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The Nature of Gas Hydrates on the Nigerian Continental Slope

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Abstract

*Gas hydrates have been collected in 6-meter piston cores during surface geochemical exploration (SGE) surveys in the deep and ultra deepwaters of Nigeria in 1991, 1996, and 1998. To date, gas hydrates have been collected in ~*21 *cores out of the >800 core collections on the Nigerian margin. This represents a 2.5% recovery ratio of gas hydrated cores on this margin at sites that are potential conduits for the upward migration of hydrocarbons (i.e., core locations are sited based on 2-D and 3-D seismic over faults, mounds, acoustic wipe-outs, etc.). Unlike the northern Gulf of Mexico where the authors have retrieved a significant percentage of thermogenic hydrates in piston cores, all the gas hydrate collections offshore Nigeria to date have been primarily biogenic in nature (methane >99% of the hydrocarbon gases;* **d** ^{13C} *generally light, -60 to –117* $^{0}/_{00}$*). A few of these gas hydrated sites do contain a mixed thermogenic gas component (ethane to butane gases up to a few hundred ppm of total hydrocarbon gas), but even at these sites the primary gas in the hydrates is methane.*

There is migration of liquid hydrocarbons to shallow sediments that is common on the Nigerian continental margin. For example, a SGE coring survey on the Nigerian ultra deep water continental margin in 1996 collected 10 cores out of 130 with visible liquid hydrocarbons within portions of the 4.0 to 5.0 meters of sediment generally retrieved by the piston cores. However, in many cases there is little gas associated with these sites and the collection of gas hydrated cores is generally independent of the macroseepage of liquid hydrocarbon core sites. Bottom Simulating Reflectors (BSRs) are often associated with the marcoseepage core sites in Nigeria. BSRs are common *on the seismic records of the Nigerian continental slope. The subbottom depth of the BSRs range between ~200 to ~500 meters and are often associated with various geological structures such as faults. When gas hydrates are collected in cores they often consist of disseminated nodules of a few centimeters in diameter within the mud matrix a few meters subbottom or are massive (5 to 10+ cm thick) and come up as the bottom of the core. The depth of the BSRs are generally similar or at shallow depths than the calculated base of the methane hydrate stability zone using known bottom water temperatures and thermal gradients for the region. The average heat flow for the Nigerian continental margin is 58.2 mW/m*^{2} *with a range from 18.8 to 123 m/Wm*^{2}.

Introduction

Although gas hydrates have been known to exist in upper continental shelf sediments for many years (1,2), they have not been commonly collected. The global distribution of gas hydrates has been deduced primarily from bottom simulating reflectors (BSRs) and the occasional collection, generally hundreds of meters deep in the subsurface in deep-sea drilling (i.e., DSDP and ODP) cores. Brooks and co-workers (3-8) have documented the occurrence of gas hydrates in shallow subsurface marine sediments overlying several of the hydrocarbon generative basins throughout the world (i.e., Gulf of Mexico, northern California and offshore Nigeria). The gas hydrates have generally been collected from the upper 5 meters of piston cores taken in water depths greater than 400 m. These gas hydrates occur in close proximity to faults and other conduits for gas migration. In the Gulf of Mexico, biogenic and thermogenic hydrates have been observed from submersibles to outcrop at the seafloor (7, 9). The observations of gas hydrates at the seafloor in water depths near their upper stability zone suggests that slight changes in bottom water temperature or pressure could cause the hydrates to disassociate and thereby dramatically increase the release of gas to the ocean surface. It is not clear to what degree shallow hydrates act as barriers to the seepage of gas from the seafloor because bubbling gas seeps are common in areas containing extensive shallow hydrates (5, 10).

Nigerian Margin Geological Setting

The Niger Delta occupies the central region of West Africa's Gulf of Guinea. With a land area of some 75,000 km^2 it forms the largest delta system in Africa (11). The delta owes its size to the focus provided by the Benue arm of the Niger Triple Junction for sediment delivery from interior Africa to the Atlantic Ocean. The modern delta began its growth in the late Eocene (12, 13). Since that time the delta top, as defined by the 200 meter isobath, has prograded south and south-westwards from the Cretaceous shelf-edge hinge line some 300 km across previously deepwater settings. The distal edge of the delta lies some 80 to 170 km further seawards. The continental slope forms the intermediate region and has been the focus of SGE cores containing the hydrates reported here.

The Eocene and younger delta succession is divided into three younger units moving seaward. These are, from the bottom upwards, the Akata Formation, the Agbada Formation and the Benin Formation (13). The Akata Formation comprises deep marine shales and, as was predicted more than twenty-five years ago, deepwater sands (12). Shelf to paralic sediments define the Agbada Formation and the uppermost unit, the Benin Formation, consists of primarily non-marine, delta top sands and clays. Delta top loading has been sufficient to mobilize the Akata Formation clays and the entire 10-12 km succession is being actively displaced oceanwards. The result is a generally clearly defined frontal toe thrust (14) behind which are stacked clay cored diapir belts associated with the lateral translation of the delta slope towards the ocean. Doust and Omatsola (13) and more recently by Cohen and McClay (15) provide a comprehensive account of the history of development of the delta in terms of depobelts.

The modern anatomy of the delta is summarized on Fig. 1. Superimposed are the oil producing region and some of the most significant of the deepwater discoveries. Our own work based on piston-core recovered oils collected in 1996 and 1998, together with comparisons with offshore and nearshore produced oils, indicates that the predominant offshore source, at least to present exploration limits, is a mid-Tertiary or younger marine claystone with strong deltaic influences (although Cretaceous-sourced seeps are present locally). These oils and seeps group to form GeoMark's Tertiary Deltaic Oil Family (16) regarded as derived from the Akata Formation. The mixed Type II/III source rocks which would supply these oils and the accompanying gases have been described from the Akata Formation to the west of Bioko Island in Equatorial Guinea (17). Mixed oil and gas prone kerogens are also described from the Bonga discovery in OPL 212 and the Ngolo-1 well in OPL 219 (18). Little is known concerning the younger Cretaceous and older Tertiary source rocks, although their presence is suspected beneath the slope given that source rocks of this age are developed. Considering the prevalence of mature oil seepage to shallow sediments and the large oil/gas discoveries occurring along the continental margin, there are multiple possible sources of gas to the hydrate stability zone.

Sea Floor Gas Hydrate Collections

The initial hydrate discoveries in the Gulf of Mexico, offshore West Africa, northern California and elsewhere have resulted from piston cores acquired for the purpose of geochemical exploration. SGE studies are used to define the aerial distribution of oil, condensate and gas seepage on the continental margin. These studies high grade areas and prospects by defining areas of active oil migration and charge through gas and high molecular weight hydrocarbon analysis methods. This active migration acts to charge accompanying reservoirs in the same geological system. From many such studies, especially in Tertiary delta systems in west Africa, the Gulf of Mexico and elsewhere, we know that there is considerable macroseepage of 'live' oil and gas into seafloor sediments throughout broad regions from the shelf/slope break extending to the ultra deep waters (>1,500 m).

Core locations for SGE studies are chosen from both 2-D and 3-D seismic data where there are possibly deep conduits (i.e., faults and fractures) for the upward migration of hydrocarbons. The optimum targets are deep cutting faults that link the source succession to the seabed. These are best developed where there is ongoing tectonism, for example in clay diapir or salt tectonic provinces. However, even in tectonically quiet regions breaks are usually present, especially where the section is thick and/or where there has been differential movement and reactivation across basement features such the Benue and Charcot Fracture Zones in Nigeria. The ideal faults are those associated with: (1) amplitude anomalies ("flags") and/or BSRs, (2) seabed constructional features such as carbonate accumulations and mud-gas mounds, (3) gas vent pits, and (4) gas chimneys. Thus, the sites chosen for SGE studies are very focused to optimise the chance for retrieving upward migrated gaseous and liquid hydrocarbons.

Cores are acquired with a 900 kg piston corer with collapsible piston, 6-meter of pipe and core liner. All cores are positioned with differential GPS positioning to a precision of ±5 meters, generally within ±30 meters of preselected locations. Often either precision bathymetric or subbottom (3.5 kHz or Chirp sonar) profiling is used to further refine core positions in the field. Seismic data acquired by Mabon Limited was used for both the 1996 and 1998 Nigerian programs discussed below. Core site selection is enhanced where 3-D seismic and/or swath bathymetry are available.

Gas hydrates are recognized visually in many of the cores upon retrieval on deck as most often white ice-like nodules or lenses in the core. They are also inferred by large gas expansion pockets in some cores upon retrieval on the ship's deck. If large gas nodules are present, the hydrate is sometimes placed in a 23-cc Parr bomb to collect the hydrate decomposition gas into a high pressure cylinder (8). In our SGE studies, all the cores are sampled at three depths in the bottom half of the core for headspace gas. Headspace gas analysis refers to the determination of interstitial light hydrocarbon gases (C_1-C_5). The light hydrocarbon gases are not very soluble in water, so they can be extracted from a sediment by a gas/water partitioning procedure (19).

Geographic Distribution

The Gulf of Mexico has been the most geographically prolific area for collection of gas hydrates in near surface sediments. Gas hydrates were first collected in shallow cores in the Gulf of Mexico in 1984 during surface geochemical exploration programs conducted by the author (4). The Gulf of Mexico remains one of the few documented site of predominantly thermogenic gas hydrate collections in shallow cores. There have been numerous gas hydrate collections in the Gulf of Mexico (3-9). Table 1 documents the sites where the authors have collected cores for SGE programs and the estimated number of gas-hydrated cores obtained. The table shows that there is more than double the chance in water depths >500 meters of obtaining a gas-hydrated core in the Central/Eastern Gulf compared to Nigeria (6.6% vs. 2.5%). Although this is no doubt geologically controlled, it may also be skewed in that more sites in the Gulf were targeted based on 3-D seismic data whereas most of the sites elsewhere (i.e., West Africa and offshore California) were target based on 2-D seismic data. Clearly, targeting core locations based on 3-D seismic data increases ones ability to select the best locations for hitting upward migrated hydrocarbons in shallow sediments using deep fault extensions into shallow sediments along with amplitude anomalies and edge maps.

Brooks et al. (5) noted that collections of shallow gas hydrates in the Gulf ranged in water depths from 439 to 1360 meters, although Anderson et al. (20) have shown that thermogenic gas hydrates could exist in water depths as shallow as 220 meters. Table 2 lists locations of some additional hydrate sites in the Gulf of Mexico to water depths of 2,324 meters. In the Gulf, most thermogenic hydrates have been recovered in the 400 to 800 meter depth range, while biogenic hydrates predominate at greater water depths. Table 2 shows the carbon isotopic content of recent hydrates collections in the Gulf of Mexico in depths >1,000 meters to be biogenic in nature. The gas hydrates recovered at seven sites between water depths of 510 and 642 m offshore northern California in the Eel River Basin (Table 1) also were predominantly biogenic gas (6).

Tables 1 and 3 indicated that 21 gas hydrated cores have been acquired in three surveys consisting of >800 cores in water depths >500 meters offshore Nigeria. Fig. 2 shows the locations of the Nigerian gas hydrate collections. The sites ranged in water depths from 440 to 1,528 meters. While most of the cores had small, dispersed, gas hydrates either throughout the core or in the bottom of the cores, several cores bottomed into a massive hydrate 10 to 15 cm in thickness that came up plugging the end of the core. All Nigerian gas hydrates were white, contained mostly methane, and were found predominately in clay-rich sediment. All the hydrated cores contained hydrogen sulifde gas indicating anoxic conditions. Since most sediments on the slope are not anoxic in the top 3-4 meters subbottom, the presence of H_2S in the hydrated cores indicates active bacterial sulfate reduction has occurred possibly using the gaseous hydrocarbons as the subtrate.

An interesting feature is the often noted shallow seafloor depression at gas-hydrated core sites. Fig. 3 shows a Chirp subbottom record across a gas hydrated site in over 1,300 meters of water. The core site was chosen because the 2-D seismic indicated a fault at this location possibly reaching the seafloor. The subbottom profile indicated by the turbid nature of the seismic record that the surficial sediments at this location are gassy. The core was retrieved slightly upslope of an active fault.

Hydrate Origin and Gas on the Nigerian Margin

The nature of the hydrate gas offshore Nigeria can be inferred from the examination of headspace gases obtained from the shallow piston cores. Table 4 shows the headspace gas concentration in the cores containing the gas hydrates. Unless noted otherwise, the values are the average of three measurements in the bottom half of each core. The $C_1/(C_2+C_3)$ ratios indicate that the molecular compositions are mostly biogenic gas (22), although small thermogenic components might be present at locations with $C_1/(C_2+C_3)$ ratios less than 1,000. With one exception, methane makes up greater than 99% of the hydrocarbon gases. This is consistent with other headspace gas carbon isotopic ratios from high gas containing cans from these same Nigerian SGE surveys (Table 5). Table 5 lists the carbon isotope values reported as $\delta^{13}C_{PDB}$ ($^o/_{oo}$) measured in alkane gases of concentration greater than 500 ppmV in the headspace of the selected cans from the 1998 program. The data in Table 5 with values more negative (lighter) than -100 $^o/_{oo}$ represent cores that contain only biogenic gas. Whereas thermogenic gas is typically represented by $\delta^{13}C_{PDB}$ of methane from -40 to -50 $^o/_{oo}$, values between -50 to -85 $^o/_{oo}$ are routinely observed in sediment gases with higher-than-biogenic levels of C_{2+} alkane gases. We interpret these sites as having some component of thermogenic gas mixed with predominately biogenic gas. This small component of thermogenic gas does not change the basic biogenic nature of the gas hydrated cores.

The distribution of the alkane gases obtained from ~230 cores taken in the ultra deep water (generally >1,500 meters water depth) is shown in Fig. 4. The figure illustrates that 92% of the samples contain sediment light hydrocarbon alkane gases totalling less than 100 ppmV. Concentrations ranging from 1 to 100 ppmV total alkane gases in these marine sediments are considered background, with the predominant hydrocarbon gas being methane in all samples. Fig. 4 shows that of the remaining 8% (55 total) “above-background” samples, 36 contain alkane gases totaling 100 to 1,000 ppmV and 19 more contain alkane gases totaling more than 1,000 ppmV. Light hydrocarbon concentrations greater than 100 ppmV may be indicating upward migrating thermogenic gas.

Fig. 5 shows the occurrence of the non-methane (C_{2+}) alkane gases in the sediment samples. The figure illustrates that 93% of the samples contain C_{2+} alkane gases totaling less than 2 ppmV. The remaining 45 samples contain C_{2+} alkane gases totaling 2 ppmV or more. Concentrations ranging from 0.02 to 2 ppmV C_{2+} alkane are considered background for marine sediments in this area. The natural presence of high levels of C_{2+} alkane gases serves as a good indicator of migrating thermally-sourced gas, because C_2-C_5 alkanes are not microbially produced at these levels in marine sediments. However, the absence of high levels of the C_{2+} alkane gases does not necessarily mean that thermogenically-sourced gas is not present.

Fig. 6. illustrates the range of concentrations of light hydrocarbon alkane gases in the sediments from both the 1996 and 1998 Nigerian studies by comparing the values of the non-methane (C_{2+}) component of the alkane gases to the values of the total alkane gases for each core section. Typical background levels of total-alkane-gases range from about 1 to 100 ppmV, whereas typical concentrations of C_{2+} hydrocarbons range from about 0.02 to 2 ppmV. Because we are reporting gas data by volume rather than by mass, the 1%, 20%, and 100% lines represent percent-by-volume boundaries. Volumes of gases are proportional to their mole quantities; therefore, these lines also represent mole fractions of 1%, 20%, and 100%. Note that a value of 100% means that essentially all of the gas is C_{2+}, with insignificant fractions of methane. Mole fractions of the C_{2+} alkane gases from 1% to 20% in a produced or

seeping natural gas would be indicative of a thermogenic "wet gas" origin for the gas, but in marine sediments the normal background levels of ethane and propane are typically high enough with respect to the background methane to produce these percentages. Such mole fractions, without further indicators, are not extraordinary. However, when the non-methane alkane fraction falls in this range *and* the methane concentration is high compared to background, then the sample deserves further consideration as having a thermogenic component.

Figs. 7 and 8 show the distribution of C_{2+} alkanes greater than 100 ppmV and the presence of hydrogen sulfide in the core bottom relative to the BSRs mapped by Cunningham et al. (21). Most of the high gas containing cores are outside of the areas of mapped BSRs possibly indicating that the hydrate could form a partial barrier to the upward migration of gas. However, an examination of the seismic data at sites were macroseepage of liquid hydrocarbons exist in the ultra deep water (Fig. 9) show that BSRs are generally present. Thus, we do not believe that the BSRs are acting as a significant barrier for the upward migration of liquid and therefore gaseous hydrocarbons along deep cutting faults on the slope. No gas hydrated cores (Table 3) contained visible liquid hydrocarbons, although several contained significant amounts of liquid hydrocarbon microseepage (i.e., liquid hydrocarbons only detected analytically). In general, the presence of gas hydrated cores on the Nigerian margin is decoupled from the seepage of liquid hydrocarbons to the seafloor which is consistent with the biogenic nature of the gas hydrates. The presence of reducing conditions in the cores as indicated by the presence of hydrogen sulfide in the bottoms of the cores did not show any coupling with the presence of the BSRs (Fig. 8).

Bottom Simulating Reflectors

Fig. 9 shows an example of a BSR over a macroseepage core site offshore Nigeria. Cunningham et al. (21) have mapped the BSRs using 2-D regional seismic data offshore West Africa and reported that BSRs are extensive on the continental margin off the Niger and Congo River Delta, but absent elsewhere in the Nigerian to Angolan corridor of west Africa. This corresponds to the collection of gas hydrates reported here offshore Nigeria in shallow cores but the complete lack of any shallow gas hydrate collections offshore Angola in >1,300 cores collected using the same techniques and core settings as used in Nigeria (Table 3). Cunningham et al. (21) reports that the cumulative surface area of BSR areas offshore Nigeria and Congo are 11,000 and 4,000 km^2, respectively. Fig. 2 shows the sites of gas hydrate core collections offshore Nigeria and the correspondence with the BSRs reported by Cunningham et al. (21). An amazing observations is that most of the seafloor collections of gas hydrates are shoreward of the major BSR trends, despite the fact that many cores were obtained over faults in the BSR regions.

In Nigeria, the BSRs are generally associated with complex structural types that are contractional in origin (i.e., imbricated and fault-related folds) in water depths greater than 1,200 meters (10, 21). Hovland et al. (10) reports from his studies in the OPL-213/215 area that the BSRs cover 8.5% of the study area and tend to follow the up dipping strata formed by the anticlinal compressional ramp structures, where the mud volcanoes tend to form at the summit of these ramps. Our examination of the BSRs along the Nigerian margin generally correspond to those areas identified by Cunningham et al. (21) and Hovland et al. (10). The BSRs are common along the distal portions of the prodelta where large thrust faults create bathymetric highs adjacent to the flat Atlantic seafloor. Fig. 10 illustrates the relationship of an extensive BSR to a large thrust fault. The BSR occurs at approximately 500 meters below the seafloor and the water depth is 2400 meters. There is little blanking above the BSR at this location. Fig. 11 is a 2-D seismic profile that illustrates the nature of occurrence of an extensive BSR in water depths of 1350 meters. The BSR is 300 milliseconds two-way travel-time below the seafloor, which is approximately 270 meters at a sediment velocity of 1800 m/sec. The BSR is above and on the flanks of a diapiric structure. There is extensive blanking above and below the BSR. Fig. 12 illustrates the development of a well-defined BSR in water depths of 1800 meters and 175 milliseconds twtt below the seafloor. The BSR extends below a seafloor depression and there is extensive blanking above the BSR.

The water depth and the depth below the seafloor of BSR’s in the offshore portions of Nigeria determined from an extensive 2-D regional seismic survey is presented in Fig. 13. The equation for the line of best fit was determined to be:

$$\text{Water Depth (sec twtt)} = 0.2647 + 5.6593\ \text{BSR Depth Below Seafloor (sec twtt)}$$

This equation has an R^2 value of 0.76. The BSRs depths graphed in Fig. 13 are at similar geographic locations to those presented by Cummingham et al. (21) and shown in Fig. 2.

Hovland et al. (10) concluded that the mean maximum amount of gas hydrates and free gas residing in sediments above and below the Nigerian BSRs is 1-3% and 1-5% by volume, respectively. They argue that BSRs and natural gas hydrates form at locations where there is a relatively high flux of methane to shallow sediments from fluid migration and the Nigerian margin is an area of active fluid flux. Our studies support these arguments since:

- Most of the sites of known liquid oil macroseepage to the surface are associated with BSRs thus these sites must have vertical fluid migration occurring or having occurred in the recent past;
- All our gas hydrate-containing sites were over conduits (i.e., faults, mud mounds, and depressions) for the upward migration of fluids and hydrocarbons; and
- Gas hydrates as well as macroseepage of oil and gas are common on the Nigerian margin.

There is the general assumption (21) that the deeper BSRs in the complex structural zones are fed by upward migrating thermal gas from the active petroleum systems that exists on the Nigerian continental margin. While to some extent intuitively this must be true considering the extent and amount of thermogenic liquid hydrocarbons in seafloor sediments over faults as well as the presence of active petroleum systems, the actual collections indicate that most of the gas forming the shallow hydrates are predominately biogenic methane. Our analyses indicate that while some thermogenic gas components are sometimes present, the thermal gas is a minor component. A few of the hydrate sites actually have significant levels of thermogenic liquid hydrocarbon microseepage but even these sites are still predominately methane (>99%) with light isotopes (δ^{13}C –50's to –70's $^{0}/_{00}$). Cunningham et al. (21) reports that one of the gas hydrated sites had a δ^{13}C of –54 $^{0}/_{00}$ indicating a considerable thermogenic component even though it was >99% methane. Our conclusion is that while there are thermogenic gas components in some of the hydrates as evidence by the presence of small amounts of C_{2+} gases and carbon isotopes of methane in the –50's to –70's $^{o}/_{oo}$ range, the hydrate gas is predominately being supplied by biogenic process presumably in the shallow (upper few hundred meters) subsurface.

Regional Heat Flow and Geothermal Gradient on the Nigerian Margin

Regional heat flow measurements were conducted on the continental margin offshore Nigeria in June 1998 (Fig. 14) for the primary purpose of determining basal heat flow for thermal maturation studies of the petroleum systems. Heat flow measurements were acquired at 112 sites in water depths between 500 and 3,400 meters using the Dalhousie Heat Flow probe from Dalhousie University, which measures the geothermal gradient at 8 depths in the first 5 meters of sediment and the *in situ* thermal conductivity at the corresponding intervals. Details of the instrument and measurements can be found in Hutchison and Owen (23). Sites were chosen away from conduits for fluid migration (i.e., faults) and in quiescent zones to best reflect the regional heat flow of the area. Heat flow in the study area ranged from 18.8 to 123.7 mW/m^2, with an average of 58.2 mW/m^2. Fig. 14 is a bar chart of the distribution of heat flows for the 112 sites. The chart shows a great predominance of heat flows between 40 and 70 mW/m^2. Fig. 16 shows the bottom water temperature at each site as a function of water depth as well as the dissolution boundary for methane hydrates from literature values (24, 25) as a function of water depth. This figure illustrates that the sediment surface at every site except the most shallow one (500 m) is at a temperature and pressure regime within the stability zone for methane hydrates. The thickness and the bottom of the hydrate stability zone for each of these sites thus depends on the temperature/pressure regime within the sediment.

The bottom of the stability zone can be predicted (to a first order) if the composition of the hydrate, bottom water temperature, water depth, and geothermal gradient are known. Fig. 17 shows the geothermal gradient (in milliKelvins per meter) vs. the water depth measured at each of the 112 heat flow sites. The figure illustrates that there is no distinct trend of geothermal gradient with increasing water depth at the stations measured. Because of this, an average thermal gradient cannot be assumed for predictions of the bottom of the hydrate stability zone in the region. However, we have measured the bottom water temperature, the geothermal gradient, and the water depth at each heat flow site, as well as the composition of gas in hydrates recovered at a few sites. Based on these measurements, the predicted bottom of the methane hydrate stability zone can be calculated for each site.

Fig. 18 shows the calculated bottom of the methane hydrate stability zone vs. water depth for each site. The figure also shows the calculated zone-bottom if the average geothermal gradient measured for the region is used. The plotted values generally follow the trend shown by the average gradient, but deviations from this trend line illustrate the effect of higher or lower than average heat flows at the various sites.

Fig. 19 plots the same data as Fig. 18, but it also contains the depth values measured on the seismic records that were interpreted as BSRs. The BSR depth values generally fall at somewhat deeper depths than would be predicted from the calculations of the bottom of the methane hydrate stability zone. At water depths >1,200 meters, the linear best fit BSR line is at increasing deeper depths than the similar line from the calculated base of the methane hydrate stability zone. The difference could be easily explained by the variability in heat flow for the region (i.e., the predicted based of the methane hydrate stability zone easily overlaps the observed BSR depth considering the range of measured heat flow on the slope). Other explanations for the difference include (1) the inclusion of non-methane gases that shift the hydrate stability to deeper depths; and (2) the estimate of 1,800 m/sec for the sound speed of all sediments is high. One could argue that the BSR is deeper than predicted for a base of the methane hydrate stability zone because of the inclusion of other more thermal hydrocarbons (C_2-C_5). While there is a general coincidence of the calculated gas hydrate stability zone from the thermal data and the observed depth of the BSR, we suggest it may be unreliable for the reasons noted above to use the depth of the BSR as a means of predicting regional heat flow for the region.

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Table 1. Gas hydrate recovery rates in offshore continental slope regions (>500 meters water depth) collected from SGE piston coring programs.

	# of Cores	Hydrate Cores	Percent
Northern Gulf of Mexico[a]			
Central/Eastern Gulf (1997-1999)	425	28	6.6
Western Gulf of Mexico (1997-1999)	361	8	2.2
Total Northern Gulf	786	36	4.6
West Africa			
1994 Nigerian Deep Water[b]	310	6	1.9
1996 Nigerian Deep & Ultra Deep	186	6	3.2
1998 Nigerian Deep & Ultra Deep	330	9	2.7
Total Nigeria	826	21	2.5
Gabon (1994-1998)	307	0	0.0
Congo (1997-1998)	16	0	0.0
Angolan (1994-1998)	1,330	0	0.0
Namibia (1994)	90	0	0.0
Total Non-Nigeria	1,743	0	0.0
Northern California[c]			
Eel River	74	7	9.5
Point Arena	90	0	0.0

[a] These Gulf of Mexico core numbers only represent those cores obtained by the author since 1996 and do not include several thousand additional SGE cores obtained prior to 1996.

[b] After Brooks et al. (5)

[c] After Brooks et al. (6)

Table 2. Carbon Isotope Ratios ($^{o}/_{oo}$) of Hydrate Gases from the Gulf of Mexico Collected in Parr Bomb.

Station Number	Latitude	Longitude	Water Depth (m)	Methane $\delta^{13}C$	Lease Area/ Block[a]
CGC 083A	27° 50.12’ N	88° 15.76’ W	2,324	-69.5	AT-166
CGC 077	27° 43.17’ N	88° 26.91’ W	2,140	-58.3	AT-250
CGC079	27° 43.84’ N	88° 23.32’ W	2,309	-73.1	AT-252
WGM 167	27° 05.12’ N	92° 48.99’ W	1,085	-68.5	GB-908
WGM 168A	27° 05.57’ N	92° 49.40’ W	1,067	-72.6	GB-908

[a] AT = Atwater lease area; GB = Garden Banks lease area.

Table 3. Locations of Gas Hydrates offshore Nigeria.

Sample ID	Latitude	Longitude	Water Depth (m)	Comment
N-074C3	3^{o} 33.7’ N	6^{o} 31.8’ E	677	Reference 5
N-074C4	3^{o} 33.7’ N	6^{o} 31.8’ E	675	Reference 5
N-082C3	3^{o} 31.4’ N	6^{o} 20.9’ E	770	Reference 5
N-138C2	3^{o} 57.6’ N	5^{o} 16.6’ E	560	Reference 5
N-138C3	3^{o} 57.6’ N	5^{o} 16.6’ E	560	Reference 5
N-138C6	3^{o} 57.6’ N	5^{o} 16.6’ E	563	Reference 5
PEF005	3^{o} 40.9’ N	7^{o} 25.3’ E	549	Nodules 2.0-2.6 m subbottom; largest nodule was 4-7 cm thick; H_2S present
PEF013	3^{o} 40.9’ N	7^{o} 45.9’ E	440	Present near bottom of 4.6 m core; inferred site; H2S present
PT028a	3^{o} 17.1’ N	6^{o} 01.0’ E	1,528	H_2S present
PT028b	3^{o} 17.1’ N	6^{o} 01.0’ E	1,528	White massive hydrate; H_2S present
PEX005a	5^{o} 31.5’ N	4^{o} 15.2’ E	1,176	Massive white hydrate in bottom at 2.2 m (TD), H_2S present
PEX05d2	5^{o} 31.5’ N	4^{o} 15.2’ E	1,172	Small white hydrates, H_2S present
NGC102	3^{o} 15.0’ N	6^{o} 42.4’ E	1,147	Inferred based on large gas voids; H_2S present
NGC103	3^{o} 14.1’ N	6^{o} 42.0’ E	1,185	10-cm of solid white hydrate in core catcher; H_2S present
NGC226	4^{o} 56.9’ N	4^{o} 19.2’ E	1,341	White hydrates present; in depression, H_2S present
PCO005	3^{o} 29.7’ N	6^{o} 54.8’ E	738	Hydrates throughout 0.4 m core; in depression; H_2S present
PTX004	3^{o} 28.7’ N	5^{o} 34.1’ E	1,378	Small white hydrate nodules; in small depression; H_2S present
PTX017	3^{o} 34.6’ N	5^{o} 24.6’ E	1,333	Hydrates in bottom of 2.2 m core; In abrupt depression; H_2S present
PTX026	3^{o} 28.2’ N	5^{o} 33.6’ E	1,405	Abundant hydrates; H_2S present
PAG008	4^{o} 52.2’ N	4^{o} 41.8’ E	569	Hydrate present; H_2S present
PAG013	4^{o} 48.2’ N	4^{o} 29.3’ E	971	Hydrates in 0.2 to 0.4 m subbottom; H_2S present

Table 4. Headspace Gas Concentrations in Gas Hydrated Cores on the Nigerian Continental Slope[a].

Sample ID	Methane (ppm)	Ethane (ppm)	Propane (ppm)	i-Butane (ppm)	n-Butane (ppm)	C1/ (C2+C3)
N-074C3	6,250	108	8.7	2.7	1.4	54
N-074C4	35,700	116	6.0	0.7	0.2	292
N-082C3	29,600	12	3.4	0.3	0.3	1,920
N-138C2	75,100	11	0.4	0.0	0.4	6,590
N-138C3	69,800	5.6	0.5	0.0	1.5	11,400
N-138C6	77,000	6.6	0.4	0.0	0.0	11,000
PEF005	37,600	17.2	1.2	0.3	0.2	1,990
PEF013	36,000	94.3	23.8	1.5	0.3	300
PT028a	16,400	5.2	0.9	0.7	0.5	2,250
PT028b	27,100	10.2	4.5	l.7	1.0	1,560
PEX005a [b]	5,470	41.6	4.4	0.9	0.2	116
NCG102 [b]	44,500	23.3	1.6	0.4	0.5	1,720
NGC103	106,000	79.1	2.1	0.9	0.4	1,280
NGC226 [b]	81,500	13.6	3.6	0.9	0.4	4,440
PCO005	423,000	101	3.1	2.1	2.1	3,910
PTX004	50,200	68.3	2.3	0.1	0.1	709
PTX017	62,800	19.3	2.4	0.2	0.2	2,840
PTX026 [c]	1,240,000	3,340	2,080	738	125	198
PAG008	35,900	21.8	37.0	9.9	7.1	474
PAG013	59,700	55.7	3.3	5.2	0.9	917

[a] Unless otherwise noted, concentrations are the average of three headspace cans distributed in the bottom half of the core generally at (1) the bottom, (2) bottom minus 1-meter, and (3) near the middle of the core.

[b] Concentration represents the can from the bottom of the core.

[C] The reason the headspace volume is over 100% methane is that the can was over-pressurized. This one sample is not the averaged, but the concentration in the bottom can taken from this core.

Table 5. Carbon Isotope Ratios of Selected Headspace Gases Offshore Nigeria (1998 Program).

CORE #	SECT	Methane	Ethane
NGC124	22	-77.5	
NGC128	21	-117.1	
NGC151	25	-116.2	
NGC158	26	-106.1	
NGC190	25	-71.5	
NGC206	22	-85.0	
NGC219	19	-73.0	
NGC224	19	-62.3	
NGC226	18	-67.6	
NGC230	09	-53.5	-34.3

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Figure 17. Cross-plot of the measured geothermal gradient vs. water depth for all heat flow sites.

Figure 18. Plot of the calculated bottom of methane hydrate stability zone vs. water depth for all heat flow sites. The average depth of methane hydrate stability is show as a solid line using the average geothermal gradient (58.2 mW/m^2).

Figure 19. Comparison of the calculated bottom of methane hydrate stability zone (Fig. 17) to actual measured depth of the BSR from an examination of the seismic records. The linear best fit for the BSR is shown ($y = 5.6593x + 0.2647$); $R^2 = 0.7632$).