

# Massive vein-filling gas hydrate: relation to ongoing gas migration from the deep subsurface in the Gulf of Mexico

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## Abstract

A gas hydrate mound that contains massive, vein-filling, structure II gas hydrate occurs on the upper continental slope (~540 m water depth) of the Gulf of Mexico, southwest of the Mississippi Delta. The mound is located in the Green Canyon (GC) Block 185, adjacent to Jolliet Field in GC 184. Jolliet Field contains oil and gas that filled fault traps caused by salt deformation during late Pleistocene–Holocene time. In contrast to reservoir oil in Jolliet Field, which shows bacterial oxidation effects, the C<sub>1</sub>–C<sub>5</sub> reservoir gas is unaltered by bacterial oxidation. Disassociated gas is assumed to have recently entered from the subsurface hydrocarbon system. Vertical migration of gas along faults is ongoing, manifested on the sea floor by gas vents, gas hydrate, complex chemosynthetic communities, and by a large gas plume that extends from the vents to the sea surface. The isotopic properties of C<sub>1</sub>–C<sub>5</sub> hydrocarbons from reservoirs, gas vents, and gas hydrate correlate closely. Although outcropping gas hydrate is transiently stable because of variations in seawater temperature, the bulk of buried gas hydrate at GC 185 is stable and perhaps increasing in volume because of the copious gas flux. The massive accumulation of gas hydrate at the GC 185 site is attributed to the gas that has recently entered the vents, largely from Jolliet Field, and to the synchronous activation of fault conduits allowing gas migration to the sea floor. Synchronous late gas charge and faulting could also explain the wide distribution of gas hydrate across the upper Gulf slope. © 2001 Elsevier Science Ltd. All rights reserved.

**Keywords:** Hydrocarbons; Gas hydrate; Gulf of Mexico

## 1. Introduction

Gas hydrate is a potential energy resource (Kvenvolden, 1999), and has been suggested as an agent of sudden climate change (e.g. Bains, Corfield, & Norris, 1999; Dickens, O'Neil, Rea, & Owen, 1995; Dickens, Castillo, & Walker, 1997; MacDonald, 1990; Max, Dillon, Nishimura, & Hurdle, 1999). It is important to understand the processes that give rise to localized but massive gas hydrate vein fillings on the continental slope of the Gulf of Mexico. Gas hydrate mainly occurs in the Gulf as massive vein-fillings in fracture porosity of hemipelagic mud (Sassen et al., 1999a), and as nodular growths (Brooks, Kennicutt, Fay, McDonald, & Sassen, 1984; Brooks et al., 1986). The concentration of gas hydrate in sediment is greater near discrete

migration conduits in the Gulf slope (Sassen et al., 1999a) than in sediment from the Blake Plateau (Paull & Matsumoto, 2000) where gas hydrate is mainly disseminated in pore space. From the perspective of economic geology, a concentrated deposit in the deep sea is more likely to be economically viable than a disseminated deposit (Glasby, 2000; Hovland, 2000). From the perspective of climate change, improved insight to the stability and fate of hydrate-bound greenhouse gas in the Gulf of Mexico could help constrain models of global climate change (Kvenvolden, 1999).

Gas hydrate is an ice-like crystalline mineral in which hydrocarbon gases and non-hydrocarbon gases are held within rigid cages of water molecules. Structure I gas hydrate has a body-centered cubic lattice, structure II gas hydrate has a diamond lattice, and structure H gas hydrate has a hexagonal lattice (Sloan, 1998). Structure I gas hydrate, which occurs in the Gulf as well as in other basins, is usually dominated by bacterial methane

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formed at relatively low temperatures and shallow sediment depths (Kvenvolden, 1995). The  $\delta^{13}\text{C}$  and  $\delta\text{D}$  of bacterial methane from sea floor gas vents and from structure I gas hydrate in the Gulf are thus far consistent with a primary origin from methanogenesis via  $\text{CO}_2$  reduction in sediment (Sassen et al., 1999b).

Structure II hydrate contains mainly thermogenic  $\text{C}_1\text{--C}_4$  hydrocarbon molecules (Sloan, 1998) that originate from the subsurface petroleum system. The varied and complex molecular and isotopic properties of hydrocarbons that form thermogenic gas hydrate are useful to study, because these molecules preserve unique information on the origin and alteration of vent gas and gas hydrate that is otherwise unobtainable.

Gas hydrate sites extend along the Gulf slope offshore Texas and Louisiana over a distance  $>500$  km, and the maximum width of the belt is  $>100$  km. Solid gas hydrate has been recovered from shallow sediments ( $<6$  m) by piston coring and by research submersibles from  $>50$  localities on the Gulf slope (Fig. 1). The distribution of mapped gas hydrate sites corresponds to a late Pleistocene depocenter (Gallaway, Ganey-Curry, Li, & Buffler, 2000, Fig. 18). The minimum observed water depth of occurrence of gas hydrate in the Gulf of Mexico is  $\sim 440$  m and the maximum depth is  $>2400$  m (Sassen et al., 1999a). The thickness of the gas hydrate stability zone (GHSZ) increases with water depth. Calculations of stability, based on free gas with 90.4% methane, suggest that thickness of the GHSZ may be as much as  $\sim 450$  m at 540 m water depth, and  $>1$  km at 1930 m water depth in the Gulf (Milkov & Sassen, 2000).

Jolliet Field and the associated GC 185 seep mound (Figs. 2 and 3) offer a unique opportunity in which the geology and the hydrocarbon geochemistry may be synthesized to constrain the origin and timing of massive gas hydrate at a representative site on the upper Gulf slope. Conclusions from the Gulf study area cannot be generalized to encompass the origin of all massive deposits of gas hydrate, but can at least provide an analog and constrain models of gas hydrate origin in similar geologic settings. The objectives of the present study are to consider the relationship of massive gas hydrate at the sea floor at GC 185 to structural evolution of the area, multiple episodes of gas and oil migration that filled Jolliet Field, and the relative timing of gas migration and fault growth.

### 1.1. Geologic and geochemical setting

The main structural feature of the US Gulf area is the Gulf of Mexico Salt Basin, which formed during Late Triassic rifting. The basin was then floored by thick salt (Louann Formation) during Middle Jurassic marine incursions (Salvador, 1987). During the Tertiary, the structural style of the basin was strongly influenced by salt movement and faulting driven by rapid loading by siliclastic sediment. The Gulf continental slope, in particular, is affected by large salt thrusts pierced by salt withdrawal basins in which thick and relatively undeformed sediment accumulated (Worrall & Snelson, 1989).

The bulk of oil and gas in reservoirs beneath the central Gulf slope originated from prolific Mesozoic source rocks that began to generate oil in the recent geologic past beneath

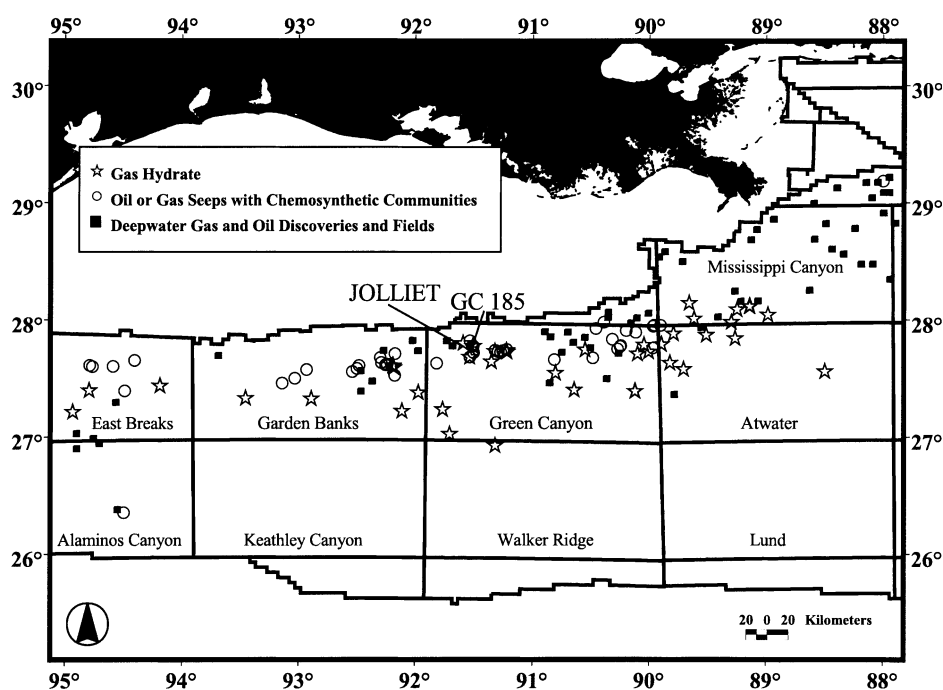


Fig. 1. Map showing the study area (Jolliet Field and the GC 185 gas vent and hydrate site) in context of other gas hydrate occurrences, seeps with chemosynthetic communities and subsurface hydrocarbon discoveries.

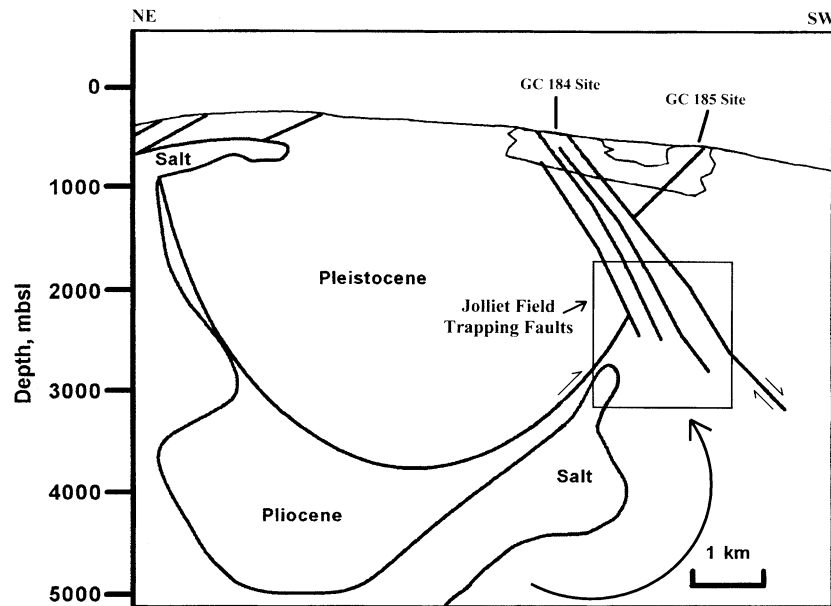


Fig. 2. Diagrammatic cross section (north east–south west) through Jolliet Field on GC 184 and the GC 185 gas hydrate site. The normal faults on GC 184 constitute the trap at Jolliet Field. Gray area associated with normal and antithetic faults indicates modeled subsurface morphology of thermogenic gas hydrate at the site based on measured vent gas properties from the GC 185 site (modified from Cook & D'Onfro, 1991; Milkov & Sassen, 2000). Long arrow indicates hypothesized active migration conduit along salt from the deep subsurface.

the thick sections of sediment deposited within the large salt withdrawal basins (e.g. Wenger, Goodoff, Gross, Harrison, & Hood, 1994). The actively moving allochthonous salt bodies, salt scars in the sediment from past movement of salt, and active faults provide efficient conduits of vertical migration to the sea floor along the rims of the salt withdrawal basins. Gas hydrate is concentrated at the rims of the salt withdrawal basins, where migration conduits to the sea floor are common, rather than within the relatively undeformed interiors of the salt withdrawal basins (Sassen et al., 1999a).

Production of oil and gas at Jolliet Field in the eastern portion of GC 184, is from Pleistocene turbidite reservoir sands at burial depths in the ~1.7 to 3.1 km range (Table 1 and Fig. 2). Rapid subsidence and filling of a salt withdrawal basin to the east in GC 185 occurred during the late Pleistocene–Holocene. Oil and gas is produced from structural traps sealed and compartmentalized by normal faults that attained their present configuration in the late Pleistocene–Holocene (Cook & D'Onfro, 1991). Shallow reservoirs at Jolliet Field contain oil altered by bacterial oxidation. The bacterial oxidation of oil in shallow reservoirs is shown by preferential depletion of *n*-alkanes and increased sulfur content (Kennicutt, Brooks, & Denoux, 1988; Sassen et al., 1993). Deep reservoirs contain oil that is not substantially altered by bacterial oxidation or other non-thermal processes (Thompson & Kennicutt, 1990). Although the shallow oil of Jolliet Field is affected by bacterial oxidation (Fig. 4), the overall degree of non-thermal alteration is relatively minor

when compared to that noted elsewhere in reservoirs of the Gulf shelf (e.g. Thompson & Kennicutt, 1990). The absence of major non-thermal alteration effects in Jolliet Field is consistent with geologically recent migration and accumulation of oil and gas.

The geology of the GC 185 salt withdrawal basin (Fig. 2) favors migration along active fault conduits. For example, the major growth faults on the eastern edge of Jolliet Field that intersect the sea floor on GC 184 (Fig. 2) are active sites of hydrocarbon venting (Brooks et al., 1984, 1986). The faults breached the sea floor and created persistent sea-floor scarps during late Pleistocene–Holocene time (Cook & D'Onfro, 1991). Although multiple sites are known in the area, the most significant site of ongoing gas venting occurs in western GC 185.

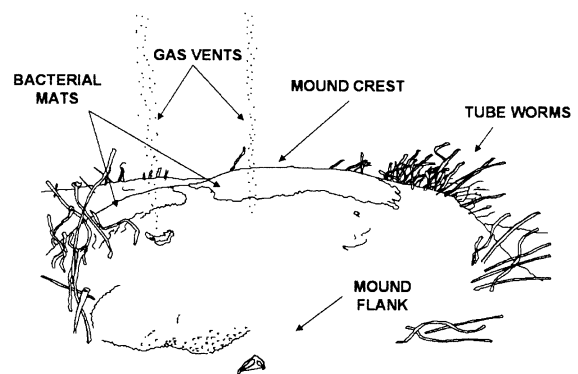


Fig. 3. Features of typical thermogenic gas vents associated with a gas hydrate mound (~2 m across) and chemosynthetic organisms (tube worms) at GC 185 (after Sassen et al., 1999b).

Table 1  
Molecular and isotopic properties of reservoir gas, vent gas, and gas hydrate

Sample location (well)	Sample (sand)	Depth (m)	$\delta^{13}\text{C } \text{C}_1$	$\delta\text{D } \text{C}_1$	% $\text{C}_1$	$\delta^{13}\text{C } \text{C}_2$	% $\text{C}_2$	$\delta^{13}\text{C } \text{C}_3$	% $\text{C}_3$	$\delta^{13}\text{C } i\text{-C}_4$	% $i\text{-C}_4$	$\delta^{13}\text{C } n\text{-C}_4$	% $n\text{-C}_4$	$\delta^{13}\text{C } i\text{-C}_5$	% $i\text{-C}_5$	$\delta^{13}\text{C } n\text{-C}_5$	% $n\text{-C}_5$
<i>Jolliet reservoir gas</i>																	
A8	Reservoir gas	2084	−45.8	−196	90.5	−29.5	6.0	−26.8	2.3	−27.5	0.3	−25.7	0.6		0.2		0.1
A3ST	Reservoir gas	3076	−44.9	−191	90.2	−29.2	6.5	−26.7	2.3	−27.3	0.3	−25.6	0.5		0.1		0.1
A14ST	Reservoir gas	2104	−46.9	−200	86.2	−30.2	8.3	−27.2	3.8	−27.8	0.5	−25.9	0.9		0.2		0.2
A13	Reservoir gas	2091	−47.0	−199	87.1	−29.9	7.5	−27.1	3.5	−27.7	0.5	−25.8	0.9		0.2		0.2
A3DST	Reservoir gas	2182	−46.5	−199	87.8	−29.7	7.1	−27.0	3.3	−27.6	0.5	−25.7	0.9		0.2		0.2
A19ST	Reservoir gas	2293	−46.1	−199	87.0	−29.5	7.7	−26.9	3.4	−27.7	0.5	−25.7	0.9		0.2		0.2
A18	Reservoir gas	2280	−48.7	−206	87.4	−30.0	6.9	−27.1	3.5	−27.8	0.6	−25.8	1.1		0.3		0.3
A14DST	Reservoir gas	1900	−48.1	−200	91.4	−30.0	5.1	−27.0	2.4	−27.7	0.4	−25.7	0.6		0.1		0.1
A2DST	Reservoir gas	2167	−48.7	−204	87.3	−30.1	7.4	−27.1	3.4	−27.7	0.5	−25.8	0.9		0.2		0.2
A9	Reservoir gas	2128	−47.1	−201	88.1	−29.7	7.3	−27.0	3.1	−27.6	0.5	−25.7	0.8		0.2		0.1
A1	Reservoir gas	2713	−45.9	−197	84.6	−29.6	8.9	−26.9	4.1	−27.7	0.7	−25.7	1.2		0.3		0.3
A15D	Reservoir gas	1855	−48.1	−199	89.8	−29.9	5.5	−27.0	2.8	−27.7	0.5	−25.6	0.9		0.3		0.2
A7	Reservoir gas	2610	−45.1	−194	85.7	−29.4	8.4	−26.8	3.7	−27.6	0.6	−25.6	1.0		0.3		0.3
A6	Reservoir gas	1740	−47.2	−206	86.6	−30.0	7.3	−27.3	3.8	−27.8	0.6	−25.9	1.1		0.3		0.3
A11	Reservoir gas	2310	−47.0	−200	87.3	−29.8	7.4	−27.0	3.7	−27.4	0.5	−25.8	0.7		0.2		0.2
A9DST	Reservoir gas	2035	−46.9	−200	86.5	−29.8	7.8	−27.1	3.6	−27.7	0.6	−25.8	1.0		0.3		0.2
Mean			−46.9	−200	87.7	−29.8	7.2	−27.0	3.3	−27.6	0.5	−25.7	0.9		0.2		0.2
<i>Green canyon 185 vent gas</i>																	
GC 185	Vent gas	~ 540	−46.0	−198	95.9	−29.7	2.4	−25.0	12		< 0.1	−22.6	0.3	−26.1	0.2		< 0.1
GC 185	Vent gas	~ 540	−44.1	−200	90.4	−30.2	4.5	−26.3	3.7	−27.9	0.6	−23.3	0.6	−26.1	0.2		< 0.1
GC 185	Vent gas	~ 540	−44.9	−171	93.4	−29.4	4.1	−26.2	1.5	−29.8	0.3	−24.4	0.5		0.3		< 0.1
Mean			−45.0	−190	93.2	−29.8	3.7	−25.8	2.1	−28.9	0.5	−23.4	0.5	−26.1	0.2		< 0.1
<i>Green canyon 185 vent gas</i>																	
GC 185	Gas hydrate	~ 540	−42.9	−163	83.1	−28.6	7.6	−24.9	8.1	−27.2	0.9	−22.1	0.2				
GC 185	Gas hydrate	~ 540	−42.2	−190	71.7	−29.0	10.6	−25.5	12.6	−27.6	2.6	−22.8	1.7	−26.2	0.8		
GC 185	Gas hydrate	~ 540	−43.5	−177	80.2	−29.7	9.4	−25.5	7.3	−27.9	1.6	−23.0	1.2	−24.8	0.3		
GC 185	Gas hydrate	~ 540	−42.5	−193	72.1	−29.2	12.4	−25.7	11.4	−27.8	2.3	−22.7	1.6	−24.7	0.3		
GC 185	Gas hydrate	~ 540	−42.9	−115	85.7	−28.6	6.3	−25.6	6.1	−26.8	1.1		0.8				
GC 185	Gas hydrate	~ 540	−43.6	−167	72.1	−29.8	10.5	−26.1	12.4	−28.1	2.5	−24.0	1.7		0.7		< 0.1
Mean			−42.9	−168	77.5	−29.2	9.5	−25.6	9.7	−27.6	1.8	−22.9	1.2	−25.2	0.5		

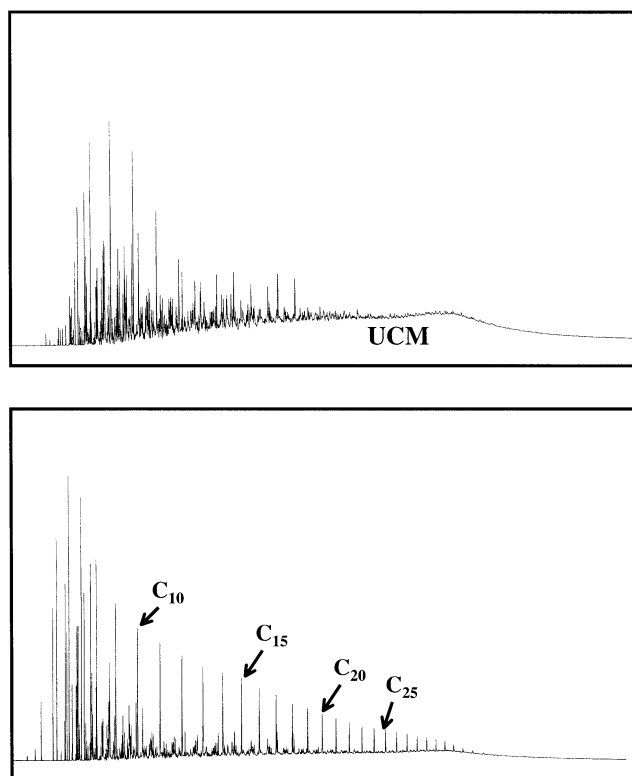


Fig. 4. Whole-oil chromatograms illustrating variation in bacterial oxidation of oil in Jolliet Field reservoirs. Bacterially altered oil at top (~1.7 km depth) shows selective loss of *n*-alkanes, whereas the unaltered oil below (~2.6 km depth) appears pristine.

The GC 185 vent site, at ~540 m water depth, has been extensively sampled by research submarine and by piston cores. The site (27°45.7'N and 91°30.5'W) is a seep mound that receives hydrocarbon gas along a fault that is antithetic to the growth faults that trap the oil and gas of Jolliet Field on GC 184 (Fig. 2). Thermogenic hydrocarbon gas vents copiously to the water column from gas hydrate mounds and other sea floor features (Sassen et al., 1999a,b). The GC 185 site comprises mounds of structure II gas hydrate that outcrop on the sea floor (MacDonald et al., 1994; Sassen et al., 1993), with the occasional occurrence of structure H hydrate (Sassen & MacDonald, 1994). The presence of structure II hydrate is generally consistent with crystallization from relatively unaltered vent gas at a high rate of flux (Sassen et al., 1999a). Mounds (Fig. 3) are draped by sulfide-oxidizing bacterial mats (*Beggiatoa*), deformed hemipelagic mud, bacterially oxidized crude oil and free gas, dispersed gas hydrate nodules, authigenic carbonate depleted in  $^{13}\text{C}$ , and  $\text{H}_2\text{S}$ . The site is also known as 'Bush Hill' because of its complex chemosynthetic communities including abundant clusters of tube worms (Fig. 3).

The GC 185 site has a distinct acoustic reflection signature as a consequence of near-pervasive hydrocarbon seepage in deformed sediment (Sager, Lee, MacDonald, & Schroeder, 1999). During the August 2000 cruise of the Research Vessel (RV) Edwin Link, single beam echo

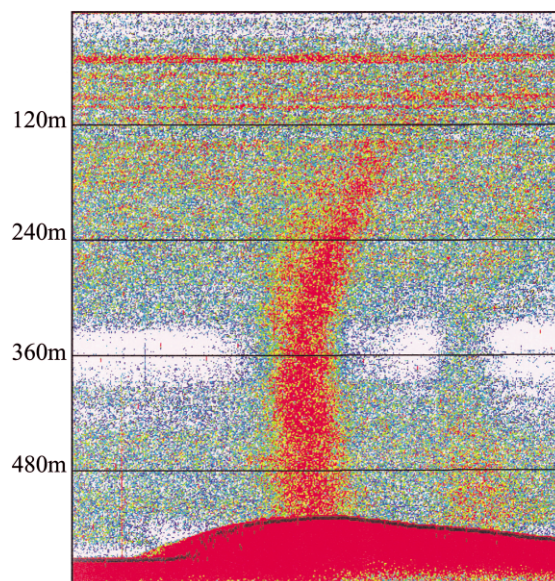


Fig. 5. Echo sounder record of a gas bubble train entering the water column from gas vents on the GC 185 gas hydrate site. The mound-like seep feature is at ~540 m water depth, and the plume rises close to the sea surface (see vertical scale). The base of the plume is estimated to be ~600 m across. Over the site, gas bubbles 2–3 cm across breach the sea surface, associated with oil, demonstrating direct transfer of thermogenic greenhouse gas to the atmosphere. Image courtesy of Jesse Hunt, US Minerals Management Service.

sounder records showed a gas plume with a base ~600 m wide extending from the mound at the sea floor to near the sea surface (Fig. 5). Gas bubbles with oil (~2–3 cm in diameter) were observed to breach the sea surface and create natural oil slicks. These observations are consistent with high flux of thermogenic greenhouse gas to the water column, and to the atmosphere (Hovland, Judd, & Burke, 1993; Judd et al., 1997). Natural gas bubbles and oil slicks at the sea surface have been persistently observed at this site for years (e.g. Kennicutt et al., 1988; Sassen, Sweet, Milkov, DeFreitas, & Kennicutt, 2001).

## 2. Methods

Reservoir gas was sampled at Jolliet Field in stainless steel pressure vessels. The basic approach to measuring of isotopic properties of hydrocarbon gas from reservoirs is described by Schoell, Jenden, Beeunas, and Coleman (1993). Isotopes of reservoir gas were determined using similar procedures by Isotech Laboratories. Seafloor vent gas in association with structure II gas hydrate was sampled from the GC 185 site using research submersibles, as described by Sassen et al. (1999b). Analytical procedures for  $\text{C}_1$ – $\text{C}_5$  gas chromatography (precision =  $\pm 5\%$ ), and measurement of isotopic properties of hydrocarbon gases from sediment are described by Sassen et al. (1999b), and are basically similar to those used on reservoir samples. The

$\delta^{13}\text{C}$  values are reported as parts per thousand (‰) relative to the PeeDee Belemnite standard (precision =  $\pm 0.2\text{‰}$ ), and the  $\delta\text{D}$  values are reported as ‰ relative to the Standard Mean Ocean Water (SMOW) standard (precision =  $\pm 5\text{‰}$ ).

### 3. Results

#### 3.1. Reservoir gas, vent gas, and gas hydrate

Molecular and isotopic properties of  $\text{C}_1$ – $\text{C}_5$  hydrocarbons from gas caps of the oil reservoirs of Jolliet Field ( $n = 16$ ) are shown in Table 1. Methane is the main component (mean = 87.7%), and relative abundance of higher hydrocarbons generally decreases with increasing carbon number (Table 1). The methane is largely thermogenic in origin with mean  $\delta^{13}\text{C}$  of  $-46.9\text{‰}$  and mean  $\delta\text{D}$  of  $-200\text{‰}$ . Mean relative abundance of  $\text{C}_{2+}$  hydrocarbons is in the order of ethane (7.2%), propane (3.3%), isobutane (0.5%), normal butane (0.9%), isopentane (0.2%), and normal pentane (0.2%). The mean  $\delta^{13}\text{C}$  values of ethane ( $-29.8\text{‰}$ ), propane ( $-27.0\text{‰}$ ), isobutane ( $-27.6\text{‰}$ ), and normal butane ( $-25.7\text{‰}$ ) show only small variation ( $<1\text{‰}$ ) within the samples (Table 1).

Some differences exist between the vent gas ( $n = 3$ ) and the reservoir gas (Table 1). Methane is the main hydrocarbon of the vent gas (mean = 93.2%). The methane of vent gas (mean  $\delta^{13}\text{C} = -45.0\text{‰}$  and mean  $\delta\text{D} = -190\text{‰}$ ) is enriched both in  $^{13}\text{C}$  and D relative to reservoir methane (Table 1). Relative abundance of other hydrocarbons decreases with increasing carbon number. Mean relative abundance of the  $\text{C}_{2+}$  hydrocarbons is in the order of ethane (3.7%), propane (2.1%), isobutane (0.5%), normal butane (0.5%), isopentane (0.2%), and normal pentane ( $<0.1\%$ ). Compared to reservoir gas, methane is more abundant in the vent gas, whereas ethane, propane, and butanes are less abundant in the vent gas (Table 1). The mean  $\delta^{13}\text{C}$  values of ethane ( $-29.8\text{‰}$ ), propane ( $-25.8\text{‰}$ ), isobutane ( $-28.9\text{‰}$ ), and normal butane ( $-23.4\text{‰}$ ) are generally similar to reservoir gas, within  $\sim 2\text{‰}$  (Table 1). The mean  $\delta^{13}\text{C}$  values of ethane in vent and reservoir gas ( $-29.8\text{‰}$ ) are identical, but the mean  $\delta^{13}\text{C}$  values of both propane and normal butane in vent gas are slightly enriched in  $^{13}\text{C}$  when compared to reservoir gas (Table 1).

Gas hydrate ( $n = 6$ ) has a dissimilar molecular composition when compared to vent gas. Methane occurs in lower percentage (mean = 77.5%) than in vent gas. Hydrate-bound methane from GC 185 is enriched in  $^{13}\text{C}$  (mean =  $-42.9\text{‰}$ ) and D (mean =  $-168\text{‰}$ ) relative to vent gas (Table 1). Mean relative abundance of the  $\text{C}_{2+}$  hydrocarbons of hydrate are in the order of propane (9.7%), ethane (9.2%), isobutane (1.8%), normal butane (1.2%), isopentane (0.5%), and normal pentane ( $<0.1\%$ ). The mean  $\delta^{13}\text{C}$  values of hydrate bound ethane ( $-29.2\text{‰}$ ), propane ( $-25.6\text{‰}$ ), isobutane ( $-27.6\text{‰}$ ), normal butane ( $-22.9\text{‰}$ ), and mean  $\delta^{13}\text{C}$  of the pentanes is within  $<1\text{‰}$  of the vent gas (Table 1).

### 4. Discussion

Molecular distributions of reservoir gas from Jolliet Field are typical of thermogenic gas from subsurface reservoirs containing relatively unaltered crude oil (e.g. James & Burns, 1984). Bacterial methane oxidation is associated with a kinetic isotope effect;  $^{12}\text{C}$  and  $^1\text{H}$  are preferentially used from the methane reactant pool, resulting in enrichment of  $^{13}\text{C}$  and D in the residual methane (Coleman, Risatti, & Schoel, 1981). The  $\delta\text{D}$  of reservoir methane from Jolliet Field is in the narrow range from  $-191$  to  $-206\text{‰}$ . Because  $\delta\text{D}$  is particularly sensitive to kinetic isotope effects from bacterial oxidation (Coleman et al., 1981), the narrow range of methane  $\delta\text{D}$  ( $\sim 16\text{‰}$ ) is not consistent with meaningful bacterial oxidation effects. The small variation in the isotopic properties of  $\text{C}_{2+}$  reservoir gases is not consistent with meaningful kinetic isotope effects from bacterial oxidation.

Bacterial oxidation of hydrocarbon gas usually precedes or accompanies bacterial oxidation of crude oil in reservoirs (e.g. Winters & Williams, 1969). If oil in shallow reservoirs displays compositional variation from bacterial oxidation (Kennicutt et al., 1988; Sassen et al., 1993), it is difficult to explain why the isotopic properties of the gas are so uniform in Jolliet Field. One hypothesis that satisfies the observations is that a late charge of hydrocarbon gas entered Jolliet Field in the recent geologic past, after an earlier filling episode and the alteration of oil in shallow reservoirs by bacterial oxidation.

Kennicutt et al. (1988) first established a geochemical correlation between reservoir gas from Jolliet Field and seep gas from the GC 185 site. The data of the present study allows us to confirm previous work, and to better compare molecular and isotopic properties of reservoir and vent gas in terms of processes related to either gas hydrate crystallization or to its decomposition. Such data on gas hydrate stability are important in geologic context, and may help explain why massive gas hydrate vein-fillings occur at the GC 185 site.

The hypothesized late gas charge may have initiated leakage from Jolliet Field along the active fault conduits that compartmentalize the reservoirs of the field (Cook & D'Onfro, 1991), permitting rapid vertical migration to the sea floor. The GC 185 vent gas site occupies the sea-floor expression of an active fault antithetic to the major growth fault complex at the eastern boundary of Jolliet Field (Cook & D'Onfro, 1991). Loss of gas from Jolliet Field and vertical migration along faults is geologically reasonable in this dynamic structural setting with ongoing deformation of salt (Fig. 2). Some fraction of gas could be from active migration conduits not related to Jolliet Field, but this hypothesis is more difficult to prove.

The molecular distribution of the vent gas is consistent with stripping  $\text{C}_{2+}$  hydrate-forming molecules originally present in vent gas as a consequence of active gas hydrate crystallization during migration in the subsurface (Table 1). Structure II gas hydrate from the site is rich in ethane,

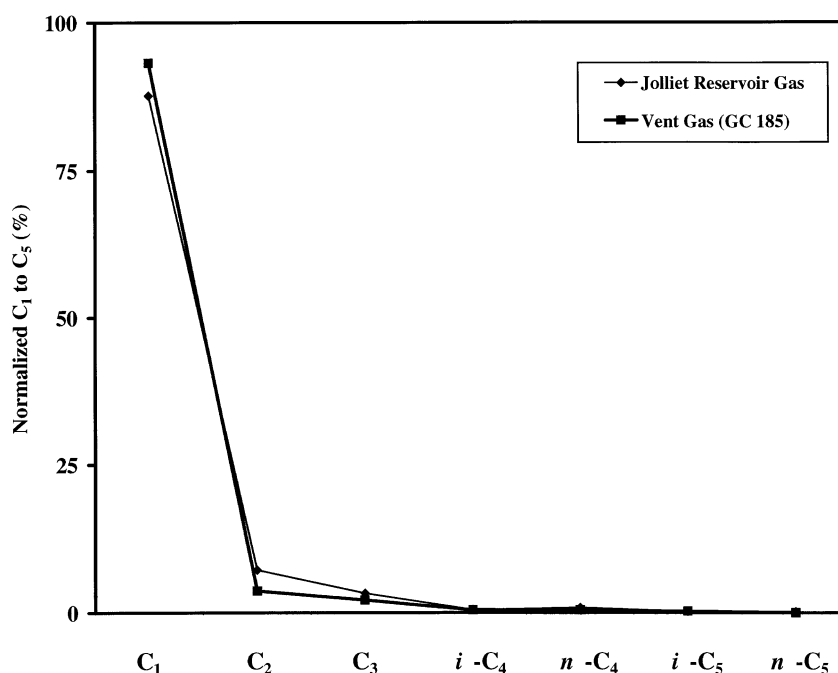


Fig. 6. Mean C<sub>2</sub>–C<sub>5</sub> molecular compositions of gas from Jolliet Field compared to vent gas from GC 185. The reservoir gas appears unaltered, whereas vent gas shows stripping of hydrate-forming ethane, propane, and butanes.

propane, and butanes. If hydrate crystallization is quantitatively significant at present, the vent gas would show selective stripping of the hydrocarbons that characterize structure II gas hydrate. This is observed. The vent gas shows increased methane and decreased relative abundance of hydrate-forming hydrocarbons such as ethane, propane, and butanes when compared to reservoir gas (Fig. 6). An alternate hypothesis is also examined. If gas hydrate decomposition is quantitatively significant at present, then the molecular properties of gas venting from hydrate-bearing sediment should be consistent with decomposition of the gas hydrate (Sassen et al., 2001). The C<sub>1</sub>–C<sub>5</sub> hydrocarbon distributions of gas from decomposition of gas hydrate would be rich in diagnostic hydrate forming molecules such as ethane, propane, and butanes. This is not observed (Fig. 6). The vent gas displays no meaningful evidence of gas hydrate decomposition. Molecular evidence of gas-stripping by gas hydrate crystallization and a lack of evidence of gas hydrate decomposition are consistent with the suggestion that gas hydrate at present is stable and is perhaps undergoing net accumulation at the GC 185 site (Sassen et al., 2001).

The isotopic correlation of the gas hydrate to the vent gas at Bush Hill is important, because if the vent gas is the result of ongoing loss from Jolliet Field, then the massive gas hydrate shares the same origin. If gas from the deep subsurface did not vent prolifically at present, then we would not expect to observe the large gas plume or the massive gas-hydrate fabric at GC 185. Although there is strong molecular fractionation during gas hydrate crystallization, which favors hydrate-forming molecules (such as ethane, propane, and butanes), there is no evidence of isotopic frac-

tionation of hydrocarbons during crystallization (e.g. Brooks et al., 1986). Isotopic properties of hydrocarbons are thus useful in correlating the vent gas and the associated gas hydrate. The enrichment in <sup>13</sup>C and D is interpreted to be the result of preferential bacterial oxidation of hydrate-bound methane with increasing time of exposure at the sea floor (Sassen et al., 1999b). However, the C<sub>2+</sub> isotopic properties of the gas hydrate provide a strong isotopic correlation (Fig. 7), and substantiate that the gas hydrate crystallized from the associated vent gas at GC 185 (Kennicutt et al., 1988; Sassen et al., 1999b).

The sediment fabric at the GC 185 site is distinctive because of the outcropping gas hydrate mounds and because of massive vein filling by gas hydrate, which are consistent with copious gas flux. Veins of gas hydrate are sometimes >40 cm in thickness, and thus occupy a considerable volume of total sediment. Sassen et al. (1999a) suggest a mechanism of vein filling. Gas pressure appears to open tension fractures along sub-horizontal planes of weakness in the mud. These tension fractures fill rapidly with gas hydrate, which props them open, and veins probably continue to expand by pressure of crystallization. Sediment is highly deformed in association with vein fillings and angular clasts of gas hydrate are observed suspended in mud matrix. Sea floor experiments are consistent with the suggested mechanism of vein formation in that gas hydrate crystallization can be induced to occur within seconds or minutes of mixing natural gas and water at the GC 185 site (Sassen & MacDonald, 1997). This observation is consistent with the model suggested by Clennell, Hovland, Booth, Henry, and Winters (1999).

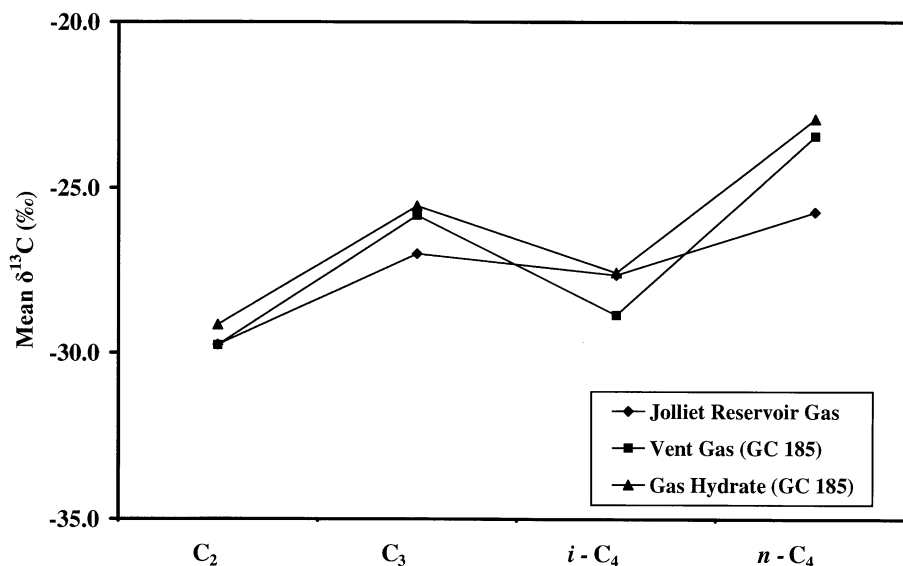


Fig. 7. Mean  $\delta^{13}\text{C}$  of  $\text{C}_1$ – $\text{C}_4$  hydrocarbons from Jolliet Field reservoirs, GC 185 vent gas and gas hydrate. The similarity in isotopic properties confirms the earlier correlations between the field, the vent, and gas hydrate.

## 5. Conclusions and synthesis

To study the Gulf slope is to study the dynamic evolution of a leaky oil and gas province. The GC 185 site is adjacent to Jolliet Field (GC 184), which contains gas and oil in fault traps (1.7–3.1 km depth) that formed during the late Pleistocene–Holocene (Fig. 2). Some shallow reservoir oil displays alteration effects from bacterial oxidation, but the  $\text{C}_1$ – $\text{C}_5$  reservoir gas is relatively uniform and unaltered by bacterial oxidation throughout the fields (Table 1). Reservoirs cannot have filled until the fault traps formed during the late Pleistocene–Holocene (Cook & D’Onfro, 1991), defining a short span of geologic time within which the field filled and then reached a spill point or experienced seal failure. The observed lack of reservoir gas alteration is consistent with the geologically recent and ongoing charge to Jolliet Field of disassociated gas from the subsurface hydrocarbon system.

Vertical migration of gas along faults near the field is manifested by gas hydrate mounds, massive vein-filling gas hydrate, a large gas plume which extends from sea floor vents (~540 m water depth) to the sea surface, and by fresh natural oil slicks. The new observation of the large size of the gas plume (Fig. 5) provides unambiguous evidence of high gas flux to the GC 185 site. High gas flux appears necessary to form massive gas hydrate vein-fillings in hemipelagic mud (Ginsburg & Soloviev, 1998; Clennell et al., 1999; Sassen et al., 1999a). In contrast, areas with disseminated gas hydrate filling pore space are here assumed to be often associated with little or no hydrocarbon gas flux. This is because methane is primarily derived from the activities of indigenous methanogenic bacteria (Whelan et al., 1986).

The isotopic properties of  $\text{C}_1$ – $\text{C}_5$  gas from reservoirs,

vents, and gas hydrate correlate closely. More importantly to the present work, vent gas shows molecular evidence of stripping of hydrate-forming hydrocarbons in the subsurface. There is no molecular evidence of meaningful decomposition of gas hydrate (Sassen et al., 2001). The bulk of gas hydrate at GC 185 thus appears to be stable or perhaps increasing in volume at present. The massive accumulation of gas hydrate at the GC 185 site can be largely attributed to the geologically recent gas migration from the deep subsurface to Jolliet Field, and simultaneous activation of efficient fault conduits for gas migration from depth to the sea floor. Multiple charge episodes occurred. However, the radiometric measurements of Aharon, Schwarcz, and Roberts (1997) on authigenic carbonate suggest that the most recent phase of seepage at GC 185 commenced near the close of the Pleistocene and continues at present (12.3–0.0 ka). The timing of authigenic carbonate may define the timing of the late gas migration and gas loss from Jolliet Field, as well as the formation of the GC 185 site much as it is seen today.

Late gas migration appears a common process affecting many reservoirs in the Gulf of Mexico (e.g. Thompson & Kennicutt, 1990). The association of oil and gas fields with gas hydrate across much of the upper Gulf slope roughly corresponds to a large Pleistocene depocenter defined by Galloway et al. (2000). Accumulation of sediment in the depocenter may have deformed salt, breaching seals and causing remigration of gas from former traps downdip. Thus, the dynamic processes that gave rise to the late charge of thermogenic gas at Jolliet Field, fault activation, and the massive vein-filling gas hydrate near Jolliet Field may be generalized to explain the distribution of gas hydrate across a large area of the upper Gulf slope (Fig. 1).

It is useful to consider gas hydrate from a three dimensional



perspective (Fig. 2). Only a thin skin of gas hydrate outcrop appears transiently stable at GC 185, probably because of episodic changes in seawater temperature (MacDonald et al., 1994; Roberts, Wiseman, Hooper, & Humphrey, 1999). Most gas hydrate at GC 185, however, buried at depth in sediment >2 m, appears to be insulated from short-term variability in seawater temperature (Milkov, Sassen, Novikova, & Mikhailov, 2000). Buried structure II gas hydrate could be stable at depths as much as ~450 m in sediment at GC 185 (Milkov & Sassen, 2000). The lack of molecular evidence of gas hydrate decomposition in gas venting from hydrate-bearing sediment suggests that the decomposition process is not quantitatively significant at present. Models of climate change that involve sudden decomposition of gas hydrate have been presented, based only on indirect evidence (Bains et al., 1999; Dickens et al., 1995, 1997; MacDonald, 1990; Max et al., 1999). Given advances in our understanding of gas hydrate geochemistry, is prudent to constrain such models in future using geochemical data from the rock record wherever possible.

The implication of massive and vertically extensive gas hydrate at GC 185 to future exploitation as a source of clean burning energy is clear. A concentrated resource is potentially more economic than a disseminated resource in the deep sea (Glasby, 2000; Hovland, 2000). The large plume of thermogenic gas in the water column at GC 185 may be significant with respect to climate issues, perhaps at present more relevant than the gas hydrate itself. Given the unambiguous empirical evidence of strong flux of thermogenic gas to the water column and the atmosphere from venting in the Gulf of Mexico, it may be prudent to include thermogenic methane and other hydrocarbons in the budget of greenhouse gases in models of climate change. In the geologic past, synchronous oil and gas generation could have occurred globally on continental margins, releasing large volumes of thermogenic greenhouse gas in relatively short spans of geologic time. The exclusive generalization that bacterial methane has been the most significant hydrocarbon greenhouse gas over long spans of geologic time should be given further scrutiny as it may be an oversimplification.

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