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The geochemical signatures of variable gas venting at gas hydrate sites

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Abstract

Diverse evidence suggests that gas-venting rates at sites of hydrate crystallization are variable in space and time, but the magnitude of these variations has been difficult to quantify. The hydrate crystallization model of Chen and Cathles [J. Geophys. Res. (Solid Earth) 108 (2003)] is used here to analyze 10 years of vent gas chemistry measurements at the Bush Hill hydrate mound and gas-venting site, Green Canyon 185, offshore Louisiana, Gulf of Mexico. The analysis suggests that, at any instant of time, gas vents at variable rates in different gas channels at the same site, and that the compositional differences in these vent gases are nearly as large as can be produced by hydrate crystallization. Almost two orders of magnitude differences in venting rate between individual gas channelways are suggested. Changes in the average vent gas composition over the last 10 years suggest the average venting rate varied by a factor of ~ 2 or more over a few years. The average $C_3 + C_4$ composition of Bush Hill hydrates are leaner than could be crystallized from vent gases sampled over the last decade, indicating that the venting gas flux was slower in the past by a factor of ~ 2 . This is compatible with geologic generalizations that venting evolves from fast (mud volcano), to intermediate (hydrate crystallization), to slow (carbonate precipitation) if venting organized into more discrete vents with time.

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1. Introduction

Gas hydrate is an ice-like crystalline mineral in which a rigid cage of water molecules encloses hydrocarbon and non-hydrocarbon gas molecules (Sloan, 1998). Natural gas hydrates occur worldwide in Polar Regions and in sub-thermocline oceanic environments, especially in areas of onshore and offshore permafrost and in sediments on continental margin slopes (Kvenvolden, 1998). The Gulf of Mexico is a classic area of gas hydrate occurrence. Hydrates have been sampled at more than 50 sites where the water depth exceeds ~ 440 m (Booth, Rowe, & Fischer, 1996; Kennicutt et al., 1985; Kvenvolden & Keith, 1995; MacDonald, Guinasso, Sassen, Brooks, Lee, & Scott, 1994; Sassen & MacDonald, 1994; Sassen et al., 2001a,b). Milkov & Sassen (2001) estimate that there is $10\text{--}14 \times 10^{12} \text{ m}^3$ of gas entrapped in hydrate in the northwestern Gulf of

Mexico, and suggest that $\sim 80\%$ occur near faults at the margins of salt withdrawal minibasins where thermogenic gas has vented.

Many of the thermogenic, fault-related hydrate sites in the Gulf of Mexico are also sites of active gas and oil venting. MacDonald et al. (1993) documented 60 active oil seeps in the northern Gulf by analysis of satellite remote sensing data, but recent, more comprehensive data indicate that this estimate is too low by an order of magnitude (MacDonald et al., 2000; 2002). Manned submersible observations and seafloor mapping has documented a range of venting rates with characteristic physical, chemical and biological features (Roberts, 2001; Roberts & Carney, 1997). The most rapidly erupting vents discharge massive quantities of sediment and hydrocarbon rich fluids that produce mud volcanoes and mudflows. Gas venting at intermediate rates supports viable and widespread chemo-synthetic communities, crystallization of surface and near-surface gas hydrates, and spatially variable small-scale mud volcanoes. Slow gas seepage is associated with mounded or

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chimney-like authigenic carbonates or other less impressive forms of seafloor lithification, such as hardgrounds, slabs, and nodules, and exotic minerals like barite in localized areas. Although not necessarily always the case, these systems have evolved from fast to slow venting in at least some cases. In the Green Canyon Block 338 area, for example, barite chimneys characteristic of slow gas venting are establishing themselves on Pleistocene mud flows (Roberts & Carney, 1997).

The Bush Hill hydrate mound and gas vent is the best-studied intermediate vent site in the Gulf of Mexico and perhaps the world. It is located where antithetic faults to a major growth fault system intersect the sea floor in Green Canyon Block 185 (Brooks, Kennicutt, Fay, MacDonald, & Sassen, 1984, Brooks et al., 1986). The main fault system contains the Jolliet oil and gas reservoirs (Cook & D'Onfro, 1991; Sassen et al., 2001a). Present-day gas venting at Bush Hill produces a plume that is dramatically visible on echo sounder records. Gas bubbles 2–3 cm in diameter breach the sea surface over the site, leaving oil slicks as they dissipate (Sassen et al., 2001a). Bush Hill hosts abundant chemosynthetic communities, authigenic carbonates, and bacterial mats. Hydrates are exposed on the surface of a mound 800 m in diameter. Numerous sites of gas venting are situated on this mound. Gases and hydrates at these vent sites have been sampled by submersibles at least five times in the last decade (see Table 1). A separate mud vent site lies to the side of the Bush Hill hydrate mound.

The composition of the vent gas at Bush Hill is consistent with stripping of C₂₊ hydrate-forming gases from Jolliet reservoir gas by hydrate crystallization (Sassen et al., 2001a). Since there is no isotopic fractionation during hydrate crystallization, the isotopic similarity of the Jolliet reservoir gases, the vent gases, and the Bush Hill hydrates is very strong evidence that all the gasses are from a common source (Roberts, 2001; Sassen et al., 2001a). Based on this common source, a kinetic model of gas venting and hydrate crystallization at the Bush Hill was constructed by Chen and Cathles (2003). Analysis of the Bush Hill vent with this model showed that, on average over the 10 000 year history of hydrate accumulation, ~9% of the vent gas is crystallized as hydrate in the subsurface and the compositions of vent gases and hydrates are controlled almost entirely by the variation in the rate of gas venting. The purpose of this paper is to examine the changes in vent gas composition that have been observed over the last 10 years at Bush Hill in more detail, and to suggest how these variations could be related to vent evolution. The changes in vent chemistry suggest a dynamic, constantly changing nexus of subsurface gas pathways that are progressively organized so that venting occurs at fewer locations of smaller total area as the overall venting rate gradually wanes. This progressive vent consolidation is an aspect of gas vent evolution that to our knowledge has not been previously specifically discussed.

Table 1
Observed composition of Bush Hill vent and hydrate gases

No.	Year	T (°C)	C ₁	C ₂	C ₃	i-C ₄	n-C ₄	i-C ₅	n-C ₅	C ₃ + C ₄
V-a	1993	7.35	88.0	8.0	2.1	0.3	1.2	0.4	<0.1	0.036
V-b	1993	7.35	88.0	7.5	2.2	0.5	1.1	0.6	<0.1	0.038
V-1	1995	9.10	93.2	4.3	1.5	0.3	0.6	0.3	<0.1	0.024
V-2	1995	9.10	93.5	4.3	1.4	0.2	0.4	0.2	<0.1	0.020
V-3	1995	9.10	94.7	3.9	0.7	0.1	0.5	0.2	<0.1	0.013
V-4	1995	9.10	94.6	3.8	0.7	0.1	0.5	0.3	<0.1	0.013
V-5	1995	9.10	91.1	4.8	1.8	0.4	1.2	0.8	<0.1	0.034
V-6	1997	7.00	90.4	4.5	3.7	0.6	0.6	0.2	<0.1	0.049
V-7	1997	7.00	95.9	2.4	1.2	<0.1	0.3	0.2	<0.1	0.015
V-8	1998	7.00	93.4	4.1	1.5	0.3	0.5	0.3	<0.1	0.023
V-9	2000	6.50	92.7	4.6	1.7	0.3	0.6	0.2	<0.1	0.026
Mean		7.00	92.32	4.75	1.68	0.31	0.68	0.34	<0.1	0.02645
H-1			83.1	7.6	8.10	0.9	0.2	0.0	0	0.092
H-2			71.7	10.6	12.6	2.6	1.7	0.8	0	0.169
H-3			80.2	9.40	7.30	1.6	1.2	0.3	0	0.101
H-4			72.1	12.4	11.4	2.3	1.6	0.3	0	0.153
H-5			85.7	6.30	6.10	1.1	0.8	0.0	0	0.080
H-6			71.8	3.40	18.8	5.7	0.3	ND	ND	0.248
H-7			73.9	4.90	16.3	4.6	0.2	ND	ND	0.211
H-8			72.1	10.5	12.4	2.5	1.7	<0.1	0.7	0.166
Mean			76.33	8.1375	11.625	2.6625	0.9625	0.175	0.0875	0.1525

MacDonald et al., 1994; Sassen and MacDonald, 1994, 1997; Sassen et al., 1998, 1999a,b. All temperature data and vent gas sample-V-9 is unpublished data from Sassen, R.

2. Chemical analysis of Bush Hill venting

2.1. Kinetic model of gas venting and hydrate crystallization in Bush Hill

The kinetic model for hydrate crystallization from a gas stream is fully presented in Chen and Cathles (2003). The most important aspects of this model are reviewed here. The model addresses the rate at which gas is crystallized from a gas stream, (DM/Dt) , in a coordinate system moving with the gas:

$$\frac{DM}{Dt} = -k(X_{3+4}^{v\text{-gas}} - X_{3+4}^{\text{equ}})\exp\left(\frac{E^*}{R}\left(\frac{1}{T^*} - \frac{1}{T}\right)\right). \quad (1)$$

Here k ($\text{kg/m}^3 \text{ a}$) is the product of the kinetic rate constant and the actively crystallizing hydrate surface area per unit volume, $X_{3+4}^{v\text{-gas}}$ is the $\text{C}_3 + \text{C}_4$ mass fraction composition of the vent gas, X_{3+4}^{equ} is the $\text{C}_3 + \text{C}_4$ mass fraction composition of the gas that would be in equilibrium with hydrate at the pressure and temperature selected, E^* is the activation energy of the reaction, R is the gas constant, T^* is an arbitrary reference temperature which was taken to equal 273.15 K, and T is the temperature at the location of the gas packet in K.

Eq. (1) applies at depths below the sea floor where gas hydrate is stable (e.g. $X_{3+4}^{v\text{-gas}} - X_{3+4}^{\text{equ}} > 0$). It is solved by propagator methods. First we use the methods of Sloan (1998) to calculate the subsurface depth interval over which hydrate can crystallize, which we will refer to subsequently as the potential hydrate stability zone (HSZ). This calculation is made, assuming pore fluids have seawater salinity, by determining the depth at which gas with the composition of a selected Jolliet reservoir gas, $X_{3+4}^{J\text{-gas}}$, begins to crystallize hydrate. The potential HSZ extends to the surface because we assume that venting can be very fast and because gas discharge is observed at Bush Hill. The HSZ is then divided into a number of depth intervals. The gas is moved, unchanged in composition to the middle of the first depth interval in the HSZ, X_{3+4}^{equ} is calculated for the pressure and temperature there, and the rate of hydrate crystallization is computed from Eq. (1). The fractional crystallization of gas that occurs in the time the gas takes to transit the layer (at a mass flux q ($\text{kg/m}^2 \text{ a}$)) is then computed, and the composition of vent gas is adjusted to account for hydrate crystallization. The composition of the hydrate crystallized

is a function of P , T and $X_{3+4}^{v\text{-gas}}$ (Chen & Cathles, 2003; Sloan, 1998). The gas is then introduced to the next layer and the calculations repeated.

2.2. The causes of vent gas compositional changes at Bush Hill

In the broadest interpretive context, the analysis of vent gas compositions predicted here shows that (of the variables considered) only variations in venting rate could account for the observed variations in Bush Hill vent gas composition. Source gas compositions cannot account for the chemistry of the vent gases because the $\text{C}_3 + \text{C}_4$ range of Jolliet reservoir gas does not span the observed range in vent gas composition. With venting-rate variation, a feed gas with the average Jolliet reservoir gas composition can account for all but the wettest (most enriched in $\text{C}_3 + \text{C}_4$) observed vent gases at Bush Hill. For these few highly enriched vent gases a source gas slightly wetter than the average Jolliet reservoir gas is required. We constrain these conclusions by calculating the range of vent gas compositions that could result by varying all the controlling parameters over their full possible range using the methods of Chen and Cathles (2003).

Four observed parameters influence vent gas composition: source gas composition ($X_{3+4}^{J\text{-gas}}$), seafloor temperature (T_{sf}), subsurface temperature gradient (G), and gas-venting rate (q). The ranges of these parameters are shown in Tables 1 and 2. The mass fraction of $\text{C}_3 + \text{C}_4$ in Jolliet reservoir gas (the assumed source gas) ranges from 0.031 to 0.06. Seafloor temperatures of 6–7 °C are normal for 540 m water depth (Walker, Huh, & Rouse, 1993) and temperatures recorded at the seafloor at 540 m in GC 185 range between 6 and 11 °C with a mean of 7 °C (MacDonald et al., 1994; Sassen & MacDonald, 1994). Loop current eddies spinning off from the Gulf Stream can have cores that reach 14 °C at a water depth of 500 m (MacDonald et al., 1994; MacDonald, Buthman, Sager, Peccini, & Guinasso, 2000; Roberts, 2001; Roberts & Carney, 1997). Seafloor temperature ranges from 6 to 14 °C at Bush Hill. Eighteen Jolliet reservoir temperature measurements updated in Bascle, Nixon, and Ross (2001) and 19 subsurface measurements define the geothermal gradient in Bush Hill area at 20.1 °C/km (Chen & Cathles, 2003). The geothermal gradient can, however, be affected by rapid vertical fluid flow (Roberts,

Table 2
Ranges of parameters used to calculate Fig. 1

	1	2	3	4	5	6
$X_{3+4}^{J\text{-gas}}$	0.031–0.06	0.031–0.06	0.031–0.06	0.04675	0.04675	0.04675
T_{sf} (°C)	5–15	7	7	7	5–15	5–15
G (°C/km)	20	15–50	20	15–50	20	15–50
q ($\text{kg/m}^2 \text{ a}$)	1.84	1.84	0.55–55.26	0.55–55.26	0.55–55.26	1.84

$X_{3+4}^{J\text{-gas}}$ is the measured range of Jolliet reservoir gases (Sassen et al., 2001a); T_{sf} is the seafloor temperature in °C; G is the subsurface geothermal gradient in °C/km; q is gas mass flux in $\text{kg/m}^2 \text{ a}$. The numbers in the first row correspond to the x -axis labels of the vertical line bars in Fig. 1.

2001; Roberts & Carney, 1997). Observation at other sites show that rapid pulses in mud discharge can increase the surface temperature by $>10\text{ }^{\circ}\text{C}$ (MacDonald et al., 2000; Roberts, 2001). A range of the subsurface geothermal gradient from 15 to $50\text{ }^{\circ}\text{C}/\text{km}$ should span all plausible subsurface geothermal gradients at Bush Hill. Venting rates that impact hydrate composition vary from 0.55 to $55\text{ kg}/\text{m}^2\text{ a}$ as we will show below.

Fig. 1 shows the consequences for vent gas composition of varying the six possible pairs of these four parameters ($X_{3+4}^{\text{J-gas}}$, T_{st} , G , and q as defined in Table 2) that control vent gas composition. The observed ranges in vent gas and hydrate composition are shown as gray bands. The black bars and circles indicate the range in reservoir gas and the mean reservoir gas composition, respectively.

The first thing to notice in Fig. 1 is that the range in Jolliet reservoir gas composition (lower black bar) covers at most half of the range in Bush Hill vent gas composition that has been measured over the last 10 years, and that the gases in hydrate are all heavier than the reservoir gases (upper black bar). The heavier gas components preferentially fractionate

into hydrate as it crystallizes. The reservoir gases can thus be converted to the compositions of the vent gases by crystallizing hydrate (Sassen et al., 2001a). If the venting is very rapid, little gas will be crystallized, and the vent gas will have very nearly the same composition as the reservoir gas. The heaviest vent gas (top of gray band in the lower plot) is just slightly heavier (more enriched in $\text{C}_3 + \text{C}_4$) than the mean Jolliet reservoir gas (black dot on lower figure). Variation in venting rate (and/or other factors) could thus account for nearly the full range in observed vent gas compositions, but some heavier-than-average reservoir gas must contribute to some vent pathways to account for the vent gases heavier than the mean Jolliet reservoir gas.

The vertical lines in Fig. 1 show the vent gas and hydrate compositions predicted by our model where the indicated pairs of variables are varied across their permissible ranges as shown in Table 1. Only the vertical lines that include the gas-venting rate, q , as a variable cross the full observed range of either hydrate or vent gas composition. Although to span the full range in vent gas composition, the source gas composition must be varied slightly, the most important

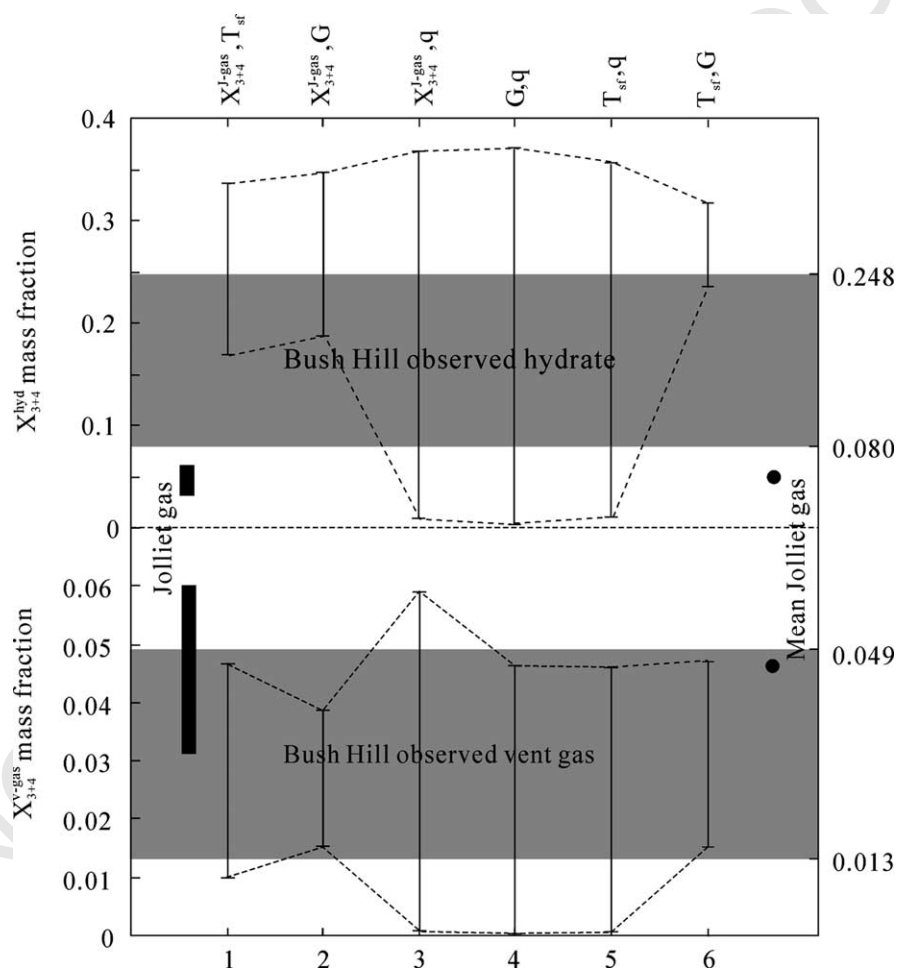


Fig. 1. Ranges in vent gas and hydrate composition computed for the parameter ranges defined in Table 2. The numbers on the x -axis refer to the crossed parameters in Table 2. The crossed parameters that are varied across their permissible range are shown above the top axis. Gray shading shows the range of observed vent and hydrate gas compositions. Black dots in both diagrams show the mean Jolliet reservoir gas composition. Black bars in both diagrams show the composition range of Jolliet reservoir gases.

conclusions to draw from Fig. 1 is that, of the factors considered, variation in venting rate is the most important factor controlling vent gas and hydrate composition. This factor alone can account for nearly the entire range of vent gas and hydrate composition.

2.3. The compositional span of vent rate variations

Fig. 2 plots (solid line) the predicted compositions of vent gas and hydrate crystallized near the seafloor as a function

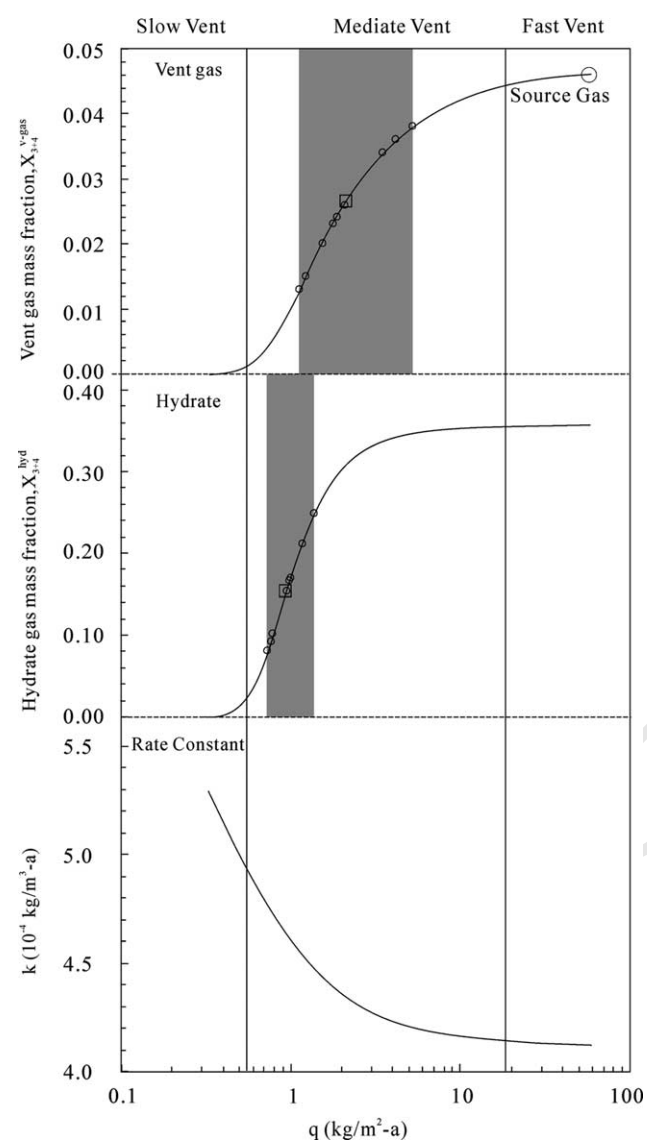


Fig. 2. Vent gas and hydrate compositions calculated as a function of gas vent rate for $T_{sf} = 7^\circ\text{C}$, $G = 20^\circ\text{C/km}$, and a source gas composition equal to the mean Jolliet reservoir gas. The boundaries of fast, intermediate and slow venting are indicated by vertical lines. Gray shading indicates the compositional range of sampled vent gases ($X_{3+4}^{v-gas} = 0.013\text{--}0.049$ with corresponding computed gas mass flux $q = 1.13\text{--}5.21\text{ kg/m}^2\text{ a}$) and hydrate gases ($X_{3+4}^{hyd} = 0.08\text{--}0.248$ with corresponding computed gas mass flux $q = 0.73\text{--}1.38\text{ kg/m}^2\text{ a}$) at Bush Hill. Open circles are the sampled vent and hydrate gas compositions and squares are their average values. The bottom figure shows how the rate constant must be adjusted if a hydrate mound containing an average 2 vol% hydrate is to accumulate in 10 000 years.

of gas vent rate, q . Measured vent gas and hydrate composition are indicated by symbols, and the range of observed compositional data is indicated by gray bands. The calculations assume a surface temperature of 7°C , a temperature gradient of 20°C/km , and a pore salinity of 3.54%. An additional constraint used in constructing this figure is that after 10 000 years of venting, the average hydrate accumulation equals 2 wt% of the sediment volume as required by observations and geological constraints at Bush Hill (see, Chen & Cathles, 2003). All thermodynamic calculations are made using the CSMHYD program (Sloan, 1998) as discussed in Chen and Cathles (2003).

At very slow model venting rates, the heavy gas components are all crystallized as hydrate below the seafloor, and the gas wetness (as measured by the $C_3 + C_4$ mass fraction) is zero in both the vent gas and hydrate. At model gas mass fluxes greater than $\sim 0.5\text{ kg/m}^2\text{ a}$, vent gas and surface hydrates contain a sufficient mass fraction of $C_3 + C_4$ hydrocarbons that hydrate can crystallize. The compositions of vent gas and hydrate depend strongly on venting rate up to venting rates of $\sim 20\text{ kg/m}^2\text{ a}$. At very fast model venting rates, the vent gas approaches the source gas composition (average Jolliet reservoir gas in this case), and the hydrates crystallized near the surface are as heavy as thermodynamics and the source gas wetness allow.

The constraint that the average hydrate accumulation equal 2 wt% after 10 000 years of venting was imposed by varying the kinetic rate constant, k . The bottom panel in Fig. 2 shows how k had to be varied to meet this constraint. The range in k required is quite small (from 4.1 to $5.3 \times 10^{-4}\text{ kg/m}^3\text{ a}$). This relationship illustrates that, as discussed in Chen and Cathles (2003), the kinetic rate constant is not a particularly important variable once it is empirically calibrated. The rate of hydrate crystallization does not depend strongly on venting rate until the venting rate becomes so weak that near-surface hydrate crystallization is strongly impaired.

Finally, Fig. 2 shows that the mass fractions of $C_3 + C_4$ hydrocarbons in hydrates at Bush Hill suggest a slower venting rate than do vent gases collected over the last 10 years (e.g. the gray band enclosing the hydrate compositions lies to the left of the gray band enclosing the vent gas compositions). If the hydrates are older than 10 years this suggests the venting rate has been increasing with time. At face value, this contradicts intuition that a gas blow out from the overpressured zones in a basin should be rapid at first and then decline, and the geological inferences of Roberts and his colleagues (Roberts, 2001; Roberts & Carney, 1997) that the gas-venting rate decreases with time as a vent matures from the mud volcano stage through hydrate/chemosynthetic to carbonate stage. These stages are roughly demarcated by the vertical lines in Fig. 2. This apparent discrepancy can be resolved if the area of venting collapses with time, as discussed below.

Table 3 summarizes additional features of the three zones (slow, medium, and fast venting) in Fig. 2. For fast venting,

Table 3
Boundaries of fast, intermediate and slow venting classes as defined by observed and computed parameters

Vent type	X_{3+4}^{v-gas}	X_{3+4}^{hyd}	ΣF (%)	F_{10} (%)	q (kg/m ² a)
Fast	>0.044	>0.355	<0.9	0.1	>18.42
Intermediate	0.001–0.044	0.022–0.355	0.9–23	0.1–2.8	0.55–18.42
Slow	<0.001	<0.022	>23	No hydrates	<0.55

X_{3+4}^{v-gas} is the mass fraction $C_3 + C_4$ in the vent gas, X_{3+4}^{hyd} is the mass fraction $C_3 + C_4$ in the hydrate crystallised at or near the surface, ΣF is the total fraction of venting gas crystallized as hydrate, F_{10} is the fraction of venting gas crystallized in the uppermost 10% of the hydrate stably zone (surface to ~60 meters deep), and q is the gas mass flux (venting rate) in kg/m² a. The venting rate is calculated assuming there is 2 vol% hydrate in a numerical Bush Hill hydrate mound that is 600 m diameter at the surface and extends to depth as calculated in Chen and Cathles (2003).

the venting gas and surface hydrates are rich in $C_3 + C_4$ hydrocarbons, a small fraction of the gas crystallizes as hydrates in the subsurface (<0.9%), and a proportional amount of hydrate crystallizes in the uppermost 10% of the HSZ (0.1% of the gas flux). At intermediate venting rates, the vent gas and hydrate compositions depend strongly on venting rate, up to 23% of the venting gas crystallizes as hydrate, and a proportional amount still crystallizes in the shallowest 10% of the HSZ. At slow venting rates over 23% of the gas stream crystallizes as hydrate in the subsurface, but the hydrate crystallization is all at substantial depth. No hydrate crystallizes in the shallowest 10% of the HSZ. Note we arbitrarily define the HSZ here with reference to the source gas composition. It extends from the depth at which hydrate is first stable for this source gas to the surface regardless of venting rate.

Fig. 3 shows how the model vent gas and model hydrate compositions change with depth as a function of venting

rate. The solid lines indicate the model venting rates that match the observed compositional data in Fig. 2. This figure again emphasizes that the hydrate samples suggest a slower venting rate than do the vent gas samples collected in the last 10 years.

2.4. Interpretation of a decade of Bush Hill vent gas chemistry

Vent gas and hydrate samples have been collected during multiple submersible visits to Bush Hill since 1993. Table 1 lists all available data. The hydrate samples are of indeterminate age and show signs of (minor) bacterial oxidation (Sassen et al., 1999a). The mound appears to have accumulated over several thousand years. Carbonates in the mound have been dated at 1.4–3.2 ka (Roberts & Aharon, 1994). The $C_3 + C_4$ mass fraction of vent gases are plotted as a function of sampling time in

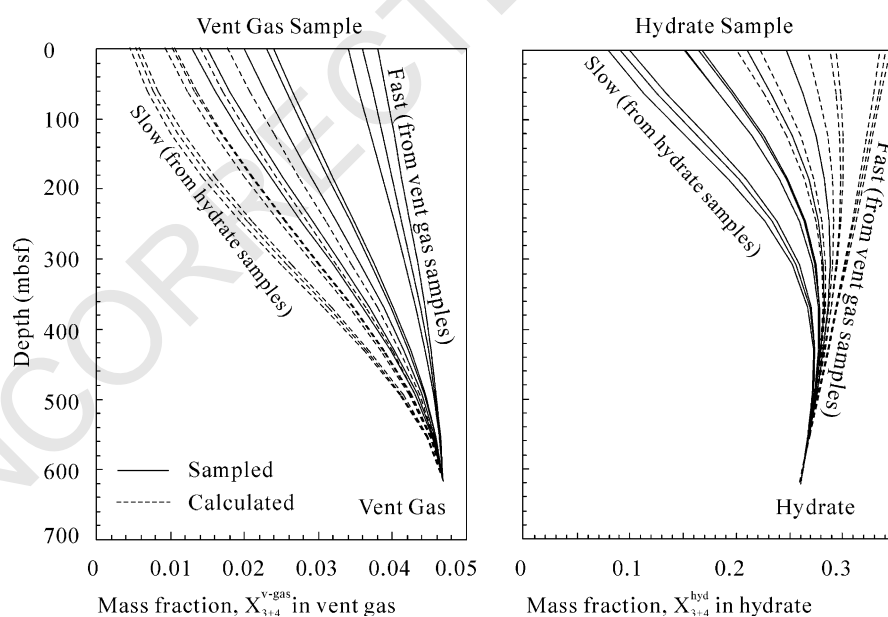


Fig. 3. Calculated changes in the vent gas and hydrate compositions that are plotted in Fig. 2 are extended to depth in this figure. The solid lines show surface data extrapolated to depth using the model. The dashed lines are for reference. They show the extrapolated lines from the other figure (e.g. superimposed $X_{3+4}^{v-gas}(z)$ on the $X_{3+4}^{hyd}(z)$ plot and visa versa).

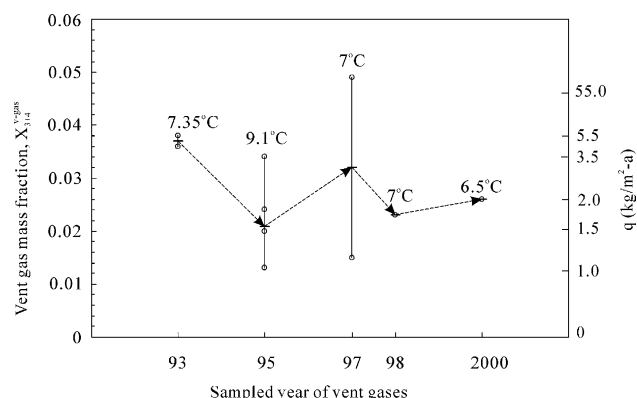


Fig. 4. Bush Hill vent gas compositions plotted against the year sampled. Seafloor temperatures at the time of sampling are shown. The right axis shows the gas mass fluxes suggested by the vent gas compositions.

Fig. 4. The variation in vent gas composition at any particular sampling time is greater than the variation between samplings. The mean mass fraction $C_3 + C_4$ composition changes by a factor of ~ 2 between submersible samplings.

There are very little data, but the implications of these data in terms of the modeling analysis presented are profound. If the composition differences between different bubble streams sampled at the same site on the same submersible visit are the result of variations in the mass flux of the individual bubble streams, an almost two order of magnitude variation in mass flux is required (right hand vertical axis in Fig. 4). The data suggest that at any instant of time gas may be venting from depth to the surface through a number of independent channelways at very different rates. The gas venting from channelways where the venting rate is slow is depleted in $C_3 + C_4$, while the channelways in which the venting rate is fast have $C_3 + C_4$ mass fractions approaching those in the source reservoir gas. The changes in vent gas composition between submersible visits suggest that the venting rate (gas mass flux) in individual channels is also changing with time.

Table 4 provides the details of these calculations. It shows the total fraction of gas, ΣF , that was crystallizing as hydrate from each bubble stream when it was measured, the composition of the surface hydrate crystallizing from the gas, and the gas mass flux calculated for the bubble stream for the seafloor temperature measured at the time of sampling (as listed in Table 1) or a sea floor temperature of 7°C if none was measured.

2.5. Synthesis

Fig. 5 suggests a synthesis of the analysis presented above and the geologically indicated evolution of vents suggested by seafloor observations summarized in Roberts (2001) and Roberts and Carney (1997). This figure depicts

Table 4

Gas mass flux, q , calculated for observed vent gas mass fraction X_{3+4}^{v-gas}

No.	Year	X_{3+4}^{v-gas}	ΣF	X_{3+4}^{hyd}	q (kg/m ² a)	
					q_a	q_b
V-a	1993	0.036	0.041	0.342	4.19	3.83
V-b	1993	0.038	0.033	0.346	5.21	4.74
V-1	1995	0.024	0.089	0.295	1.87	0.99
V-2	1995	0.020	0.106	0.268	1.54	0.81
V-3	1995	0.013	0.141	0.202	1.13	0.59
V-4	1995	0.013	0.141	0.202	1.13	0.59
V-5	1995	0.034	0.049	0.337	3.50	1.89
V-6	1997	0.049	None	None	None	None
V-7	1997	0.015	0.130	0.224	1.23	1.23
V-8	1998	0.023	0.093	0.289	1.78	1.78
V-91	2000	0.026	0.080	0.306	2.07	2.32
Mean	1993–2000	0.0264	0.078	0.309	2.12	2.12

ΣF is the total fraction of venting gas crystallized as hydrate, X_{3+4}^{hyd} is the $C_3 + C_4$ mass fraction of hydrate crystallized at the seafloor. Gas mass flux, q_a , is calculated for a mean seafloor temperature of 7°C ; gas mass flux, q_b , is calculated for the sea floor temperatures measured at the time the samples were collected (see Table 1).

the early, mud volcano stage of venting as having the largest total gas venting Q , but shows this venting spread over a broad area (Fig. 5a). Because the venting is spread over a broad area, the gas mass flux, $q = Q/A$, is low. Hydrates crystallize from the base of the HSZ to the surface, but because rapid mud flow may warm the subsurface (and even the sea floor) the depth interval of hydrate crystallization may be slightly reduced as shown by the dashed line in the figure. Fig. 5b depicts the gas venting as focused to a much smaller area at the hydrate/chemosynthetic stage of venting. The total gas discharge rate, Q , is smaller in the figure but the gas flux, q , is larger because the area of discharge is reduced more than the total venting Q is reduced. Finally, when the venting rate drops below that required to sustain hydrate crystallization at the surface venting occurs only in a very few widely scattered locations and the vent enters its carbonate evolutionary stage (Fig. 5c). In this stage, the carbon tied up in hydrates or dissolved in pore water may be slowly converted to carbonate, producing carbonate mounds and hardgrounds.

If this progressive channel organization occurred at Bush Hill, it could explain the observed relationship between hydrate and vent chemistry even if the overall venting rate were decreasing with time. If the gas flux, q , controls the vent and hydrate gas chemistry as suggested by our modeling, the higher mass fraction $C_3 + C_4$ in vent gases sampled in the last 10 years compared to the vent gas compositions suggested by the (presumably older) hydrates in the Bush Hill mound could reflect the progressive organization of venting into channelways of smaller total cross section and higher mass flux.

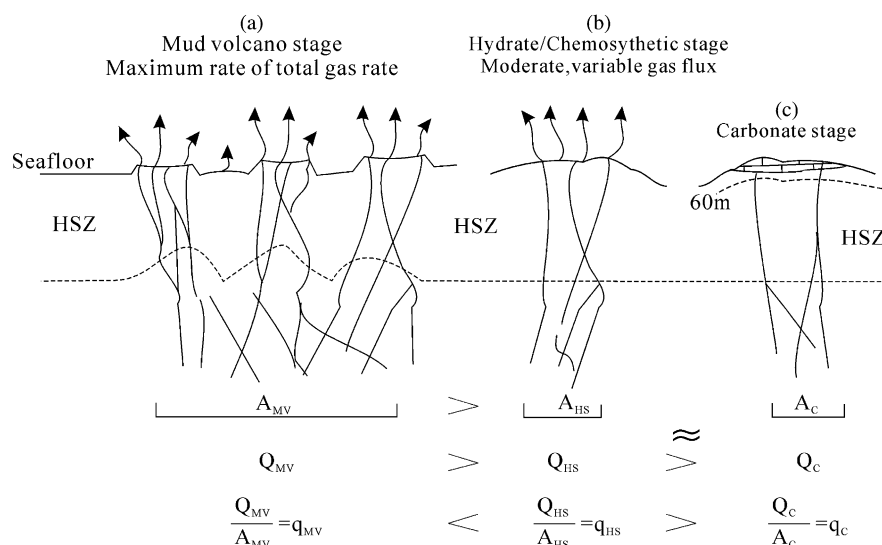


Fig. 5. Cartoon showing the evolution of a typical gas vent. The total gas venting, Q , is most rapid at the mud volcano stage, but the venting occurs over a broad area, A , and the gas mass flux, q , is consequently low. Venting is progressively organized so the area of discharge is reduced, and q is increased. At the same time the total venting rate Q decreases. The three stages shown correspond to those geologically inferred by Roberts and co-workers as discussed in the text.

3. Discussion

The critical presumption in our analysis is that venting rate and gas and hydrate chemistry are related. Bubble streams fed by subsurface flow pathways through which gas transit is fast discharge gases and crystallize hydrates rich in $C_3 + C_4$. Bubble streams fed by gas flow pathways with slow transit times discharge gas and crystallize surface hydrates lean in $C_3 + C_4$ hydrocarbons. Kinetic models of gas venting and hydrate crystallization display these systematics. Although there are many uncertainties in the models as discussed in Chen and Cathles (2003), and the subsurface flow pathways may be complex (with slow transit in some places and fast in others), it is hard to imagine how kinetically controlled hydrate crystallization could avoid these systematics. We therefore suggest that the very different chemistry of different individual bubble streams at a site sampled during the same submersible visit (see especially 1995 and 1997 in Fig. 4) is due to the different rates at which the discharging gas traversed the HSZ.

We cannot prove that the (HSZ) transits times of different bubble streams are different, so this explanation for the different chemistries is a suggestion. The suggestion can however be tested in several ways. Fig. 3 shows that if the vent gas chemistry is controlled by venting rate, the variability in vent gas and hydrate chemistry should decrease with depth to the variability of the source gas (which is taken to be zero in this figure since the source gas is the average Joliet reservoir gas). This prediction could be tested by drilling the Bush Hill hydrate mound. The hypothesis that individual vents are variable in their venting rate and that this directly affects the composition of the vented gases could be tested by monitoring the venting rate and composition of a single bubble stream. This experiment

has been attempted several times but for practical reasons (plugging of the instrument with hydrate, difficulty positioning and calibrating measuring devices, etc.) has proven to be very difficult. The importance of venting rate and its variations in time and space to our understanding of the hydrate system (as made clear by the models we have constructed) reinforces the importance of making these difficult measurements.

Using the connection between venting rate and gas and hydrate chemistry we further suggest that, because virtually all the hydrate samples collected at Bush Hill indicate (when analyzed by our models) the venting rates were slower than at present when they crystallized, the gas mass flux at Bush Hill is greater today than in the past (e.g. the average transit time across the HSZ is less today). We do not know that the hydrates sampled are older than 10 years, but we know they are incompatible with the present vent gas chemistry and cannot (as a whole) have crystallized from it. Given that the hydrate mound accumulated over thousands of years it is likely the samples are older than 10 years. We also do not know that some other process, such as bacterial attack, may not have altered the hydrate chemistry. However, judging from their isotopic alteration, the heavy components of the hydrates sampled at Bush Hill are not altered whereas the C_1 component is altered (somewhat) in a fashion consistent with bacterial oxidation (Sassen et al., 1999a). This suggests that bacteria attack the C_1 component of hydrate first, and that the Bush Hill hydrates would be enriched in their $C_3 + C_4$ components by whatever bacterial oxidation they have suffered. Our chemical dilemma is that the hydrates are not rich enough in $C_3 + C_4$ to be compatible with gases venting over the last 10 years. Bacterial oxidation cannot help resolve this dilemma because it shifts the hydrate

compositions the wrong way. The simplest explanation that we can think of is that the venting rates were slower in the past than they have been over the last 10 years.

The venting rate at Bush Hill seems to be quite variable, so this is perhaps no surprise. In addition to the data in Fig. 4, echo sounder images of the Bush Hill plume seem to be quite variable. In August 2000, echo sounder images showed the Bush Hill plume originated from a 600 m interval at the seafloor centered on the Bush Hill hydrate mound and nearly reached the sea surface. The image was robust to echo sounder tuning and visually dramatic. In June 2002, the vent imaged by echo sounding was about one third the size, less robust to tuning, and visually weaker. At both visits, bubbles of gas were observed breaking the surface leaving iridescent oil slicks. However, if there were no systematic trends, venting variability should not show such as systematic difference between present venting rates and almost *all* hydrates sampled to date. It seems, therefore, that the current venting rate is unusually fast compared to that which pertained over whatever prior period is spanned by the hydrate samples.

On the face of it discharge rates more rapid today than in the past contradicts both common sense and geological inference, and thus warrants some discussion. There seems little question that the fluid venting at Bush Hill derives from zones where fluid pressure is known to be above hydrostatic starting at depths of ~ 6500 ft below the seafloor. Rupture events, probably related to fault movements, tap these high-pressure zones. It is hard to imagine that when this happens the discharge would not be rapid at first and then decrease with time. This is also suggested from the geomorphological, geochemical and biological features summarized in Roberts and Carney (1997). Admittedly, it is a jump to interpret the observed spectrum of venting rates to indicate a progression from fast to slow venting in all cases. Bush Hill may not have had a mud-volcano pre-cursor, and discharge rates could have increased there as the result of recent fault movement or seal rupture rather than because of a general progression from fast to slow gas discharge.

However, there is another possibility that is suggested by broad observations. Roberts and Carney (1997) describe how the vents in slow discharge areas are weak, rare, and scattered compared to sites venting at intermediate rates. It seems that the number of vents tends to decrease as the system evolves (assuming the intermediate sites evolve to weak venting sites). If this is the case, it is possible that the gas transit time could decrease even as the overall venting rate decreases. We offer this as a possible way that the gas mass flux rate at Bush Hill could have could have systematically increased with time.

4. Conclusion

This paper explores the relationship between the gas venting rate and the gas and hydrate chemistry in the Bush

Hill vent site, Green Canyon Block 185, offshore Louisiana, Gulf of Mexico using the kinetic model developed by Chen and Cathles (2003). This model is applied to the Bush Hill vent taking the widest plausible ranges of seafloor temperature, thermal gradient, source gas composition, and gas venting rate. Our analysis shows that venting rate is the principal control on vent gas and hydrate chemistry (Fig. 1).

The Bush Hill vent gas and hydrate chemistries are then examined in terms of gas venting rates (Fig. 2). If venting rates are slow ($q < \sim 0.5$ kg/m² a), hydrate crystallization will not reach the sea floor. If venting rates are fast ($q > \sim 20$ kg/m² a), the vent gas has almost the same composition as the source gas, and the heaviest possible hydrates are crystallized at the surface. Between these extremes both the vent and hydrate gas compositions depend strongly on venting rate. The hydrates sampled from the Bush Hill mound are dryer (contain less C₃ + C₄) than the hydrates that would crystallize from the vent gases sampled over the last decade (Fig. 2). If the sampled hydrates were crystallized more than 10 years ago, their comparative dryness suggests that the gas flux was lower (and the vent gas dryer) in the past.

Changes in vent gas chemistry observed at five repeat submersible visits to the Bush Hill site are interpreted in terms of venting rates (Fig. 4). The range in vent gas chemistry is greater at any instant in time than the changes in the average vent gas chemistry between submersible visits. Nearly a two order of magnitude variation in venting rate (1–55 kg/m² a) is suggested by the chemical differences at any instant. We suggest that the different chemistry of different bubble streams sampled at the same time reflects different rates of movement across the HSZ. Changes in average venting rate between submersible visits of a factor of 2 over a few years are suggested by changes in the vent chemistry.

Fig. 5 summarizes a suggestion of how venting systems such as that at Bush Hill may in general evolve. In the initial mud volcano stage of venting, total gas venting, Q , is maximum but spread over a broad area. With time the gas venting is increasingly organized into fewer venting of smaller cross-sectional areas, and the gas flux (mass of gas crossing a unit area per unit time), q , increases. This increasing organization is reflected in the chemical disparity between the vent gas sampled in the last decade and the older hydrates. Eventually, the Bush Hill venting may decrease to the point hydrates no longer crystallize at the surface, and the hydrate mound will dissolve and be partially replaced by carbonate.

There are many uncertainties in our modeling analysis and the suggestions we draw from it, and an important aspect of the vent-rate-control-on-vent-chemistry hypothesis is therefore that it can be tested by monitoring the chemistry and venting rate of a single gas stream, by further documenting variation in the venting rate of individual bubble streams at a single site during the same submersible

visit, or by drilling the Bush Hill (or a similar) hydrate mound to determine if the gas and hydrate chemical variability changes with depth as predicted in Fig. 3.

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