THERMOGENIC GAS HYDRATES, GULF OF MEXICO CONTINENTAL SLOPE

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INTRODUCTION

The Gulf of Mexico continental slope is a natural laboratory for gas hydrates that contain hydrocarbons from deeply buried thermogenic sources. Thermogenic hydrocarbons (oil and gas) from actively generating Mesozoic source rocks (>6 km burial depth) migrate vertically along conduits associated with actively-moving salt structures and faults to subsurface reservoirs (2-4 km) of Tertiary age[1]. The hydrocarbon trapping system is so "leaky" that large volumes of thermogenic hydrocarbons reach the sea floor[1], and enter the water column[2].

Although biogenic gas hydrates are abundant on the Gulf slope[3], oil and gas from deep source rocks create a geochemically complex and physically dynamic environment for thermogenic gas hydrates at the sea floor. Structure II gas hydrate containing C_1-C_4 thermogenic hydrocarbon gases was first sampled in 1984 by piston cores in 530-560 m water depths on the Gulf slope offshore Louisiana[4]. Identification of the hydrate as structure II was based on the relative abundance of the C_3 and *i*-C_4 hydrocarbons[4]. The structural assignment was corroborated using solid-state nuclear magnetic resonance (NMR)[5]. Research on gas hydrates of the Gulf slope, however, has advanced rapidly in the last few years, and our objective here is to summarize new results.

THE BUSH HILL STUDY AREA

The Bush Hill site in the Green Canyon area of the Gulf slope offshore Louisiana is a well-documented site for study of thermogenic gas hydrates (27°47.5' N and 91°15.0' W). Bush Hill is a fault-related sea-floor mound about 500 m wide, with relief of about 40 m[6]. Water depth of the mound crest is about 540 m, where mean water temperature is about 7° C (range = 6 to 11° C) Phase equilibria models indicate that Bush Hill is within the stability zone of thermogenic gas hydrates (Sloan, E.D., pers. communication).

Sea-floor sediments contain crude oil and related free hydrocarbon gases. Bacterial oxidation of these hydrocarbons produces CO_2 which precipitates as authigenic carbonate rock with isotopically-light $\delta^{13}C$ values[7]. The crest of the mound is colonized by seep-dependent chemosynthetic organisms including bacterial mats, vestimentiferan tube worms, and methanotrophic mussels[8]. Persistent natural oil slicks appear on satellite remote sensing images of the sea surface over Bush Hill[2].

Thermogenic gas hydrates and gases that vent to the water column at the mound crest are readily sampled by research submarines. Copious streams of gas vent continuously to the water column where subsurface migration conduits intersect the sea floor[9,10]. Thermogenic gas hydrates form around the orifices of gas vents. The gas hydrates at vents are not dispersed in sediments as nodules or thin seams, but instead occur as continuous masses. Lens-shaped masses of yellow to orange gas hydrates breach the sea-floor at numerous locations on the crest of Bush Hill[9,10]. The hydrates form sediment-draped mounds 30-50 cm high and up to several m in width, with exposed gas hydrate visible at the edges of mounds[10].

Vent Gases

The C_1-C_5 hydrocarbons of the vent gases are dominated by methane (C_1 = 91.1-94.7%), and $\delta^{13}C$ values of C_1 are within the narrow range of -42.4 to -45.6 ‰ PDB (Table 1). The C_1-C_5 distributions and $\delta^{13}C$ of C_1 of the vent gases (Table 1) correlate to gases from underlying subsurface reservoirs of Jolliet Field[11].

Table 1. Normalized C_1-C_5 hydrocarbon compositions and methane $\delta^{13}C$ of vent gases and thermogenic gas hydrates (Structure II and Structure H) at Bush Hill. Number in superscript indicates the citation to the data.

Sample	C_1	$\delta^{13}C$	C_2	C_3	i-C_4	n-C_4	i-C_5
Vent Gas [10]	93.2	-43.3	4.3	1.5	0.3	0.6	0.3
Vent Gas [10]	93.5	-42.5	4.3	1.4	0.2	0.4	0.2
Vent Gas [10]	94.7	-45.6	3.9	0.7	0.1	0.5	0.2
Vent Gas [10]	94.6	-43.8	3.8	0.7	0.1	0.5	0.3
Vent Gas [10]	91.1	-42.4	4.8	1.8	0.4	1.2	0.8
Hydrate (II)[10]	71.7	-36.3	10.6	12.6	2.6	1.7	0.8
Hydrate (II)[10]	80.2	-38.5	9.4	7.3	1.6	1.2	0.3
Hydrate (II)[10]	72.1	-39.9	12.4	11.4	2.3	1.6	0.3
Hydrate (H)[6]	21.2	-29.3	9.5	7.5	2.5	17.5	41.1

Structure II hydrate
Hydrocarbon compositions of massive hydrate lenses of Bush Hill are shown in Table 1. The C_1-C_5 hydrocarbons of the hydrate gases are dominated by C_1 (71.7-80.2%). The $\delta^{13}C$ values of C_1 are in the range of -36.3 to -39.9 ‰ PDB, somewhat heavier than vent gases, possibly because of bacterial activity[10]. The C_2 and C_3 hydrocarbons are both present in similar but relatively high percentages compared with the vent gas (Table 1). Preliminary NMR of an intact hydrate sample preserved in liquid nitrogen is consistent with structure II hydrate (Ripmeester, J., pers. communication).

Structure H gas hydrate
Structure H hydrates produced in the laboratory can enclose larger molecules than structure I or II hydrates, including common thermogenic hydrocarbons such as i-C_5. Given the widespread occurrence of petroleum, it was postulated in 1993 that structure H hydrate could co-exist in nature with structure II hydrate[12].

Evidence for the natural occurrence of structure H gas hydrate at the Bush Hill locality was first reported in 1994[6]. Massive amber-colored gas hydrate breached the sea-floor. It had been exposed when a buoyant lobe of hydrate broke free of the sediment and floated upwards into the water column. Identification of structure H hydrate was based on abundant i-C_5, which represented 41.1% of the total C_1-C_5 hydrocarbon distribution of the sample (Table 1). The δ^{13} C of C_1 from the sample is heavy (-29.3 ‰ PDB), possibly because of bacterial activity[6].

Experimentally-Precipitated gas hydrate
Gas hydrate was experimentally precipitated at the crest of Bush Hill in 1995 using natural vent gases as the starting material[10]. Water temperatures during experiments were 9.0-9.2°C. Precipitation of white to yellow gas hydrate was noted to occur within minutes.

The hydrocarbon compositions of experimentally precipitated gas hydrates are similar to vent gas compositions[10]. The C_1-C_5 hydrocarbons of the experimentally precipitated gas hydrates gases are dominated by methane (C_1 = 87.7-93.9%), and the $\delta^{13}C$ values of C_1 are within the -40.5 to -45.3 ‰ PDB range.

CONCLUSIONS
Thermogenic gas hydrates occur on the Gulf of Mexico continental slope because of active vertical migration of oil and gas to the sea floor within their stability zone. The Bush Hill seep site on the Gulf slope is an important case history. Massive thermogenic gas hydrates occur in association with the orifices of hydrocarbon vents. Both structure II and structure H hydrates appear to co-exist in this

environment. Gas hydrate is also rapidly precipitated in sea-floor experiments using natural vent gas as the starting material. More sophisticated sampling and experiments from research submarine platforms could significantly enhance our understanding of thermogenic gas hydrate formation in the deep sea.

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