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Types of Gas Hydrates in Marine Environments and Their Thermodynamic Characteristics

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ABSTRACT

The hydrates in marine environment can be grouped into two categories, diffusion gas hydrates and vent gas hydrates. The diffusion gas hydrates occur widely in an area where bottom simulation reflector (BSR) was recorded in seismic profiles, and is a thermodynamic equilibrium system of hydrates and water with dissolved methane within gas hydrate stability zone (GHSZ). The hydrates are buried in a distance apart from the seafloor and are characterized by low concentrations. The vent gas hydrates occur in an area where gas vents out of the seafloor. It is a thermodynamic disequilibrium system of hydrate, water and free gas, occurs in a zone that extends from the base of GHSZ to the seafloor, and is characterized by high concentration. Reported evidences show that these two types of hydrates are possibly occurring in the South China Sea.

(Key words: Classification, Gas hydrate, Thermodynamics, Methane solubility, Hydrate ridge, South China Sea)

1. INTRODUCTION

Gas hydrate is an ice-like crystalline mineral distributed on continental slopes worldwide where temperature and pressure are suitable for hydrate stability (Sloan 1998; Kvenvolden and Lorenson 2001). In the last decade, tremendous data have been accumulated from geophysical surveys, the Ocean Drilling Program (ODP), direct seafloor observation and samplings devoted to gas hydrate. Enormous progresses have been made toward a better under-

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standing of hydrate occurrence and formation in marine sediments (e.g., Paull et al. 2000; Trehu et al. 2003).

The evidence for the occurrence of gas hydrate as bottom simulation reflector (BSR) in seismic profiles (e.g., Hyndman and Davis 1992) was identified in a great number of marine sites worldwide (Sloan 1998; Kvenvolden and Lorenson 2001). ODP in areas where BSR typically occur yields results demonstrating that gas hydrate accumulates in the subsurface in a distance apart from the seafloor and that no free gas occurs within the GHSZ (Paull et al. 2000; Trehu et al. 2003, 2004). At the same time, seafloor observation and sampling and ODP drilling found that gas hydrate outcrops on the seafloor where gas actively vents into the overlying ocean to form a gas plume in a seawater column (Suess et al. 1999; Sassen et al. 2001; MacDonald et al. 2002, 2003; Heeschen 2003; Leifer and MacDonald 2003), and free gas exists within the GHSZ (Milkov et al. 2004).

ODP 204 drilled at the southern summit of Hydrate Ridge (Trehu et al. 2003) shows the difference in hydrate occurrence (Fig. 1). Very high concentrations of gas hydrates are present in about 30 - 40 % of the pore space that extends from the seafloor to ~30 mbsf (zone C) where gas venting is known on the seafloor, while no gas hydrate is present in the upper ~45 mbsf away from this southern summit. Between ~45 mbsf and the base of the GHSZ (zone B), gas hydrate occupies only 2 - 4 % of the pore space (Trehu et al. 2004). ODP 164 at the Blake Ridge yields similar characteristics of hydrate occurrence. Hydrate occupies on average 4 - 6 % of the porosity in sediments at 186 - 451 mbsf in Sites 994, 995 and 997 where the BSR occurs (Paull et al. 2000). However, hydrate was recovered from all five boreholes at Site 996 at depths ranging from just below the seafloor to ~60 mbsf over the Blake Ridge Diapir where gas actively vents (Paull et al. 2000), and the hydrate concentrations are estimated to be about 10% of the pore space on average (Paull et al. 2000).

As a result, remarkably distinct characteristics of hydrate occurrence and different thermodynamics of gas hydrate system have been observed in continental slopes in the world. However, no literature is available in regard to systematic classification of gas hydrates in such a marine environment based on the thermodynamics and distribution of gas hydrates that occur in the areas where BSR occurs (named diffusion gas hydrate) and or in the gas vent sites (named vent gas hydrate). Here, we will address the characteristics of occurrence and thermodynamics of diffusion gas hydrates and vent gas hydrates, and then use the methane equilibrium solubility of these two types of hydrates to constrain their possible occurrences. Finally, we will discuss the possible occurrences of these two types of hydrates in the northern South China Sea.

2. GAS HYDRATE END MEMBERS IN CONTINENTAL SLOPE

2.1 Two-Phase Hydrate: Diffusion Gas Hydrate

Diffusion gas hydrate is defined as gas hydrate that occurs in an area where BSR was identified in seismic record profile. Within the GHSZ, there are hydrate and water with dissolved methane rather than free gas. Dissolved methane in pore water migrates by the diffusion process. Therefore, this type of gas hydrate was named as Diffusion Gas Hydrate.

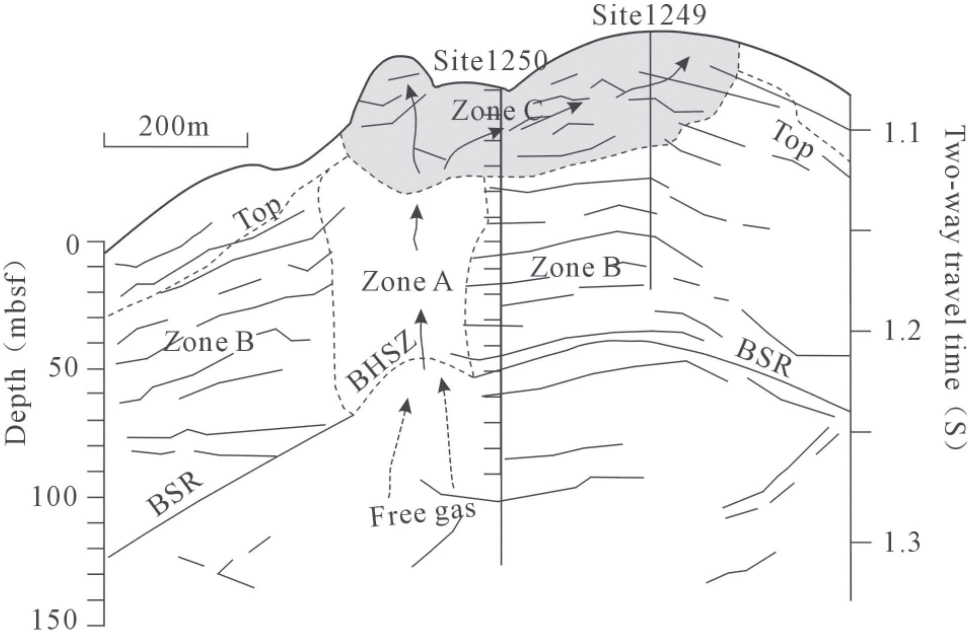

Fig. 1. Schematic illustration of gas hydrate occurrence across the southern summit of Hydrate Ridge (after Trehu et al. 2004). BHSZ is the base of the hydrate stability zone. Zone C and possibly zone A are a three-phase hydrate system, while zone B is a two-phase hydrate system. Arrows show the route of gas venting. Vent gas from a free gas zone under BSR may migrate to zone C through zone A where is a wipeout zone in seismic profile.

Most of the ocean floor is within the appropriate regime of pressure and temperature for gas hydrate to be stable (Fig. 2a), but an adequate gas source for hydrate accumulation is normally restricted to some regions on continental slopes. Biogenic methane either from in situ conversion of organic carbon within the GHSZ or from free gas zone beneath the GHSZ is the major source of gas (Zatsepina and Buffett 1997; Xu and Ruppel 1999). Dissolved methane may precipitate as hydrate in the subsurface when methane concentration in pore water exceeds the equilibrium solubility of methane in water and hydrate system (Fig. 2b) (Buffett and Zatsepina 2000; Davie and Buffett 2003). However, if dissolved methane is not significant in amount, free gas will not be formed within the GHSZ suggesting that this type of gas hydrate is a two-phase system of hydrate and water.

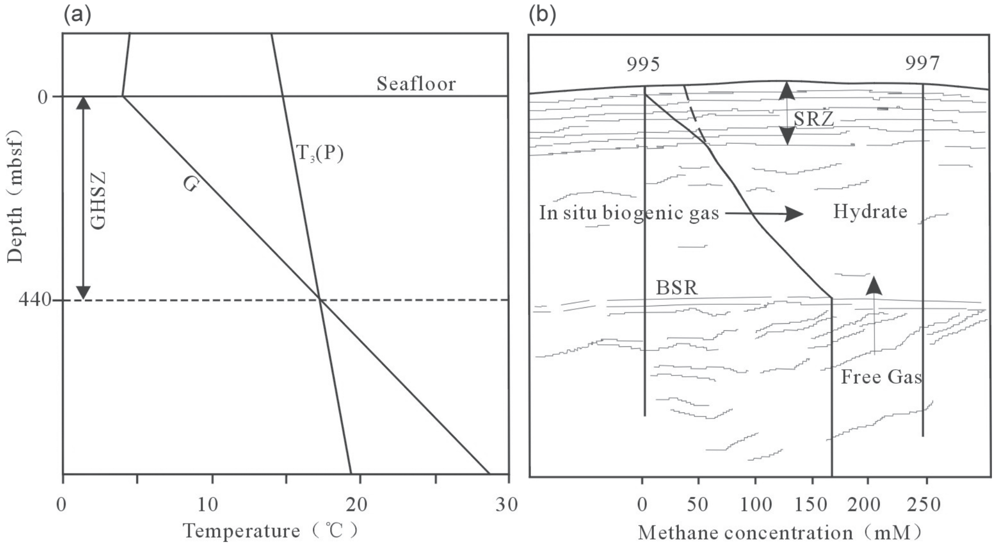

Fig. 2. Schematic profile of diffusion gas hydrate at Blake Ridge. (a) Shows the range of temperature and pressure that constrain the gas hydrate stability zone (GHSZ). GHSZ extending from 440 mbsf to the seafloor shows that hydrate could be accumulated within the GHSZ. G is the thermal gradient, and $T_3(P)$ is the stability curve of methane hydrate as calculated by using the program CSMHYD (Sloan 1998). (b) Shows the content of dissolved methane in pore water (solid line) and the equilibrium solubility of methane (dashed line) in a hydrate-water system across Blake Ridge (after Davie and Buffett 2003). The concentration of dissolved methane in pore water must exceed the equilibrium solubility of methane in hydrate-water system in order for hydrate to be accumulated. Hydrate accumulates at a distance apart from the seafloor within the GHSZ since the dissolved methane will vanish within the sulfate reducing zone (SRZ) through a microbiological process.

ODP 164 drilled at Black Ridge and ODP 204 at Hydrate Ridge where BSR occurs shows that gas hydrate do not occur right on the seafloor but is buried at a distance apart from the seafloor (Paull et al. 2000; Trehu et al. 2003). This is because anaerobic methane oxidation ($CH_4 + SO_4^{2-} \rightarrow HS^- + HCO_3^- + H_2O$) in sulfate reduction zone consumes methane in the uppermost sediments (Valentine and Reeburgh 2000). The decrease in sulfate concentration with depth is approximately linear until the sulfate concentration vanishes completely, and the concentration of dissolved methane also decreases to almost zero in this microbiological process.

Therefore, the concentration of methane in the sediment pore water of sulfate reduction zone is lower than the methane equilibrium solubility in water and hydrate system, and no hydrate will be accumulated in the uppermost sediments (Fig. 2) (Davie and Buffett 2003).

Below the sulfate reduction zone and due to microbiological conversion of available organic carbon to methane, dissolved methane will have a concentration that is high enough to achieve the methane equilibrium solubility in water and hydrate system; hence, hydrate can be crystallized within the GHSZ. Since the rate of diffusion of methane is extremely low within the GHSZ, all excess methane relative to the methane equilibrium solubility in water and hydrate system will be precipitated as hydrate in the subsurface. Finally, the hydrate-water system with dissolved methane tends to achieve a thermodynamic equilibrium (Xu and Ruppel 1999; Buffett and Zatsepina 2000). Consequently, the kinetics for hydrate accumulation doesn't have to be taken into account when this thermodynamic equilibrium system of hydrate, water with dissolved methane is considered. By using the thermodynamic equilibrium theory for hydrate-water system, a steady state model can be applied to ODP Site 997 at the Blake Ridge for calculation of hydrate that was distributed from 180 to 450 mbsf, and it was found that hydrate occupies no more than 7% of the sediment pore on average (Davie and Buffett 2001, 2003).

2.2 Three-Phase Hydrate: Vent Gas Hydrate

A gas vent is known as a common natural phenomenon distributed widely in marine environments across the world (Kvenvolden and Rogers 2005; Dimitrov 2002; Mazurenko and Soloviev 2003). Free gas migrates from a deep source along conduits toward the seafloor. The vent gas partially precipitates as hydrate within the GSHZ (Chen and Cathles 2003, 2005; Chen et al. 2004a; Cathles and Chen 2004), and partially converts into CO_2 to precipitate as seep carbonate in the seafloor and subsurface through microbial process (e.g., Valentine and Reeburgh 2000). Remaining vent gas emerges into the overlying water column to form gas plume in seawater column and is dramatically visible on echo sounder records (e.g., MacDonald et al. 2002; Sassen et al. 2004). Figure 3 shows a concept of this gas vent system in a marine environment.

Gas hydrate was collected on the seafloor at many gas vent sites around the world (MacDonald et al. 2002, 2003; Trehu et al. 2003; Paull et al. 2000; Sassen et al. 2004; Milkov 2000). More recently, free gas was considered to be co-existent with hydrate and water in the shallow sediments at the southern summit of Hydrate Ridge (Milkov et al. 2004) where gas vents and hydrate outcrops on the seafloor (Suess et al. 1999). This evidence suggests that a gas vent site is a co-existent system of hydrate, water and free gas. Thermodynamically, gas could be completely precipitated because the shallow subsurface is within the GHSZ, but gas actively vents out of the seafloor in free gas form. Therefore, we name this type of gas hydrate as a Vent Gas Hydrate. Hence it can be concluded that the hydrate, water and free gas at gas vent site have not reached thermodynamic equilibrium, the hydrate accumulation in the subsurface is kinetically controlled, and the accumulated hydrate within the GHSZ is not stable as a result of the latent heat of hydrate crystallization and the advection of heat by gas flow (Chen and Cathles 2003, 2005; Cathles and Chen 2004; Chen et al. 2004a).

Based upon the compositional difference of heavier hydrocarbon between source gas and seafloor vent gas, Chen and Cathles (2003) developed a composition-based kinetic model for hydrate crystallization from a vent of thermogenic gas, and applied it to the Bush Hill vent site in the Gulf of Mexico. The result shows that about 10% of the vent gas crystallizes as hydrate in the subsurface (Cathles and Chen 2004; Chen et al. 2004a). Recently, Cathles et al. (2006) noted that a 30 t yr^{-1} gas vent 3 m in diameter with 30% porosity will plug with hydrate in ~40 years, suggesting that higher content of gas hydrate can be possibly accumulated in a short time in the subsurface at gas vent site.

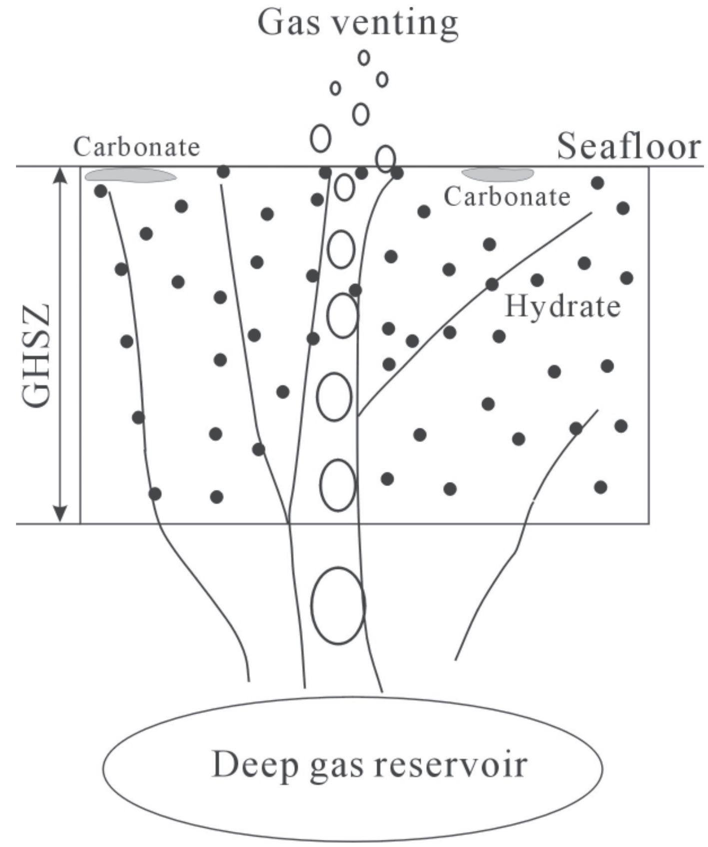

Fig. 3. Conceptual sketch at gas vent site in marine environment. Vent gas partially precipitates as hydrate and partially converts into CO_2 to precipitate seep carbonate through microbial process in the subsurface. The remaining gas vents into an overlying seawater column to form a gas plume. It is a three-phase (free gas, hydrate, and water) system occurring within the GHSZ.

2.3 Calculation of The Equilibrium Solubility of Methane

The occurrence of diffusion gas hydrate can be constrained by using the diagram illustrating the relationship between methane solubility and temperature (depth) (Fig. 2b) (Davie and Buffett 2003; Buffett and Zatsepina 2000; Zatsepina and Buffett 1997; Xu and Ruppel 1999). The equilibrium solubility of methane in the hydrate-water system, X_2 in millimole fraction [mM fraction], can be calculated by using an empirical equation derived from Davies et al. (2004):

$$X_2 = X_3 \exp(\frac{T - T_b}{\alpha}) \quad , \tag{1}$$

Where X_3 [mM fraction] is the equilibrium solubility of methane in a three-phase system of seawater, hydrate, and free gas at the base of the GHSZ (see equation 4). α is 14.5°C for seawater (Davie et al. 2004). T_b [°C] is the temperature at the base of the GHSZ, and T [°C] is the temperature within GHSZ, and can be calculated as:

$$T = T_0 + Gz \quad , \tag{2}$$

where T_0 [°C] is the seafloor temperature, G [°C m^{-1}] is the geothermal gradient, and z [m] is the depth below the seafloor.

The equilibrium solubility of methane in the three-phase system consisting of hydrate, pure water, and free gas, X_3^0 [mM fraction], can be calculated by using a data-fitting empirical equation developed by Anderson (2004):

$$X_3^0 = 0.0025T^2 + 0.0628T + 1.083 \ (R^2 = 0.9999) \quad . \tag{3}$$

The salinity of the pore water will affect the equilibrium solubility of methane in hydrate-water-free gas system. By using the method described by Davies et al. (2004), the equilibrium solubility of methane in hydrate-seawater-free gas system with salinity correction is as follows:

$$X_3 = X_3^0(1 - \beta S) \quad , \tag{4}$$

where $(1 - \beta S)$ is the correction factor for salinity of pore water, $\beta = 0.1$ mole^{-1} (Davies et al. 2004), S [mole 1^{-1}] is the pore water salinity.

Figure 4 and Table 1 shows the calculated results of equilibrium solubility of methane by using the measured parameters from Site 1249 of ODP 204 at the southern summit of Hydrate Ridge. The calculated GHSZ is 114 mbsf that is entirely coincident with the depth where the BSR occur (Trehu et al. 2004). The hydrate crystallizing and free gas bobbling on the seafloor requires that dissolved methane in pore water of the seafloor sediment should be larger than ~1.31 mM fraction at the southern summit of Hydrate Ridge (Table 1). The measured concentration of methane in pressure core samples from 13.5 to 14.5 mbsf depth is ~67.7 - 83.2 mM fraction (Trehu et al. 2003) that is extremely higher than the equilibrium solubility of methane (X_3 = ~1.37 mM fraction) (Table 1), consistent with the fact of that massive hydrate and free gas occurs in the upper most sediments on the seafloor (Suess et al. 1999; Milkov et al. 2004).

3. HYDRATE OCCURRENCE IN THE NORTHERN SOUTH CHINA SEA

To explore the gas hydrate potential in the South China Sea, a number of projects have been launched since 1996, and more than 200000 km seismic reflection profiles have been

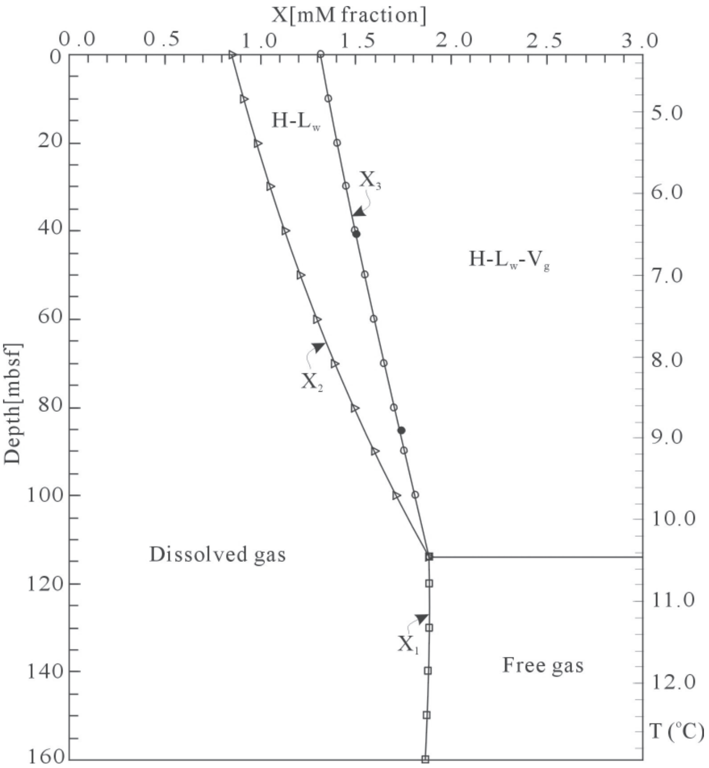

Fig. 4. Equilibrium solubility of methane at site 1249 in the southern summit of Hydrate Ridge. $H-L_w$ is hydrate-water system, and $H-L_w-V_g$ is hydrate-water-free gas system. Black dots are measured data from Servio and Englezos (2002) and is consistent with our calculated phase curve of hydrate-gas-seawater system.

Table 1. The calculated equilibrium solubility of methane at Site 1249 of ODP 204 at the southern summit of Hydrate Ridge.

z (mbsf)	T (°C)	X_1 [mM Fraction]	X_2 [mM Fraction]	X_3 [mM Fraction]
0	4.31		0.86	1.31
10	4.85		0.92	1.35
13.5	5.04		0.94	1.37
14.0	5.07		0.95	1.37
14.5	5.09		0.95	1.37
20	5.39		0.99	1.40
30	5.93		1.06	1.45
40	6.47		1.13	1.49
40.6	6.50		-	1.50*
50	7.01		1.21	1.54
60	7.55		1.30	1.59
70	8.09		1.39	1.64
80	8.63		1.49	1.70
85	8.90		-	1.73*
90	9.17		1.60	1.75
100	9.71		1.71	1.81
110	10.25		1.84	1.86
114	10.47	1.89	1.89	1.89
120	10.79	1.88		
130	11.33	1.88		
140	11.87	1.87		
150	12.41	1.87		
160	12.95	1.86		

Note: X_2 and X_3 are the equilibrium solubility of methane in hydrate-water system and hydrate-water-free gas system, respectively. X_1 is the equilibrium solubility of methane in water-free gas system calculated by using the method as described in Duan et al. (1992). The calculated parameters are that the seafloor temperature is ~4.31°C at water depth of ~775 m, the average temperature gradient is ~54°C km^{-1}, and average salinity is 3.6 wt% in sediment pore water below 23.41 mbsf (Trehu et al. 2003). The calculated GHSZ is 114 mbsf that is entirely coincident with the depth where the BSR occurs (Trehu et al. 2004). The methane solubility marked with star (X^3 = 1.50 at 6.5°C, and 1.73 at 8.9°C) is the measured data in the hydrate-gas-pure water system (Servio and Englezos 2002) with salinity correction (equation 4) by using the S = 0.64 for 3.6 wt% salinity.

collected. BSR was found in reflection seismic records at many locations in the South China Sea (Chow et al. 2000; Chi et al. 1998; Song et al. 2001; Wu et al. 2005; Liu et al. 2006). Mud volcanoes and shale diapirs were reported both on-land and offshore Taiwan (Chi et al. 1998; Chow et al. 2000, 2001; Yang et al. 2004; Chiu et al. 2006) and in the Qiangdongnan Basin (Chen et al. 2004b) in the South China Sea. More recently, some abnormally high methane concentration were found in sea waters and cored sediments (Chen and Tseng 2006; Chuang et al. 2006; Yang et al. 2006). Meanwhile, Chen et al. (2005, 2006a, b) reported seep carbonate in the northeastern South China Sea. Chemosynthetic communities and seep carbonates occurred in an area more than 400 km^2 were found on the northern slope of the South China Sea, where water depth is about 500 - 1000 m (Zhang et al. 2005). This evidence shows that two types of hydrates possibly occur in the South China Sea. By using parameters from Site 1144 of ODP 184 in the northern South China Sea, the equilibrium solubility of methane in two-phase and three-phase hydrate systems is shown in Fig. 5 and Table 2. The calculated GHSZ is 697 mbsf at Site 1144 where the BSR is possibly located at 654 - 730 mbsf (Song et al. 2001). Hydrate accumulation and gas bubbling on the seafloor at Site 1144 requires dissolved methane in pore water larger than ~1.23 mM fraction (Table 2).

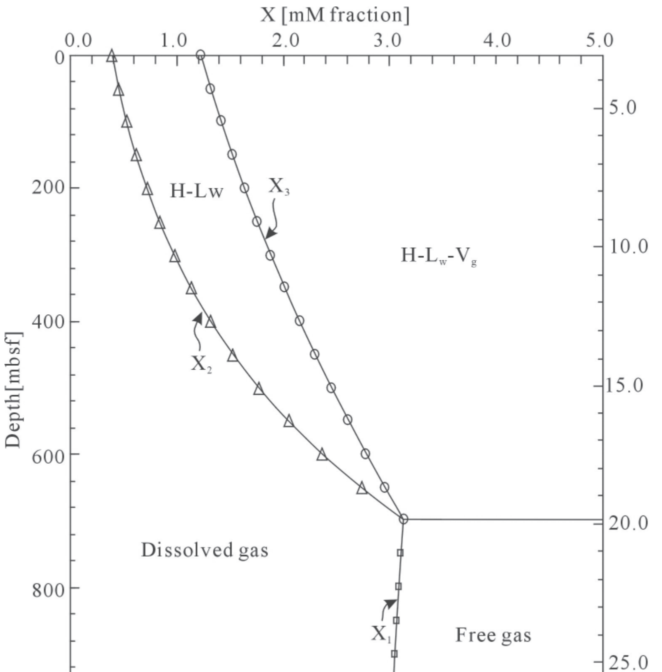

Fig. 5. Equilibrium solubility of methane at site 1144 of ODP 184 in northern South China Sea.

Table 2. The calculated equilibrium solubility of methane at Site 1144 of ODP 184 in northern South China Sea.

z (mbsf)	T (°C)	X_1 [mM Fraction]	X_2 [mM Fraction]	X_3 [mM Fraction]
0	3.1		0.39	1.23
50	4.3		0.45	1.32
100	5.5		0.53	1.42
150	6.7		0.62	1.53
200	7.9		0.72	1.64
250	9.1		0.84	1.76
300	10.3		0.98	1.88
350	11.5		1.14	2.02
400	12.7		1.32	2.16
450	13.9		1.53	2.30
500	15.1		1.77	2.46
550	16.3		2.05	2.62
600	17.5		2.37	2.78
650	18.7		2.74	2.96
697	19.8	3.13	3.13	3.13
750	21.1	3.10		
800	22.3	3.08		
850	23.5	3.07		
900	24.7	3.05		
950	25.9	3.03		
1000	27.1	3.02		

Note: The calculated parameters are that the seafloor temperature is ~3.1°C at water depth of 2037 m, and the temperature gradient is ~24°C km^{-1} in the uppermost 150 mbsf. No salinity data are available for site 1144, hence we use an average of 3.16 wt% in sediment pore water at site 1146 (Prell et al. 2003) as the salinity in our calculation. The calculated GHSZ is 697 mbsf at Site 1144 that is consistent with the depth where the BSR is located at 654 - 730 mbsf (Song et al. 2001).

4. CONCLUSIONS

Gas hydrates in a marine environment can be grouped into two categories, the diffusion gas hydrate and the vent gas hydrate. These two types of gas hydrate show distinction in occurrence, gas source, manner of gas migration, and thermodynamics of system. The gas source for diffusion gas hydrate is mainly in situ biogenic methane. Methane dissolves in pore water, no free gas exists within the GHSZ, and the hydrate system is a thermodynamically equilibrium system of water and hydrate (two-phase). Hydrate accumulation is thermodynamically controlled and hydrate occurs in a distance apart from the seafloor and generally in low concentration. Vent gas hydrate occurs at a gas vent site and is a thermodynamically disequilibrium system of water, hydrate, and free gas (three-phase). Gas consists mainly of thermogenic gas originating from deep oil and gas reservoirs and hydrate is imbedded in shallow sediments with high content. Hydrate accumulation is kinetically controlled. Available data reported to date show that both the diffusion gas hydrate and the vent gas hydrates possibly occur in the South China Sea.

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