

Geology and Geochemistry of Gas Hydrates, Central Gulf of Mexico Continental Slope

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ABSTRACT

The Gulf slope is unique in that larger volumes of gas hydrate are concentrated in smaller volumes of sediment near the sea floor than in any other known basinal setting. Gas hydrates are ice-like crystalline solids (minerals) in which hydrocarbon and nonhydrocarbon gases are held within rigid cages of water molecules. Most thermogenic gas hydrate occurrences in the central slope are linked to vertical migration of oil and gas from deep Upper Jurassic source rock facies. Migration focuses the formation of thermogenic gas hydrates at the edges of actively charged salt-withdrawal mini-basins, over salt ridges, and near the Sigsbee Escarpment. Bacterial methane hydrates also occur, and are differentiated from thermogenic gas hydrates by molecular and isotopic properties. Isotopic fractionation of hydrocarbons does not occur during gas hydrate crystallization from vent gas. The detailed isotopic properties of individual hydrocarbons from gas hydrate samples could provide insight to subsurface accumulations of either thermogenic hydrocarbons or bacterial methane. At high pressures and low temperatures of the deep sea floor, rapid crystallization of gas hydrates creates sea-floor mounds and tabular vein-fillings at vent sites, deforming hemipelagic sediments. Gas hydrates exist in a relatively unstable environment at the sea floor, and hydrate decomposition further contributes to sediment instability. The Gulf slope is atypically prone to gas hydrate hazards.

INTRODUCTION

Gas hydrates are abundant at the sea floor in the vicinity of major oil and gas fields and along potential pipeline routes in the central Gulf of Mexico continental slope, and thus impact the energy industry. Experiments from research submarines show gas hydrates crystallize rapidly on the deep sea floor simply given the presence of water and hydrocarbon gases at high pressures and low temperatures (Sassen and MacDonald, 1997). Basic knowledge of gas hydrate geology and geochemistry is important to continued effective and safe exploration and exploitation on the Gulf slope, as well as in other deep water oil and gas provinces globally.

Gas hydrates are ice-like crystalline minerals in which hydrocarbon and nonhydrocarbon gases are held within rigid cages of water molecules. Structure I gas hydrate has a body-centered cubic lattice, structure II hydrate has a diamond lattice, and structure H hydrate has a hexagonal lattice (Sloan, 1998). Structure I hydrate, which is the most abundant gas hydrate type globally, is usually dominated by bacterial methane and also contains gases such as CO₂ formed by bacterial activity (Kvenvolden, 1993, 1995).

Other gas hydrates of the Gulf slope contain thermogenic (generally oil-related) gases migrated to shallow sediments from deep hot subsurface hydrocarbon systems. Structure II gas hydrate includes C₁-C₄ hydrocarbons (methane through isobutane), and structure H hydrate includes C₁-C₅ hydrocarbons (methane through isopentane)

(Sassen and MacDonald, 1994). Thermogenic gas hydrates also contain CO₂ formed either in the deep subsurface hydrocarbon system, or by low-temperature bacterial activity (Sassen et al., 1998). The Gulf of Mexico slope is unique in that gas hydrates with three crystal structures exist (Kvenvolden, 1993, 1995; Brooks et al., 1984, 1986; Booth et al., 1996; Sassen and MacDonald, 1994, 1997; Sassen et al., 1998). Each gas hydrate crystal structure has a different range of stability regimes, compositions, and physical properties (Sloan, 1998). Complex thermogenic gas hydrates (structure II and H) are stable at lower pressures and higher temperatures than methane gas hydrates (structure I).

One median estimate of the volume of methane in shallow gas hydrate across the entire Gulf slope is 38 thousand trillion cubic feet (Collett and Kruskraa, 1998). At some time in the future gas hydrates will be a major resource, but the impact of gas hydrates on deep water exploration and exploitation of conventional subsurface reserves is immediate. Objectives of the present paper are to document the significance of gas hydrates of the central Gulf slope with respect to (1) geologic setting and relation to selected oil and gas fields, (2) new insights to gas hydrate geochemistry, and (3) potential effects of hydrate-related sediment instability as a sea-floor hazard.

GEOLOGIC SETTING

A large structural complex was formed during the Tertiary across much of the central Gulf of Mexico continental slope by syndepositional loading of an unstable salt substrate. The deep interiors of resultant salt-withdrawal basins contain recently mature source rock facies, generating crude oil and gas that migrates vertically along salt and normal fault conduits to traps. Sands accumulated in many of the salt withdrawal basins, providing shallow reservoir facies (Pratson and Ryan, 1994). In the geologically dynamic setting of the Gulf slope, trapping efficiency is poor, and the bulk of hydrocarbons from the subsurface hydrocarbon system are ultimately dispersed in the subsurface or lost at the sea floor. Analyses of oil biomarkers from reservoir and seep samples are consistent with an origin of thermogenic gas hydrates from Upper Jurassic (Tithonian) source rock facies as defined by Gross et al. (1995) across much of the central slope.

Gas hydrates are so abundant in the leaky central Gulf slope because free hydrocarbon gases rapidly vent into a sea-floor temperature and pressure regime in which the gas hydrate is stable. Gas hydrate occurrences are mapped along a large belt spanning much of the central Gulf slope that contains sea-floor gas vents, oil seeps, chemosynthetic communities, and subsurface oil and gas fields (Fig. 1; Roberts and Aharon, 1994; Sassen et al., 1994; MacDonald et al., 1996; Sassen et al., 1998). Although bacterial gas hydrates are widely distributed, our Green Canyon and Mississippi Canyon study areas shown in Figure 1 are characterized by multiple localities of thermogenic gas hydrates. Most gas hydrates have been found at shallow depths in sediment (<6 m) by piston coring at water depths in the approximate 400 to 2,000 meter range (Fig. 2). Calculations using Sloan's (1998) model show that the maximum preservation

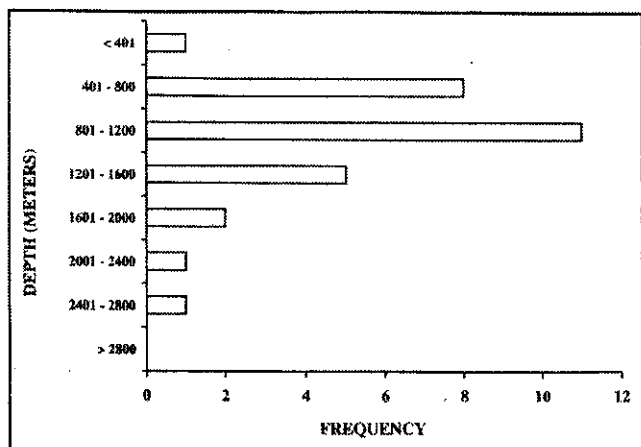


Figure 2. Preliminary data on water depth distribution of gas hydrates recovered by piston cores on the Gulf slope

of vent methane is -44.9% PDB and the δD is -171% SMOW; the $\delta^{13}C$ of individual C_2 - C_4 hydrocarbons from vent gas is also shown in Table 1. The $\delta^{13}C$ of thermogenic CO_2 from vent gas is $+13.2\%$ PDB.

Mean sea-bottom pressure is about 5,400 kPa and water temperature is about $7^\circ C$ (MacDonald et al., 1994), within the predicted stability range of structure II and structure H gas hydrates (Sloan and Mehta, personal communication), both of which coexist at the site (Sassen and MacDonald, 1994). Gas hydrate crystallizes from the vent gas rapidly during sea floor experiments from research submarine platforms under these conditions (Sassen and MacDonald, 1997). Research submersible dives have revealed a cluster of gas hydrate mounds, each approximately 1-3 meters across, with white to orange gas hydrate exposed to sea water, where it is easily sampled (Sassen et al., 1998).

Structure II gas hydrate is abundant at Bush Hill, and shows some variation in composition and isotopic properties across the site, and from year to year. Vein-filling gas hydrate is typically found at sites with rapid fluid flow (Ginsburg and Soloviev, 1994; Ginsburg, 1998). Vein-filling gas hydrates were collected at a vent site in 1998 (Fig. 3) using the JSL research submarine. The C_1 - C_5 molecular compositions of vent gases and gas hydrates are different (Table 1 and Fig. 4). The change in phase from vent gas to solid structure II gas hydrate involves molecular fractionation that favors hydrocarbon molecules of appropriate sizes (Sloan, 1998). Relative to vent gas from which it precipitated, hydrate-bound methane occurs in lower percentage (72.1%), and the C_2 , C_3 , and i - C_4 hydrocarbons occur in substantially higher percentages. The molecular composition is diagnostic of structure II gas hydrate, which has been confirmed at this site by solid-state nuclear magnetic resonance (Sassen and MacDonald, 1997).

Meaningful isotopic fractionation does not occur during gas hydrate formation as a consequence of crystallization itself (Brooks et al., 1986; Kennicutt et al., 1988; Sassen et al., 1998). The $\delta^{13}C$ of the Bush Hill hydrate methane is -43.6% PDB and the δD is -167% SMOW, similar to that of the vent gas. The $\delta^{13}C$ values of C_2 - C_4 hydrocarbons from the gas hydrates also closely overlap the vent gases (Fig. 4). The $\delta^{13}C$ of CO_2 from gas hydrate is $+17.5\%$ PDB, a value similar to that of the vent gas.

The similar isotopic properties of the 1998 gas hydrate samples from Bush Hill are consistent with a recently crystallized and relatively unaltered structure II gas hydrate. However, given long expo-

sure at the sea floor, other gas hydrates sampled at this locality in previous years show a wider range of molecular and isotopic properties (Sassen et al., 1998). Isotopic properties of hydrate-bound methane and CO_2 are sometimes altered by bacterial oxidation effects during sea floor exposure, whereas C_2 - C_4 hydrocarbons appear relatively unaltered (Sassen et al., 1998).

Ursa Field in Mississippi Canyon

A sea-floor mound (>1 km across) with widespread high amplitudes overlies a shallow salt body at the boundary of Mississippi Canyon (MC) blocks 852 and 853. This mound could be one of the more volumetrically significant gas hydrate accumulations in the central Gulf. Gas hydrates are abundant at a vent site in MC 853 ($28^\circ 7.4' N$, $89^\circ 8.2' W$) in 1060 m water depth (Fig. 1). The site is near the edge of the salt withdrawal basin in which Ursa Field was delineated by exploration wells in MC 854 and MC 810. The reservoir section of Ursa is overlain by thick, relatively unfaulted sediments. A lack of hydrocarbon seeps directly over Ursa Field suggests that the unfaulted section is relatively impermeable. Part of the subregional fluid flow is channeled laterally along sand carrier beds out of the basin to a major fluid flow release point over the shallow salt on MC 852 and 853.

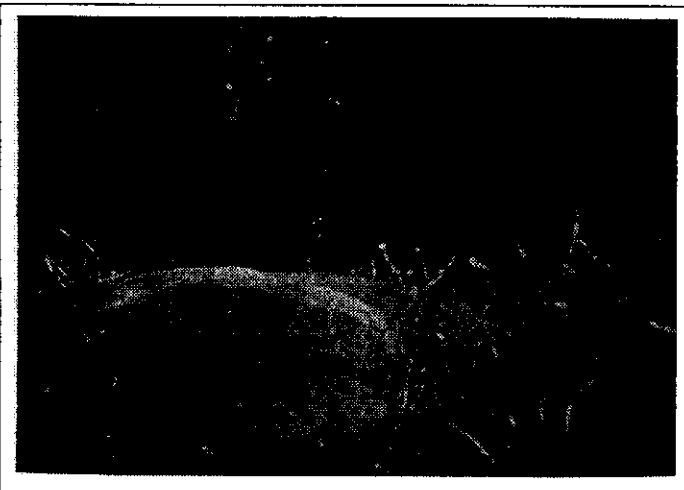


Figure 3. Example of outcropping gas hydrate at sea floor, Green Canyon Block 185. The mound is >1 meter across, and is surrounded by chemosynthetic tube worms. Note gas venting from the gas hydrate mound to the water column.

Piston cores recovered structure II gas hydrate samples at MC 852 and 853 sites in 1991, 1994, 1995, and 1998, suggesting that gas hydrates are abundant and persistent at the site. The gas hydrates were recovered in association with high concentrations of biodegraded crude oil. Crude oil of Ursa Field is likely from an Upper Jurassic source rock facies (see Gross et al., 1995). Whether or not complex chemosynthetic communities occur at this deep site is unknown.

Vein-filling structure II gas hydrate from the MC 853 site collected in 1998 by piston core contains 76.2% methane, whereas C_2 (9.0%) and C_3 (9.6%) occur in roughly equal percentages, and i - C_4 is present in lesser percentage (4.7%). Other hydrocarbons occur in small percentages (Table 1 and Fig. 4). The $\delta^{13}C$ of methane is -44.7% PDB and the δD is -161% SMOW. With the exception of C_3 ,

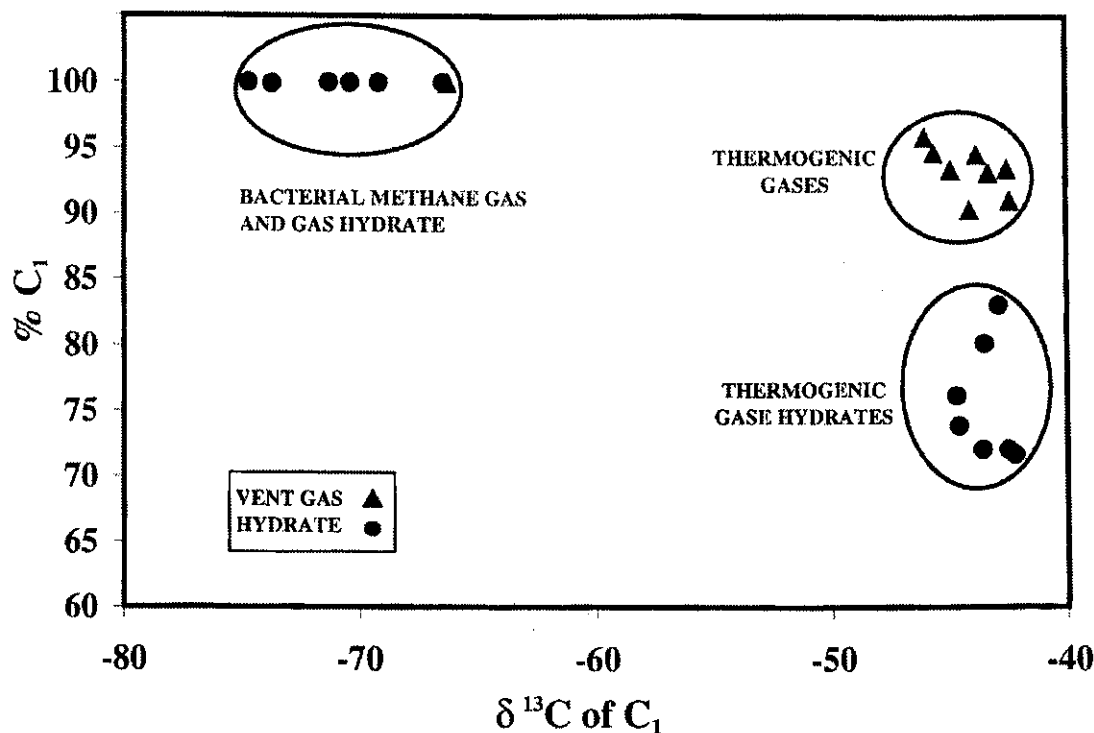


Figure 5. Diagram showing $\delta^{13}\text{C}$ of methane versus normalized per cent of methane to illustrate differences between thermogenic and bacterial methane vent gases and gas hydrates. (Table 1; Brooks et al., 1984, 1996; Sassen and MacDonald, 1997; Sassen et al., 1998).

EXPLORATION SIGNIFICANCE

Although the value of thermogenic gas hydrate as a proximity indicator to areas with known subsurface discoveries of oil is obvious (Fig. 1), our results suggest that gas hydrate geochemistry nevertheless has been underutilized as a tool in hydrocarbon exploration. Clayton (1991) emphasizes the value of carbon isotope measurements of hydrocarbon gases as a thermal maturity indicator. Measurements of (1) molecular composition, (2) $\delta^{13}\text{C}$ and δD of methane, and (3) $\delta^{13}\text{C}$ of individual $\text{C}_2\text{-C}_3$ hydrocarbons of thermogenic gas hydrates could provide information on subsurface hydrocarbon systems to supplement standard analyses of oil seep samples to include oil biomarkers.

The relatively unaltered thermogenic hydrocarbons of gas hydrates sampled at both GC 185 and MC 853 show isotopic similarities consistent with an origin from the same or similar Upper Jurassic source facies at a broadly similar level of thermal maturity. Moreover, as shown in Figure 5, there appears to be similarly small isotopic variation in thermogenic gas hydrates from additional sites where Upper Jurassic source facies are thought to be volumetrically significant. The isotopes of hydrate-bound thermogenic hydrocarbon gases have not been previously suggested as useful for purposes of geochemical correlation, and this could be a focus of future research. Recognition of subtle bacterial alteration effects on the isotopic properties of hydrate-bound hydrocarbons is important in interpretation of such data (Sassen et al., 1998).

Composition and isotopic properties easily differentiate bacterial methane gas hydrate from thermogenic gas hydrate (Fig. 5). The origin of bacterial methane accumulations in the subsurface merits further study. Isotopic properties suggest that the Atwater Valley methane hydrates we sampled are derived from bacterial CO_2 reduction by methanogens, an origin shared by bacterial methane accumulations in the deep subsurface of the Gulf. Some bacterial methane in

seeps and in gas hydrates could be the result of leakage from subsurface reservoirs, providing a new exploration tool for bacterial gas accumulations in the deep waters of the Gulf and elsewhere.

SEDIMENT INSTABILITY

Since the energy industry has shifted into deeper water, oil and gas exploration and production is now occurring in the realm of gas hydrates. Rapid crystallization or decomposition of gas hydrate masses deforms shallow hemipelagic sediments episodically. Where gas hydrate is abundant at the sea-floor, sediment instability could directly impact pipelines and other sea-floor infrastructure. Moreover, pipeline plugging and damage by gas hydrates has long been recognized as a significant problem (Sloan, 1998). Another potential problem is crystallization of gas hydrate in drilling mud of deep water wells, altering mud properties. The Gulf slope is thus unusually prone to gas hydrate hazards.

Sudden increases in gas pressure along deep normal or antithetic faults in shallow hemipelagic muds appear to open tension fractures along sub-horizontal planes of weakness in hemipelagic muds. These fractures fill with gas hydrate, and probably expand by pressure of crystallization. Experimental precipitation of gas hydrates at the sea floor occurs rapidly (on a scale of seconds or minutes), particularly at the interface between free gas and ambient seawater (Sassen and MacDonald, 1997).

Complex gas hydrate and sediment fabrics are observed from research submersibles and in piston cores that are best explained by multiple episodes of gas pressure increases, tensional deformation, and rapid crystallization in open spaces. Visual observations of gas hydrates suggest that early-formed vein-fillings can later undergo brittle fracture accompanied by soft-sediment deformation. Evidence includes rotated angular blocks of gas hydrate and smaller brecciated clasts of gas hydrate suspended in sediment, as well as

Sample	Location	Water Depth	C ₁	δD C ₁	C ₂	C ₃	<i>i</i> -C ₄	<i>n</i> -C ₄	<i>n</i> -C ₅	<i>i</i> -C ₅	δ ¹³ C CO ₂
Vent Gas	Green Canyon	540 m	93.4%	(-44.9)	4.1%	1.5%	0.3%	0.5%	<0.1%	0.3%	(+13.2)
Gas Hydrate	Green Canyon	540 m	72.1%	(-43.6)	10.5%	12.4%	2.5%	1.7%	<0.1%	0.7%	(+17.5)
Gas hydrate	Mississippi Canyon	1060 m	76.2%	(-44.7)	9.0%	9.6%	4.7%	<0.1%	<0.1%	<0.1%	
Gas Hydrate	Atwater Valley	1076 m	99.9%	(-74.7)	0.1%						
Gas Hydrate	Atwater Valley	1230 m	100.0%	(-73.7)							

Table 1. Molecular and isotopic properties of recently collected (1998) vent gas and gas hydrate samples from Green Canyon, Mississippi Canyon, and Atwater Valley areas. Normalized percentages of C₁-C₅ hydrocarbons are shown, and isotope values are given in parentheses beneath the percentage value. Carbon isotopes (δ¹³C) are reported as parts per mil (‰) relative the PDB (Pee Dee belemnite) standard, and hydrogen isotopes (δD) as ‰ relative to the SMOW (standard mean ocean water) standard.

- Rice, D.D., and C.N. Threlkeld, 1990, Bacterial gas analyses from offshore Gulf of Mexico: GCSSEPM Foundation, Ninth Annual Research Conference Proceedings, p. 367-371.
- Roberts, H.H., and P. Aharon, 1994, Hydrocarbon-derived carbonate buildups of the northern Gulf of Mexico slope: A review of submersible investigations: *Geo-Marine Letters*, v.14, p.135-148.
- Roberts, H.H., and R.S. Carney, 1997, Evidence of episodic fluid, gas, and sediment venting on the northern Gulf of Mexico continental slope: *Economic Geology*, v. 92, p. 863-879.
- Sassen, R., and I.R. MacDonald, 1994, Evidence of structure H hydrate, Gulf of Mexico continental slope: *Organic Geochemistry*, v. 23, p. 1029-1032.
- Sassen, R., I.R. MacDonald, A.G. Requejo, N.L. Guinasso, Jr., M.C. Kennicutt II, S.T. Sweet, and J.M. Brooks, 1994, Organic geochemistry of sediments from chemosynthetic communities, Gulf of Mexico slope: *Geo-Marine Letters*, v. 14, p. 110-119.
- Sassen, R., and I.R. MacDonald, 1997, Hydrocarbons of experimental and natural gas hydrates, Gulf of Mexico continental slope: *Organic Geochemistry*: v. 26, p. 289-293.
- Sassen, R., I.R. MacDonald, N.L. Guinasso, S. Joye, A.G. Requejo, S.T. Sweet, J. Alcalá-Herrera, D.A. DeFreitas, and D.R. Schink, 1998, Bacterial methane oxidation in sea-floor gas hydrate. Significance to life in extreme environments: *Geology*, v. 26, p. 851-854.
- Sassen, R., J.S. Watkins, C.L. Decker, D.A. DeFreitas, and A. Milkov, 1999, Structural setting of gas hydrates, Gulf of Mexico slope: Abstracts, 1999 Annual AAPG Meeting, San Antonio, Texas, p. A31.
- Sloan, E. D. (1998) *Clathrate Hydrates of Natural Gases*, 2nd Edition: Marcel Dekker, New York, 705 p.