

Association of gas hydrates and oil seepage in the Gulf of Mexico

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Abstract—Gas hydrates were recovered from eight sites on the Louisiana slope of the Gulf of Mexico. The gas hydrate discoveries ranged in water depths from 530 to 2400 m occurring as small to medium sized (0.5–50 mm) nodules, interspersed layers (1–10 mm thick) or as solid masses (> 150 mm thick). The hydrates have gas:fluid ratios as high as 170:1 at STP, $C_1/(C_2 + C_3)$ ratios ranging from 1.9 to > 1000 and $\delta^{13}C$ ratios from -43 to -71% . Thermogenic gas hydrates are associated with oil-stained cores containing up to 7% extractable oil exhibiting moderate to severe biodegradation. Biogenic gas hydrates are also associated with elevated bitumen levels (10–700 ppm). All gas hydrate associated cores contain high percentages (up to 65%) of authigenic, isotopically light carbonate. The hydrate-containing cores are associated with seismic “wipeout” zones indicative of gassy sediments. Collapsed structures, diapiric crests, or deep faults on the flanks of diapirs appear to be the sites of the shallow hydrates.

Key words: gas hydrates, oil seepage, carbon isotopes, Gulf of Mexico, shallow seismic

INTRODUCTION

Gas hydrates are ice-like inclusion compounds that form at high pressures and low temperatures when gas in excess of solubility is present. In practicality, hydrocarbons (methane through butane) and possibly carbon dioxide and hydrogen sulfide are the only gases found in deep-sea sediments in sufficient concentrations to form gas hydrates. The shallowest limit for methane hydrate stability in marine sediments is usually quoted as *c.* 500 m water depth and 7°C bottom water temperature (Kvenvolden and McMenamin, 1980). However, a number of factors can influence these limits. First, the inclusion of higher molecular weight hydrocarbons (ethane and higher) can stabilize the hydrate structure at higher temperatures and/or lower pressures and allow it to exist at a shallower depth. The opposite effect results from increasing salinities in the pore waters. The size of molecules that can be occluded within the hydrate structures is determined by the structure of the hydrate cage. Structure I hydrate can only occlude molecules as large as ethane while Structure II hydrate can occlude molecules at least as large as isobutane (Davidson *et al.*, 1978). There is also evidence that *n*-butane can fit into Structure II hydrate cages in limited quantities (Ng and Robinson, 1976).

Gas hydrates are rare occurrences in deep-sea sediments. This is because gas hydrates can only form where there is significant biogenic methane production, or where there is upward migration of thermogenic gases from deeper horizons. Thermogenic gases do not form hydrates at their sites of production because the zone of hydrate stability is well below the temperatures necessary for their formation. Before the recent discovery of gas hydrates

in a Louisiana slope core in the northern Gulf of Mexico (Brooks *et al.*, 1984), the only direct observation of gas hydrates in shallow cores was from the Black Sea (Yefremova and Zhizhchenko (1974). The other subsequent findings of gas hydrates were from Deep Sea Drilling Project (DSDP) cores at sub-bottom depths of hundreds of meters on the Blake Outer Ridge of the Atlantic (DSDP Leg 76; Brooks *et al.*, 1983) and in the Middle America Trench off Guatemala and Mexico (DSDP Legs 66, 67 and 84; Shipley and Didyk, 1982; Harrison and Curiale, 1982; Brooks *et al.*, 1985). These early findings all represented gas hydrates of biogenic origin consisting of predominately methane. This report will describe biogenic and thermogenic gas hydrates and associated sediments collected from eight sites on the Gulf of Mexico continental slope.

ASSOCIATED GEOLOGY

The continental slope off Louisiana is a bathymetrically complex region underlain by extensive salt diapirs, stocks, and ridges interconnected at shallow depths (Ewing and Antoine, 1966; Antoine and Bryant, 1969; Wilhelm and Ewing, 1972; Martin and Bouma, 1981). The geologic features of the area include mass movement deposits (slumps), intraslope basins with thick sediment accumulations, graben structures over shallow diapirs, and growth and normal faults (Bouma, 1982). Processes actively occurring are continuous growth of diapirs, growth faulting, slumping and sediment creep. Lateral as well as vertical movement by sediment loading and progradation has been suggested as a mechanism for the formation of diapiric provinces on the margin (Antoine and Bryant, 1969; Amery, 1969; Humphris,

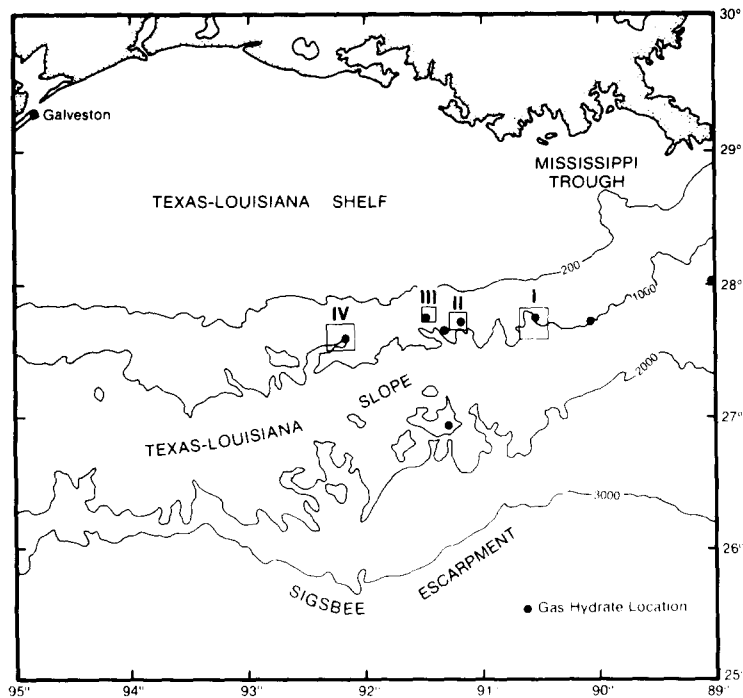


Fig. 1. Gas hydrate locations on the Louisiana slope. The boxes represent areas where intensive high resolution shallow seismic data have been obtained.

1978). As a result of this movement, secondary features such as radial and concentric faulting, slumps, growth faults and localized fans have been developed and identified on the slope (Walker and Ensminger, 1970; Martin and Bouma, 1978; Bouma *et al.*, 1981; Trippet, 1981).

Approximately 462 nmi of high resolution seismic data have been collected on the Louisiana continental slope on three cruises of the *R/V Gyre* (see Fig. 1 for locations). This data was acquired in areas where gas hydrates had been collected. The purpose was to determine the geological setting associated with the occurrence of gas hydrates with particular reference to gas "wipeout" zones. The first thermogenic hydrate discovery (Green Canyon Block 184; Brooks *et al.*, 1984) was associated with a seismic "wipeout" zone appearing on a subbottom profiler. The seismic data consists of high-quality, shallow subbottom records acquired by a 3.5 kHz subbottom profiler and a 40 tip, 800 J minisparker system. Penetration of up to 300 msec (two-way travel time) on the minisparker records was obtained and maximum resolution was 1.3 m. The subbottom profiler penetrated up to 200 msec and the resolution was 0.5 m.

As an example of the type of geological setting associated with gas hydrates in the Gulf of Mexico, Fig. 2 shows the shallow subbottom structures associated with the Green Canyon (GC) Block 204 thermogenic hydrate discovery. The bathymetry indicates a large trough-like feature extending south across the area. This was formed by two large diapirs flanking the trough. A prominent fault scarp exists

over the eastern diapir which may indicate recent movement of the underlying diapir. The large gas "wipeout" zone mapped in Fig. 2 is generally over the crest and western flank of the eastern diapir. This is the location where the gas hydrate core was recovered. Figure 3 shows a subbottom profiler record over the diapiric crests showing the fault scarp and faults associated with gas "wipeout" zones. These types of structures are typical of the areas where hydrates have been found. A fault associated with a scarp or collapsed structures provide numerous conduits for the upward migration of gas from sources at depth. The faults may result from the upward movement of the diapirs causing a lateral extension and multiple fracturing of the sediment. Collapsed structures may be the result of dissolution of shallow salt by seawater entering through extension faults.

All the shallow gas hydrate areas that have been seismically studied in detail (Fig. 1 shows those locations) are associated with seismic "wipeout" zones which are usually indicative of gassy sediments. However, every core taken within a seismic "wipeout" zone in a gas hydrate-containing area does not yield hydrates. Hydrates occur sporadically in these zones. For example, in the GC-234 area 10 piston cores were recovered in or near "wipeout" zones before gas hydrates were cored. Cores from the seismic "wipeout" zones, at least in the GC lease area on the Louisiana slope, yield gas hydrates, oil-stained cores and/or gassy sediments in various combinations. The gas "wipeout" zones surveyed and mapped are associated with either collapsed structures or

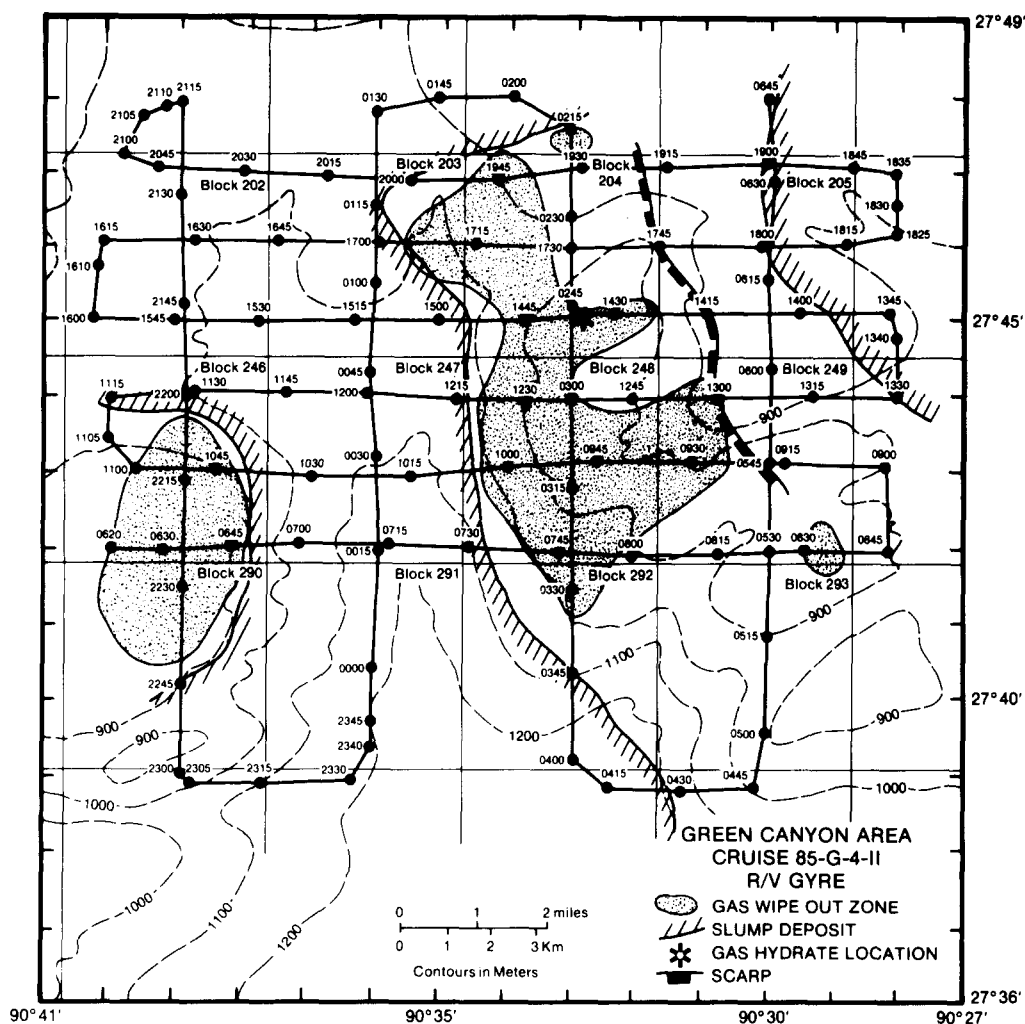


Fig. 2. Ship tracks and shallow subbottom features at the GC-204 site (Area I on Fig. 1).

diapiric crests or deep faults on the flanks of diapirs. The tectonic action of salt diapirs on the slope creates structural traps for hydrocarbons and conduits for the upward migration of gas and oil. Since there are numerous diapirs on the slope and numerous seismic "wipeout" zones, gas hydrates presumably exist in many areas of the northwest Gulf of Mexico continental slope.

EXPERIMENTAL

Sampling

The gas hydrates recovered on DSDP Leg 96 from the Orca Basin (Site 618) were obtained from a 40–60 m subbottom depth in the northern lobe of this anoxic, hypersaline basin [see Shokes *et al.* (1977), Wiesenburg (1980), Sackett *et al.* (1979), and Wiesenburg *et al.* (1985) for descriptions of this basin]. The samples were taken immediately from the core liner, inserted into a cloth bag and stored under liquid nitrogen for laboratory analysis. The seven shallow cores were taken using a 1000 kg, 6 m piston core and the gas hydrate-containing sections recovered were immediately frozen in liquid nitrogen or placed immediately into a Parr bomb.

Analytical

Gas hydrate samples were removed from the liquid nitrogen storage dewars and placed in a tray of liquid nitrogen, then broken into small pieces for analysis. These pieces were placed in a 23 cm³ Parr bomb equipped with a pressure gauge and sampling port. The hydrate was allowed to decompose and the gas sampled for molecular and isotopic compositions. The bomb was then opened and the water/sediment mixture centrifuged to determine the water content for calculating gas:fluid ratios.

The molecular composition of the hydrate gas was determined using two Hewlett-Packard (HP) 5790 gas chromatographs equipped with FI and TC detectors for hydrocarbons and fixed gases, respectively. Gaseous components for isotopic analysis were separated chromatographically, combusted to CO₂ in a Craig-type combustion system, and then analyzed on a Finnigan MAT 251 Isotope Ratio Instrument. All values are reported as $\delta^{13}\text{C}$ (‰) relative to PDB. The organic carbon content of sediment subsamples was determined using a Leco inductive furnace. Carbonate was determined by acidification followed by CO₂ detection with an infrared analyzer. Extractable organic matter was gravimetrically determined with a Cahn Electrobalance after a 12 hr hexane Soxhlet extraction. The extracts were subsequently blown dry with a purified air stream, brought up in 100 μl of methylene chloride and injected onto a HP

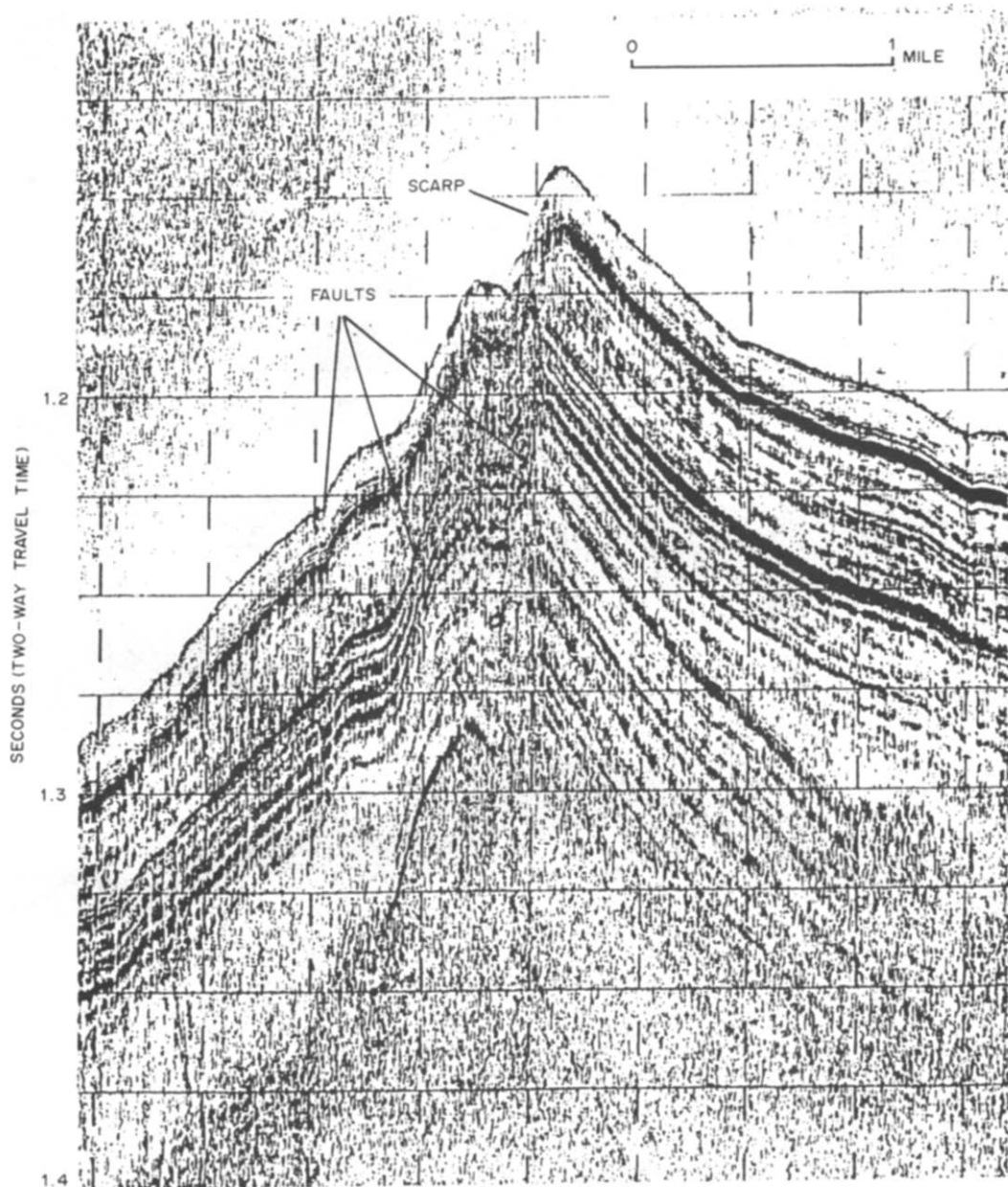


Fig. 3. Subbottom profiler record of scarp and faults associated with the GC-204 hydrate.

5880 gas chromatograph equipped with a 25 m fused silica capillary column. The gas chromatograph was interfaced with a HP-1000 computer for data storage and subsequent data analysis using Laboratory Automation Software (LAS).

RESULTS

Eight gas hydrate sites have been identified on the Gulf of Mexico northwest continental slope by conventional piston coring (Fig. 1). Six of these cores were taken during surface geochemical surveys directed towards determining the concentration of upward migrated hydrocarbons in surface sediment overlying oil-gas prospects. The core locations were

usually over or near deep faults previously identified by seismic profiling. Of the *c.* 800 shallow piston cores taken in water depths greater than 500 m on the Gulf slope, only eight have contained hydrates (this does not include intensive coring in very localized areas already identified as containing gas hydrates). All gas hydrates have been released for this study. Additional gas hydrate samples were obtained at Site 618 in the Orca Basin on DSDP Leg 96 and on *R/V Gyre* Cruise 84-G-12 in the oil seep area identified by Anderson *et al.* (1983). Table 1 lists the gas hydrate areas, their locations, water depths and the nature of the occluded gases.

Table 1. Gulf of Mexico gas hydrate locations, water depth and the nature of the occluded gases

Area	Location	Water depth (m)	Nature
Orca Basin	26°56'N, 91°19'W	2400	Biogenic
Green Canyon-184	27°47'N, 91°30'W	530	Thermogenic
Green Canyon-204	27°45'N, 90°33'W	850	Thermogenic
Green Canyon-234	27°44'N, 91°13'W	590	Thermogenic
Garden Banks-388	27°36'N, 92°11'W	850	Biogenic
Green Canyon-257	27°43'N, 90°06'W	880	Biogenic
Green Canyon-320	27°39'N, 91°21'W	800	Biogenic
Mississippi Canyon	28°03'N, 88°59'W	1300	Thermogenic

Physical description

The three GC thermogenic cores all had similar appearances. Gas hydrates have been recovered in six cores taken at GC-184. The gas hydrates recovered varied in size from 1–2 mm to several chunks 40–50 mm in diameter. The larger chunks were bulbous, nodule-like and somewhat spherical in shape. The GC-234 gas hydrate was recovered twice with core penetrations of only 2.8 and 1.2 m. This site contained the largest sized gas hydrate, a solid plug > 150 mm in length. Since the core did not completely penetrate the hydrate, this massive hydrate could have been several meters thick. The GC-204 hydrate was recovered at water depths of 850 m. Because of mechanical problems, the sediment was not removed from the core barrel until 30 min after retrieval. Nevertheless, gas hydrates were found dispersed in the sediment at a subbottom depth of 1.4–4.2 m. The hydrates ranged in size from 2–5 mm chips to chunks 10–30 mm in diameter. All three of these cores containing thermogenic gas hydrates had visually oil-stained sediment. The gas hydrates were yellow-brown in color and had a strong oil, H₂S odor. However, the massive hydrate from GC-234 was whitish-yellow in color. All of the cores contained large amounts of gravel-sized carbonate material interspersed with the gas hydrates. The depth distribution of the gas hydrates, oil-stained sediment and carbonate gravel-sized material in the cores was difficult to determine in some cases because of the severe core disruption caused by gas hydrate decomposition.

The fourth thermogenic gas hydrate was recovered in 1300 m of water in the Mississippi Canyon (MC) area, approximately 60 nautical miles south of the Mississippi delta. Only small pieces of gas hydrates (< 2 mm) were observed in the bottom section of this 3.8 m core. However, due to the 40 min recovery time for this deep core, these gas hydrates may represent larger pieces that had partially decomposed. No oil-staining was visually detected in this core.

All four predominantly biogenic gas hydrates were collected from water depths greater than 850 m. These biogenic gas hydrates were not associated with oil-stained sediments and were either composed of small nodules or flat, sheet-like layers. The biogenic hydrates were visually distinct from the thermogenic hydrates in that they were pure white in comparison

to the yellow-brown noted for the thermogenic hydrates. Like the thermogenic hydrates, they were found in core sections that had coarse sediments, with carbonate rubble and/or shell hash. The biogenic gas hydrates from the shallow cores appeared to be less dispersed within the core and also not as easily resampled by subsequent coring. Gas hydrates from the GC-257 area were recovered from 4.2 and 4.8 m below the seafloor. The hydrates recovered from this core were 3 mm wide and 10 mm long and consisted of flat white masses amid sandy muds and gravel-sized authigenic carbonate particles. GB-388 core contained two gas hydrate samples of 2 and 10–20 mm thicknesses at 2.8 and 3.8 m below the seafloor, respectively. The GC-320 gas hydrate was found in the interval from 3.2 to 3.6 m subbottom in a matrix of coarse sediment. It was almost visually identical to the GC-257 hydrate consisting of 2 mm wide and 10 mm long white layers. The hydrates of GC-257 were intermingled with large chunks of carbonate rubble. This hydrate had a strong H₂S odor, whereas the GC-257 had no such odor. The deepest biogenic hydrate was recovered in 2400 m of water from Orca Basin. Small 1–4 mm bead-sized hydrates were dispersed sporadically from 20–40 m subbottom and were often associated with sandy sediments.

Thermogenic hydrates

Four of the hydrates were classified as being predominantly thermogenic in origin (Table 1). Tables 2 and 3 lists the isotopic and molecular compositions, and the gas:fluid ratios of these hydrates. These gas hydrates had $\delta^{13}\text{C}$ ratios for methane ranging from –43 to –56‰. The molecular composition of the GC hydrates were characterized by the following hydrocarbon distributions: methane > propane > ethane > isobutane > normal butane. Methane concentrations ranged from 62 to 74% except for the MC gas hydrate which contained a much higher percentage of methane (93.4%). CO₂ was also a major component ranging from 0.2 to 4.0%. The CO₂ was isotopically heavy compared to the carbonate carbon (Table 4). Gas:fluid ratios varied from 70:1 to 177:1. The highest ratio was obtained from a sample that was immediately placed in a pressure container in the field. All other ratios were determined on stored nonpressurized samples.

Table 2. Stable isotopic composition ($\delta^{13}\text{C}$ in ‰) of the occluded hydrate gas and gas:fluid ratios

Area	Methane	Ethane	Propane	Butanes	CO ₂	Gas:fluid ratio
Orca Basin	-71.3	—	—	—	—	N.D.
Green Canyon-184	-44.6	-29.3	-18.6	-28.6	+18.5	70:1
Green Canyon-204	-56.5	-35.1	-24.6	-26.5	—	85:1
Green Canyon-234	-43.2	-27.9	-28.5	-28.6	+0.4	177:1
Garden Banks-388	-70.4	—	—	—	—	68:1
Green Canyon-257	-69.2	—	—	—	—	35:1
Green Canyon-320	-66.5	—	—	—	—	66:1
Mississippi Canyon	-48.2	—	—	—	—	N.D.

N.D. = not determined because of the small amount of hydrate available.

Table 3. Molecular compositions (assuming hydrocarbons + CO₂ = 100%) of the occluded hydrate gas

Area	C ₁	C ₂	C ₃	<i>i</i> -C ₄	<i>n</i> -C ₄	CO ₂	C ₁ /(C ₂ + C ₃)
Orca Basin	99.1	0.34	0.28	—	—	0.24	159
Green Canyon-184	70.9	4.7	15.6	4.4	0.3	4.1	3.2
Green Canyon-204	61.9	9.2	22.8	4.5	1.3	0.2	1.9
Green Canyon-234	74.3	4.0	13.0	3.2	0.86	4.6	4.4
Garden Banks-388	99.5	0.12	—	—	—	0.26	829
Green Canyon-257	99.7	—	—	—	—	0.26	> 10000
Green Canyon-320	99.7	0.08	—	—	—	0.12	1246
Mississippi Canyon	93.4	1.2	1.3	—	—	4.0	37.4

The chemical analysis of the sediment from the thermogenic gas hydrated cores is presented in Table 4. Hexane extractable organic matter was as high as 7% in the GC thermogenic gas hydrate associated sediment. The hydrocarbons extracted from GC cores containing thermogenic hydrates were severely biodegraded (Fig. 4). The gas chromatograms were generally composed of only an unresolved complex mixture (UCM) peaking around *n*-C₂₉ and the complete absence of normal and isoprenoid hydrocarbons. The lower concentration of hydrocarbons associated with the MC gas hydrate core were char-

acterized by the complete suite of *n*-alkanes with an odd over even carbon preference in the > *n*-C₂₃ range and a bimodal UCM. The sediments were elevated in organic carbon, total sulfur and calcium carbonate compared to typical deep-sea sediments. The highest carbonate levels in the cores were associated with isotopically light carbonate.

Biogenic hydrates

Four gas hydrates were classified as predominantly biogenic in nature (Table 1). The occluded gases from these samples were composed of predominantly

Table 4. Analysis of thermogenic gas-hydrated sediment

Area	Depth (cm)	Extract %	Org. C %	Sulfur %	CaCO ₃ %	$\delta^{13}\text{C}$ -CaCO ₃ ‰
Green Canyon 204	0-5	0.05	1.1	1.16	13.0	-2.9
	100-105	7.2	5.2	1.64	23.6	-27.9
	160-165	2.1	3.0	1.36	26.1	-21.5
	240-245	1.4	3.4	1.09	12.5	-7.2
	260-265	1.4	2.9	1.46	8.4	+0.8
	320-325	1.6	3.1	1.32	7.4	+1.0
	380-385	0.4	1.7	1.96	8.0	+1.0
Green Canyon 234	420-425	0.2	1.6	0.09	8.2	+1.3
	0-5	1.1	2.7	0.93	6.7	-2.4
	20-25	1.3	3.3	1.19	6.8	-4.8
	60-65	1.1	3.0	1.24	5.2	-2.7
Green Canyon 184	80-85	1.2	3.2	1.25	5.4	-5.3
	0-5	2.7	3.8	0.76	44.9	-17.1
	80-85	0.8	3.0	0.51	65.0	-18.2
Green Canyon 184	160-165	0.4	1.1	1.20	16.9	-2.9
	200-205	0.6	1.6	1.37	8.2	-1.1
	240-245	0.5	1.7	1.68	7.2	+2.0
	260-265	0.4	1.4	1.66	14.2	+1.9
	280-285	0.3	1.3	1.87	10.0	-2.5
	Miss. Canyon	0-5	0.007	1.2	1.84	17.5
80-85		0.01	0.6	0.44	12.0	-5.7
120-125		0.01	0.6	0.30	11.3	-0.8
180-185		0.02	0.4	0.34	11.2	-1.2
220-225		0.03	0.5	0.59	11.5	-2.0
280-285		0.01	0.7	0.73	26.0	-29.4
320-325		0.02	0.4	0.56	10.8	-5.5
360-365		0.03	0.5	0.18	12.8	-1.0

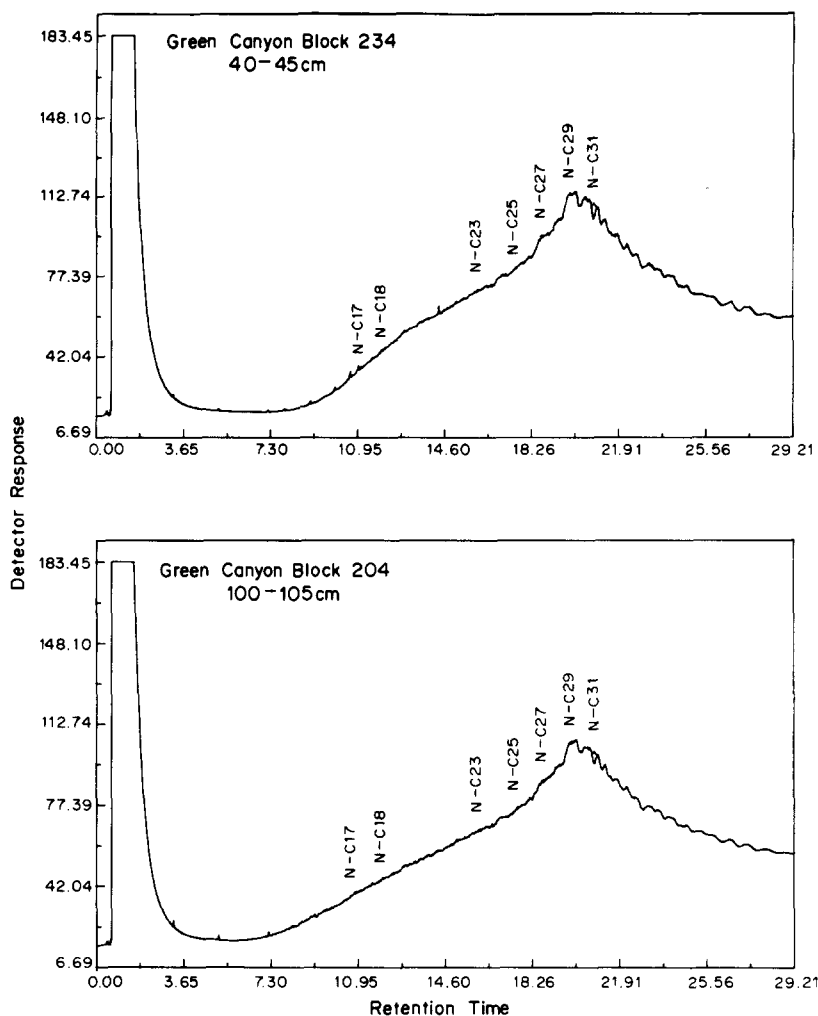


Fig. 4. Gas chromatograms (FID) of sediment extracts from thermogenic gas hydrate cores in Green Canyon.

methane (Table 3) with low concentrations of ethane, propane and CO_2 . Isotopically the methane ranged from -66 to -71% . Table 5 presents the analyses of the sediments associated with the shallow gas hydrates. In these cores, extractable organic matter was 1–2 orders of magnitude less than for the sediment containing thermogenic hydrates (< 200 ppm for the GC cores and < 700 ppm for the GB core). Typical gas chromatograms of extracts from the shallow cores are presented in Fig. 5. These chromatograms are characterized by a bimodal UCM, *n*-alkanes from *n*- C_{14} to *n*- C_{34} with an odd/even preference in alkanes $> \text{C}_{23}$, and varying degrees of biodegradation. As shown in Fig. 5 for the GB-388 area, a number of cores show more extensive biodegradation in the shallower sediment sections.

The molecular analysis of the gas produced on decomposition of the Orca Basin hydrate was primarily methane with trace amounts of ethane, propane and CO_2 . The 92 m core was gassy throughout and vacutainer samples from pockets created by gas

expansion were obtained. The $\delta^{13}\text{C}-\text{C}_1$ for the hydrate was the same (-71.3%) as for the gas collected in a vacutainer in the same core section. However, there was an anomalous C_1/C_2 ratio (18,400) in the vacutainer gas from the hydrate section compared to the vacutainer gas samples obtained from 15 other sections in the core (range 3200–8400). The anomalous C_1/C_2 ratio may have been due in part to the presence of the hydrate since ethane and propane concentrations, while low, are much higher than those found in the gas pockets. This data suggests that hydrate formation involves no isotopic fractionation of methane but may involve a preferential incorporation of ethane and propane.

Figure 6 shows the vertical distribution of a number of parameters in the Orca Basin core (a core from the nearby Pigmy Basin is shown for comparison). Total organic carbon concentrations are relatively uniform (range 0.6–1.0%; averaged $0.6 \pm 0.1\%$, $n = 16$). Carbon to nitrogen elemental ratios are indicative of a predominance of terrestrially derived

Table 5. Analysis of biogenic gas-hydrated sediment

Area	Depth (cm)	Extract %	Org. C %	Sulfur %	CaCO ₃ %	$\delta^{13}\text{C-CaCO}_3$ (‰)
Green Canyon 257	0-5	0.008	2.0	1.36	28.4	-42.9
	80-85	0.009	1.0	1.00	33.4	-37.6
	160-165	0.02	1.0	0.96	18.2	-30.5
	220-225	0.01	1.1	1.27	10.3	-6.5
	280-285	0.01	2.0	1.58	11.7	-7.6
	360-365	0.008	1.5	1.19	15.0	-8.2
	420-425	0.001	1.2	1.39	15.8	-11.7
	480-485	0.008	1.4	1.18	11.2	-12.6
Garden Banks 388	0-5	0.04	0.6	0.84	37.1	-32.9
	80-85	0.06	0.7	0.50	32.2	-26.8
	120-125	0.07	0.7	0.53	26.8	-14.5
	180-185	0.03	0.8	0.87	17.7	-3.1
	240-245	0.02	0.8	1.07	17.2	-4.0
	280-285	0.02	1.0	0.71	18.7	-1.8
	320-325	0.02	1.1	0.85	18.2	-2.0
	380-385	0.02	1.2	0.95	19.9	-2.5
Green Canyon 320	0-5	0.005	1.1	0.22	9.2	-0.5
	60-65	0.008	0.9	1.13	34.8	-36.5
	120-125	0.004	0.9	0.92	47.2	-41.7
	160-165	0.01	1.7	0.92	56.0	-47.5
	220-225	0.02	0.9	1.30	16.1	-8.6
	260-265	0.01	0.7	1.11	14.1	-6.1
	280-285	0.01	0.7	1.14	15.1	-8.5
	330-305	0.01	0.8	0.97	14.4	-5.7

organic matter. This interpretation is supported by $\delta^{13}\text{C}$ -organic matter which ranges from -25.5 to -26.8 ‰. Sulfate was below detection limits beyond a depth of 3 m in the core. Concentrations of extractable organic matter are relatively high, variable (ranging from 99.1 to 393 ppm) and show no apparent vertical trends [for comparison see Kennicutt *et al.* (1986) for levels in DSDP cores from slope sediments from the Mississippi Fan]. Gas chromatographic analyses demonstrate a hydrocarbon distribution representing a mixture of biogenic and thermogenic hydrocarbons (Fig. 7).

DISCUSSION

A model (after R. Malone, DOE) for the possible formation of gas hydrates in deep-sea sediments is depicted in Fig. 8. In this model gas hydrates initially form small disseminated crystals followed by larger nodules and hydrate layers interspersed with mud. With increased hydrate growth, a solid gas hydrate mass is finally formed. Although this model of hydrate formation is oversimplified, the hydrates obtained from the Gulf slope exhibit all these physical forms. The biogenic hydrates mainly consist of crystals and small nodules, while the thermogenic hydrates represented various conditions from nodules to cm thick layers to a massive hydrate. If these stages actually represent degrees of hydrate growth, then the thermogenic hydrates are more mature hydrates in which a greater supply of gas was available for hydrate formation. However, hydrate growth in the cores may be influenced by factors such as sediment texture (sand and carbonate content), formation of authigenic carbonate rubble, and shallow faulting and fracturing of the sediments. In a number of the

cores, it was visually evident that the hydrates were associated with sandy layers, or high carbonate-containing sediments. Anderson *et al.* (1983) showed that near the GC-234 area, oil-stained cores were stained along fractures. It is therefore possible that the hydrates initially form along fractures, faults, and/or cavities in coarse grained sediments.

All the cores recovered contain significant amounts of calcium carbonate which was authigenic as evidenced by their light $\delta^{13}\text{C}$ carbonate values in high carbonate containing sections (Tables 4 and 5). The high concentrations and light carbonate are generally restricted to the upper portions of the cores. In the cores containing thermogenic hydrate, this carbonate presumably originates from the bacterial degradation of the oil, producing CO_2 supersaturation and calcium carbonate precipitation in the sediment. The bacterial degradation of the oil is indicated by the almost complete depletion of the *n*-alkanes and isoprenoids in the oil-stained cores. The predominance of these processes in the upper portions of the cores is indicated not only by carbonate content and isotopic distributions but also by decreasing degrees of biodegradation of the bitumens with depth in a number of cores (Fig. 5).

High calcium carbonate levels are also observed in the upper portions of the cores containing biogenic hydrate. As evidenced by the gas chromatographic determined concentrations (Table 6 and Fig. 5), even the cores containing biogenic hydrate have significant levels of presumably upward migrated oil. However, this oil is not as extensively biodegraded as in material of the thermogenic cores and probably did not produce significant amounts of *in situ* CO_2 from oil degradation. One explanation for the production of excess CO_2 for carbonate precipitation in the cores

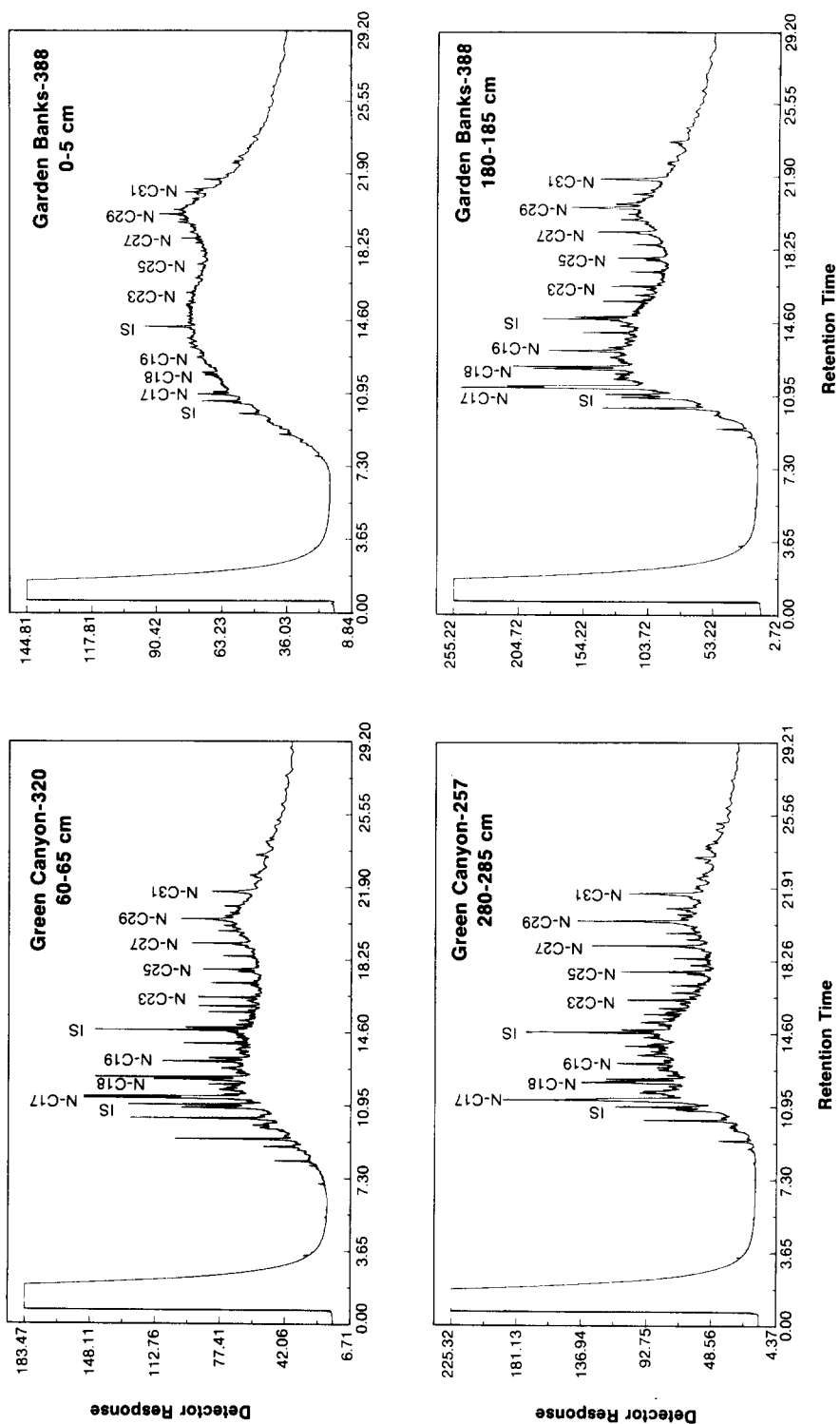


Fig. 5. Gas chromatograms (FID) of sediment extracts from the shallow biogenic hydrated cores.

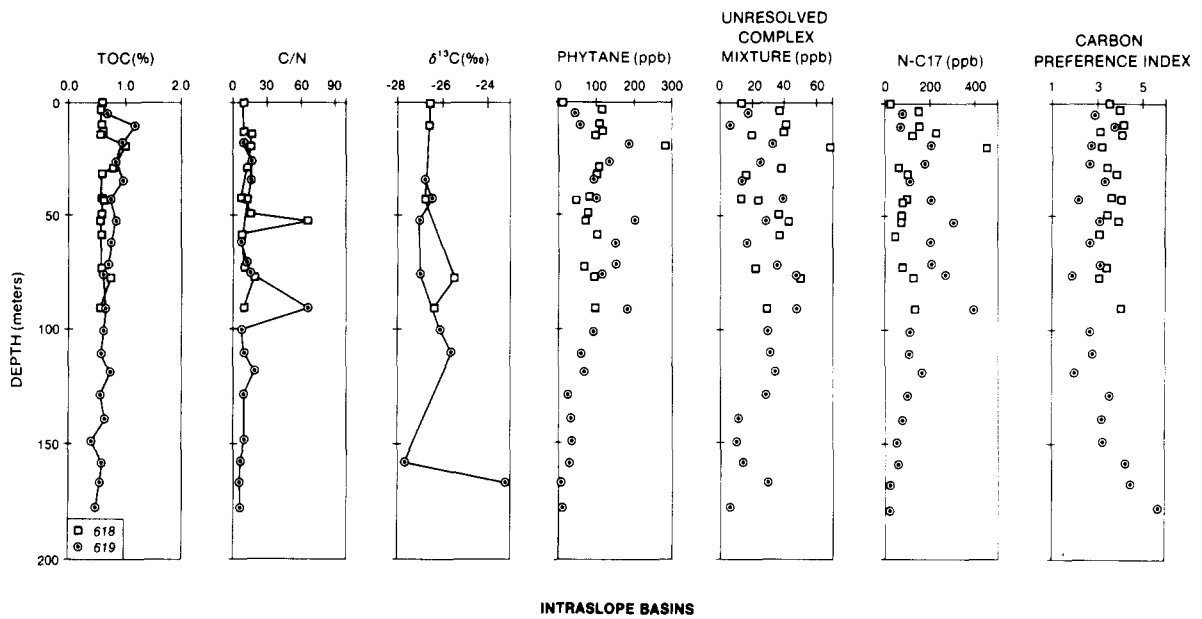


Fig. 6. Vertical distributions of selected parameters from the Orca (Site 618) and Pigmy (Site 619) Basins.

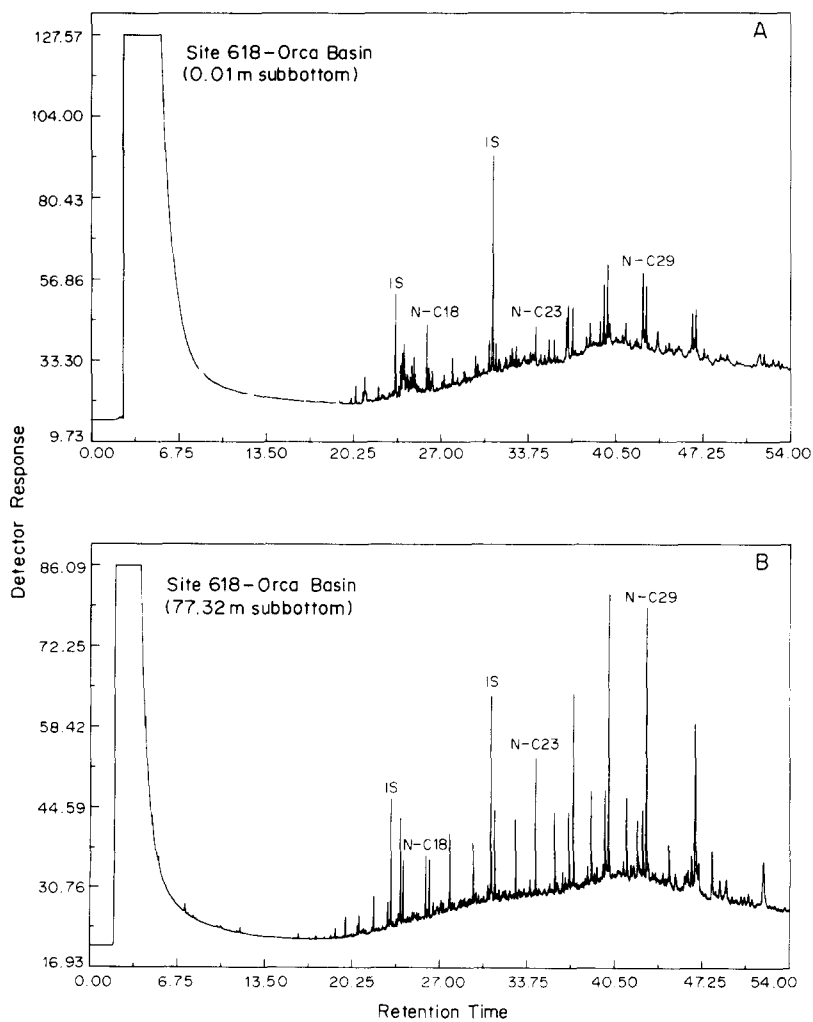


Fig. 7. Gas chromatograms (FID) of sediment extracts from the Orca Basin (DSDP Leg 96, Site 618).

Postulated Evolution of Hydrate Deposits

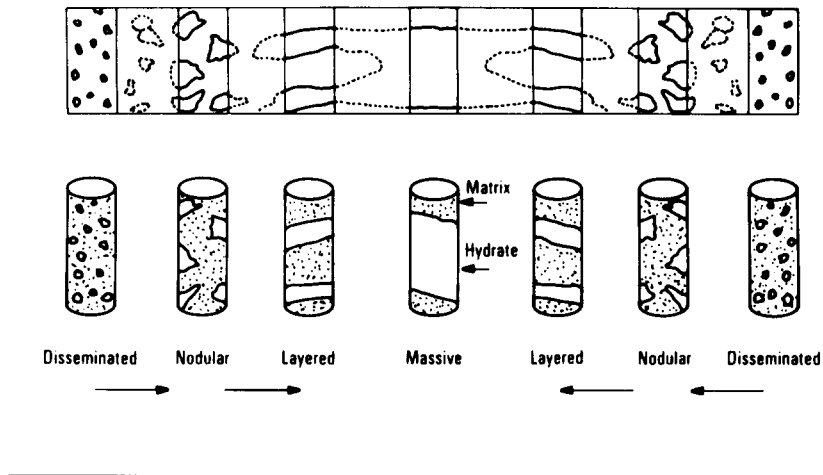


Fig. 8. Postulated evolution of hydrate deposits (after R. Malone, Morgantown Energy Technology Center, U.S. Dept. of Energy, 1984).

containing biogenic hydrates is bacterial oxidation of upward migrating or locally produced biogenic methane. The isotopically lighter carbonate in the biogenic as compared to the thermogenic hydrated cores suggests that methane is being oxidized.

The effects of authigenic carbonate precipitation on the formation of the gas hydrates is unclear. Core sections containing hydrates are not exclusively associated with high carbonate containing sections indicating that hydrate formation is not completely dependent on the coarse grained sediments associated with authigenic carbonate precipitation. There appears to be a very complicated carbon cycle in the hydrate cores. There may be an exchange or fractionation process that produces heavy CO_2 in the hydrate lattice in an environment in which there is isotopically light CO_2 and calcium carbonate from the bacterial breakdown of oil and/or gas. Alternatively, there may be early formation of light CO_2 that is incorporated into the authigenic carbonate followed by sequential late formation of heavier CO_2 that is incorporated into the gas hydrate lattice.

The thermogenic hydrates that exist at the 500–600 m depth on the slope are probably relatively near-surface phenomenon. The bottom water at these depths is in the 6–8°C range which is outside of the stability zone for pure methane hydrate. The large amounts of higher hydrocarbons and CO_2 no doubt act to stabilize the hydrate. However, these effects are somewhat offset by the elevated salinities in the pore waters from at least the GC-184 core (Brooks *et al.*, 1984). Since the shallow hydrates obtained in this study are near their stability limits, they cannot exist very deep into the sediment column because of the

increasing temperature with depth. However, the hydrated cores obtained at deeper depths could represent only the surface expression of hydrates that exist throughout a fairly extensive sedimentary column. This is especially true if the gas from near-surface formations results from the upward migration from deeper horizons as it does of necessity for thermogenic hydrates. The molecular analysis of the gas hydrates indicates that the biogenic hydrates were composed of predominantly Structure I hydrate while the thermogenic hydrates were composed of predominantly Structure II hydrate.

The classification of the nature of the gas hydrates into biogenic and thermogenic is based on the molecular and isotopic compositions of the gas released upon decomposition. Bernard *et al.* (1977) have shown that gases with $\delta^{13}\text{C}-\text{C}_1$ values $< -60\text{‰}$ and $\text{C}_1/(\text{C}_2 + \text{C}_3)$ ratios > 1000 are diagnostic of gas from a microbial origin and that a $\delta^{13}\text{C}-\text{C}_1$ greater than -50‰ and a $\text{C}_1/(\text{C}_2 + \text{C}_3)$ ratio < 50 are indicative of a thermogenic origin. Although there are diagenetic, bacterial utilization and mixing effects that can obscure these ranges, the gas from these hydrates fall clearly into the ranges for gases of these discrete origins. There is considerable evidence that there is no isotopic fractionation on the formation/decomposition of hydrates (Brooks *et al.*, 1983; Pflaum *et al.*, 1986) that would effect these classifications. The petrogenic nature of four of the gas hydrates is indicated by the (1) presence of oil in the cores, (2) very low $\text{C}_1/(\text{C}_2 + \text{C}_3)$ ratios and (3) heavy carbon isotopic ratios. The biogenic hydrates have molecular and isotopic compositions indicative of biogenic gas. However, these hydrates may have

Table 6. Concentrations of hydrocarbons in hydrated cores

File	Area	Depth (cm)	Unresolved complex mixture			Sum of normal alkanes		
			UCM		Total UCM (ppm)	< n-C ₂₃ (ppm)	> n-C ₂₃ (ppm)	Total (ppm)
			< C ₂₃ (ppm)	> C ₂₃ (ppm)				
RL3130	GC 204	0-5	54	147	201	0.85	1.28	2.12
RL3131	GC 204	100-105	5688	4988	10656	5.49	196.30	201.79
RL3132	GC 204	160-165	1735	6514	8249	7.20	9.74	16.94
RL3133	GC 204	240-245	940	3992	4932	1.93	3.54	5.48
RL3134	GC 204	260-265	864	3816	4680	5.77	19.64	25.40
RL3135	GC 204	320-325	455	2070	2525	5.58	9.93	15.51
RL3136	GC 204	380-385	269	826	1095	2.53	4.18	6.71
RL3137	GC 204	420-425	223	532	755	4.40	2.75	7.14
		Avg.	1276	2861	4137	4.22	30.92	35.14
RL3138	GC 234	0-5	404	4446	4850	1.54	15.23	16.77
RL3139	GC 234	20-25	459	3848	4307	1.12	6.40	7.52
RL3140	GC 234	30-35	313	2811	3124	0.87	14.49	15.76
RL3141	GC 234	40-45	493	4746	5239	1.02	15.97	16.99
		Avg.	417	3963	4380	1.14	13.12	14.26
RL3142	GC 257	0-5	19	20	39	0.26	0.47	0.73
RL3143	GC 257	80-85	27	25	52	0.78	0.80	1.58
RL3144	GC 257	120-125	40	59	99	0.81	1.17	1.98
RL3145	GC 257	180-185	59	35	94	0.79	1.49	2.29
RL3146	GC 257	240-245	27	38	65	1.12	1.93	3.05
RL3147	GC 257	280-285	24	31	55	1.26	1.81	3.06
RL3148	GC 257	320-325	21	27	48	0.71	1.07	1.77
RL3149	GC 257	380-385	22	27	49	0.70	1.78	2.48
		Avg.	30	33	63	0.80	1.31	2.12
RL3150	GB 388	0-5	118	406	524	0.95	2.12	3.07
RL3151	GB 388	80-85	149	182	331	0.31	0.79	1.09
RL3152	GB 388	120-125	82	86	168	0.19	0.39	0.59
RL3153	GB 388	180-185	49	77	126	1.65	1.81	3.46
RL3154	GB 388	240-245	53	90	143	1.25	1.02	2.26
RL3155	GB 388	280-285	43	74	117	0.71	0.76	1.47
RL3156	GB 388	320-325	39	48	87	0.72	0.58	1.30
RL3157	GB 388	380-385	56	62	118	2.13	0.95	3.08
		Avg.	74	128	202	0.99	1.05	2.04
RL3158	Miss Can.	0-5	15	35	50	0.27	0.49	0.76
RL3159	Miss Can.	80-85	48	48	96	1.25	1.34	2.59
RL3160	Miss Can.	120-125	52	66	118	3.03	3.47	6.50
RL3161	Miss Can.	180-185	42	85	127	0.56	1.81	2.37
RL3162	Miss Can.	220-225	24	60	84	0.39	2.02	2.40
RL3163	Miss Can.	280-285	39	68	107	1.25	2.50	3.75
RL3164	Miss Can.	320-325	25	62	87	0.87	2.58	3.45
RL3165	Miss Can.	360-365	40	85	125	1.56	3.28	4.84
		Avg.	36	64	99	1.15	2.19	3.33
RL3166	GC 320	0-5	32	22	54	0.34	0.36	0.70
RL3167	GC 320	60-65	28	45	73	1.35	1.07	2.42
RL3168	GC 320	120-125	14	13	27	0.60	0.55	1.16
RL3169	GC 320	160-165	23	24	47	0.67	0.72	1.38
RL3170	GC 320	220-225	36	33	69	1.46	1.17	2.63
RL3171	GC 320	260-265	32	184	216	1.27	4.43	5.70
RL3172	GC 320	280-285	30	21	51	1.07	0.63	1.71
RL3173	GC 320	300-305	16	15	31	0.69	0.76	1.45
		Avg.	26	45	71	0.93	1.21	2.14

small thermogenic components based on the presence of thermogenic high-molecular-weight hydrocarbons in the bitumens.

There appears to be upward migration of oil in all eight of the cores containing hydrate. The cores containing thermogenic hydrates have 2-3 orders of magnitude higher levels of upward migrated thermogenic hydrocarbons than observed for those containing biogenic hydrates. However, even the biogenic hydrated cores have elevated hydrocarbon levels compared to many slope sediments (Kennicutt *et al.*, 1986). The high bitumen levels in the GC thermogenic cores can be generically related to oil reservoirs in the subsurface by GC-FID, GC-FPD,

GC-MS and stable isotopic measurements. The correlation of surface bitumens with subsurface oils will be addressed in another report.

The existence of gas hydrates at 20 to 40 m sub-bottom depths in Orca Basin is probably related to the hypersaline salinity gradient that exists within the basin. Salinity distributions decrease from *c.* 220 ppt at the seawater/sediment interface to *c.* 50 ppt at the 50 m subbottom depth level. It is possible that the high interstitial salinities in the upper 50 m of the subbottom either destabilize the methane hydrate or lower methanogenesis rates.

The importance of oil and gas seepage associated with gas hydrates in the Gulf of Mexico are

significant for several reasons. First, the gas hydrates and oil stained cores can have significant effects on the benthic ecology in the areas where they are recovered. Kennicutt *et al.* (1985) have recently shown that at least two of the Green Canyon hydrate areas contain chemosynthetic marine ecosystems that are probably fueled by H_2S . Second, gas hydrates can have significant influences upon marine geotechnical properties that are largely unknown. It is possible that the formation and/or decomposition of hydrates can act to destabilize sediments resulting in slumps, mass sediment movements, and the loss of bearing capacity. Third, the large amounts of oil associated with the gas hydrates have significant ramifications to offshore environmental baseline studies on the continental slope. Fourth, the formation of hydrates has significant effects on diagenetic processes occurring in the sediments. There is a very complex organic and inorganic carbon cycle driven by oil and gas seepage in at least the thermogenic gas hydrated areas. There is precipitation of isotopically light carbonate from CO_2 supersaturation in the pore waters, accompanied by isotopically heavy CO_2 within the gas hydrate lattice. The biodegradation of the upward migrating oil and gas accompanied by formation and decomposition of the hydrates in the sediment column most surely produces unique diagenetic pathways, products and rates in these areas. Fifth, hydrates could possibly represent a future energy resource with their large gas:fluid ratios.

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