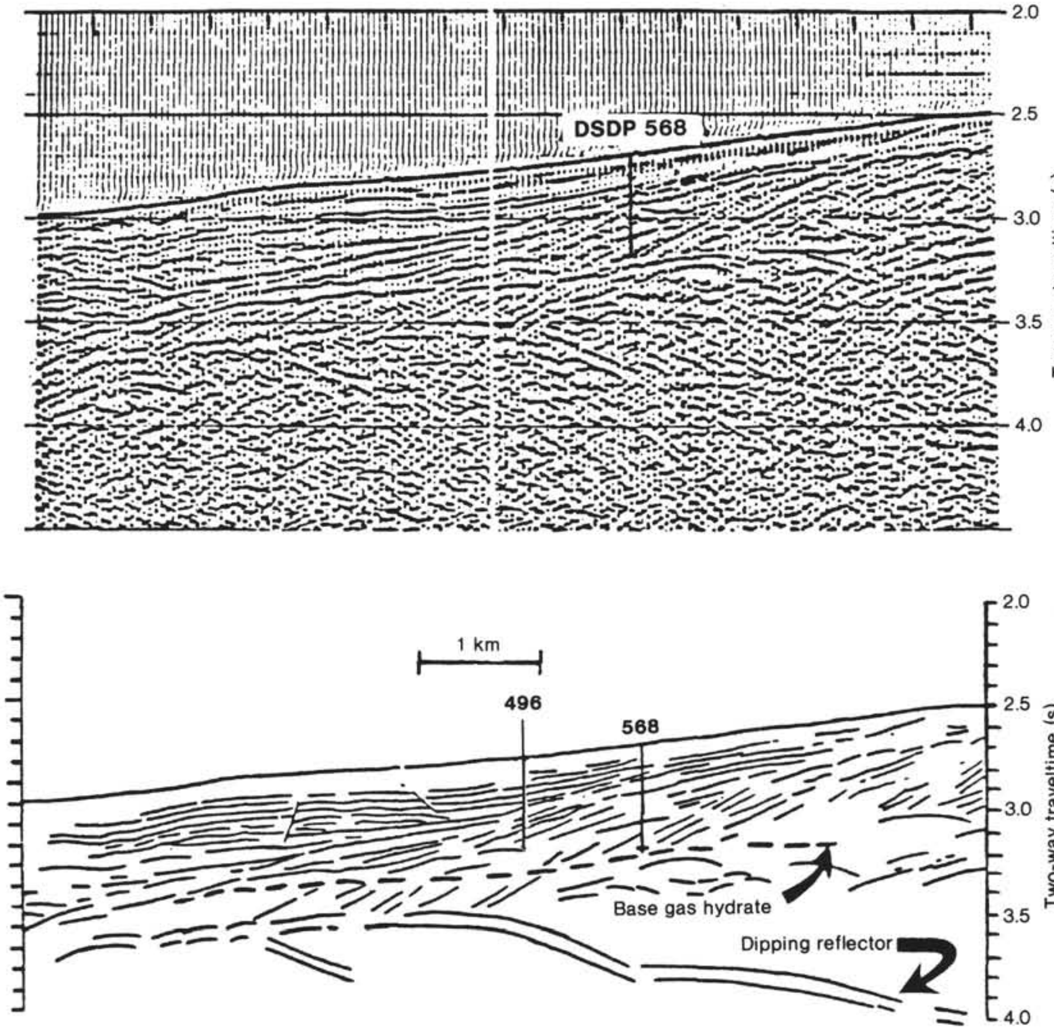

Figure 6. Part of seismic record GUA-13 taken across the midslope where Site 496 (Leg 67) and Site 568 (Leg 84) were drilled, and an interpretive sketch showing the structure of the slope deposits and the base of the gas hydrate reflector (BSR). (Modified from von Huene et al., 1982.)

Site 568, concentrations of C_{3+} are significantly larger in core gas as compared with hydrate gas. This difference in concentration may be attributable to the preferential exclusion of C_{3+} from the gas hydrate structure. Our results imply that Structure I gas hydrates are present; their lattice framework is made up of "cages" that are large enough to include C_1 and C_2 but not C_{3+} (Hand et al., 1974). If the Leg 84 natural gas hydrates are indeed Structure I, then the C_{3+} hydrocarbons found in the gas resulting from gas hydrate decomposition (though at lower concentrations than in core gas) may be loosely associated with the gas hydrate but not included in the gas hydrate structure.

The observation that C_{3+} hydrocarbons are apparently reduced in abundance in natural gas hydrates leads to the idea that in sediment cores, where gas hydrates are dispersed and not visually evident, the gas released may have less C_{3+} than do sediments without gas hydrates. Such reasoning leads to the inference that dispersed hydrates are present at Site 568 in the sub-bottom depth interval between 190 and 345 m (see Site 568 report, this volume, for details). The lower C_{3+} abundances in these intervals can be seen in Figure 2C and particularly Figure 3B. Also, in the interval 391 to 410 m, where gas hydrates were observed at 404 m, the amount of C_{3+} in core gas in lower than that in sediment intervals above and below. At Site 565 the level of C_{3+} concentrations of core gas decreases toward the bottom of the hole where gas hydrates were encountered (Figs. 2A and 3A). In contrast, at Site 570 (Fig. 2E) the abundance of C_{3+} in core gas increases and remains high in the interval from 246 to 274 m sub-bottom where solid gas hydrates are common. The increase may reflect sampling of C_{3+} gases that were excluded from the gas hydrates and that now reside in nonhydrated sediments. Thus, one cannot confidently infer the presence of dispersed gas hydrates in sediments on the basis of the relative concentrations of C_{3+} hydrocarbons.

In summary, gas hydrates were observed in sediments at Sites 565, 568, and 570. These gas hydrates filled the pore space of coarse-grained sand and ash, occupied fractures in mudstone, and occurred as a massive hy-

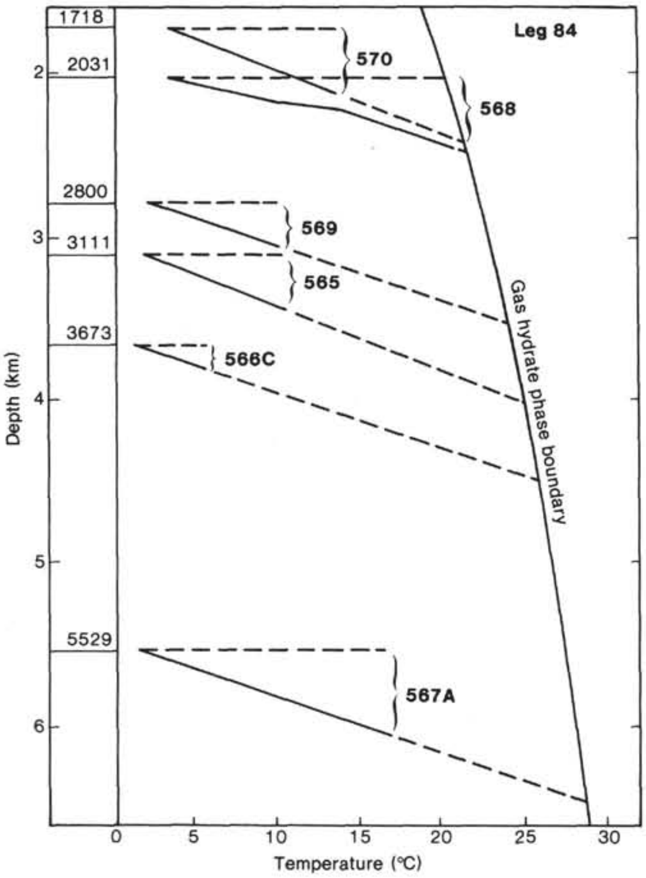

Figure 7. Pressure (depth)–temperature diagram showing gas hydrate phase boundary and the pressure–temperature conditions at each site drilled during Leg 84. All sites are within the pressure–temperature region where gas hydrates are stable. The left-hand column shows the depth in meters of the ocean bottom at each site. The slanted solid lines indicate the measured or inferred geothermal gradients at each site, starting on the left at the temperature of the bottom water. These gradients are extrapolated (slanted dashed lines) to their intersection with the gas-hydrate phase boundary. These intersections predict the base of the zone of gas hydrate stability for each site and the depth at which BSRs would be expected. The brackets indicate the depth in the sediment of the holes.

drate presumably filling a very large fracture. That gas hydrates also were dispersed in fine-grained sediment was inferred, but the evident is equivocal. Upon decomposition, gas hydrates sampled on Leg 84 released from 4 to 133 volumes of C_1 per volume of water. These ratios show that more C_1 was present than could be dissolved in that volume of water. The large ratios indicated that, indeed, gas hydrates had been sampled. Finally, analyses showed that the hydrocarbon gas included in the gas hydrates was mainly C_1 and C_2. C_{3+} hydrocarbons were present but in lower concentrations that in samples of core gas from sediments near where gas hydrates were found.

Pressure Core Barrel

The pressure core barrel (PCB), described in detail by Kvenvolden et al., (1983), was deployed three times at Site 568 to obtain sediments at *in situ* pressure and to test for the presence of gas hydrates. Sediment cores were recovered at sub-bottom depths of 89, 155, and 282 m. On retrieval of each PCB, *in situ* pressures were measured by means of a pressure transducer, and each PCB was placed in a vertical standpipe filled with water, the temperature of which was monitored. Hydrostatic pressure was released, and attempts were made to measure and collect venting gas. Results are given in Table 5.

PCB-1

A gas-water mixture was vented from PCB-1. An attempt was made to measure the volume of gas released by means of a wet-test meter. This attempt failed because the meter became flooded with water. This flooding resulted from the fact that only a short sediment core (1.05 m) was recovered at *in situ* pressure. The remainder of the pressurized section (~5 m) was filled with water.

PCB-2

This PCB also released gas and water, but water was trapped before the gas reached the wet-test meter. About 7.4 L of gas were released from a 1.61-m core. The volumetric ratio of gas relative to sediment pore water was determined to be 0.7. If gas hydrates had been present, this ratio would have been greater than about 4.

PCB-3

This PCB failed to recover any sediment in the pressurized section of the barrel.

The results of the PCB deployments were disappointing in that there was only partial core recovery in two of three attempts. Where gas measurements were successfully made, there was no evidence for the presence of gas hydrates.

Effects of Gas Hydrates on Chlorinity

Hesse and Harrison (1981) and Harrison et al. (1982) observed that the chlorinity of pore waters decreases with depth at Sites 496 and 497 of Leg 67. They attributed this decrease to the presence of gas hydrates. On Leg 84 we observed decreasing chlorinities of pore waters with depth at Sites 565, 568, 569, and 570 (Fig. 5). These chlorinity profiles suggest that gas hydrates could be present in sediments at sub-bottom depths as shallow as 25–50 m. Below these depths, chlorinity decreases rather systematically to the bottom of the holes at Sites 565, 568, and 569 implying increasing amounts of gas hydrates with depth. The chlorinity profile at Site 570 supports this idea, although the number of data points is minimal. From near the surface to a sub-bottom depth of about 235 m, chlorinity decreases slightly from ~19.5 to ~18.5‰ suggesting minor amounts of gas hydrates. Below 235 m the chlorinity appears to decrease rapidly with a value of 8.9‰ measured at a depth of 337 m. In the interval between 235 and 337 m, abundant evidence for gas hydrates was recovered (Table 2), including the massive gas hydrate previously discussed.

At three of these sites (565, 568, 570) we observed gas hydrates and showed that the water of the gas hydrate had very low chlorinities ranging from 0.5 to 3‰. Thus, a correlation between the presence of gas hydrates and

Table 2. Description of gas hydrates encountered on Leg 84.

Site and section	Sub-bottom depth (m)	Total depth (m)	Comment
565-30-6	285	3396	White, frothing gas hydrate (~0.3 cm^3) was observed through the core liner in a region of degassing sediment. Two pieces were recovered but they decomposed before appropriate measurements could be made.
565-33,CC	319	3430	Pieces of muddy, gas-releasing sandstone were expelled from the end of the core barrel. When broken open, the sandstone showed increased evolution of gas.
565-33,CC	319	3430	White, frothing gas hydrate (~1.5 cm^3) was recovered from stiff mud at top of core catcher; sample used for gas analysis.
568-43-4	404	2434	White gas hydrate was recovered from fractures in a tuffaceous mudstone (Fig. 8A); ~10.4 cm^3 used for gas analysis.
568-43-4	404	2434	Same as above; sample had decomposed for ~15 min before gas analysis; ~7.1 cm^3 used for analysis.
570-21-1	192	1910	Ash laminated with gas hydrate at top of core; ~32 cm^3 used for gas analysis.
570-26-5	246	1965	White gas hydrate in fractures of mudstone (Fig. 8B).
570-27-1	249	1968	White gas hydrate in fractures of dolomite; ~18 cm^3 used for analysis. This sample is at the base of the massive gas hydrate.
570-27-1	249	1968	Massive gas hydrate ~1.05 m long (Fig. 8C). Sample of this gas hydrate decomposed in closed can. Gas was transferred to evacuated aluminum canister from which gas was removed for analysis.
570-28	259–268	1977–1986	White gas hydrate in fractures of mudstone.
570-29-3	273	1991	Same as above.
570-32-4	303	2021	Gas hydrate associated with ash.
570-36-1	338	2055	Gas hydrate associated with sand.

Table 3. Analyses of gas hydrates from Leg 84.

Section	C_1 (%)	C_2 (ppm)	C_3 (ppm)	i-C_4 (ppm)	n-C_4 (ppm)	neo-C_5 (ppm)	i-C_5 (ppm)	n-C_5 (ppm)	CO_2 (%)	C_1/C_2	Volume gas/ volume fluid	Chlorinity (‰)	Comment
565-33,CC	89	440	5	0.2	—	—	0.1	—	0.03	2000	133	0.51	Pressure vessel
568-45-4	64	1200	0.3	1.4	—	0.04	—	—	0.10	530	30	3.2	Pressure vessel
568-45-4	—	—	—	—	—	—	—	—	—	—	7	3.1	Pressure vessel, second sample after 15 min. decomposition
570-21-1	44	390	0.9	0.7	0.2	—	—	—	0.34	1100	4?	—	Pressure vessel
570-27-1	58	2600	79	37	45	3.5	34	12	0.30	220	29	0.65	Pressure vessel
570-27-1	69	1600	48	23	28	1.0	17	8	0.25	440	29	0.65	Repeat gas analysis
570-27-1	74	1200	31	10	7	0.6	6	3	—	600	—	—	Aluminum cannister
570-28	75	890	11	2	7	0.06	4	2	0.24	840	24–42	—	Pressure vessel
570-28	75	1200	14	3	9	0.16	6	3	0.24	620			Repeat gas analysis
570-29-3	—	—	—	—	—	—	—	—	—	—	12	—	Pressure vessel

Note: — indicates not detected.

the decreasing chlorinity of pore waters seems reasonable. Although gas hydrates were not observed at Site 569, the decreasing chlorinity of pore waters suggests that gas hydrates were also present there.

Chlorinity profiles may provide clues to the distribution of gas hydrates in sediments, but there are problems in reconciling some pore water chlorinities and the presence of gas hydrates. At Sites 565 and 568 chlorinities decrease regularly down the holes, yet visual evidence for gas hydrates was found only near or at the bottom of these holes. The chlorinity profiles imply that gas hydrates are present starting near the surface. A possible explanation is that gas hydrates may be finely dispersed in sediments at these sites but that these small crystals of gas hydrate do not survive the drilling and recovery process and are thus not visible in cores. Perhaps only large pieces of gas hydrate are recoverable by the drilling process. If this interpretation is correct, the occurrence of visible gas hydrates cannot adequately define how gas hydrates are distributed in many sediments. The chlorinity profile at Site 570 (Fig. 5) is of interest in that a significant decrease in pore water chlorinity does not occur until below ~235 m sub-bottom; most of the visual evidence for gas hydrates was found below this depth. In this case the chlorinity decrease and the observed gas hydrates correlate well.

The chlorinities of the waters of decomposed gas hydrates are much lower than the chlorinities of squeezed pore water. For example, the lowest pore water chlorinity measured was ~9‰ at Site 570 whereas the highest chlorinity measured in gas hydrate water was 3‰ at Site 568 (Table 3). Thus, in gas hydrate formation, ions are excluded and the resulting water has low chlorinities. The chlorinities of squeezed pore waters most likely results from waters of decomposed gas hydrates and ordinary pore water. A major problem is accounting for the

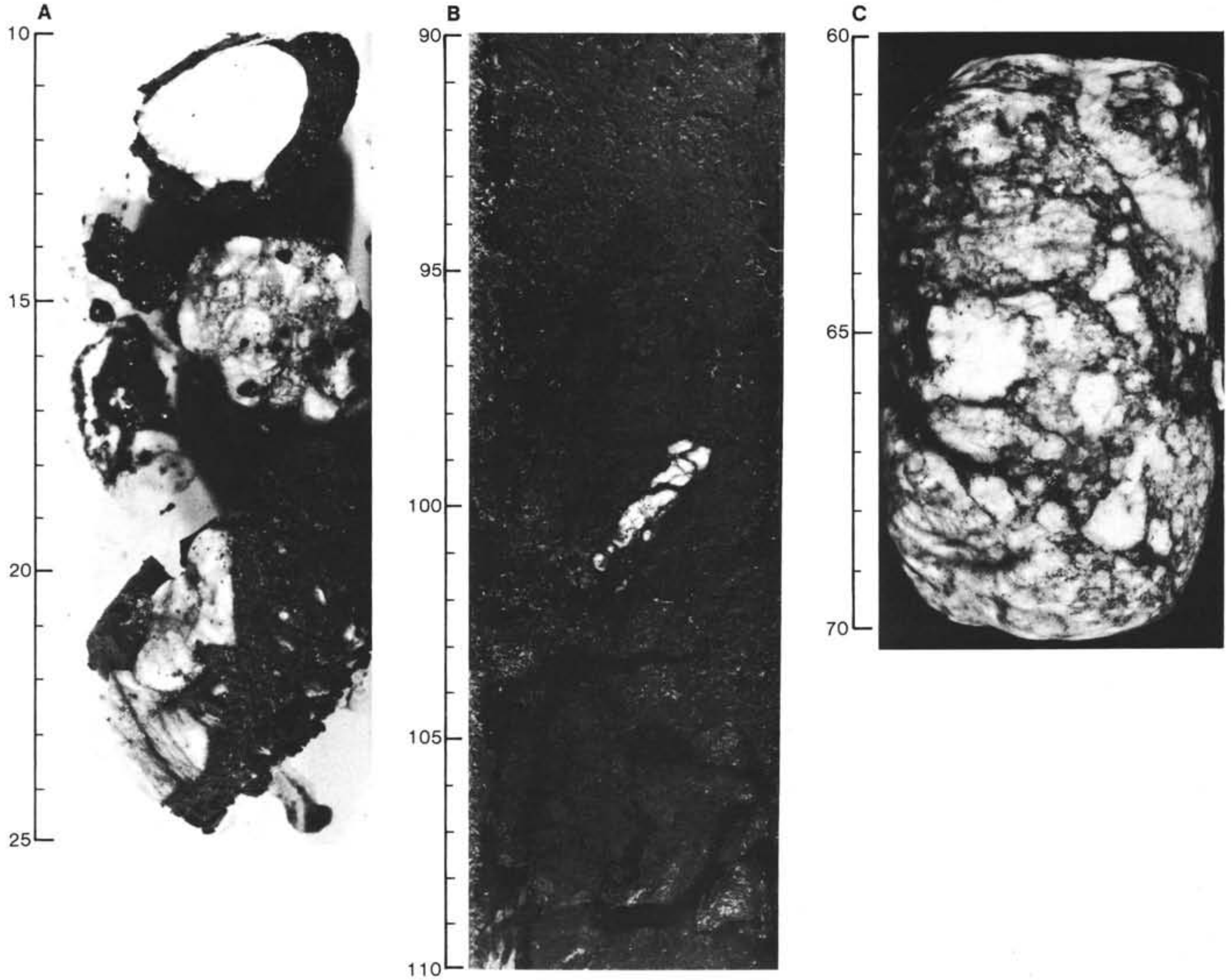

Figure 8. A–C. Photographs of examples of gas hydrates recovered at Sites 568 and 570 of Leg 84 (Sections 568-43-1 [A]; 570-26-5 [B]; and Core 570-27 [C]).

high chlorinity water that must have been excluded during gas hydrate formation. Hesse and Harrison (1981) considered this problem in detail and suggested that measurements of pore water taken with an *in situ* sampler may resolve the problem. The *in situ* pore water sampler was deployed successfully at Sites 565 and 568, but the resulting measurements, including chlorinities (Fig. 5), were similar to measurements made on pore water obtained by squeezing sediments, with the exception of two *in situ* water samples taken near the bottom of the hole at Site 568. The high chlorinity values of these samples probably resulted from seawater contamination of the *in situ* probe. Thus, the problem of accounting for the ions excluded from water during gas hydrate formation remains unsolved.

Gases in Fractured Serpentinite

Holes at Sites 566 and 570 bottomed in fractured serpentinite from which gas was escaping. These gases contained surprisingly high concentrations of hydrocarbons (Table 6) and had distributions different from the gases in the sediments. C_1/C_2 ratios were low: 410 and 160 at Site 566 and 190 and 85 at Site 570. Concentrations of C_{3+} generally exceeded concentrations of C_2. This distribution is the reverse of that discussed previously for gas hydrates in which C_{3+} concentrations were much lower than C_2 concentrations because of the exclusion of C_{3+} hydrocarbons from the cages of the hydrate structure. Because of their unique hydrocarbon composition, the gases in the serpentinite were assumed to have sources different from the gases found in overlying sediments and in gas hydrates. The low C_1/C_2 ratios and the relatively high concentrations of C_{3+} signaled thermogenic processes and suggested that the gases migrated into the serpentinite. The $\delta^{13}C_1$ of the gas from Hole 566C, however, was about $-60‰$ and does not support the idea that the gas is entirely thermogenic. In contrast, gas from serpentinite at Site 570 has $\delta^{13}C_1$ values of -41 and $-40‰$, which does suggest thermogenic processes. However, studies by Jeffrey et al. (this volume) and Claypool et al. (this volume) indicate that C_1 isotopic compositions of about $-40‰$ for gas from cores and

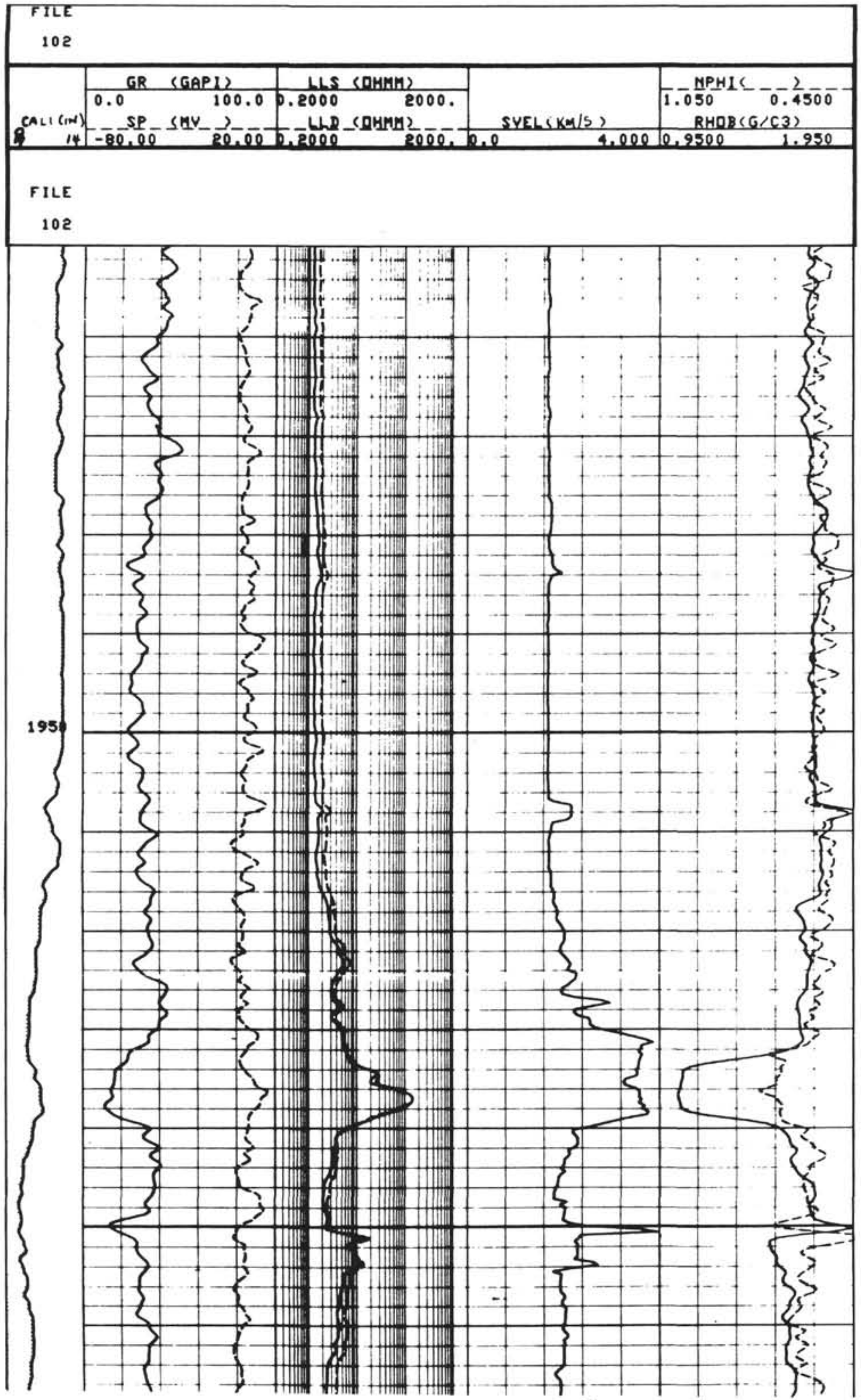

Figure 9. Schlumberger well log showing the log responses for a portion of the hole at Site 570. From left to right the logs are caliper, gamma ray, self potential, resistivity (shallow and deep), sonic velocity, neutron porosity, and bulk density. Depth (water plus sediment) scale (m) is on the left. Each division represents 1 m. The top of the massive gas hydrate is indicated at a total depth of ~1965 m. The subbottom depth of the top of the gas hydrate is at ~249 m.

Table 4. Comparision of C_2 and C_{3+} normalized to C_1 = 100% for gas released from gas hydrates and from sediments near where gas hydrates were found.

Site	Core-section	Depth (m)	C_1 (%)	C_2 (ppm)	C_{3+} (ppm)
565					
Hydrate	33,CC	319	89	500	6
Core Gas	34-1	320	69	400	14
568					
Hydrate	43-4	404	64	2000	3
Core Gas	43-4	404	65	1000	3
570					
Hydrate	21-1	192	44	900	4
Core Gas	21-2	193	65	200	21
570					
Hydrate	27-1	249	64	3300	300
Core Gas	26-4	246	56	2500	1300
570					
Hydrate	28	259–268	75	1400	40
Core Gas	28-6	267	71	2400	640

gas hydrate in the lower part of the hole at Site 570 (below ~250 m sub-bottom) may result from biogenic processes operating in very heavy CO_2.

Thus, the molecular compositions of gases from serpentinite suggest thermogenic sources, whereas carbon isotopes provide an equivocal interpretation. Certainly the gas in the serpentinite must have migrated from elsewhere because *in situ* production of gas within this rock type seems impossible. This gas may have been present in the serpentinite as both Structure I and II gas hydrate because of the large relative abundances of C_{3+} hydrocarbons. In Structure II gas hydrates, the cages are large enough to include C_1, C_2, C_3, and i-C_4 but not n-C_{4+} (Hand et al., 1974). Table 6 shows that the abundance of hydrocarbons as large or larger than n-C_4 (n-C_{4+}) is much lower than the abundance of the smaller hydrocarbons. Thus, circumstantial evidence points to the possibility that Structure II gas hydrate may have been present in the serpentinite.

Origin of Leg 84 Gas Hydrates

Most of the C_1 sampled at sites in Leg 84 is believed to be biogenic as suggested by large C_1/C_2 ratios (Table 7). At Sites 565, 568, and 570, where gas hydrates were recovered, C_1/C_2 ratios in the first 100 m of sediment exceed 30,000. These ratios decrease with increasing depth because of the exponential increase in C_2 that apparently results from the low temperature breakdown of organic matter. Hydrocarbon gases from cores of the deepest sediments sampled still contain >99% C_1. Likewise, the hydrocarbon gases resulting from gas hydrate decomposition are >99% C_1. Much of the biogenic C_1 is produced in the first 100 m of sediment as suggested by headspace analyses of sediments from Sites 565 and 568 (Fig. 3A and B). The production of C_1 depends on sufficient organic carbon in the sediments to support methanogenic processes. In the sediments examined at sites where gas hydrates were observed, organic carbon values are generally >0.5% and reach a maximum of 4.2% at Site 568 (Fig. 4). Claypool and Kaplan (1974) calculated that C_1 production in sediments requires a minimum of ~0.5% organic carbon. Thus, there appears to be sufficient organic carbon in Leg 84 sediments to permit the *in situ* generation of biogenic C_1 for gas hydrate formation.

C_1 in all core gas samples from Sites 565, 567, and 569 has carbon isotopic compositions lighter than −60‰ suggesting a biogenic source (Jeffrey et al., this volume). Core gas samples from the upper 150 m of sediment at Site 568 and the upper 210 m of sediment at Site 570 also had $\delta^{13}C_1$ values lighter than −60‰. Below these depths, however, $\delta^{13}C_1$ values increased to values as heavy as −40‰. C_1 from the massive gas hydrate at Site 570 has a carbon isotopic composition of −44‰ (Jeffrey et al., this volume). C_1 of this heavy isotopic composition is generally considered to be of thermal origin. However, this isotopically heavy C_1 is accompanied by isotopically very heavy CO_2. (Jeffrey et al., this volume; Claypool et al., this volume), and they suggest that the isotopically heavy C_1 could have been derived from the isotopically heavy CO_2 by biogenic processes. Thus, evidence based on the molecular composition of hydrocarbon gases and isotopic compositions of C_1 and CO_2 favor a mainly biogenic source for C_1 in gas hydrates found at sites on Leg 84.

The formation and occurrence of gas hydrates in slope sediments of the Middle America Trench can be explained at least in part by the model proposed by Claypool and Kaplan (1974). In this model C_1 is produced within the sediments by microbial processes. These processes go on concurrently with sedimentation. When the amount of C_1 exceeds its solubility in water and the pressure–temperature conditions are correct gas hydrates form. The zone of gas hydrates will continue to thicken as sedimentation proceeds. When the base of the gas hydrate zone is buried to a depth where temperatures are too high relative to pressure to stabilize the hydrate, the gas

Table 5. Results from pressure core barrel, Site 568.

PCB number	Core number	Sub-bottom depth (m)	Core recovered (m)	(L)	Initial pressure (psig)	Pressure before venting (psig)	Sediment water (%)	Gas released (L)	Gas/water volume ratio
1	11	89.4–98.8	1.05	14	3000	3000	50	nd[a]	nd
2	21	185.7–195.4	1.61	22	2900	3100	52	7.4	0.7
3	31	282.3–292.0	1.16[b]	—[c]	2000	2300	—	—	—

Note: psig = lb./in.^{2}, gauge.

[a] nd = not determined.

[b] Unpressurized core.

[c] Not relevant, because sample was not in pressurized section of the core barrel.

Table 6. Hydrocarbons in serpentinite.

Section	Sub-bottom depth (m)	C_1 (%)	C_2 (ppm)	C_3 (ppm)	i-C_4 (ppm)	n-C_{4+} (ppm)	$\delta^{13}C_1$ (‰)
566C-6-1	118	49	2500	1100	1100	85	−60.5
566C-7-1	128	45	6200	3100	3300	350	−60.2
570-41-2	386	69	5200	7000	2000	300	−41.2
570-42-1	394	25	12000	15000	3600	640	−40.2

Note: C_2, C_3, and i-C_4 are normalized to C_1 = 100%. $\delta^{13}C_1$ values are from Jeffrey et al. (this volume).

hydrate will decompose. The base of the gas hydrate zone is sometimes manifested as a BSR on seismic records, such as at Site 568 (Fig. 6).

The massive gas hydrate found at 249 m sub-bottom at Site 570 is so unusual, however, that very special circumstances must have prevailed during its formation. This gas hydrate is 3–4 m thick, but its lateral extent is unknown. It contains little sediment; during the crystallization process the hydrate either filled existing void space or created space for itself. The hydrocarbon gases composing this gas hydrate must have moved from the enclosing sediment into the region where this hydrate formed. Details of the processes of formation of this unique gas hydrate are unclear.

SUMMARY

Drilling on DSDP Leg 84 has shown that gas hydrates are common in landward slope sediments of the Middle America Trench offshore Guatemala and Costa Rica. The six drilled sites were all located within the pressure (depth)–temperature zone of gas hydrate stability. At only one site (568) did seismic records show an anomalous, bottom-simulating reflector indicating the presence of gas hydrates. Nevertheless, gas hydrates were recovered at three sites (565, 568, and 570) and were inferred, from both organic and inorganic evidence, to be present at two other sites (566 and 569). Wherever gas hydrates were recovered, they appeared as pieces of white, icelike substances occupying fractures in mudstone or as ash or sand in which the pore space contained gas-hydrate, as indicated by the rapid evolution of gas. At Site 570 at least seven examples of gas hydrate were noted, the most spectacular of which was a 1.05-m core of massive gas hydrate. Samples of this core were preserved in special pressure vessels for onshore studies. Downhole logging showed that the massive hydrate was actually 3 to 4 m thick and provided the first *in situ* measurements of the physical properties of a nearly pure gas hydrate.

Table 7. C_1/C_2 ratios at six sites, Leg 84.

Site 565		Site 566		Site 567		Site 568		Site 569		Site 570	
Depth (m)	C_1/C_2	Depth (m)	C_1/C_2	Depth (m)	C_1/C_2	Depth (m)	C_1/C_2	Depth (m)	C_1/C_2	Depth (m)	C_1/C_2
56	31000	118	410	203	7500	18	290,000	38	6200	5	—
177	7700	128	160	212	5500	28	260,000	49	7500	11	92,000
195	7800			219	6200	39	240,000	59	8300	26	92,000
204	8300			225	5200	47	123,000	63	8600	30	74,000
209	8700			237	5900	56	174,000	69	8300	41	60,000
217	6100			250	5700	68	113,000	78	8800	53	50,000
236	6100			255	5700	75	122,000	90	8200	61	55,000
243	4200			268	4900	85	58,000	105	6700	69	55,000
250	3500			278	4700	104	75,000	110	7300	78	74,000
270	2300			281	4400	114	63,000	117	6900	88	74,000
293	2500			291	5000	126	23,000	129	6000	96	92,000
320	2500			301	4500	135	16,000	136	14,000	130	31,000
				313	4900	145	16,000	153	8100	136	29,000
				319	3600	153	15,000	156	9000	151	20,000
				336	3600	160	13,000	175	10,000	157	18,000
				346	3200	176	10,000	186	11,000	164	12,000
				352	2900	184	13,000	195	9200	176	10,000
				359	63,000	203	6000	207	5800	183	9300
				377	1900	208	7400	219	6900	195	5000
				412	2900	220	6500	224	7600	205	5800
				421	2600	232	6800	238	6900	214	2200
				430	1000	247	470	244	7600	224	2300
				438	490	259	350	248	8100	235	1000
				446	1700	270	6100	258	9700	246	400
				486	2000	281	4400	275	9600	267	410
						300	6100	294	7900	274	450
						310	5900	304	7700	284	630
						319	4700	333	9300	289	950
						327	4400			302	900
						339	4500			317	1900
						346	5000			329	1200
						358	3300			337	1000
						363	1500			346	750
						374	1300			386	190
						386	1300			394	80
						398	950				
						404	970				
						414	718				

Samples of gas hydrates from Sites 565, 568, and 570 were allowed to decompose in a closed, pressure-measuring container. The volumetric ratio of released C_1 to water was greater than the amount of C_1 that could be dissolved in water at the *in situ* pressure–temperature conditions of the samples. Comparison of the distribution of hydrocarbon gases released from gas hydrates with the distribution of hydrocarbon expelled from the cores suggests that Structure I gas hydrates are present. Concentrations of C_2 are generally larger in the gas hydrates than in core gas, and at the same time, concentrations of C_{3+} are lower in the gas hydrates than in the core gas. These results probably reflect the preferential inclusion of C_2 and preferential exclusion of C_{3+} that are expected because of the sizes of the cages that are present in Structure I gas hydrates.

At all sites where gas hydrates were recovered (565, 568, and 570) the chlorinity of pore waters squeezed from the sediments decreased as the depth of the sediment increased. This observation, also made on Leg 67, suggests that the presence of gas hydrates may be predicted on the basis of pore-water chlorinity. Profiles of decreasing chlorinities with increasing depth suggest however, that gas hydrates may be present through much of the cored section, whereas samples of gas hydrates were usually near or at the bottom of the holes. A possible explanation is that gas hydrates may be finely dispersed in much of the sediment at these sites but that the small gas hydrate crystals do not survive the drilling and recovery process. Perhaps only when large pieces of gas hydrate are present can they be successfully recovered by the drilling process. Thus, the occurrence of visible gas hydrates in cores does not adequately describe the distribution of gas hydrates in sediments. The chlorinity profile with depth may provide a better clue to overall distribution of gas hydrates in sediment.

Most of the C_1 sampled on Leg 84 is probably of biogenic origin, as is indicated by the generally large ratios of C_1/C_2. This biogenic gas was likely generated *in situ* and incorporated into gas hydrates as recovered at Sites 565, 568, and 570. Carbon isotopic compositions of C_1 generally support a biogenic source for the gas. However, with increasing depths at Sites 568 and 570, $\delta^{13}C_1$ values increase to $-40‰$, in a range usually considered to represent a thermal origin. This isotopically heavy C_1 is also accompanied by isotopically heavy CO_2; the isotopically heavy C_1 could have been derived from the isotopically heavy CO_2 by biogenic processes. Thus, we conclude that C_1 in the gas hydrates recovered on Leg 84 was mainly derived *in situ* by biogenic processes, whereas C_2 in these hydrates probably resulted mainly from low-temperature diagenetic processes. Some C_1 was also produced during low-temperature diagenesis, but the amount was most likely small relative to the amount of C_1 formed biogenically.

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