Occurrence and origin of marine gas hydrates

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Natural gas hydrates are common in continental margin sediments in all major oceans at water depths greater than about 500 m. The occurrence of these gas hydrates has been inferred mainly from anomalous acoustic reflectors seen on marine seismic profiles. Direct, visual evidence for marine gas hydrates has been obtained at four localities where chemical analyses have shown that the gas is mainly methane accompanied by minor amounts of heavier hydrocarbons and carbon dioxide. The molecular composition of the hydrocarbons and the carbon isotopic composition of methane indicate that the methane is of biological origin. The gas probably is produced from bacterial alteration of organic matter, and the process of gas-hydrate formation may be concurrent with sedimentation. Gas hydrates may be expected in outer continental margin sediments where high rates of sedimentation bury sufficient organic matter so that enough methane is produced to initiate and stabilize the formation of gas hydrates.

Dans tous les océans, à des profondeurs d'eau supérieures à 500 m, on rencontre fréquemment des hydrates de gaz naturel dans les sédiments de la marge continentale. On a surtout déduit l'existence de venues d'hydrates naturels à partir de réflexions acoustiques anormales observées sur les profils sismiques sous-marins. On a pu directement observer la présence de ces hydrates sous-marins en quatre endroits; les analyses chimiques ont démontré que le gaz est surtout du méthane, accompagné de quantités mineures d'hydrocarbures plus lourds et de gaz carbonique. La composition moléculaire des hydrocarbures et la composition isotopique du carbone dans le méthane indiquent que ce dernier a une origine biologique. L'altération bactérienne de la matière organique a probablement donné naissance aux gaz, et la formation des hydrates accompagné la sédimentation. On s'attend à trouver des hydrates de gaz naturel dans les sédiments de la portion extérieure du plateau continental, où la sédimentation est rapide et où sont enfouies des quantités importantes de matière organique, qui produisent suffisamment de méthane pour provoquer la formation d'hydrates de gaz naturel et assurer la stabilisation de ceux-ci.

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Introduction

Natural gas contains mainly methane, often accompanied by higher molecular weight hydrocarbons, ethane, propane, and butanes, as well as inorganic gases such as nitrogen, carbon dioxide, and hydrogen sulphide. Under appropriate conditions of high pressures and low temperatures that are found in deep oceanic sediments, natural gas may combine with water to crystallize as a clathrate or three-dimensional framework of water molecules that is stabilized by the included gas molecules (Hand *et al.* 1974). This water clathrate of natural gas is commonly called a gas hydrate. In oceanic sediments, gas hydrates can form at water depths greater than about 500 m where bottom-water temperatures approach 0°C. Below about 500 m of water depth, the zone where gas hydrates are stable extends from the upper continental slope through the continental rise to the abyssal basins. The thickness of the zone increases with increasing water depth.

Besides pressure and temperature, two other factors influence the occurrence of gas hydrates in oceanic sediments. First, the amount of methane must be sufficient to initiate and stabilize the gas hydrate. Only methane present in excess of the amount soluble in water at the given conditions of temperature and pressure is available for gas-hydrate formation. Because of this requirement for very high concentrations of methane, the occurrence of gas hydrates in sediments of the abyssal basins is not likely even though conditions of temperature and pressure are satisfied. Thus, most gas hydrates will be found in continental slopes and rises. The second factor influencing gas hydrates is the geothermal gradient. The fact that the temperature of sediments increases with depth leads to temperature conditions at which gas hydrates are no longer stable and therefore decompose. The base of the gas-hydrate zone follows a pressure–temperature surface that represents the maximum depth at which the gas hydrate is stable. Thus, the gas-hydrate zone may overlie accumulations of free gas.

The base of the gas-hydrate zone often correlates with anomalous acoustic reflectors in marine seismic data obtained from a number of areas on outer continental margins (Shipley *et al.* 1979). The anomalous reflector approximately parallels the sea-floor but deepens with increasing water depths. The depths at which this reflector occurs can be predicted based on considerations of the pressure–temperature stability field for gas hydrates and the geothermal gradient. This reflector is commonly called a bottom-

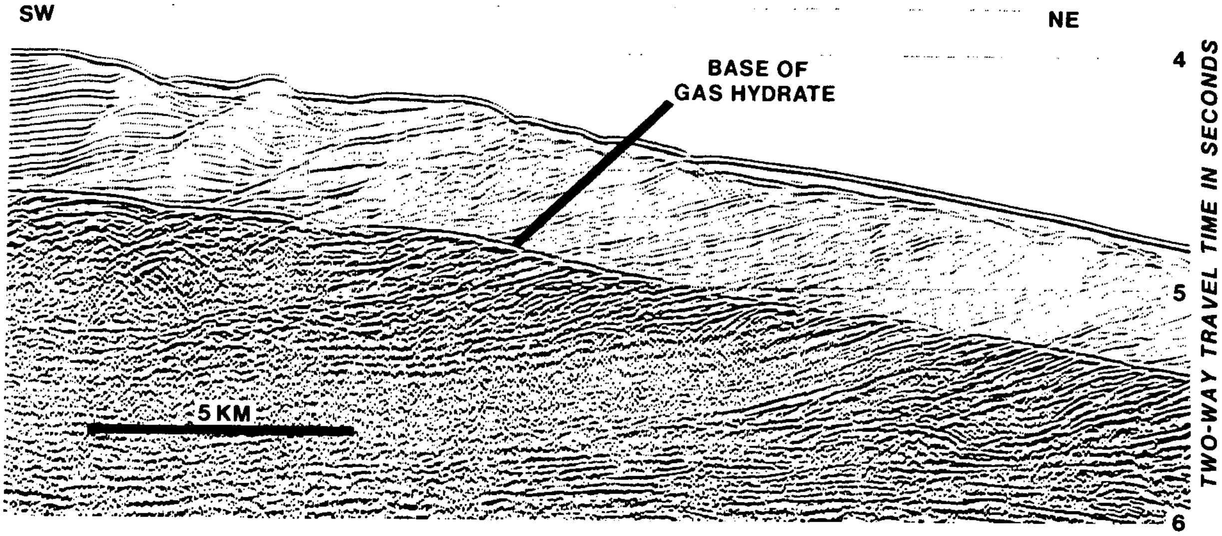

FIGURE 1. A 12-fold multichannel seismic reflection profile from the crest and eastern flank of the Blake Outer Ridge, off-shore south-eastern United States. The reflector at the base of the gas hydrate follows the topography of the sea-floor and transects dipping bedding reflectors (Shipley *et al.* 1979, Fig. 3, p. 2206).

simulating reflector (BSR). The reflector probably results from the velocity contrast between the sediment cemented with gas hydrate and the underlying sediment where lower velocities occur because of the absence of gas hydrate and the possible presence of free gas. In an example of a seismic profile with a well-developed BSR (Figure 1), the BSR closely mimics the topography of the sea-floor and cuts across dipping bedding reflectors. The acoustically transparent region above the BSR may result from acoustic impedance differences caused by the presence of gas hydrate.

Kvenvolden and McMenamin (1980) have summarized the geological occurrence of natural gas hydrates and listed areas where marine gas hydrates can be inferred based on observations of BSR's on marine seismic records. Kvenvolden and Barnard (1982) expanded this list to include a number of as yet unpublished occurrences. Since these lists were prepared, new areas with suspected gas hydrates have been identified, and one purpose of this paper is to update the documented occurrences of hydrates in oceanic sediments. This update includes occurrences (1) inferred from seismic profiles, (2) inferred from other geological evidence, and (3) confirmed by direct sampling. After the ubiquity of marine gas hydrates has been established, this paper considers possible processes that could lead to the generation of methane for the subsequent formation of marine gas hydrates.

Gas Hydrates Inferred from BSR's

Early seismic profiles in the area of the Blake Outer Ridge in the western Atlantic Ocean off south-eastern United States, by Markl *et al.* (1970) and Stoll *et al.* (1971) showed an anomalous reflector that intersected bedding reflectors, paralleled closely sea-floor bathymetry, and appeared to deepen with increasing water depth. In later profiles from the same region (*see* Figure 1 for example), the well-developed BSR was correlated with the base of the gas-hydrate zone (Dillon *et al.* 1980; Paull and Dillon 1981; Shipley *et al.* 1979; Tucholke *et al.* 1977). A comprehensive study of BSR's on seismic profiles by Shipley *et al.* (1979) has shown the possible presence of gas hydrates along the east coast of the United States, the western Gulf of Mexico, the coasts of northern Colombia and northern Panama, and along the Pacific side of Central America in areas extending from Panama to near Acapulco, Mexico. Now BSR's, thought to be caused by gas hydrates, have been observed on seismic profiles obtained in a number of areas on outer continental margins in all major oceans (Table 1).

In four areas listed on Table 1, extensive seismic profiling has provided sufficient information so that the minimum areal extent of the gas hydrate can be determined. At the Blake Outer Ridge, the gas hydrate extends over an area of approximately 80,000 km^2 [estimated from maps given by Dillon *et al.* (1980) and Paull and Dillon (1981)]. To the north

TABLE 1. Gas hydrates in oceanic sediment

Location	Water depth in m or s (2-way)	Evidence	BSR Subbottom depth in m or s (2-way)	Reference
ARCTIC OCEAN				
Beaufort Sea, off Alaska, USA	400–2500 m	BSR	100–800 m	Grantz *et al.* (1976) Grants and Dinter (1980)
ATLANTIC OCEAN				
Labrador Shelf, off Newfoundland, Canada	~ 2000 m	BSR	Not reported	Taylor *et al.* (1979)
Continental Rise, off New Jersey and Delaware, USA	2500–3800 m	BSR	470–590 m	Tucholke *et al.* (1977)
Blake Outer Ridge, off south-eastern USA	2500–4000 m	BSR, gassy cores, solid gas hydrate	450–600 m	Markl *et al.* (1970) Ewing and Hollister (1972) Tucholke *et al.* (1977) Shipley *et al.* (1978) Shipley *et al.* (1979) Dillon *et al.* (1980) Paull and Dillon (1981) Sheridan *et al.* (1982)
Western Gulf of Mexico, off Mexico	1200–2000 m	BSR	Not reported	Shipley *et al.* (1979)
Western Gulf of Mexico, location not specified	~ 2.7–3.1 s	BSR	~ 0.5 s	Hedberg (1980)
Caribbean Sea, off Panama and Columbia	1500–3000 m	BSR	Not reported	Shipley *et al.* (1979)
Continental slope and rise, off South West Africa	~ 2000 m	Surficial slumps and slides. High organic matter content	Not mentioned	Summerhayes *et al.* (1979)
PACIFIC OCEAN				
Mid-America Trench, off Mexico	~ 2.5–5.0 s	BSR, gassy cores, solid gas hydrate	~ 0.5–0.7 s	Shipley *et al.* (1979) Shipley *et al.* (1980) Moore *et al.* (1979)
Mid-America Trench, off Guatemala	Not reported	BSR	Not Reported	Shipley *et al.* (1979)
Mid-America Trench, off Guatemala	2000–5500 m	No BSR, gassy cores, solid gas hydrate	Not observed	von Huene *et al.* (1980)
Off-shore Nicaragua	800–2400 m	BSR	~ 0.4–0.5 s	Shipley *et al.* (1979)
Off-shore Costa Rica	~ 1.0–1.8 s	BSR	~ 0.2–0.5 s	Shipley *et al.* (1979)
Off-shore Panama	~ 2.5–2.8 s	BSR	~ 0.4–0.5 s	Shipley *et al.* (1979)
Continental slope, east of North Island, New Zealand	1000–2500 m	BSR	0.36–0.85s	Katz (1981)
INDIAN OCEAN				
Gulf of Oman, continental margin off Pakistan and Iran	3000 m	BSR	600–700 m	White (1979)
Timor Trough off northern Australia	2315 m	High gas concentrations, trend in inorganic ion concentrations	Not mentioned	McKirdy and Cook (1980)
OTHERS				
Black Sea, USSR	2000 m	Solid gas hydrate at 6.5 m subbottom, high gas concentrations	Not mentioned	Yefremova and Zhizhchenko (1974)

of the Blake Outer Ridge on the continental rise east of New Jersey and Delaware, Tucholke *et al.* (1977) showed that a gas hydrate may cover at least 20,000 km^2 [estimated from their map, Fig. 4]. Mapping by Grantz *et al.* (1976) and Grantz and Dinter (1980) of the western Beaufort Sea, Arctic Ocean, showed a minimum areal extent of gas hydrates of about 7,500 km^2. Finally, Katz (1981) calculated that 10,000 to 20,000 km^2 of continental slope east of New Zealand appear to be underlain by gas hydrates. These four examples plus the other areas listed in Table 1 attest to the widespread occurrence of BSR's that likely are caused by marine natural gas hydrates.

Gas Hydrates Inferred from Other Evidence

At least two areas exist where gas hydrates are inferred based on evidence over than seismic profiles. In the Timor Trough off the northern coast of Australia (*see* Table 1) a geochemical study of sediments at a site on DSDP Leg 27 by McKirdy and Cook (1980) showed that between 5 and 310 m of sediment-depth methane concentrations were above average. In conjunction with gas analyses, measurements were also made of various inorganic ions. Changes in the trends of the alkalinity and salinity profiles with depth were postulated to result from the presence of methane hydrate with has effected fluid migration pathways.

A reconnaissance study of surficial slides and slumps on the continental slope and rise off South West Africa (*see* Table 1) showed high concentrations of gas associated with slides and slumps (Summerhayes *et al.* 1979). The source of the gas affecting sediment stability may be from decomposing gas hydrates. The gas hydrates are thought to result from the generation of methane by microbiological processes.

Gas Hydrates Sampled Directly

The first observation of solid gas hydrate in oceanic sediment was made by Yefremova and Zhizhchenko (1974) in samples from the Black Sea (*see* Table 1). At water depths of about 2000 m, microcrystalline aggregates of gas hydrates were recovered from depths of 6.5 m below the sea-floor. The hydrates, containing mainly methane and carbon dioxide, decomposed rapidly. Coring during the Deep Sea Drilling Project (DSDP) Leg 42B in the Black Sea failed to recover solid gas hydrates, but most cores contained gases that expanded as cores reached the surface. Some cores contained sufficient gas to blow sediment out of the core barrel. Gases were mainly methane with small amounts of carbon dioxide and other hydrocarbon gases. The carbon isotopic composition of methane, according to Hunt and Whelan (1978) ranged from −63 to −72 per mille. [All isotopic data cited in this paper are referred to the PDB standard.]

Gas hydrates were recovered at three sites from continental margin sediment during DSDP Leg 66 in the Pacific Ocean on the inner wall of the Mid-America Trench (*see* Table 1) where a BSR strongly suggests that gas hydrates should be found. Samples of gassy frozen sediment produced about 20 ml of gas per ml of pore fluid. The gas was mainly methane; the volume of methane produced was about five times the solubility of methane in seawater at equivalent conditions, indicating the presence of gas hydrates (Moore *et al.* 1979).

On DSDP Leg 67 in the Pacific Ocean off Guatemala, also on the inner wall of the Mid-America Trench (*see* Table 1), no BSR was observed but gas hydrates were recovered in vitric sands near the bottom of holes at two sites. Evidence for gas hydrates was based on observations that high gas pressure was present and that decomposition of the suspected hydrates produced greater quantities of gas than are soluble in water at *in situ* pressures and temperatures. As in Leg 66 the gas was mainly methane (von Huene *et al.* 1980).

A principal objective at one site of DSDP Leg 76 on the Blake Outer Ridge in the Atlantic Ocean (*see* Table 1) was to recover samples of gas hydrate. The presence of gas hydrates here had been predicted based on the well-developed BSR (*see* Figure 1) and the previous observations made in the same area on DSDP Leg 11 (Ewing and Hollister 1972). At three sites on Leg 11, high concentrations of methane were observed in sediments; ethane and heavier hydrocarbon gases were present in minor amounts. The carbon isotopic composition of methane ranged from −70 to −88 per mille (Claypool *et al.* 1973).

Pressure–volume measurements, visual observations, chemical analyses, and pressure core-barrel experiments conducted at one site on Leg 76 confirmed that gas hydrates are present. Expansion of many sediment cores indicated that high concentrations of gas were present. A sediment sample containing gas hydrate was recovered at a sediment depth of 240 m. This sample vigorously frothed. Thin mat-like layers of white crystals were present. The volume of gas released during decomposition was about 20 times the volume of pore fluid, a result similar to that obtained from a sample of sediment containing gas hydrate from Leg 66. Gases recovered from cores and decomposing gas hydrates were mainly methane accompanied by very small concentrations of heavier hydrocarbon gases and carbon dioxide. Experiments with a pressure core barrel produced pressure relief patterns that suggest some gas hydrate was present (Sheridan *et al.* 1982).

Gas hydrates recovered on DSDP Legs 66, 67, and 76 did not occur in massive, solid, thick units but rather in a few thin layers which usually, but not always, were associated with higher porosity intervals. On Legs 66 and 67 the gas hydrates were associated with vitric sands. The single occurrence of solid gas hydrate noted on Leg 76 was in hemipelagic sediment not unlike the rest of the sediment in the core. Pressure core-barrel experiments on Leg 76 suggest that some gas hydrate occurs in fine-grained sediment, but much of this gas hydrate may have decomposed during both conventional and pressure core-barrel drilling. This decomposition may explain why no solid gas hydrate was observed on Leg 11 and only a single occurrence was noted on Leg 76. Where direct evidence for gas hydrates was recovered by coring at sites on Legs 66 and 76, seismic profiling had shown well-developed BSR's. These two examples strongly support the inferred relation between gas hydrates and BSR's.

Origin of Marine Gas Hydrates

The gases associated with marine gas hydrates sampled thus far are methane-rich; that is, methane generally constitutes more than 99.9 per cent of the hydrocarbon gases present. Ethane and heavier hydrocarbons usually occur in the low parts per million range. Natural gas with this kind of composition can result from two very different processes. During microbial alteration of organic matter, methane is the only hydrocarbon generated in significant amounts. Likewise, during the evolution of organic matter, methane is the major product resulting from the thermal cracking of existing hydrocarbons (Hunt 1979, p. 178). Because of its occurrence in shallow marine sediments at temperatures less than 50°C, the natural gas in marine gas hydrates is most likely derived from biological processes rather than thermochemical processes. Carbon isotopic compositions of methane support this contention, at least indirectly. Carbon isotopic compositions of methane recovered on DSDP Leg 11 from the Blake Outer Ridge (Claypool *et al.* 1973) and on DSDP Leg 42B from the Black Sea (Hunt and Whelan 1978) range from -63 to -88 per mille. These values fall within the range -50 to -90 per mille that is generally considered to indicate biogenic methane (Fuex 1977). On the other hand, methane produced during thermal cracking of hydrocarbons has a range of carbon isotopic compositions between -25 and -40 per mille (Fuex 1977). The observed carbon isotopic compositions of methane from areas where marine gas hydrates have been recovered clearly lie outside the range of values attributed to high temperature thermal processes. Therefore, both molecular and isotopic compositions of hydrocarbons suggest that most of the methane in marine gas hydrates sampled so far has resulted from bacterial alteration of organic matter buried in the sediment.

In the formation of marine gas hydrates, methane can enter the zone of gas hydrate stability either from below or from within. That gas for hydrate formation migrates from below from deeper parts of the sedimentary section has been suggested in order to account for the large volumes of methane required for gas-hydrate stability (for example, *see* Lancelot and Ewing 1972). Seismic profiles showing BSR's truncating dipping bedding reflectors suggest that gas hydrates may form from upward-migrating gas and then act as seals trapping methane that continues to migrate from deeply buried sediment up the dipping beds (Dillon *et al.* 1980; Hedberg 1980). These ideas would be particularly attractive if the methane had resulted from thermal alteration of organic matter as would be expected for methane from deeply buried sources. However, the molecular composition of the hydrocarbons and the isotopic composition of methane associated with gas hydrates clearly indicate that the methane observed thus far is biogenic and not thermogenic. Of course, biogenic methane could be involved in the migration process from below the zone of gas-hydrate stability, but this source would be limited at great depth because of the lack of current biological activity there.

An alternate way to account for marine gas hydrates composed of biogenic methane has been outlined by Kvenvolden and Barnard (1982) and involves methane entering the zone of gas-hydrate stability from within. On continental margins where high rates of sedimentation ensure the deposition of metabolizable organic matter, an ecological succession of metabolic processes is established that varies with time and depth in the marine sedimentary column (Claypool and Kaplan 1974). Two biochemical zones result and in the lower zone methane production takes place. When the ecological succession is established the biochemical zones move together upward with time as new sediment is added at the sediment-water interface. Where these biochemical and geological processes occur under pressure and temperature conditions suitable for gas-hydrate stability, and where sufficient methane is generated from an adequate supply of organic matter, the gas hydrates will form. The process of gas-hydrate formation may be concurrent with sedimentation. The zone of gas hydrate will thicken until its base subsides into a region where temperatures make the gas hydrate unstable. In this region, the gas hydrate may form a seal for the methane released from gas-hydrate decomposition and for any methane generated below the gas hydrate (Rice and Claypool 1981). Thus, both models for gas-hydrate formation lead to the possible trapping of free gas below the base of the gas-hydrate zone. If the interface between the base of the gas-hydrate zone and free methane zone intercepts porous and permeable beds, a situation may be created where the gas hydrate traps free gas in a reservoir. Such traps may provide a source of methane for future energy needs.

Conclusions

Natural gas hydrates commonly occur in continental margin sediments of all major oceans at water depths greater than about 500 m. Evidence for this wide-spread occurrence comes mainly from seismic profiles. These profiles exhibit an anomalous acoustic reflector that approximately parallels the sea-floor at depths predicted from considerations of the pressure–temperature requirements for gas-hydrate stability. The anomalous reflector is often described as a bottom-simulating reflector or BSR. Fourteen areas on continental margins have been identified where the presence of gas hydrate has been inferred from BSR's. At four of these areas, Blake Outer Ridge, Atlantic margin off New Jersey, Beaufort Sea, and east New Zealand, extensive seismic profiling provides the basis for mapping the areal extent of gas hydrates which range from 7500 to at least 80,000 km^2.

Direct evidence for marine gas hydrates exists from visual observations in four areas: Black Sea, Mid-America Trench off Mexico, Mid-America Trench off Guatemala, and Blake Outer Ridge off south-eastern United States. Where solid gas hydrates have been sampled the gas is composed mainly of methane accompanied by minor amounts of heavier hydrocarbons and carbon dioxide. The molecular composition of the hydrocarbons and the carbon isotopic composition of the methane indicate that most of the methane is of biological origin. The gas was probably produced by the bacterial alteration of organic matter buried in the sediment. In the formation of marine gas hydrates, methane can enter the zone of gas-hydrate stability either from below or within. Because the gas hydrates examined thus far do not show evidence of thermogenic hydrocarbons, the idea that gas-hydrate formation is concurrent with sedimentation and takes place in a downward direction is favoured at present. Marine gas hydrates contain, and may trap, large quantities of methane that could serve as an important energy resource if the methane could be released and produced.

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