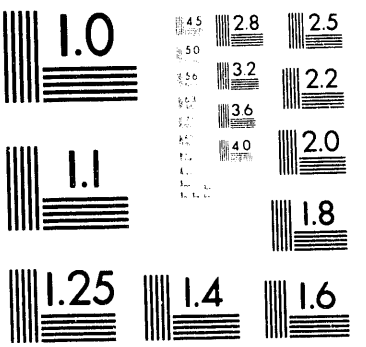
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SOURCES OF BIOGENIC METHANE TO FORM MARINE GAS HYDRATES: IN SITU PRODUCTION OR UPWARD MIGRATION?

by

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ABSTRACT

Potential sources of biogenic methane in the Carolina Continental Rise - Blake Ridge sediments have been examined. Two models were used to estimate the potential for biogenic methane production: 1) construction of sedimentary organic carbon budgets, and 2) depth extrapolation of modern microbial production rates. While closed-system estimates predict some gas hydrate formation, it is unlikely that >3% of the sediment volume could be filled by hydrate from methane produced in situ. Formation of greater amounts requires migration of methane from the underlying continental rise sediment prism. Methane may be recycled from below the base of the gas hydrate stability zone by gas hydrate decomposition, upward migration of the methane gas, and recrystallization of gas hydrate within the overlying stability zone. Methane bubbles may also form in the sediment column below the depth of gas hydrate stability because the methane saturation concentration of the pore fluids decreases with increasing depth. Upward migration of methane bubbles from these deeper sediments can add methane to the hydrate stability zone. From these models it appears that recycling and upward migration of methane is essential in forming significant gas hydrate concentrations. In addition, the depth distribution profiles of methane hydrate will differ if the majority of the methane has migrated upward rather than having been produced in situ.

INTRODUCTION

Gas hydrates are a solid phase composed of water and low molecular weight gases (predominantly methane) which form under conditions of low temperature and high pressure[1], conditions that are common in the upper few hundred meters of rapidly accumulated continental margin sediments

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where significant amounts of biogenic gas may be present[2]. Gas hydrates are usually detected in marine sediments with seismic reflection data because they produce a bottom simulating reflector (BSR)[3]. The BSR often cuts across normal sediment bedding planes, thus clearly distinguishing itself as an acoustic response to a diagenetic change rather than a depositional horizon. BSR's are believed to represent the base of the gas hydrate stability zone which occurs between about 200 and 600 meters below the sea floor of continental rises[4-6]. The pore space of sediments above BSR's are partly filled with gas hydrates while the sediments below may contain a free gas phase. The existence of bubbles in interstitial pore fluid from below the inferred base of the hydrate stability has been observed in recent ODP holes on Legs 141 and 146 [7,8] and apparently occurs in patches beneath the BSR.

Enormous volumes of natural gas may be associated with sediments containing gas hydrate[9]. Large quantities of gas may be stored in these sediments because up to 164 times the saturation concentration of gas at STP condition can be contained in methane hydrate per unit volume[1]. It is estimated that there are about 10^4 Gt (Gt = 10^{15} gm) of methane carbon stored in gas hydrates, which is about two times the estimate for the carbon in all other fossil fuel deposits[6,9]. Moreover, there may be considerable volumes of free gas trapped beneath the overlying solid gas hydrate-cemented zones that are associated with the BSR. Geophysical estimates suggest that a large percent of the total sediment volume may be filled with gas hydrates in some parts of the Carolina Continental Rise - Blake Ridge area (e.g., >16%[10]; up to 35%[11]; up to 5%[12]).

In this paper we consider the importance of in situ production as compared with migration of biogenic methane in providing methane for biogenic gas hydrate formation in the Carolina Continental Rise - Blake Ridge area. Three distinct sources are in situ biogenic production, recycling of methane at the base of the gas hydrate stability field, and distillation of methane from pore fluids contained in the sediment column beneath the base of gas hydrate stability field.

Sources of the Methane (in situ Production or Upward Migration?)

In order to have gas hydrate formation by in situ microbial methane production, the following sequence of events must occur within the

sediments, as they are buried: 1) Microbial sulfate reduction must consume the sulfate dissolved in the pore fluids, because microbial methane production is inhibited by the presence of sulfate[13]; 2) Microbial methane production will commence near the base of the sulfate reduction zone and pore fluid methane concentrations will increase until methane saturation occurs; and 3) After saturation is achieved, any additional methane production will result in either gas hydrate formation or continued gas bubble formation, depending on pressure and temperature conditions. The amount of methane produced between the depth of sulfate depletion, and the base of the hydrate stability zone, must exceed the amount necessary for fluid saturation before hydrates can form. Conversely, if in situ production of biogenic methane is not adequate to generate saturation within the gas hydrate stability zone, then additional methane must migrate from below if hydrate is present in the sediment column[14].

Once a gas hydrate zone is established, high concentrations of biogenic gas may accumulate as a result of recycling of methane gas below the base of this zone. As continental rise sediments are progressively buried, they experience an increase in temperature associated with the geothermal gradient. At some point, the sediment will subside below the base of the gas hydrate stability zone. Methane released by gas hydrate decomposition below the base of the hydrate stability zone may move buoyantly upward and re-enter the overlying gas hydrate stability zone. Additional methane may come from below the base if the gas hydrate stability zone because of continued microbial methane production and bubble formation with decreasing methane saturation.

Methane Saturation Levels

The existence of gas bubbles at a BSR is required by the phase rule, if the BSR in fact reflects the base of hydrate stability. Thus, the methane concentration in the pore waters at a BSR can be estimated from methane saturation data[15] as shown in Figure 1. The concentration of dissolved methane necessary to reach saturation decreases with depth (i.e., increasing pressure and temperature) to a sub-bottom minimum. Assuming that pore fluid within this sediment column is at hydrostatic pressure, a water depth of 3 km, seawater-like sodium chloride concentrations (35°/oo), a temperature gradient of 30°C / km, and the

base of the hydrate stability zone at 600 meters, the concentration of methane saturation is 193 mM per liter. Thus, in order to form gas hydrate, methane concentration in the pore fluids must equal or exceed the saturation value of 193 mM at the base of the hydrate stability zone. Beneath the base of hydrate stability, the concentration of methane that is needed to obtain saturation decreases to a minimum value of 171 mM per liter at 4.5 km (1.5 km sub-bottom).

METHANE SOURCES FOR CAROLINA CONTINENTAL RISE - BLAKE RIDGE HYDRATES:

Existing isotopic ($\delta^{13}C$ and δD) and compositional data (methane/ethane ratios) at the Carolina Continental Rise - Blake Ridge gas hydrate field suggest that the methane is biogenic[16-19]. However, these data do not require that the gas was formed where it was sampled. Here we consider whether the gas hydrates in the Carolina Continental Rise - Blake Ridge area can be sustained by <u>in situ</u> production of microbial methane and whether the observed amounts of methane require upward migration of gas from below.

<u>Can Enough Methane Be Produced by *in situ* Production?</u>

a. Organic Carbon Limitation

The amount of methane that could be produced in a closed system (i.e., no gas migration) is ultimately controlled by the amount of metabolizable organic carbon that the sediments contain at the time they are deposited on the sea floor. Methanogenesis[2] consumes two moles of organic carbon for each mole of CH_4 produced:

$$2\,CH_2O \rightarrow CH_4 + CO_2 \qquad (1)$$

Theoretically, the CO_2 that is produced may also be further reduced to methane if there is an adequate supply of hydrogen:

$$CO_2 + 4\,H_2 \rightarrow CH_4 + 2\,H_2O \qquad (2)$$

Although, it is still not known how important these reactions are at moderate burial depths in deep-sea sediments[20], we will use these stoichiometric reactions to estimate the maximum amount of methane that could be produced.

Unfortunately, neither the original amount nor quality of sedimentary organic carbon can actually be determined for buried sediment. However, modern sediments in similar continental rise settings rarely have total organic carbon concentrations that exceed 1%, and one-half or more of the total organic carbon is thought to be unavailable to microorganisms[21]. The Holocene sediments in Carolina Continental Rise - Blake Ridge area today average <1% organic carbon[22], of which only about one-half may be metabolized by bacteria.

Hydrate-bearing sediments from the Blake Ridge area have surprisingly high porosity values for silty-claystones[23]. Data collected by the DSDP at Site 102 indicates that the porosity is 40 to 50% at 600 meters[24]. At DSDP Site 533[25], the porosity remains near 57% from the surface to the base of the hole (399 meters). These observations suggest that normal porosity reduction during sediment subsidence and compaction may be arrested by gas hydrate in-filling. Our calculations below will use a porosity value of 40% for the sediment near the base of the gas hydrate stability field.

It is possible to calculate the amount of methane hydrate which can form in a given volume of sediment (Table 1). One liter of fluid-saturated, clay-rich sediment that has 1% total organic carbon by dry weight (~0.5% metabolizable organic carbon), 40% porosity, and a clay mineral density of 2.6 gm/cm^3, would contain 7.8 gms of organic carbon. If this is all converted to methane and diffusive losses are ignored, 260 mM of methane could be produced per liter of wet sediment.

Given that the pore fluid will remain at methane saturation (~193 mM per liter of pore fluid), the pore fluid in this liter of sediment will contain 77 mM of dissolved CH_4. Thus, 183 mM of CH_4 will be available to form hydrate. Each 1% by volume of gas hydrate formed in the pore space (assuming a porosity of 40%, a gas hydrate density of 0.91 gm/cm^3 and stoichiometry[26] of $CH_4 \cdot 5.9H_2O$) will contain 30 mM of CH_4 per liter of sediment. Under these ideal conditions, 6.1% of the pore space could be

filled with hydrate (or 2.4% of the total sediment volume) through in situ production of microbial gas. Thus, organic carbon limitation makes it unlikely that continental rise sediments which contain more than nominal amounts of biogenic methane hydrate are closed systems.

b. Extrapolation of in situ Microbial Production Rates.

Another approach in determining whether methane hydrate is formed by in situ production or requires methane migration uses depth-concentration profiles of microbial substrates and metabolic by-products (Table 2). Depth-concentration profiles of metabolic by-products can help indicate whether adequate rates of microbial gas production have occurred[2] to produce saturation levels of methane in the zone above the base of the hydrate stability zone. The relationship between idealized microbial production gradients and the resulting concentration of methane that can be produced by the time a sediment reaches the depth of the base of the gas hydrate stability zone can be estimated and compared with the saturation values (Figure 2). We assume: 1) uniform vertical distribution of organic carbon in the sediment; 2) steady-state conditions; 3) sulfate reduction proceeds by:

$$2\,CH_2O + SO_4^{-2} \rightarrow S^{-2} + 2\,CO_2 + 2\,H_2O \qquad (3)$$

and 4) the methane production rate at depth is equal to one-half the average sulfate reduction rate in the shallower sediments. Assumption 4 probably yields an excessively high methane production rate. A more realistic production rate estimate will decrease as organic carbon quality decreases with burial depth and time. In many cases, the rate of microbial activity is modeled as decreasing logarithmically with depth[27]. The rate of methanogenic gas production hundreds of meters below the sediment surface may be much lower than the sulfate reduction rate in the upper sediment column.

Piston cores from the Carolina Continental Rise - Blake Ridge area indicate that a characteristic depth of pore water sulfate depletion is about 28 meters[28]. The porosity in the upper few hundred meters of these sediments is about 50%[24]. Therefore, there are 14 mM of SO_4 per liter of sediment (28 mM in pore fluid) and thus the rate of sulfate depletion is 0.5

mM per meter. For an area of the seafloor where the sulfate depletion depth is 28 m and the BSR is at 600 meters sub-bottom depth[28], the methanogenic zone within the hydrate stability field is 572 meters thick. The average methane production rate over this 572 meter zone is optimistically estimated at one-fourth the sulfate depletion rate in the upper 28 meters.

If methanogenesis involves a complete reduction of the organic carbon by reaction (1), then 28.6 mM of CH_4 are produced per liter of sediment by 600 m sub-bottom [(572 m) * (0.125 mM/m) * (0.4 porosity)]. However, the CO_2 that is produced in reaction (1) may also be converted by reaction (2) to double the amount of methane that is produced in the system. Thus, a maximum of 143 mM of methane could be produced from one liter of sediment. Subtracting the saturation amount (saturation value of 193 mM; Figure 1) that will remain in solution at 40% porosity (77 mM), the maximum amount of the pore volume that could be filled with gas hydrate from in situ methane production is 2.2%. Thus, with these generous assumptions, only 0.9% of the sediment volume could be occupied by methane hydrate.

These calculations suggest that both the total amount of sedimentary organic carbon and optimistic depth integrated rates of organic carbon reduction are probably inadequate to produce significant amounts of gas hydrate by in situ production in the Carolina Continental Rise - Blake Ridge area under 3 km of water depth. The problem of methane availability is more significant in shallower water where the observed depth to BSR is shallower. In shallower water methane must be produced at much higher rates if methane saturation is to be achieved by in situ microbial production.

Methane Recycling: Bubble Formation and Migration.

In the continental rise there are three ways in which methane bubbles may form within the sediments at depths that are below the base of gas hydrate stability zone: 1) sustained microbial production, 2) recycling of methane, and 3) methane distillation.

1) Microbial methane production will continue with depth until the utilizable organic carbon is exhausted and as long as methanogenic bacteria survive. Although the amount of biogenic methane produced will decrease

with depth, any new methane production will increase the pore water methane concentration until saturation is achieved. Once the pore fluids are saturated with methane, continued methane production should result in the generation of methane bubbles. In a methane hydrate containing sediment column, pore fluids in the sediments at and directly beneath the base of the gas hydrate stability zone must be saturated with methane. Thus, any additional methane production will cause methane supersaturation in the pore fluids and generate interstitial bubbles.

2) In continental rise sediments, the position of the methane hydrate-methane gas phase boundary (which separates the overlying zone where gas hydrates are stable from the underlying zone where methane gas is present) is sensitive to local conditions, especially temperature, pressure and pore water composition. Predictable hydrostatic pressure and temperature changes occur within continental rise sediments with gradual subsidence. As the position of this phase boundary shifts upward within the sediment column, some gas hydrate containing sediments will pass out of the gas hydrate stability field. The methane from these decomposing gas hydrates will be added to the already supersaturated pore fluid and should ultimately form bubbles (Figure 3).

3) Beneath the gas hydrate stability zone, the methane concentration that is needed to achieve saturation (Figure 1) decreases with depth in the sediments to a minimum value at about 1.5 km sub-bottom. A consequence of this relationship is that burial of a methane-saturated pore fluid will result in a supersaturated solution, from which methane bubbles may form.

Bubbles are buoyant and may rise within the sediment column until they re-enter the gas hydrate stability zone. If methane bubbles formed within the continental rise prism sediments are efficiently mobilized upward and if methane is efficiently recaptured by gas hydrate crystallization above, then the amounts of methane gas hydrate that could occur near the base of the the gas hydrate stability zone can be estimated.

a. Estimates of methane recycling

As sedimentation and subsidence occurs on the continental rise, the base of the methane hydrate stability field moves progressively upward within the sediment column. Thus, methane hydrate will decompose at the

base of the hydrate stability field, forming methane bubbles. Buoyant methane bubbles should migrate a short distance upward and form gas hydrate after re-entering the hydrate stability field above (Figure 3). How far into the hydrate stability zone methane bubbles will penetrate is unknown but this will be influenced by local sediment permeability. If local recycling is perfectly efficient, the amount of gas that will return to the overlying hydrate stability field will be the integrated sum of all the hydrate that has decomposed at the base of the stability field throughout the history of the rise.

For example, if in situ production of methane is adequate to fill the lower 5 meters of the hydrate stability zone with 1% gas hydrate, then after 5 meters of sedimentation and subsidence under steady state conditions, enough methane should migrate upward from decomposing gas hydrate to add an additional one percent hydrate into an overlying zone of similar thickness. If all the methane from decomposing hydrate is added with the 1% in situ produce hydrates into a layer of the same thickness, in theory enough methane could be concentrated to fill all of the sediment pore space with methane hydrate after 250 m of sedimentation has occurred. However, recycling of methane by gas hydrate decomposition and the formation of increasing amounts of gas hydrate should progressively decrease the permeability of the basal hydrate zone and prevent gas bubbles from entering into the overlying hydrated zone. Gas may either accumulate at the base of the hydrate zone or migrate laterally along the base of the hydrate stability zone.

b. Estimates of methane distillation from beneath the stability zone.

At the base of the hydrate stability zone, the pore water is saturated with respect to methane. The example illustrated in Figure 1 shows that the amount of methane necessary for saturation decreases from the base of the hydrate stability zone (193 mM) to a sub-bottom depth of 1500 m (170 mM). Thus with continued burial, methane bubbles may form without any additional biogenic methane production.

The effect of this change in methane saturation can be illustrated by following a parcel of sediment through the sediment column from the base of the hydrate stability zone to the depth of the solubility minimum. For each liter of pore fluid (a 10 cm cube) that passes through this 900 meter

thick zone of decreasing methane saturation concentration beneath gas hydrate containing sediments, 23 mM of methane gas could be produced. If the sediment porosity is 40%, then 9.2 mM of methane will be produced for each liter of sediment that follows this path. Because the overlying pore waters beneath the zone of hydrate stability are already methane saturated, bubbles will not be reabsorbed as they rise. Thus, for every liter of sediment that is buried (10 cm of burial), 9.2 mM of methane will be converted into bubbles and is available to rise buoyantly upward and re-enter the base of the gas hydrate stability zone from below. After 100 meters of burial, 9,200 mM of methane gas will have been produced from the same area (100 cm^2). If this methane rises as bubbles, penetrates into the hydrate stability zone and become concentrated into a thin (5 m) zone at the base of the stability field, 184 mM of methane will be available for additional gas hydrate formation per liter of sediment. This is enough methane to fill an additional 6% of the original sediment pore space. If this process works efficiently, enough methane to fill all the original pore space with methane hydrate will become available after only 660 meters of subsidence. Clearly, this process is either not efficient or the methane is removed by other processes.

DISCUSSION

Growth of a Biogenic Methane Hydrate Deposit: Initiation and Evolution.

The consequences of the processes of methane production and migration are illustrated by examining the potential for gas hydrate development in sediments as the rise develops over the course of millions of years. Several scenarios are possible:

1) Where microbial gas production rates are low, methane saturation may never be achieved anywhere within the sediment column and neither hydrates nor bubbles are formed.

2) Microbial gas production rates are adequate to achieve methane saturation within the hydrate stability zone. Gas hydrates are formed from this level to the base of the hydrate stability zone. While gas bubbles are formed below, gas bubbles are not efficiently transported upward. Thus the gas hydrates are only composed of methane produced in situ.

3) Microbial gas production rates are moderate, gas saturation might be achieved by in situ methane production below the base of the hydrate stability zone but above the minimum in methane solubility. Both continued production and progressive burial will result in methane supersaturation and bubble formation in the interstitial spaces. These bubbles may rise in the sediment column. As the methane bubbles rise, they are reabsorbed by overlying undersaturated pore fluids, increasing the local methane concentration. However, not enough methane bubbles are transported upwards to achieve saturation at the base of the hydrate stability zone, so gas hydrates are not formed.

4) Microbial gas production rates are moderately high. Although gas saturation is not achieved at the base of the hydrate stability zone by in situ production, enough gas is transported upward in rising bubbles from below the hydrate stability zone so that saturation values are achieved and some hydrate is formed at the base of the gas hydrate stability field.

5) Microbial gas production rates are high. Microbial production is adequate to achieve saturation within the hydrate stability zone. Saturation levels are achieved in the sediments some distance above the base of the hydrate stability. The first crystal of methane hydrate will form at the level where saturation was achieved, and continued methane production leads to additional amounts of hydrate formation. Thus a few per cent of the sediment pore space might be filled with gas hydrate formed from methane produced in situ. However, this hydrate is augmented by gas hydrate formed from methane that has migrated from below. Both methane recycling by gas hydrate decomposition directly at the base of the hydrate stability zone and by methane distillation from sediment pore fluids are possible sources. The result will be that traces of gas hydrate will occur from the level at which saturation was achieved and will increase in amount downward. However, near the base of the hydrate stability zone, where methane has been supplied from below, the concentration of hydrate could approach the sediment porosity (Figure 4).

6) Microbial methane production rates in the sediment column are low but methane becomes available through lateral migration from an adjacent area down dip. This could happen when the zone near the base of the hydrate stability zone is adequately filled with hydrate to occlude most of the sediment permeability. Thus, if additional gas was provided from

beneath, the gas would accumulate and may migrate along the porous zone under the base of the hydrate stability. Where more permeable areas (less hydrate) are encountered, and the pore waters are saturated, the gas will rise and fill the zone above the base of the hydrate stability zone with hydrate. If the bubbles migrated into a zone of undersaturated pore waters, then methane bubbles would be re-absorbed by the pore fluids. Both processes would result in the lateral expansion of the zone in which gas hydrates occur.

When the formation of gas hydrate depends the migration of gas or fluid, then the distribution of gas hydrate within the sediments will be controlled by the flow characteristics of the sediments. If the fluid flow occurs pervasively through relatively uniform porosity sediments, the hydrate should be disseminated in a regular and predictable fashion. Conversely, if the gas migration is concentrated along permeable conduits, such as fractures, sand stringers or along the base of the gas hydrate stability zone, gas hydrate might occur as vein fillings.

Residence Times of Methane in the Continental Margin.

With efficient recycling, methane gas molecules may have very long residence times in Continental Rise sediment prism. In fact, the methane contained in gas hydrate could have been produced at any time during the continental rise's development and the present inventory of hydrates might include the integrated volume of all the methane hydrate that has been formed during the history of the continental rise.

However, the areas that might have very high concentrations of gas hydrate are neither that common, nor are they thick based on the presently available geophysical studies[29-32]. This suggests the following possibilities: 1) methane generated by gas hydrate decomposition is not efficiently recycled, 2) methane is lost from the system, or 3) the dynamics of methane production and storage have not operated in the same way throughout the history of the continental rise's development and, consequently, the methane currently stored in hydrates is relatively recent.

a. Methane Losses.

Methane may be lost from continental margin sediments if there are advective conduits through the gas hydrate stability zone to the seafloor that will carry gas bubbles through this zone too quickly for hydrates to form or carry methane-rich pore waters to the seafloor. Vents, faults, and other conduits for methane discharge from the sediment at abyssal depths have been theorized to occur[32-36]. At present we do not know how significant these vent systems are.

Some methane will also be lost with burial. As subsidence and burial proceed, methane that is dissolved in the pore waters and methane bubbles trapped in the sediments will become less likely to migrate upwards after a sediment parcel passes through the depth of the pore water saturation minimum.

b. Paleoclimatic Changes on Continental Rise Gas Hydrate Dynamics.

Measurements of oxygen isotopes of benthic foraminifera have provided an indication of the change in bottom water temperatures since the Mesozoic[37-38]. In the Cretaceous, it is believed that bottom waters were much warmer, about 14° C, but have cooled throughout the Cenozoic to the present temperature of about 4° C in the vicinity of the Blake Ridge. The effect of this long term bottom water temperature decrease would be a progressive thickening of the zone of gas hydrate stability through the Cenozoic. From the methane hydrate phase diagram[39], we predict that Cretaceous gas hydrates would have been stable within a zone in the sediment column only about half the thickness of the present stability zone. Thus, it would have been more difficult to form gas hydrates by <u>in situ</u> gas production in the Mesozoic. We suspect that the inventory of methane that is stored as gas hydrate may have largely accumulated during the Neogene.

<u>Bubble Distillation and the Appearance of Seismic Reflection Profiles.</u>

Under appropriate circumstances, methane bubbles should occur intermittently in the sedimentary section between the base of the zone of hydrate stability and the depth of the minimum methane solubility. Because these bubbles strongly influence the acoustic impedance of sediments, these units may be very reflective in seismic reflection profiles.

Seismic reflection profile data from the Carolina Rise - Blake Ridge area[3,28,40-42] frequently show that sedimentary units below the BSR (and are presumably beneath the base of the gas hydrate stability field) are associated with numerous high amplitude reflectors. These high amplitude reflectors may be a result of bubble formation.

CONCLUSIONS

Two models of estimating the amount of gas that can be produced within the zone of hydrate stability in marine sediments from the Carolina Continental Rise - Blake Ridge area have been considered: 1) amount of available organic carbon and 2) extrapolations of microbial depth-integrated production rates. Carbon supply ultimately controls how much of the sediment could be filled with gas hydrate produced in situ. With observed organic carbon concentrations and efficient conversion of this carbon to methane, up to a few percent of the total sediment volume near the base of the gas hydrate stability zone could be filled with in situ produced gas hydrates. Likewise, depth integration of observed microbial production rates in the sediment that overlay the Carolina Continental Rise - Blake Ridge gas hydrate field show that in situ production can only generate a few percent gas hydrate.

Estimates of the amount of gas that might be recycled at the base of the hydrate stability zone by gas hydrate decomposition and the amount of gas that can be distilled out of the underlying sediments because of decreasing gas saturation with depth suggest that there is a considerable potential to concentrate methane in the gas hydrate stability zone. In fact, given some moderate level of efficiency, the question is not how do we get enough gas, but rather where has the gas gone. We infer that some gas must be escaping upward out of the rise through conduits.

Sediments containing methane hydrate will exhibit different depth distributions of hydrate depending on the source of the methane (Figure 4). If the gas hydrates are produced in situ in favourable lithologies, there should be a gradual increase in the amount of gas hydrate with depth. However, if the methane is advected from below (either by recycling or distillation) or laterally, gas hydrate amount will increase dramatically just above the base of the gas hydrate stability field.

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Figure 1. The concentration of methane that is needed to achieve saturation is indicated with depth for a section of the continental rise where the water depth is 3 km, pressure is hydrostatic, the geothermal gradient is 30° C per km, and the initial pore waters are of 35 °/oo sodium chloride (after[15]). The position of the base of the gas hydrate stability (BGHS) zone is indicated at 600 meters sub-bottom, consistent with published phase diagrams[39] and with empirical observations of BSR depths on the Carolina Rise and Blake Ridge. Above the BGHS and to the left of the methane saturation line there is no methane hydrate and the pore waters are undersaturated. To the right of the methane saturation curve (dashed line) and above the BGHS pore waters will be saturated with methane and the sediments may contain methane hydrate crystals. Methane saturation within the gas hydrate stability zone cannot be accurately estimated with the equations of Duan et al.[15] and the position of the dashed line is only schematic. Below the BGHS, the pore water in the sediments that occur in the field to the left of the saturation curve (black line) will be undersaturated with respect to methane while the pore waters in sediments that lie in the field to the right of the saturation curve will be saturated with methane and the sediments may contain methane bubbles.

Figure 2. Examples of the relationship between possible microbial production rates, methane saturation levels, and the methane hydrate stability field (as in Figure 1) are shown. In order to have methane hydrates, methane concentration must exceed the saturation value at the base of the gas hydrate stability (BGHS) field. Line A shows a microbial methane production gradient that will achieve saturation at the BGHS. For significant amounts of methane hydrate to form from in situ production the average microbial production gradient should exceed rate indicated by line A. No hydrate will form by in situ production with gradient B; however, methane bubbles should form in the sediment beneath the BGHS where methane saturation is exceeded. If bubbles rise in the sediment, they will increase the concentration of methane in the pore waters above until saturation is reached. Given adequate transport efficiencies and amount of bubbles, methane from buoyant bubbles that are distilled from the underlying sediment section may re-enter the hydrate stability field above. No methane hydrate will form with gradient C. If methane

saturation is achieved, methane bubbles would be reabsorbed with increasing burial because this zone is beneath the minimum in the methane saturation concentration.

Figure 3. Schematic illustration showing how methane may be recycled as the base of the hydrate stability field (BGHS) moves upward in the sediment column with progressive burial and subsidence of the continental rise. At Time 1, some hydrate crystals are disseminated with the sediments above the BGHS which originated from in situ produced methane. With continued burial and subsidence, the methane hydrate produced in situ will move beneath the BGHS and decompose. This gas may rise buoyantly upward and re-enter the gas hydrate stability zone above to form more methane hydrate. Thus at Time 3, the methane that forms hydrate will be a mixture of in situ produced and recycled methane.

Figure 4. Schematic illustration of how the depth distribution of methane hydrate will vary depending on whether the methane in the sediments that forms gas hydrates has come from in situ microbial production or from recycling of methane from gas hydrate decomposition or bubble distillation as the continental rise evolves. In situ-produced gas hydrates will have a depth distribution gradient that starts at the subseafloor depth at which methane saturation is achieved and increases at a rate that is controlled by microbial production. Gas hydrate from recycled methane should be restricted to a thinner zone above the BGHS. The thickness of this zone which contains methane hydrate from recycled gas will depend on the dynamics of bubble rise, permeability of the sediment and the kinetics of methane hydrate formation.

TABLE 1: ORGANIC CARBON LIMITATION

GIVEN:

(1) **1 % Total Organic Carbon**
(0.5 % Utilizable Organic Carbon)
in 1 L wet sediment

- $Porosity_{BGHS}$ = 40 %
- 600 m subbottom
- ρ mineral = 2.6 g/cm^3
- 3 km water depth
- Stoichiometry CH_2O = 30 g /mole

260 mM CH_4
per 1 L wet sediment with 40% porosity

(2)
- Temperature gradient 30°C/km
- Hydrostatic pressure
- 3 km water depth
- BGHS at 600 m subbottom

[CH_4] Saturation = 193 mM

- $Porosity_{BGHS}$ = 40 %

193 mM x 0.40 = 77 mM

(3) **1 % pore space is methane hydrate**

- $Porosity_{BGHS}$ = 40 %
- ρ hydrate = 0.91 g/cm^3
- Hydrate Stoichiometry
  1 CH_4 : 5.9 H_2O
  122 g /mole

30 mM CH_4

per 1 L wet sediment with 1 % pore-filling hydrate

THEN:

260 mM [maximum CH4] **- 77 mM** [dissolved in pore water] **= 183 mM CH_4** [available to form hydrate]

$\frac{183\ mM}{30\ mM}$ = **6.1 %** pore space with hydrate

6.1 % x 0.40 ≃ **2.4 %** of sediment volume occupied by hydrate

TABLE 2: METHANE PRODUCTION RATE LIMITATION

GIVEN:

(1) Only SO_4 reduction in upper sediment column

[$2\,CH_2O + SO_4^{2-} \rightarrow S^{2-} + 2\,CO_2 + H_2O$]

* 1 L wet sediment
* [SO_4^{2-}] = 28 mM
* $Porosity_{shallow}$ = 50 %
* Average depth-of-no-SO_4 = 28 m

$\frac{28\ mM}{28\ m} \times 0.50 = 0.5$ mM /m SO_4 depletion rate

CH_4 production rate = 0.125 mM /m
[CH_4 production = 1/4 SO_4 depletion]

(2) * Temperature gradient 30°C /km
* Hydrostatic pressure
* 3 km water depth
* 600 m subbottom

193 mM CH_4 at saturation

[see Figure 1]

* $Porosity_{BGHS}$ = 40 %

77 mM CH_4 in pore water

(3) CH4 production below SO_4-reducing zone

* 3 km water depth
* $Depth_{BGHS}$ = 600 m
* Thickness CH_4 production zone
  600 m - 28 m = 572 m
* $Porosity_{BGHS}$ = 40 %
* CH_4 production = 0.125 mM /m

572 m x 0.125 mM /m x 0.4 = [CH_4 production]

28.6 mM CH_4 produced in 1 L wet sediment

* If reaction 2 also occurs [$CO_2 \rightarrow CH_4$]

28.6 mM x 2 = 57.2 mM CH_4 Produced

* $Porosity_{BGHS}$ = 40 %

$\frac{57.2\ mM}{0.40}$ = **143 mM CH_4 Per 1 L pore water**

THEN:

143 mM - 77 mM = 66 mM CH_4 available for hydrate

$\frac{66\ mM}{30\ mM\ per\ 1\ \%\ hydrate} \simeq$ **2.2 % CH_4 hydrate per pore fluid volume**

2.2 % x 0.40 = **0.9 % CH_4 hydrate per sediment volume**

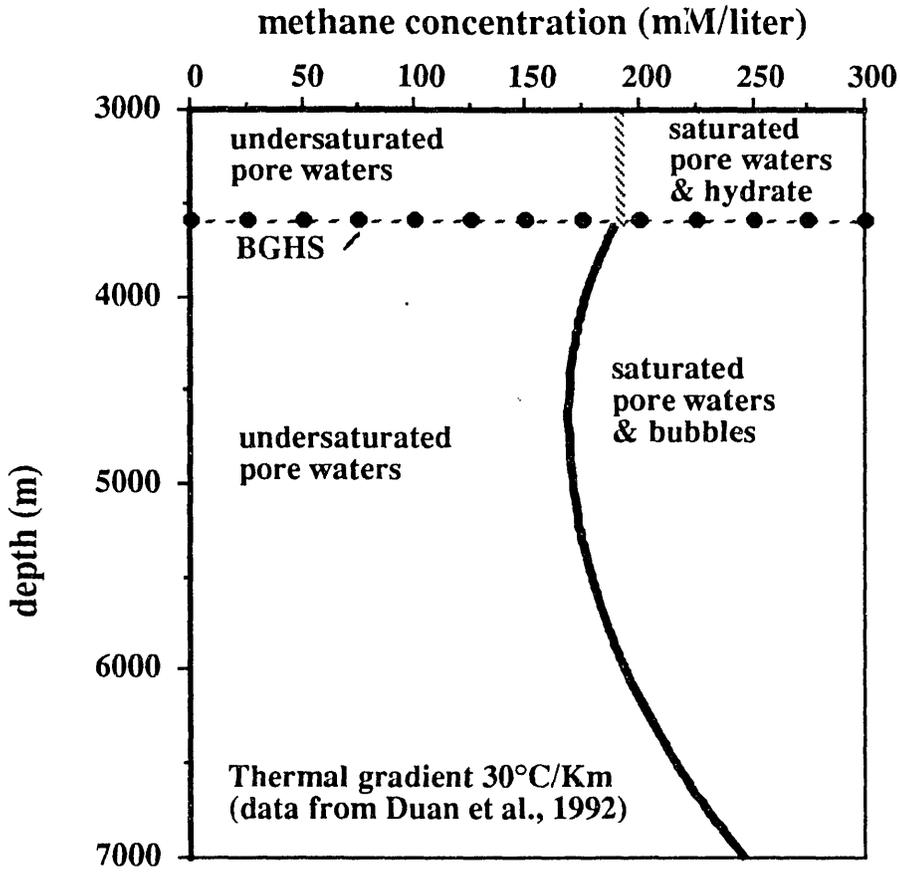
methane concentration (mM/liter)
0
50
100
150
200
250
300
3000
4000
5000
6000
7000
depth (m)
undersaturated
pore waters
saturated
pore waters
& hydrate
BGHS
saturated
pore waters
& bubbles
undersaturated
pore waters
Thermal gradient 30°C/Km
(data from Duan et al., 1992)

FIG 1

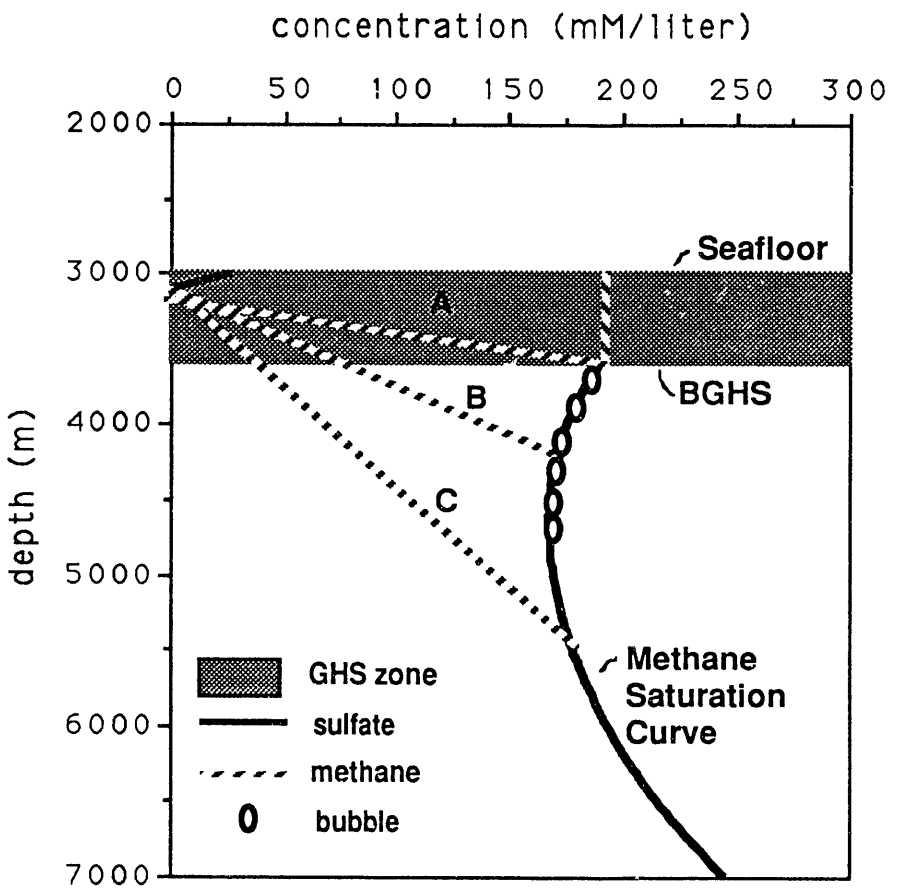
concentration (mM/liter)
0
50
100
150
200
250
300
2000
3000
4000
5000
6000
7000
depth (m)
Seafloor
BGHS
A
B
C
Methane
Saturation
Curve
GHS zone
sulfate
methane
bubble

FIG 2

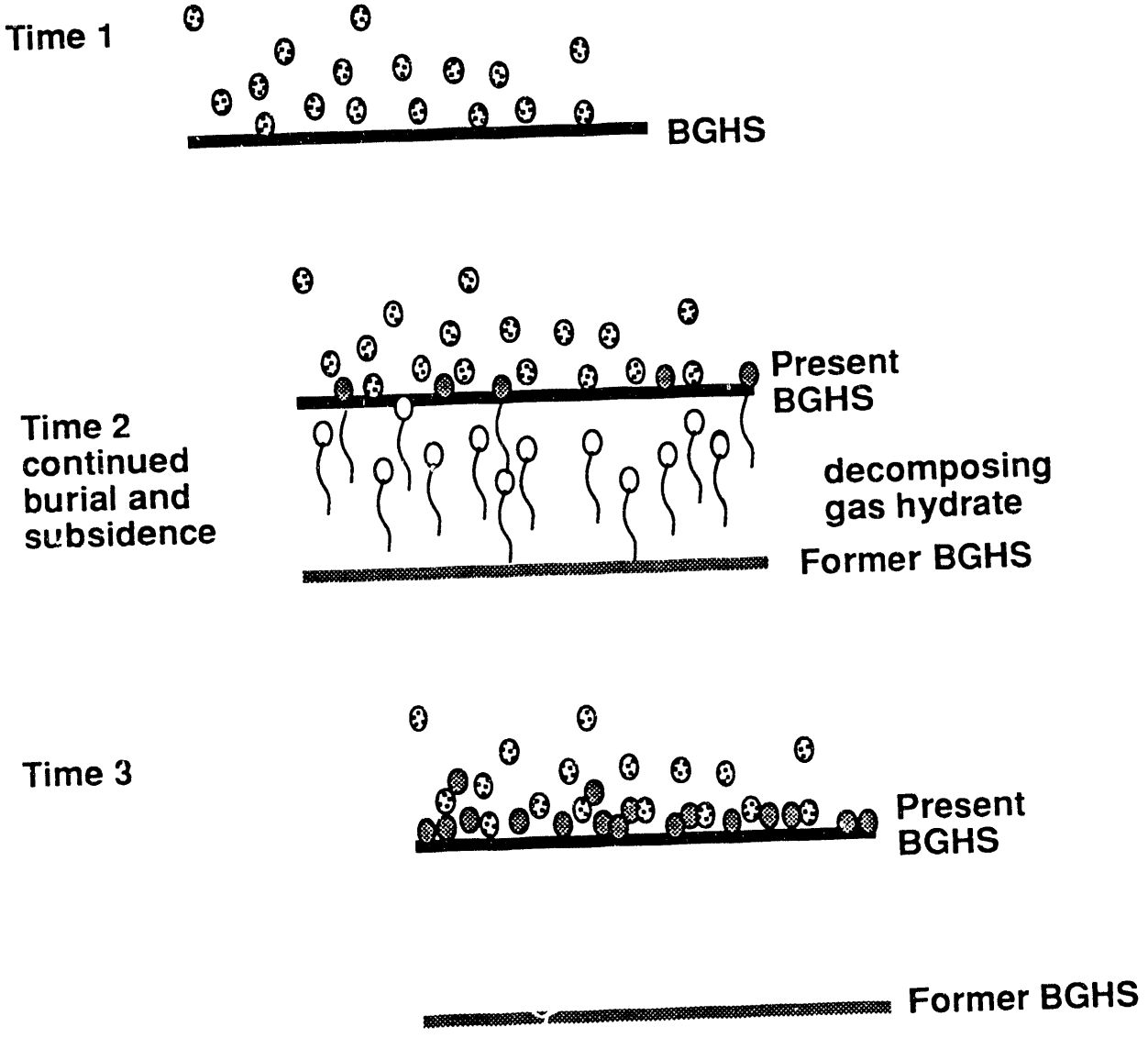
Time 1
BGHS
Time 2
continued
burial and
subsidence
Present
BGHS
decomposing
gas hydrate
Former BGHS
Time 3
Present
BGHS
Former BGHS
- in situ
methane
hydrate
- rising
methane
bubble
- recycled
methane
hydrate

FIG 3

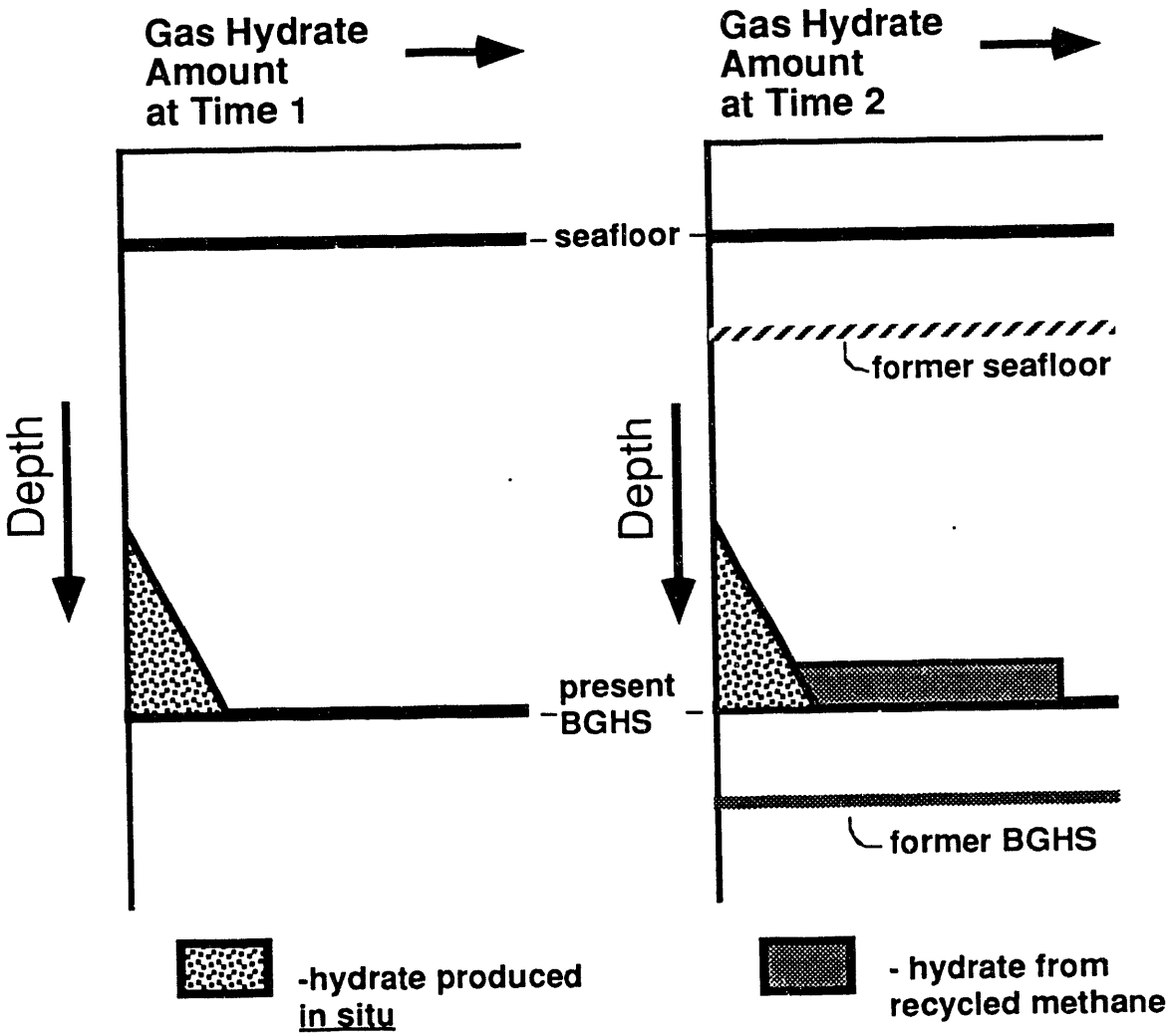
Gas Hydrate Amount at Time 1
Gas Hydrate Amount at Time 2
seafloor
former seafloor
Depth
Depth
present BGHS
former BGHS
-hydrate produced in situ
- hydrate from recycled methane

FIG 4

DATE
FILMED
11/8/93
END