1 **Testing short-range migration of microbial methane as a hydrate formation mechanism:**
2 **Results from Andaman Sea and Kumano Basin drill sites and global implications**

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Abstract

Methane gas hydrates in marine sediments often concentrate in coarse-grained layers surrounded by fine-grained marine muds that are hydrate-free. Methane in these hydrate deposits is typically microbial, and must have migrated from its source as the coarse-grained sediments contain little or no organic matter. In “long-range” migration, fluid flow through permeable layers transports methane from deeper sources into the gas hydrate stability zone (GHSZ). In “short-range” migration, microbial methane is generated within the GHSZ in fine-grained sediments, where small pore sizes inhibit hydrate formation. Dissolved methane can then diffuse into adjacent sand layers, where pore size does not restrict hydrate formation and hydrates can accumulate. Short-range migration has been used to explain hydrate accumulations in sand layers observed in drill sites on the northern Cascadia margin and in the Gulf of Mexico. Here we test the feasibility of short-range migration in two additional locations, where gas hydrates have been found in coarse-grained volcanic ash layers (Site NGHP-01-17, Andaman Sea, Indian Ocean) and turbidite sand beds (Site IODP-C0002, Kumano forearc basin, Nankai Trough, western Pacific). We apply reaction-transport modeling to calculate dissolved methane concentration and gas hydrate amounts resulting from microbial methane generated within the GHSZ. Model results show that short-range migration of microbial methane can explain the overall amounts of methane hydrate observed at the two sites. Short-range migration has been shown to be feasible in diverse margin environments and is likely to be a widespread methane transport mechanism in gas hydrate systems. It only requires a small amount of organic carbon and sediment sequences consisting of thin coarse-grained layers that can concentrate microbial methane generated within thick fine-grained sediment beds; these conditions are common along continental margins around the globe.

1. Introduction

Methane gas hydrates are widely found in continental margin sediments where methane is abundant, temperature is low, and pressure is high (Kvenvolden, 1993; Buffett, 2000; Tréhu et al., 2006). Hydrates are not uniformly distributed within sediments and their morphology depends on grain and pore size. In fine-grained, silt- and clay-rich sediments hydrates typically displace mineral grains and aggregate in veins, fractures, and nodules (e.g., Cook et al., 2014). We focus here on another end-member, gas hydrates disseminated within the pore space of coarse-grained sediment such as sand or volcanic ash. These coarse-grained layers are typically surrounded by fine-grained intervals that are hydrate-free (e.g., Torres et al., 2008). Understanding how these deposits form will improve our ability to predict where hydrates accumulate, how they dissociate due to warming of the global ocean, and their potential for release of greenhouse gases.

Methane in continental margin hydrate deposits is often of microbial origin, sourced from small amounts of particulate organic carbon (POC) buried in sediment (Claypool and Kvenvolden, 1983). Hence, methane must have migrated from its source to form hydrate in coarse-grained intervals that contain little or no organic matter. Two end-member migration scenarios have been proposed. In “long-range” migration, fluid flow through permeable layers transports methane from deeper sources into the gas hydrate stability zone (GHSZ), where it forms solid hydrate. In “short-range” migration, microbial methane is generated within the GHSZ in fine-grained muds, where small pore sizes inhibit hydrate formation. Dissolved methane can then

diffuse into adjacent coarse-grained layers, where pore size does not restrict hydrate formation and methane hydrates accumulate. Short-range migration by diffusion was suggested by Clennell et al. (1999) and modeled in detail by Malinverno (2010) and Rempel (2011). Short-range migration has been used to explain observed hydrate accumulations in a sequence of thin (<5 cm) sand layers in the northeastern Pacific Ocean (northern Cascadia margin; Malinverno, 2010) and in a 2.5 m-thick sand layer in the Gulf of Mexico (Walker Ridge; Cook and Malinverno, 2013).

In this paper, we test the feasibility of short-range migration in two additional convergent margin locations in the Indian and Pacific Ocean (Figure 1). The India National Gas Hydrate Program Expedition 1 found methane hydrates in several thin (up to 22 cm-thick) ash layers in the Andaman Sea accretionary complex (Site NGHP-01-17, Collett et al., 2008). Integrated Ocean Drilling Program Expedition 314 documented methane hydrate occurrences in up to 1.4 m-thick sand layers in the Kumano forearc basin of the Nankai Trough (Site IODP-C0002, Kinoshita et al., 2009). In both cases, gas hydrates were only found in coarse-grained layers surrounded by thicker fine-grained intervals that contained no hydrates. We first quantify observations of gas hydrate layering at these two sites and then apply a reaction-transport model to show that microbial methanogenesis and short-range methane migration can explain the observed hydrate contents. Based on the results in a total of four different settings, we argue that short migration may result in gas hydrate accumulations along many continental margin environments. Short migration only requires a relatively small amount of organic carbon available for microbial methanogenesis and fine-grained sediments (where methane is generated) that predominate in thickness over coarse-grained sediments (where gas hydrates accumulate). Finally, we present a

schematic representation of methane migration processes in gas hydrate systems that places short migration in a context of increasing distances and rates of methane transport.

2. Observations

2.1 Site NGHP-01-17 (Andaman Sea)

Site NGHP-01-17 was drilled in the Andaman accretionary complex near the top of a broad anticlinal structure over a prominent bottom-simulating reflector (Collett et al., 2008; Shankar and Riedel, 2013). The sediments are dominantly calcareous oozes with variable contents of siliceous biogenic material; thin volcanic ash layers are found between the seafloor and 165 mbsf (meters below seafloor) and between 265 mbsf and the total depth of 685 mbsf (Collett et al., 2008; Rose et al., 2014). Gas hydrates were detected in these ash layers defining a gas hydrate occurrence zone (GHOZ) between 268 mbsf and the base of the gas hydrate stability zone (GHSZ) at ~600 mbsf, which is unusually deep because of the low geothermal gradient at the site (Collett et al., 2008). In the GHOZ of Site NGHP-01-17, detailed core observations found 169 coarse-grained ash layers whose thickness ranges between 1 and 22 cm and averages 3.2 cm (Figure 2). The fine-grained sediment intervals between the ash layers are 1.5 m thick on average. The average sedimentation rate in the GHSZ is 69 m/Ma (Table 1), based on the estimated sediment age at 600 mbsf (Flores et al., 2014).

Gas hydrate content can be estimated from the chlorinity decrease in pore waters due to fresh water liberated by gas hydrate dissociation (Ussler and Paull, 2001). At Site NGHP-01-17, pore water analyses in 46 ash layers show chlorinities that are considerably less than the inferred in situ chlorinity (Figure 3A). The estimated gas hydrate contents are up to ~80% of pore volume (Figure 3B). Pore waters from immediately adjacent fine-grained sediments show little or no chlorinity decrease, indicating that gas hydrate preferentially formed in the ash layers (Collett et al., 2008; Rose et al., 2014). Gas hydrate content can also be estimated from downhole logs of porosity and electrical resistivity (e.g., Malinverno et al., 2008). The downhole logs collected at Site NGHP-01-17, however, do not have enough vertical resolution to accurately measure the thin hydrate-bearing layers observed in the cores (Shankar and Riedel, 2013).

Short-range migration requires that methane is microbially produced in situ. The origin of methane can be determined by the ratio of methane over higher hydrocarbons and from the composition of stable carbon isotopes (Claypool and Kvenvolden, 1983; Whiticar, 1999). Methane at Site NGHP-01-17 is microbial, as shown by the predominance of methane over higher hydrocarbon gases (Collett et al., 2008). The $\delta^{13}\text{C}$ of methane in the GHSZ is -60‰ to -80‰ , confirming a microbial origin (Briggs et al., 2012). However, the methanogenic Archaea that are usually observed at gas hydrate locations were not detected in a microbiological study of Site NGHP-01-17 sediments, perhaps indicating long-range transport (Briggs et al., 2012; see discussion in Section 5).

The intensity of in situ methanogenesis is limited by the amount of available particulate organic carbon (POC). Assuming that organic carbon deposition is approximately constant in time, the

amount of carbon consumed by methanogenesis can be estimated from the difference between the POC content near the seafloor and at depth (e.g., Ingall and Van Cappellen, 1990). POC content at Site NGHP-01-17 equals about 1% (dry sediment weight) at the seafloor, decreases to ~0.5% at 200-300 mbsf, and then increases downhole to ~1% at the base of the cored interval (Johnson et al., 2014). While the downhole increase at depth indicates that POC deposition has not been constant through time, the observed decrease from the seafloor to 200-300 mbsf can be taken as a measure of the amount of POC available for methanogenesis, suggesting that it should not be much more than 0.5%.

2.2 Site IODP-C0002 (Kumano basin)

Site IODP-C0002 has been drilled and reoccupied during several IODP expeditions of the Nankai Trough Seismogenic Zone Experiment (NanTroSEIZE). A 3D seismic survey near the site imaged the Kumano forearc basin as a sequence of planar, laterally continuous horizons representing sediments that are over ~900 m thick and tilted slightly to the NW. This dipping sequence is clearly cut by a bottom simulating reflector, marking the base of the GHSZ at a depth of ~400 mbsf near Site IODP-C0002. The dip of the horizons within the GHSZ is about 5° NW (Moore et al., 2009). The sedimentary sequence within the GHSZ was logged using logging-while-drilling (LWD) tools during IODP Expedition 314 (Hole C0002A, Kinoshita et al., 2009) and cored during IODP Expeditions 315 and 338 (Holes C0002K and C0002L, Strasser et al., 2009). The cores recovered from this site show a sequence of turbidites mostly composed of silt-clay muds with thin interbedded sands (typically 1-15 cm thick; Kinoshita et

al., 2009). Based on the estimated sediment age at 400 mbsf (Kinoshita et al., 2009), the average sedimentation rate within the GHSZ is 308 m/Ma.

Recovering unconsolidated sands by coring is usually problematic, as was the case at Site IODP-C0002, and a comparison with the LWD data show that <10% of the sands were recovered in the cores (Kinoshita et al., 2009). The lithostratigraphy and gas hydrate occurrence at this site have been largely interpreted from logging data. The LWD data show a number of thin, high-resistivity beds with relatively high porosity that are interpreted as hydrate-bearing intervals (gas hydrate is an electrical insulator). These resistive beds have low natural gamma ray radioactivity and are inferred to be turbidite sand layers (Kinoshita et al., 2009). Intervals between sands are interpreted as fine-grained clay and silt layers, which show no evidence of gas hydrate.

We estimate gas hydrate content from the excess electrical resistivity for the given sediment porosity (e.g., Malinverno et al., 2008). In this method, the bulk density log was first filtered with a median filter over a 3 m-thick window to eliminate low density values measured in enlarged borehole intervals (Figure 4A) and the median-filtered bulk density was used to compute the sediment porosity (Figure 4B). The same median filter was applied to the measured resistivity curve to eliminate the high-resistivity peaks due to gas hydrates, providing a smooth, general trend of resistivity with depth (Figure 4C). This resistivity trend is closely matched by the water-saturated resistivity predicted by Archie's equation (Ellis and Singer, 2007) for a best-fit cementation exponent m of 2.64. Finally, assuming a saturation exponent equal to m , we applied Archie's equation again to the ratio of measured and predicted water-saturated resistivity to estimate gas hydrate content as a fraction of pore volume (Figure 4D).

To minimize the effect of the finite vertical resolution of LWD resistivity measurements, which could result in a measured resistivity that is less than the actual resistivity of a thin layer, we used the LWD measurements having the highest resolution (~5 cm, deep button resistivity) and estimated the gas hydrate content of each layer from the local maximum (black dots in Figure 4D). We conservatively interpret high-resistivity intervals as gas hydrate-bearing when the maximum estimated hydrate content is greater than 10% of pore volume (Figure 4D). Because other factors may cause variations in the measured porosity and resistivity (e.g., lithology changes, borehole irregularities, etc.), the estimated gas hydrate content will not be exactly zero in hydrate-free intervals (e.g., below the base of the GHSZ at 400 mbsf). We assume that the 10% threshold for hydrate layer occurrence is a reasonable approximation of the detection uncertainties at Site IODP-C0002. With this 10% threshold criterion, gas hydrate layers are detected between 108 and 401 mbsf, defining the GHOSZ. Gas hydrate content increases with depth in the GHOSZ and reaches ~70% near the base of the GHSZ. Using the same detection threshold, we also reconstruct the sequence of gas hydrate-bearing sand layers within the GHOSZ (Figure 5), which closely matches the interpretation of sand layering made during IODP Expedition 314 (Kinoshita et al., 2009). Within the GHOSZ, we identify 166 gas hydrate-bearing sand layers that have an average thickness of 10.2 cm. The average thickness of fine-grained sediment intervals between the sand layers is 1.7 m.

At Site IODP-C0002, hydrate-forming methane is of microbial origin, indicated by a methane/ethane ratio of about 1000 and by a $\delta^{13}\text{C}$ of methane of -60‰ to -80‰ in the GHSZ (Kinoshita et al., 2009; Strasser et al., 2009). The POC content of the sediments cored at Site

IODP-C0002 was only measured below ~200 mbsf, and it shows a decreasing trend with depth, reaching ~0.4% at ~800 mbsf (Strasser et al., 2009). A simple linear extrapolation of this trend above 200 mbsf gives a POC content at the seafloor of ~0.8%. Near-seafloor POC contents around 0.8% decreasing to ~0.4% at depth have been measured in similar slope basin and trench settings of the Nankai Trough, IODP Site C0008 (Kinoshita et al., 2009) and ODP Site 808 (Berner and Koch, 1993). The difference between the POC content at the seafloor and at depth suggests that the amount of POC available for microbial methanogenesis should not be much more than ~0.4%.

3. Modeling

We apply reaction-transport modeling at Sites NGHP-01-17 and IODP-C0002 to test whether short-range migration could be the mechanism forming methane hydrates. This kind of modeling has been applied in various settings to predict gas hydrate content in homogeneous marine sediments (Davie and Buffett, 2001, 2003; Bhatnagar et al., 2007; Wallmann et al., 2012). Models are generally calculated in one dimension (vertical), assuming that variations with depth dominate over lateral changes, and calculations are performed until steady-state is reached with physical conditions that remain constant over time (sedimentation rate, methane generation, etc.). In these models, the calculated concentration of dissolved methane accounts for methane sources (such as microbial in situ generation) and for the effects of diffusion and sediment burial. Once the methane concentration exceeds its solubility within the GHSZ, the excess methane is assumed to combine with pore water to form gas hydrate. Typical model results suggest that

small pore space fractions become occupied by hydrate, on the order of 1-10% of pore space (e.g., Davie and Buffett, 2003; Bhatnagar et al., 2007).

Reaction-transport modeling in homogeneous sediments, however, cannot be directly applied to sequences of alternating fine- and coarse-grained sediment intervals because gas hydrate formation is affected by pore size. Similar to the freezing of water in soil, gas hydrate formation is inhibited inside small sediment pores due to capillary effects and grain surface interactions (Clennell et al., 1999; Daigle and Dugan, 2011; Liu and Flemings, 2011; Rempel, 2011). Gas hydrate formation in small pores requires an excess concentration over the free space solubility. For example, silt-clay marine sediments with a nominal pore size of 100 nm require an estimated excess concentration of about 3.3% of solubility (Henry et al., 1999). Torres et al. (2008) estimate that 0.5 °C of undercooling is necessary to form gas hydrates in fine-grained sediments, which corresponds to a similar excess methane concentration of 3.5% (from the derivative of solubility with temperature). Thus, although gas hydrate will form when the methane concentration equals the free space solubility in the larger pores of coarse-grained sediments, an excess concentration of 3-3.5% will be necessary to form gas hydrate in fine-grained sediments. We refer to this excess concentration as “supersaturation.”

Figure 5 illustrates a cartoon of the methane concentration pattern in a sequence of fine-grained sediment intervals of thickness h_{fine} separated by thin, coarse-grained layers of thickness h_{coarse} (Malinverno, 2010). As continuing sedimentation progressively buries a coarse-grained layer, the methane concentration will eventually reach the free space solubility and gas hydrate will start to form. As methane concentration can exceed free space solubility in fine-grained

sediment intervals, the concentration gradients above and below will drive a net diffusive flux of methane into the coarse-grained layer. If the methane concentration does not reach supersaturation, gas hydrate will not form in the fine-grained intervals and all of the methane will be transported by diffusion into the coarse-grained layers and form concentrated gas hydrate deposits.

The bow-shaped methane concentration profile in such fine-grained intervals can be determined by solving a simple diffusion problem in a layer where methane is internally generated and the concentrations are prescribed at the layer boundaries (Malinverno, 2010). The maximum concentration above free space solubility that will be reached in a fine-grained interval of thickness h_{fine} is

$$u_{\text{max}} = (q_{\text{max}} h_{\text{fine}}^2)/8D, \quad (1)$$

where q_{max} is the maximum rate of microbial methane generation and D the diffusion coefficient of methane in sediment. The time needed to establish this excess concentration can be estimated from the time needed to reach 90% of the steady-state value for a constant rate of methane generation, which is

$$t_0 = h_{\text{fine}}^2/4D. \quad (2)$$

For both sites examined in this paper, the value of u_{max} is well below the 3-3.5% of supersaturation needed to form gas hydrate in fine-grained sediments and the time t_0 to establish

the excess concentration in the fine-grained intervals is very short compared to the time scale of sedimentation (see Section 4).

The microbial methane generated in the fine-grained intervals is therefore transported by diffusion into the coarse-grained layers, whose gas hydrate content is equal to the content calculated in uniform fine-grained sediment times the ratio of pore space volumes:

$$V_{\text{fine}} / V_{\text{coarse}} = (h_{\text{fine}} \Phi_{\text{fine}}) / (h_{\text{coarse}} \Phi_{\text{coarse}}). \quad (3)$$

Typically, $h_{\text{fine}} \gg h_{\text{coarse}}$, and the gas hydrate content in coarse-grained layers will be much greater than that calculated in uniform, fine-grained sediment. If the porosity $\Phi_{\text{fine}} > \Phi_{\text{coarse}}$, the increase in gas hydrate concentration would be even greater. Although the porosity in sand may be less than that in compacting shales at the shallow burial depths within the GHSZ (Marion et al., 1992), we do not have reliable porosity data in volcanic ash, and therefore we neglect the possible porosity difference.

Following the reaction-transport model procedure described in Malinverno (2010), we first calculate the gas hydrate content at steady state in uniform sediment at the Andaman and Kumano basin sites. We then multiply this estimate by the ratio of the average fine- and coarse-grained bed thickness $h_{\text{fine}} / h_{\text{coarse}}$ (Table 1) to obtain the predicted gas hydrate content in periodic sequences of alternating coarse- and fine-grained sediment layers. The model assumes constant porosity and no vertical pore water advection. The only source of methane is microbial,

parameterized as a first-order reaction controlled by a prescribed quantity of POC available to methanogens and by a reaction rate constant (as in Davie and Buffett, 2003; Bhatnagar et al., 2007). More complex methanogenesis models with variable reaction rates have been proposed (e.g., Wallmann et al., 2006), but they cannot be used in the simple analytical formulation of Malinverno (2010).

The only significant update to the previous formulation is that we multiply the rate of microbial methane production (equation 6 in Malinverno, 2010) by a factor of 0.5. The prevailing pathway for methanogenesis in the marine environment is carbonate reduction, where two moles of organic carbon are converted into one mole of methane and one mole of CO₂ (Claypool and Kaplan, 1974; Whiticar, 1999). The factor of 0.5 accounts for the half of POC mass that is converted to methane and results in a required amount that is the total POC necessary to produce the model result. The required 0.11% POC originally estimated by Malinverno (2010) at IODP Site U1325 means that a total of 0.22% POC would actually need to be consumed by methanogenesis, an amount is well within the available POC content at that site.

4. Results

Modeling was carried out at each site to calculate methane concentration as a function of depth by varying the two parameters that control microbial methane generation: the amount of POC available for methanogenesis and the reaction rate constant. Starting with reasonable initial values, the available POC and reaction rate were iteratively adjusted until the predicted gas

hydrate content matched the amounts observed in the coarse-grained layers. The maximum available POC was constrained from core sample analyses at the two sites (see section 2). The reaction rate constant for methanogenesis is the least well constrained parameter in modeling gas hydrate formation (Davie and Buffett, 2001); previous studies used rate constants on the order of 10^{-13} s^{-1} (Davie and Buffett, 2003; Malinverno, 2010). For a given amount of available POC, the rate constant is adjusted to be consistent with the observed top of the gas hydrate-bearing interval. In general, a higher (lower) rate constant results in a shallower (deeper) top of gas hydrate occurrence.

We stress that this procedure does not fully explore the possible combinations of POC content, reaction rate, and other uncertain parameters (e.g., sedimentation rate) that could match the observed gas hydrate distributions. The model simulations we present, however, let us assess whether the small amount of POC available for in situ microbial methanogenesis is sufficient to produce the amounts of gas hydrate observed at each site. This is the critical test for short-range migration to be considered a viable methane transport mechanism.

Model results at Site NGHP-01-17 for an available POC of 0.6% and a reaction rate of 10^{-14} s^{-1} are shown in Figure 7. For the given microbial methane source (Figure 7A), our model first computes a predicted gas hydrate content for homogeneous sediment, assuming that hydrate forms where the steady-state methane concentrations exceed the free space solubility (Figure 7B). The resulting gas hydrate content is low, attaining a maximum slightly greater than 1% of the pore space (Figure 7C). At this site, the supersaturation within fine-grained sediment intervals is at most only 0.001% of the free space solubility (Equation 1) and the characteristic

time to reach this supersaturation is only 35 years (Equation 2). The methane generated in the fine-grained intervals therefore diffuses into nearby coarse-grained layers, and their gas hydrate content is equivalent to the gas hydrate content of homogeneous sediment (Figure 7C) multiplied by the average ratio of fine-to-coarse grained layer thickness (46 at this site; solid line in Figure 7D).

The shaded region in Figure 7D shows the range of modeled gas hydrate content for realistic bed thickness variations. Our model assumes a periodic sequence of alternating fine- and coarse-grained layers with uniform thicknesses equal to the averages at each site, and therefore the predicted gas hydrate content varies smoothly with depth. Observed gas hydrate content, however, is extremely variable (Figures 3B and 7D). This variability may simply be attributed to variations in the thickness of fine- and coarse-grained beds. For example, a coarse-grained layer that is thinner than the average, or is surrounded by fine-grained intervals thicker than the average, would have a hydrate content greater than that predicted using the average bed thicknesses. We do not take direct observations of bed thickness into account because our lithologic interpretation is incomplete as a result of partial core recovery (Figure 2). Missing even one thin layer could bias significantly the predicted gas hydrate content. Therefore, to approximate the variability due to non-uniform bed thicknesses, we assume that thin, coarse-grained layers are randomly distributed within the sequence. With this assumption, the thicknesses of the fine-grained intervals follow an exponential distribution that is fully described by the average value. Bed thicknesses of 0.288 and 1.39 times the average bound the central 50% of this distribution and correspond to ratios of fine- to coarse-grained sediment thickness of 13 and 64, respectively, at Site NGHP-01-17. The shaded region in Figure 7D shows the

corresponding range of predicted gas hydrate contents, demonstrating that realistic bed thickness variations can account for the wide range of observed gas hydrate content.

At Site IODP-C0002, our model results also fit well the observations, given an available POC of 0.4% and a reaction rate of $3.5 \times 10^{-14} \text{ s}^{-1}$ (Figure 8). The maximum supersaturation in the fine-grained intervals is 0.02% of the free space solubility (Equation 1), and the characteristic time to reach this value is only 48 years (Equation 2). Again, this implies that methane generated in the fine-grained intervals diffuses into nearby coarse-grained layers. Although the gas hydrate content computed assuming homogenous sediment layering is at most 3% of pore space (Figure 8C), the average ratio of fine- to coarse-grained sediment thickness is 17 at this site and implies an average gas hydrate content in the coarse-grained layers of up to 50% (solid line in Figure 8D). Similar to Site NGHP-01-17, the shaded region in Figure 8D illustrates the range of modeled gas hydrate content at Site IODP-C0002 assuming an exponential distribution of fine-grained bed thicknesses, and shows that plausible bed thickness variations can result in the broad range of observed gas hydrate content.

5. Discussion

The results of our modeling study show that short-range migration of microbial methane can explain the observed gas hydrate contents in coarse-grained layers at Sites NGHP-01-17 and IODP-C0002. The same approach was previously used at IODP Site U1325 in the northern Cascadia margin and successfully predicted gas hydrate content in thin (<5 cm-thick) turbidite

sand layers through the GHOS (Malinverno, 2010). Cook and Malinverno (2013) also showed that short-range migration could account for the gas hydrate content observed in a 2.5 m-thick sand layer sandwiched between two fine-grained, hydrate-free sediment intervals at the JIP Walker Ridge drill site in the Gulf of Mexico. Together with these results, we confirm that short-range methane migration mechanism can be applied in different continental margin environments and suggest that it may be a widespread process in gas hydrate formation. For this to be true, the local prerequisites are: (1) a relatively small amount of POC available for microbial methanogenesis, and (2) a sedimentary sequence with a low thickness fraction of coarse-grained layers that can concentrate methane generated in a much larger fraction of fine-grained layers. These two conditions are met along many continental slope and rise environments, where POC deposition is relatively high and the dominant sediment is fine-grained silt and clay with a small fraction of coarse-grained sand. In cases where coarse-grained sediments are extremely rare or absent, the methane supersaturation necessary to form hydrate may be reached in the fine-grained sediments. For example, at Site NGHP-01-17 and Site IODP-C0002 we predict that gas hydrates will begin forming in fine-grained layers if they are thicker than 87 m and 22 m, respectively (see Equation 1). Fine-grained intervals observed at both sites are thinner than these minimum values (Figures 2 and 5), and our analysis predicts gas hydrate formation only in the coarse-grained layers.

Similar results were obtained using models where methane is not generated in situ, but transported into sand layers by vertical fluid advection (Daigle and Dugan, 2011; Rempel, 2011). In these studies, the models assume methane concentration equal to solubility near the base of the GHSZ and compute gas hydrate content in coarse-grained sands for a given upward pore

fluid velocity. Our model provides a more stringent constraint on gas hydrate formation because the supply of microbial methane is constrained by the observed POC and is not assumed to be sufficient at the outset. The predicted gas hydrate contents in Figures 7 and 8 are computed for no upward pore fluid advection, and therefore are conservative because advection will increase dissolved methane concentration and gas hydrate content (Davie and Buffett, 2003; Malinverno et al., 2008). Fluid advection is likely to occur along convergent margins, where fluid advection can result from the dewatering of sediments deep in the accretionary complex (Bekins and Dreiss, 1992; Wang et al., 1993). At Site NGHP-01-17, for example, a modest upward fluid velocity of 28 m/Ma (40% of the sedimentation rate) would lower the POC amount required to match gas hydrate observations to about 0.5% POC, less than the 0.6% POC that we used in Figure 7. Site IODP-C0002 is also located along a convergent margin. We suggest that our conservative approach that assumes no fluid advection is the most exacting test of the viability of methane transport via short-range migration.

While these results support the short-range migration mechanism, a close comparison of model results and observations at the two sites indicates other possible modes of methane transport. At Site NGHP-01-17, the sediment porosity below ~220 mbsf is anomalously high compared to that observed in comparable sequences of biogenic sediments drilled in the Indian Ocean. Rose et al. (2014) suggest that the relatively high permeability in this depth interval enables methane transport by fluid advection. Moreover, a lack of coarse-grained volcanic ashes through the interval 165-265 mbsf at this site may be the reason that no gas hydrate accumulations were observed at these depths. In our modeling, the top of the gas hydrate-bearing interval is the depth where the calculated methane concentration reaches solubility, and we adjust the reaction rate to

result in gas hydrate formation in the depth interval where hydrates were observed (Figure 7B). It is likely that both the presence of porous lithology and high methane concentrations play a role in controlling the vertical distribution of gas hydrate occurrences at Site NGHP-01-17 (Rose et al., 2014).

Our results show that the consumption of a small quantity of available POC, if microbial methane is generated in situ, suffices to explain the observed gas hydrate occurrences at Site NGHP-01-17. A microbiological study by Briggs et al. (2012), however, did not detect methanogenic Archea, in samples from this site, even though the isotopic composition of methane carbon indicated a microbial origin. These authors suggest that microbial methane may have been generated elsewhere and transported by fluid flow to the crest of the anticline where the site is located. Other studies support fluid flow toward topographic highs when sediments exhibit an anisotropic permeability due to depositional layering (Frederick and Buffett, 2011). Thus, fluid advection at Site NGHP-01-17 could have provided at least some of the methane required to form the gas hydrate observed in the core.

At Site IODP-C0002, short-range migration alone seems insufficient to explain the large thickness fraction of hydrate-bearing sands just above the base of the GHSZ. Over the bottom 25 m of the GHSZ (376-401 mbsf), 28 gas hydrate-bearing sands have an average layer thickness of 16 cm (Figure 5). The average thickness of the hydrate-free, fine-grained layers is 73 cm, and the ratio of fine-to-coarse sediment thickness is 4.6. This ratio is 3-9 times lower than the overall average of 17 within the GHOSZ (Table 1) or in other 25 m-thick intervals at the site (where the ratio ranges between 12 and 42). Over the bottom 25 m of the GHSZ, we predict that the gas

hydrate concentration in the coarse-grained layers should be at most 14% (4.6 times 3%, the maximum predicted saturation in uniform sediment; see Figure 8D), which is well below the high gas hydrate concentrations of up to ~70% estimated directly from LWD data (Figure 4D). This implies that other methane transport mechanisms in addition to short-range migration are active near the base of the GHSZ. One possibility is gas bubble migration from below the GHSZ (e.g., Davie and Buffett, 2001), where gas hydrates that are buried below the base of stability dissociate and form gas bubbles as sedimentation proceeds. If the resulting gas bubble fraction is large enough to create a connected free gas phase of sufficient thickness, buoyancy may overcome local capillary forces and methane bubbles can migrate upward (Flemings et al., 2003). At Site IODP-C0002, gas bubbles that move along the dipping permeable sand layers and rise back into the GHSZ could reform gas hydrate and increase the hydrate concentrations in this interval. In this case, any additional methane above that predicted by short-range migration does not need to originate from a deep source or require long-range transport; gas bubble methane near the base of the GHSZ is the same microbial methane generated within the GHSZ. Within the deep interval of the GHOSZ at this site, both the short-range transport mechanism and local bubble advection may co-exist.

6. Methane transport mechanisms in gas hydrate systems

In Figure 9, we place short-range migration in the context of other possible methane transport mechanisms in gas hydrate systems. These mechanisms are described in order of increasing distance between the methane source and the occurrence of gas hydrate and of increasing rate of

methane transport. The most localized gas hydrate is in near-horizontal to near-vertical fractures or veins within fine-grained sediments. These hydrate-filled veins are found within discrete depth intervals, do not seem to be connected to free gas occurrences below the GHSZ, and thus are likely formed from in situ microbial methane (Cook et al., 2014).

In gas hydrates disseminated within the pore space of coarse-grained sediment layers, microbial methane is transported by diffusion over bedding-scale distances in short-range migration. Over longer distances, gas bubbles that dissociate from hydrate buried below the GHSZ by continuing sedimentation can migrate upward along coarse-grained, permeable layers. If the overall transport rates remain relatively low under these circumstances, free gas may reform gas hydrate near the base of the GHSZ. In long-range migration, fluid flow can transport methane over very large distances and has often been proposed as the primary migration process for gas hydrate formation in permeable sand layers (e.g., Uchida et al., 2009; Boswell et al., 2012). Methane transported over long distances by fluid flow and advection could be microbial, as in short-range migration, or thermogenic, being generated at high temperatures well below the base of the GHSZ.

In all the settings discussed so far, anaerobic oxidation typically consumes all dissolved methane at an interface near the seafloor, the sulfate-methane transition or SMT (e.g., Borowski et al., 1996). Methane concentrations increase with depth below the SMT through an interval where gas hydrates are not present because methane concentration remains below solubility (Tréhu et al., 2006). In contrast, massive gas hydrate deposits can form at the seafloor over localized methane vents (Sassen et al., 2001; Haeckel et al., 2004). When a thick gas bubble column is

present below the GHSZ, or the rates of fluid flow and methane transport are especially high, migrating gas bubbles can rise through the GHSZ and be expelled by venting into the water column. The survival of free gas in the GHSZ has been attributed to locally high salinity levels due to salt exclusion driven by gas hydrate formation along the bubble pathway (Haeckel et al., 2004; Liu and Flemings, 2007). Alternatively, it has been suggested that in these settings critical gas pressures beneath the GHSZ drive hydraulic fracturing and gas bubble transport while high pore water salinities are only present between the seafloor and ~100 mbsf (Torres et al., 2011).

In Figure 9, different mechanisms of methane transport are illustrated separately, but clearly they may co-exist. As proposed at Site IODP-C0002, once hydrate deposits formed by short-range migration are buried below the GHSZ, local bubble migration may add methane to form concentrated hydrate in a 25 m-thick zone above the GHSZ (see Section 5). As at Site NGHP-01-17, diffusive short-range migration of microbial methane may occur in conjunction with long-range migration of methane generated below the GHSZ. Such combinations of methane transport mechanisms may explain the field observations at the two sites presented in this paper.

Understanding the relative importance of different mechanisms and scales of methane transport is key to predicting the occurrence and extent of gas hydrate deposits. For gas hydrate deposits formed by short-range migration, microbial methane comes from above, as it is generated predominantly within the shallower portion of the sediment column. The resulting gas hydrate deposits are then progressively buried by sedimentation. With short-range migration, the critical requirements for gas hydrate formation are enough POC within the GHSZ and an in situ microbial population that generates methane at sufficient rates. For gas hydrate deposits formed

by long-range migration, methane (microbial or thermogenic) comes from below and is transported upward into the GHSZ. If long-range migration is the primary active methane transport mechanism, gas hydrate deposits can be predicted using a petroleum systems approach that considers the presence of deep methane sources, migration pathways, and reservoir layers (e.g., Boswell et al., 2012). With the long-range migration mechanism, the amount of methane generated in situ within the GHSZ is not a critical requirement for gas hydrate formation.

Constraining the methane transport mechanism also helps to understand the depth distribution of microbial methanogenesis. Microbial methanogenesis is expected take place mostly near the seafloor, as POC is progressively depleted and the most labile components are consumed first (e.g., Boudreau and Ruddick, 1991). Deep microbial methanogenesis driven by increasing temperature has also been hypothesized (Wellsbury et al., 1997; Burdige, 2011; Gu et al., 2011). A way to demonstrate the need for deep microbial methanogenesis is by showing that shallow methanogenesis does not generate enough methane to result in the observed gas hydrate accumulations. In our study, where most of the microbial methane is generated within the top few hundred meters of the GHSZ (Figures 7A and 8A) no additional deep methane source is required to match gas hydrate observations at the Andaman or Kumano basin sites.

7. Conclusions

In short-range migration, microbial methane generated within fine-grained sediments diffuses into adjacent coarse-grained layers, where large pore sizes favor gas hydrate formation.

Reaction-transport modeling shows that short-range migration can explain the gas hydrate content observed in coarse-grained ash layers at Site NGHP-17-01 in the Andaman Sea and in turbidite sand beds at Site IODP-C0002 in the Kumano basin. Short-range migration has been shown to be a feasible mechanism elsewhere (at sites in the northern Cascadia margin and in the Gulf of Mexico) and is likely to be a common mode of methane transport in gas hydrate systems. All that is necessary for short-range migration to be significant is a small fraction of POC available to microbial methanogenesis (on the order of 0.5%) and a small fraction of coarse-grained sediment that soaks up the methane generated in the surrounding predominant fine-grained sediments; these conditions are widespread along continental margins. Accounting for short-range migration of in situ microbial methane is a conservative and important approach to assess whether additional methane transport mechanisms or deep methanogenesis are required to match gas hydrate observations.

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- 719

Figure captions

Figure 1. Location of drill sites NGHP-01-17 (Andaman Sea) and IODP-C0002 (Kumano forearc basin, Nankai Trough).

Figure 2. Lithostratigraphy at Site NGHP-01-17 from core observations. Gray intervals correspond to recovered sediment (mostly fine-grained calcareous-siliceous ooze) and white intervals denote missing core. Thin layers of coarse-grained volcanic ash are in black.

Figure 3. (A) Measured chlorinity (circles) and inferred in situ background chlorinity (continuous gray line) at Site NGHP-01-17; (B) Estimated pore volume fraction of gas hydrate. Gas hydrates have been detected in 46 coarse-grained volcanic ash layers (filled circles in B), where the pore water chlorinity is appreciably lower than the background value.

Figure 4. Logging-while-drilling measurements at Site IODP-C0002. (A) Measured (gray line) and median-filtered bulk density in a 3 m-thick window; (B) Porosity derived from median-filtered bulk density; (C) Measured electrical resistivity (gray line), water-saturated resistivity predicted from porosity, and median-filtered resistivity in a 3 m-thick window; (D) Pore volume fraction of gas hydrate estimated from the ratio of measured and water-saturated resistivity (solid line) and gas hydrate content in 166 inferred coarse-grained sand layers where hydrate content is $\geq 10\%$ (black dots).

Figure 5. Lithostratigraphy at Site IODP-C0002 from an interpretation of LWD data. Gray intervals correspond to low-resistivity fine-grained sediments (silt and clay) and black intervals are high-resistivity, hydrate-bearing sand layers.

Figure 6. Modeling methane concentration in a sequence of alternating fine- and coarse-grained sediments. (A) In coarse-grained sediments, gas hydrates form where the local concentration of methane (continuous line) exceeds methane solubility in free space (dashed line). In fine-grained sediments the methane concentration has to reach a higher value to form gas hydrate (dotted line). (B) The different gradients in methane concentration above and below (dotted lines) induce a net diffusive flux of methane into a coarse-grained layer, where gas hydrates preferentially form.

Figure 7. Results of modeling gas hydrate saturation at Site NGHP-01-17. (A) Methane generation rate; (B) Calculated methane concentration in pore water (continuous line) and methane solubility in free solution (dashed line); (C) Calculated gas hydrate saturation in uniform sediment; (D) Calculated gas hydrate content in coarse-grained layers for the average ratio of fine- over coarse-grained sediment thickness (continuous line) compared to estimated gas hydrate contents from chlorinity (black dots; see Figure 3). The shaded region shows the range of predicted gas hydrate content for the central 50% of a random thickness distribution of fine-grained sediment intervals (see Section 4).

Figure 8. Results of modeling gas hydrate saturation at Site IODP-C0002. (A) Methane generation rate; (B) Calculated methane concentration in pore water (continuous line) and

methane solubility in free solution (dashed line); (C) Calculated gas hydrate saturation in uniform sediment; (D) Calculated gas hydrate content in coarse-grained layers for the average ratio of fine- over coarse-grained sediment thickness (continuous line) compared to estimated gas hydrate contents from LWD logs (black dots; see Figure 4). The shaded region shows the range of predicted gas hydrate content for the central 50% of a random thickness distribution of fine-grained sediment intervals (see Section 4).

Figure 9. Methane migration mechanisms and gas hydrate formation in fine-grained marine sediments (darker shade) containing coarse-grained layers (lighter shade). Methane can be generated microbially in shallow sediments below the sulfate-methane transition (SMT), or by thermogenic processes deep in the sediment column. Gas hydrate formation can take place between the seafloor and the base of the gas hydrate stability zone (GHSZ). Typically, gas hydrates occur in a gas hydrate occurrence zone (GHOZ) whose top is below the seafloor and is controlled by the depth where methane concentration in pore water reaches solubility. The settings marked A through E illustrate processes that take place as the overall rate of methane transport increases. In intervals dominated by fine-grained sediments, gas hydrate sourced from in situ microbial methane forms in veins and fractures (A). In coarse-grained layers, gas hydrate is found disseminated in the pore space. Hydrate can form from microbial methane that diffuses from adjacent fine-grained sediments as in short-range migration (B). When sedimentation buries layers below the GHSZ, methane in hydrate will turn into gas bubbles, which can migrate upward to enrich hydrate deposits just above the GHSZ (C). Fluid flow can transport dissolved methane that originates below the GHSZ as in long-range migration (D). Where large amounts

787 of gas are present below the GHSZ and/or fluid flow is intense, free gas can migrate through the
788 GHSZ forming a vent (E).

789

Table

Parameter	NGHP-01-17	IODP-C0002
Seafloor depth	1344 m	1936 m
Depth of sulfate-methane transition	25 mbsf	9 mbsf
Depth to top of gas hydrate occurrence	268 mbsf	103 mbsf
Depth to base of gas hydrate stability	600 mbsf	401 mbsf
Average porosity in gas hydrate zone	64%	45%
Temperature at the seafloor	5.6°C	2°C
Temperature gradient	19°C/km	43°C/km
Sedimentation rate	69 m/Ma	308 m/Ma
Tortuosity	2.12	2.4
Diffusion coefficient of methane in sediment	$5.55 \cdot 10^{-10} \text{ m}^2/\text{s}$	$4.82 \cdot 10^{-10} \text{ m}^2/\text{s}$
Coarse-grained sediment lithology	Volcanic ash	Turbidite sand
Number of coarse-grained layers (depth interval)	169 (265-591 mbsf)	166 (103-401 mbsf)
Average thickness of coarse-grained layers	3.2 cm	10 cm
Average thickness of fine-grained intervals	1.5 m	1.7 m
Ratio of average fine/coarse sediment thickness	46	17

Table 1. Parameters used in reaction-transport modeling at Sites NGHP-01-17 and IODP-C0002.

Figures

Figure 1 (Color on the Web,
black-and-white in print)

Site NGHP-01-17

Figure 2

Figure 3

Figure 4 (Color on the Web,
black-and-white in print)

Figure 5

Figure 6 (Color on the Web,
black-and-white in print)

Site NGHP-01-17

Figure 7 (Color on the Web,
black-and-white in print)

Site IODP-C0002

Figure 8 (Color on the Web,
black-and-white in print)

Figure 9 (Color on the Web,
black-and-white in print)

Figure 1 (black-and-white
version for print)

Figure 4 (black-and-white version for print)

Figure 6 (black-and-white
version for print)

Site NGHP-01-17

Figure 7 (black-and-white version for print)

Site IODP-C0002

Figure 8 (black-and-white version for print)

Figure 9 (black-and-white version for print)