Hydrate Occurrences in Shallow Subsurface Cores from Continental Slope Sediments

JAMES M. BROOKS, AUBREY L. ANDERSON, ROGER SASSEN, IAN R. MACDONALD, MAHLON C. KENNICUTT II, AND NORMAN L. GUINASSO, JR.

Geochemical and Environmental Research Group
Texas A&M University
833 Graham Road
College Station, Texas 77845

Department of Oceanography
Texas A&M University
College Station, Texas 77843

INTRODUCTION

Gas hydrates are "icelike" inclusion compounds that can be formed under high pressure and low temperature on the continental slopes of the world's ocean provided there is enough gas available from either in situ biogenic processes or migration from depth. It is generally assumed that free gas must exist in excess of saturation (i.e., bubble phase) for gas hydrate formation in the deep ocean. The principal gas in naturally occurring hydrates is almost always methane, although such hydrates can contain hydrocarbon gases from methane through butanes, carbon dioxide, hydrogen sulfide, and various other fixed gases (nitrogen, argon, etc.). Depending upon the biogenic or thermogenic nature of the hydrate, smaller amounts of ethane, propane, butanes, and carbon dioxide are present in the gas hydrates.2,3

The occurrence of gas hydrates in near-surface sediment on the continental slope is significant from various environmental perspectives. First, since a methane hydrate can contain up to 180 cc of methane (STP) per cc of solid hydrate, hydrates are postulated to be the largest reservoir in the global methane budget.4 If a significant proportion of this hydrate reservoir exists in shallow sediments on the upper continental slope, these hydrates can be susceptible to melting as a result of sea level changes on geological time scales. Various authors have suggested that release of methane from hydrate formations could have affected the extent of the glaciation during the ice ages.5,6 It is postulated that gas hydrates on the upper continental slope melted during the sealevel decreases of past ice ages. Melting could have also occurred as ice sheets receded from shelf sediments lowering the total overburden pressure. Since methane is a greenhouse gas and is known to have increased in concentration in the atmosphere near the end of the ice ages,7,8 the increased atmospheric methane could have contributed to increased temperatures thus accelerating the end of the ice ages.
On recent time scales, gas hydrates can become unstable due to overburden pressure decreases or temperature increases. A decrease in overburden pressure can result from slumping on the continental slope. Gas hydrates are of concern in deep water oil and gas production for three reasons. First, wet gas can form hydrates and plug conductors in deep water pipelines or wells. Second, wells flowing oil and gas produce localized warming of areas of the seafloor around platforms and this could result in melting of in situ gas-hydrated sediments. Third, the presence of hydrates in shallow sediments affects the geotechnical properties of the seafloor. The geotechnical properties of the sediment are important in the design of offshore platforms. Thus, the possibility of the unknown presence of hydrates in deep-ocean sediments can result in costly overdesign of the platform.

In summary, understanding the nature and extent of gas hydrates in shallow sediments on the upper continental slope is important for global change research, offshore production, and understanding the global carbon cycle.

**OCCURRENCES ON CONTINENTAL SLOPES**

Although gas hydrates have been known to exist in upper continental shelf sediments for many years, 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 100s of meters deep in the subsurface, in deep sea drilling program (DSDP) and ocean drilling program (ODP) cores. Most of the DSDP and ODP hydrate collections have been in the Blake Bahama Ridge offshore Florida, the Middle America Trench offshore Guatemala and Mexico, Orca Basin in the Gulf of Mexico, and offshore Peru.

**Gulf of Mexico**

The Gulf of Mexico has been the most 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 authors. The Gulf of Mexico still remains as the only documented site of thermogenic gas hydrate occurrences. Figure 1 shows the locations of over 30 gas hydrate collections in the Gulf of Mexico. Locations where actual pieces of gas hydrates have been retrieved in shallow cores range in water depths from 439 to 1360 meters. Although gas hydrates in the Gulf commonly occur in water depths greater than 400 meters, Anderson et al. have shown that thermogenic gas hydrates could exist in water depths as shallow as 220 meters. In the Gulf, there is a strong correlation between the water depth where the hydrate is recovered and its thermogenic or biogenic nature. Most thermogenic hydrates have been recovered in the 400 to 800 meter depth range, while most biogenic hydrates are recovered in water depths greater than 800 meters.
FIGURE 1. Gas hydrate locations in the northwestern Gulf of Mexico identified by recovery of hydrate specimens in cores or visual observations on the seafloor from submersibles.

**Offshore Nigeria**

In 1991, we collected gas hydrates in six cores at three sites (3° 33.7'N; 6° 31.8'W; 3° 31.4'N; 6° 20.9'W; 3° 57.6'N; 5° 16.6'W) on the continental slope offshore Nigeria. The sites ranged in water depths from 560 to 770 meters (TABLE 1). Core N-074C3 had the largest nodules of gas hydrates. They ranged in size from <1 to 1.5 cm in diameter and were concentrated at 3.2 to 3.5 meter subbottom depth. Most of the other cores had small, dispersed gas hydrates either throughout the core (N-138C2 and N-138C6) or in the bottom 0.4 to 0.6 meter of the cores. All gas hydrates were white, contained mostly methane, had hydrogen sulfide present within the sediment, and were found predominately in clay-rich sediment (TABLE 1). Molecular composi-

**TABLE 1. Headspace Gas Concentrations in Gas Hydrated Cores on the Nigerian Continental Slope**

<table>
<thead>
<tr>
<th>Core Designator</th>
<th>Depth (meters)</th>
<th>Methane (ppm)</th>
<th>Ethane (ppm)</th>
<th>Propane (ppm)</th>
<th>i-Butane (ppm)</th>
<th>n-Butane (ppm)</th>
<th>C1/ (C2 + C3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-074C3</td>
<td>677</td>
<td>6,250</td>
<td>108</td>
<td>8.7</td>
<td>2.7</td>
<td>1.4</td>
<td>54</td>
</tr>
<tr>
<td>N-074C4</td>
<td>675</td>
<td>35,700</td>
<td>116</td>
<td>6.0</td>
<td>0.7</td>
<td>0.2</td>
<td>292</td>
</tr>
<tr>
<td>N-082C3</td>
<td>770</td>
<td>29,600</td>
<td>12</td>
<td>3.4</td>
<td>0.3</td>
<td>0.3</td>
<td>1,920</td>
</tr>
<tr>
<td>N-138C2</td>
<td>560</td>
<td>75,100</td>
<td>11</td>
<td>0.4</td>
<td>0.0</td>
<td>0.4</td>
<td>6,590</td>
</tr>
<tr>
<td>N-138C3</td>
<td>560</td>
<td>69,800</td>
<td>5.6</td>
<td>0.5</td>
<td>0.0</td>
<td>1.5</td>
<td>11,400</td>
</tr>
<tr>
<td>N-138C6</td>
<td>563</td>
<td>77,000</td>
<td>6.6</td>
<td>0.4</td>
<td>0.0</td>
<td>0.0</td>
<td>11,000</td>
</tr>
</tbody>
</table>

*All concentrations are the average of three headspace cans distributed in the bottom half of the cores generally at (1) the bottom, (2) bottom minus 1 meter, and (3) near the middle of the core. Core N-138C3 is just the average of two core sections. Depth refers to water depth at the core collection site. The three sites are represented by the N-074, N-082, and N-138 designations.*
tions indicate mostly biogenic gas, although a small thermogenic component might be present at the N-074 location.

Gas hydrates may be as common on the Nigerian continental slope as in the Gulf of Mexico. Gas hydrates were collected at six of the 310 locations cored in water depths exceeding 500 meters. This percentage of hydrate recoveries is as high as what we achieve on the Gulf of Mexico continental slope. The high frequency of occurrence may in part result because most coring was concentrated over deep faults that were identified by deep and shallow seismic profiling as potential conduits for upward migration of hydrocarbons.

Eel River Basin

We have previously reported on the occurrence of gas hydrates offshore northern California in the Eel River Basin. Biogenic gas hydrates were recovered or suspected at seven sites from the Eel River Basin between water depths of 510 and 642 m. A total of seven gas-hydrated cores were recovered out of 74 cores taken in water depths greater than 500 m in the Eel River basin. The gas hydrates in northern California corresponded with a BSR, whereas no BSRs were present at the Gulf of Mexico and offshore Nigeria sites.

Thus, our experiences in the Gulf of Mexico, offshore Nigeria, and offshore northern California indicate that gas hydrates are common in shallow cores in these hydrocarbon generative basins of the world's ocean. In addition to the sites described above, methane hydrates have been found in shallow cores in the Okhotsk Sea, and the Black and Caspian Seas.

SAMPLING AND OBSERVATIONS

All the gas hydrate samples have been obtained using a 6-m long pipe, 1-kilo piston corer with collapsible piston and core liner. The corer is designed to sample the upper 4.0 to 6.0 meters of the sediment. Critical to the recovery of actual specimens of hydrate is the rapid recovery of the corer and removal of the core liner from the pipe. Small hydrate crystals usually will not survive the 15 to 20 minute retrieval time of a piston corer from >500 m water depths. Gas hydrated cores are often characterized by high pressure within the corer as a result of partial decomposition of the hydrate. The gas formed often results in partial extrusion of the core material past the core catcher or cutter. Thus, gas hydrated cores often are characterized by large gas voids in the retrieved core samples. The high pressure created within gas hydrated cores can also be a significant safety hazard if care is not exercised.

Most of the gas hydrate discoveries were made as part of surface geochemical exploration programs where the objective is to characterize gaseous and high molecular weight hydrocarbons in shallow sediments. The general strategy in these programs is to use deep seismic sections to identify the deep faults that can potentially act as conduits for the upward migration of hydrocarbons. Using precision navigation, these locations are cored to within ±30 meters of the identified
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location. Alternatively, shallow 3.5 kHz subbottom profiling is conducted over the site to further refine the indications of fault scarps, seismic "wipeout" zones, or other features indicative of migration pathways or seep features. Thus, our success in obtaining gas hydrates in continental slope sediments results largely from use of deep seismic data to selective core migration conduits. Random coring of any of these three regions should not be expected to yield the high rate of occurrence of hydrates that we have achieved.

Recovered gas hydrate samples can be preserved for molecular and isotopic analysis by immediately placing them in liquid nitrogen. Further discussion of methods for preservation and analysis can be found in previous publications.2 3

### TABLE 2. Molecular and Isotopic Composition of Bubbling Gas Seeps Collected at Three Sites on the Upper Continental Slope of the Gulf of Mexico in Regions where Gas Hydrates Are Known to Occur

<table>
<thead>
<tr>
<th>Sea Link Dive No.</th>
<th>Dive Location</th>
<th>Site Description</th>
<th>Methane (%)</th>
<th>Ethane (%)</th>
<th>Propane (%)</th>
<th>C&lt;sub&gt;1&lt;/sub&gt;</th>
<th>C&lt;sub&gt;2&lt;/sub&gt; + C&lt;sub&gt;3&lt;/sub&gt;</th>
<th>δ&lt;sup&gt;13&lt;/sup&gt;C-CH&lt;sub&gt;4&lt;/sub&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2057 GC-234</td>
<td>2061 GC-234</td>
<td>Mussel &amp; tubeworm site</td>
<td>98.0</td>
<td>1.3</td>
<td>0.5</td>
<td>53</td>
<td>−53.9</td>
<td></td>
</tr>
<tr>
<td>2061 GC-234</td>
<td>2061 GC-234</td>
<td>Mussel site</td>
<td>95.1</td>
<td>3.4</td>
<td>0.9</td>
<td>22</td>
<td>−37.6, −37.6</td>
<td></td>
</tr>
<tr>
<td>2062 GC-234</td>
<td>2062 GC-234</td>
<td>Mussel site</td>
<td>95.1</td>
<td>3.2</td>
<td>1.0</td>
<td>21</td>
<td>−51.8, −50.7</td>
<td></td>
</tr>
<tr>
<td>2062 GC-234</td>
<td>2062 GC-234</td>
<td>Mussel site</td>
<td>95.0</td>
<td>3.3</td>
<td>0.9</td>
<td>23</td>
<td>−47.0, −46.6</td>
<td></td>
</tr>
<tr>
<td>2062 GC-234</td>
<td>2062 GC-234</td>
<td>Mussel site</td>
<td>96.3</td>
<td>0.4</td>
<td>0.0</td>
<td>194</td>
<td>−52.0, −52.0</td>
<td></td>
</tr>
<tr>
<td>2063 GC-234</td>
<td>2063 GC-234</td>
<td>Tubeworm site</td>
<td>95.9</td>
<td>3.0</td>
<td>0.7</td>
<td>26</td>
<td>−51.8, −51.8</td>
<td></td>
</tr>
<tr>
<td>2063 GC-234</td>
<td>2063 GC-234</td>
<td>Tubeworm site</td>
<td>95.8</td>
<td>3.0</td>
<td>0.7</td>
<td>26</td>
<td>−47.6</td>
<td></td>
</tr>
<tr>
<td>2071 GC-272</td>
<td>2071 GC-272</td>
<td>Clam site</td>
<td>99.4</td>
<td>0.5</td>
<td>0.1</td>
<td>191</td>
<td>−52.9, −51.3</td>
<td></td>
</tr>
<tr>
<td>2074 GC-184</td>
<td>2074 GC-184</td>
<td>Mussel site</td>
<td>94.6</td>
<td>3.3</td>
<td>1.4</td>
<td>20</td>
<td>−51.3</td>
<td></td>
</tr>
<tr>
<td>2074 GC-184</td>
<td>2074 GC-184</td>
<td>Mussel site</td>
<td>94.5</td>
<td>3.4</td>
<td>1.5</td>
<td>19</td>
<td>−46.8, −46.8</td>
<td></td>
</tr>
</tbody>
</table>

**GAS VENTING**

The upper continental slope (<1000 m) of the Gulf of Mexico is an environment where gas seepage is common.14 Hovland and Judd16 have also documented the widespread occurrence of gas seepage in many regions of the ocean. During our submersible observations in numerous areas of the Gulf's upper continental slope, we commonly observe free gas bubbling from marine sediments in regions where hydrates have been either obtained from piston coring or observed at the seafloor. These gas seeps can be either continuous or intermittent streams of bubbles which are generally less than 1 cm in size in the 500 to 1000 m water depth range.

Molecular and isotopic composition of gas bubbles collected near the seafloor with the submersible JOHNSON SEA-LINK are summarized in TABLE 2. The gas was collected by placing a tube full of seawater over the bubbling seep and allowing the seep gas to replace the water in the tube. The table shows 11 collections at three sites in the Gulf of Mexico. Most collections were in Green Canyon Block 234 (a block is 3 by 3 mi), a site previously reported to contain gas hydrates2 as well as
chemosynthetic oil seep communities. All gas collections contained predominantly methane (>94%), with smaller amounts of ethane and propane indicative of thermogenic gas. There were large variations in the stable carbon isotopic composition of the methane. At the Green Canyon Block 234 sites, stable carbon isotopic values vary from −37.6 to −53.9‰. This 15‰ variation at this one block represents various admixtures of gas seeping up deep conduits from petrogenic and overmature gas sources with smaller amounts of biogenic gas no doubt derived from shallower geologic horizons. The two samples from Bush Hill in Green Canyon Block 185 (see discussion below) show less within-block variation possibly due to the smaller number of samples.

Of importance is the fact that gas hydrates in the shallow subsurface may not act as major barriers to the venting of gas into the water column since gas seeps appear to be common, although sometimes localized, in areas containing shallow hydrates. On a localized basis, the mechanical disturbance of a shallow gas hydrate with the mechanical arm of the submersible often results in a vigorous and prolonged discharge of gas (and oil in certain areas). This phenomenon has also been observed by Ginsburg et al.\textsuperscript{13} in the Okhotsk Sea. They observed the cooccurrence of active gas venting and methane hydrate deposits in 620 to 1040 m of water. The degree to which shallow hydrated sediment acts as a barrier to gas seepage is undoubtedly affected by local geological processes such as carbonate precipitation, sediment texture, and possibly brine seepage.

Although gas seepage is common on the upper continental slope of the Gulf of Mexico, certain geological features are more commonly associated with gas hydrates. Because of salt tectonics in the Gulf of Mexico, the upper continental slope is heavily faulted. These faults provide conduits for the upward migration of both biogenic and thermogenic gas. Sassen et al.\textsuperscript{14} report that these seeps are more common (1) along the edges of salt-basin “cooking pots” on the upper continental slope, (2) near oil fields associated with salt piercement structures, and (3) near deep faulting.

### NATURE OF HYDRATE GAS

Most gas hydrates obtained in shallow cores even in oil generative geological provinces often predominately contain biogenic methane. Although Brooks et al.\textsuperscript{2} report a roughly equal distribution of biogenic and thermogenic gas hydrates in the Gulf of Mexico, thermogenic gas hydrates have not been collected in any other basin in the world's ocean. Even in the Gulf of Mexico, biogenic gas hydrates can be collected within a few kilometers of active oil seeps. Ginsburg et al.\textsuperscript{13} reports, based on molecular and isotopic compositions, that gas venting in the Okhotsk Sea is biogenic in origin. However, the gas is not produced \textit{in situ} but is migrating upward from subsurface sediment layers. Thus, it would appear that most shallow gas hydrates on the continental slopes are biogenic in origin.

### EXAMPLES OF GEOLOGICAL SETTING

Two examples of the geological setting for gas hydrates follow.
Bush Hill

Bush Hill is a large topographic feature that measures ~500 m across in 540 to 580 meters of water offshore Louisiana. It is in Green Canyon lease Block 185 in the Gulf of Mexico (27° 47'N; 91° 30.4'W). The site is named for the large chemosynthetic tube worm bushes that occur on the seafloor. These tube worm communities derive their energy from hydrogen sulfide resulting from biodegradation of seeping oil at the site.\textsuperscript{17} The site is only a few kilometers away from Jolliet Field, one of the first deep water oil discoveries and deep water production facilities in the Gulf of Mexico. The topography of the site results from migration of oil and gas up an antithetic fault associated with deep faulting. \textbf{Figure 2} shows a cross section of the site modified by Sassen \textit{et al.}\textsuperscript{14} after Cook and D'Onofro.\textsuperscript{18} The deep faulting provides conduits for upward migration of gas and oil to Bush Hill. The leakage is fed to the seafloor by structural traps associated with Jolliet Field along salt and fault conduits. Interestingly, most of the gas seepage, oil-stained sediments, and chemosynthetic communities on Bush Hill are displaced westward of the projected intersection of the fault with the seafloor. Evidently at shallow subbottom depths, the major conduit ramifies into an array of smaller pathways and hydrocarbons flow the most direct route upward to the seafloor. Most of the western portion of the feature is seismically opaque at greater than 3 meters subbottom, possibly indicating extensive hydrate occurrences.

The Bush Hill vicinity is the location of the first discovery of thermogenic gas hydrates in deep ocean sediment.\textsuperscript{3} The topographic feature is characterized by numerous gas and oil seeps, authigenic carbonate, and chemosynthetic communities.\textsuperscript{14,17} Bubbling and intermittent gas streams are common at the site and are often associated with near-surface hydrates that can be excavated with a submarine's manipulator arm. Substantial hydrates have been recovered in approximately 50\% of the cores taken on the mound. The hydrates are disseminated in the core in small or midsized (few cm) nodules or in layers of a few mm to cm in thickness. During JOHNSON SEA-LINK submersible dives in 1992, thermogenic gas hydrates were observed outcropping on the seafloor. The thermogenic nature of the hydrate was inferred from the yellowish brown coloration.\textsuperscript{2} Although generally thermogenic in nature, gas hydrates with significant biogenic methane have been collected at the site.

The site is an excellent example of deep faulting producing conduits for migration of thermogenic gas to near surface sediments to form near-surface hydrates. \textbf{Table 2} shows data for two gas seep samples that were collected at the seafloor at this site. The gas analysis indicates the thermogenic nature of the seeping gas. Based on the widespread gas and even oil seepage at the site, again we note that the gas hydrates do not provide an impermeable barrier to gas seepage.

\textbf{Green Canyon 233/234 Site}

Another site where hydrates are commonly collected in piston cores and observed at the seafloor is the Green Canyon Blocks 233 & 234 (GC-233/234) region of the Gulf. A large part of the GC-233/234 blocks are in a seismically opaque area (i.e., wipeout zone). Such wipeout zones have been frequently associated with hydrate
FIGURE 2. Schematic representation of Green Canyon lease blocks 184 and 185 in the Gulf of Mexico showing the relationship of faulting to gas hydrate occurrences.\textsuperscript{14,18}
recoveries in the Gulf of Mexico. There are widespread occurrences of gas, hydrate, authigenic carbonate, and/or oil in sediment cores from the GC-233/234 area. Biogenic gas hydrates outcrop in the area and gas seepage is commonly observed during submersible surveys (see Table 2 for the molecular and isotopic compositions of 7 bubbling seeps). MacDonald et al. described a brine pool in GC-233 that appears to be associated with subsurface lenses of gas hydrates identified in the 25 kHz seismic records obtained by the submarine NR-1. A brine pool at a water depth of 650 meters is located in a series of recent slump terraces at the head of a troughlike graben. A salt diapir that penetrates upward to less than 500 m below the seafloor creates faults that provide conduits for the upward migration of gas to the brine pool. MacDonald et al. suggested that diffuse hydrates may exist below the mudline at this site because of the widespread occurrence of gas charged and gas hydrated sediment near the site, as well as a strong reflector only a few meters below the subsurface (identified in the 25 kHz subbottom records).

Figure 3 shows a postulated formation mechanism for the brine pool crater. The debris and berm around the crater suggest that an explosive event formed the crater. The breaching of a shallow subsurface hydrate layer provides one mechanism for creation of the crater. Figure 3A shows the collection of gas, supplied by the shallow faulting, below a shallow gas hydrate layer. Breaching of the hydrate layer by the free gas is shown in Figure 3B. Continued gas seepage, which is still observed from the brine pool, could provide a continuing mechanism for excavation and deepening of the crater. Once formed, the crater is filled with brine from seepage of interstitial salt into the crater. Thus, it possible that some of the crater features that are commonly observed in the Gulf of Mexico on the upper continental slope could result from events associated with gas hydrates forming temporary barriers to the escape of gas from the seafloor.

SUMMARY

Specimens of gas hydrates are commonly collected by coring or observed with submersibles on the upper continental slope in hydrocarbon generative basins of the ocean. Thermogenic hydrates have only been retrieved in the Gulf of Mexico. Biogenic hydrates are the type more commonly collected from shallow seafloor sediments. Hydrates are generally associated with faults that supply free gas to shallow sediments. The hydrates we have collected with piston cores have generally ranged in size from dispersed, very small (perhaps 1 mm) flakes, to larger nodules (up to ~5 cm) and some thin layers or bands of layers (generally <1 cm but some larger). At least one massive hydrate has been sampled and was of unknown thickness (15 cm was recovered but corer was stopped by the hydrate). Hydrate samples recovered from the Gulf of Mexico and off the coast of Nigeria have not been associated with seafloor BSRs. In the Gulf of Mexico, in addition to seafloor faults, the most common seismic record characteristic that is associated with recoveries is a diffuse acoustic amorphous zone (wipeout zone) in the upper seafloor. Seafloor seeps are not uncommon in association with the gas hydrates. The occurrence of shallow hydrates in seafloor sediments has implications for global change research, offshore production, and understanding the global carbon cycle.
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