

Discussion

Reply to comment on: “Gas hydrate growth, methane transport and chloride enrichment at the southern summit of Hydrate Ridge, Cascadia Margin off Oregon”

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1. Introduction

In the Torres et al. [1] paper we present a quantitative 1-D model for gas hydrate formation in the presence of abundant gas and conclude that: 1) transport of gaseous methane within the gas hydrate stability zone (GHSZ) is necessary to sustain the observed massive methane hydrate deposits and chloride enrichment in the pore fluids; and 2) hydrate in the shallow subsurface must be forming very fast. We also present a possible scenario for gas migration in this setting, based on the work of Clennell et al. [2,3], in which we suggest that

capillary effects inhibit hydrate formation from the base of the GHSZ to the shallow subsurface. We show that the onset of massive hydrate and pore water brines corresponds to the shallowest depth at which the internal pressures of gas bubbles and hydrate crystals can overcome the effective overburden stress. We postulate that at this depth (~30 mbsf), internal pressures are large enough to push aside the sediment grains, thus reducing methane supersaturation and enhancing methane hydrate formation.

Milkov and Xu [4] postulate an alternate conceptual scenario (Fig. 1E). They suggest that as solid hydrate forms it generates a high-salinity fluid, which shifts the hydrate stability field sufficiently to preclude additional gas hydrate formation. A similar model has been proposed by Liu and Flemings (2004, in review). This brine supports vertical methane transport as a gas phase from the bottom-simulating reflector (BSR) to the shallow surface beneath a carbonate structure known as the Pinnacle. Here, impermeable carbonates cause lateral deflection of gas flow towards the summit, resulting in the observed change in hydrate and chloride distribution at 30 mbsf beneath the summit.

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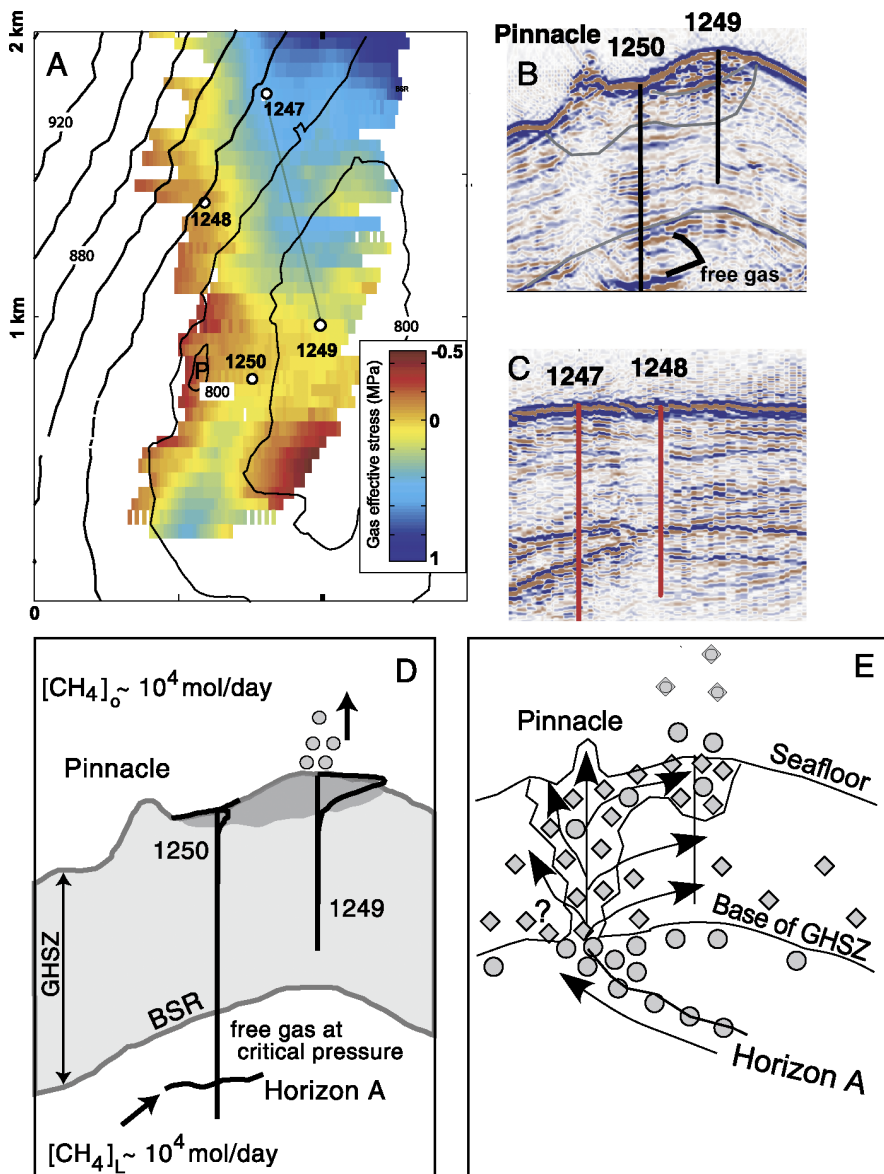


Fig. 1. A. Bathymetry of the Hydrate Ridge summit showing the location of drill sites superimposed on a map of the effective gas stress in the area. Gas effective stress was calculated from the relative depths of Horizon A, BSR and the seafloor, and the depth at which gas saturation is high enough to allow for gas to be interconnected in the pore space [from [7]]. B and C. Seismic data, showing drilled sections and acoustic blanking beneath the Pinnacle and Site 1248. D. Representation of the gas hydrate forming system at the southern summit of Hydrate Ridge used to constrain box model estimates of formation rates [1]. The bathymetry, location of the bottom simulating reflector (BSR) and Horizon A are from seismic section shown in B. The location and depth of penetration of Sites 1249 and 1250 are depicted by solid lines, on which we have superimposed schematic dissolved chloride profiles showing the depth extent of the brine. Methane discharge at the ridge summit has been estimated to be $\sim 10^4$ mol/day [14,15]. GHSZ=gas hydrate stability zone. $(\text{CH}_4)_0$ and $(\text{CH}_4)_L$ are the methane fluxes at the seafloor and the base of GHSZ, respectively. E. Postulated gas migration pathway in Milkov and Xu [4].

Milkov and Xu [4] claim that our model is invalid because it considers only one dimension and that their conceptual scenario provides a comprehensive and unique explanation for all available data. Here we argue that our simplified quantitative model does indeed provide useful insights into important physical

processes and point out several observations that are not consistent with the Milkov and Xu [4] scenario. Contrary to their view, we argue that the mechanisms and pathways of gas transport through the GHSZ in the Hydrate Ridge system are still not fully understood and thus 3-D models may be premature at this point.

2. Inconsistencies with the Milkov and Xu [4] scenario

Milkov and Xu [4] state that their model is “consistent with all available, geological, geochemical and geophysical data”. We would like to point out three major inconsistencies, which illustrate how their qualitative scenario is based primarily on gas abundance and composition obtained from pressure core sample (PCS) data from only two of the 3 sites drilled at the Hydrate Ridge summit.

2.1. Data from Site 1248

Drilling at this site was designed to test gas transport processes in a location where seismic acoustic blanking is similar to that observed beneath the Pinnacle (Fig. 1B and C). Milkov and Xu [4] recognize the significance of this site and state that it represents a present day analog to

early stages in the history of the Pinnacle, “where gas hydrates form from mixed microbial and thermogenic gas migrating from Horizon A within the wipe-out zone” [4]. However, if the acoustic blanking beneath Site 1248 (Fig. 1C) indicates gas transport supported by high-salinity fluids as suggested in [4] and [5], their model predicts the presence of high-chloride fluids at this site. Site 1248 was sited within the blanked seismic zone and no high-chloride fluids were observed at this site (Fig. 2).

In addition, the C_1/C_2 and $\delta^{13}C$ data at Site 1248, which are similar to those from Sites 1249 and 1250 (Fig. 2), are inconsistent with the idea that Site 1248 represents an “incipient” Pinnacle. If migration occurs within the wipe-out seismic zone drilled [4], there should be no discontinuity in the C_1/C_2 data, as observed at this site (Fig. 2). It is noteworthy, however, that at Site 1248 the larger hydrate content is also present in the upper 25 mbsf, consistent with the capillary inhibition approach proposed by [1].

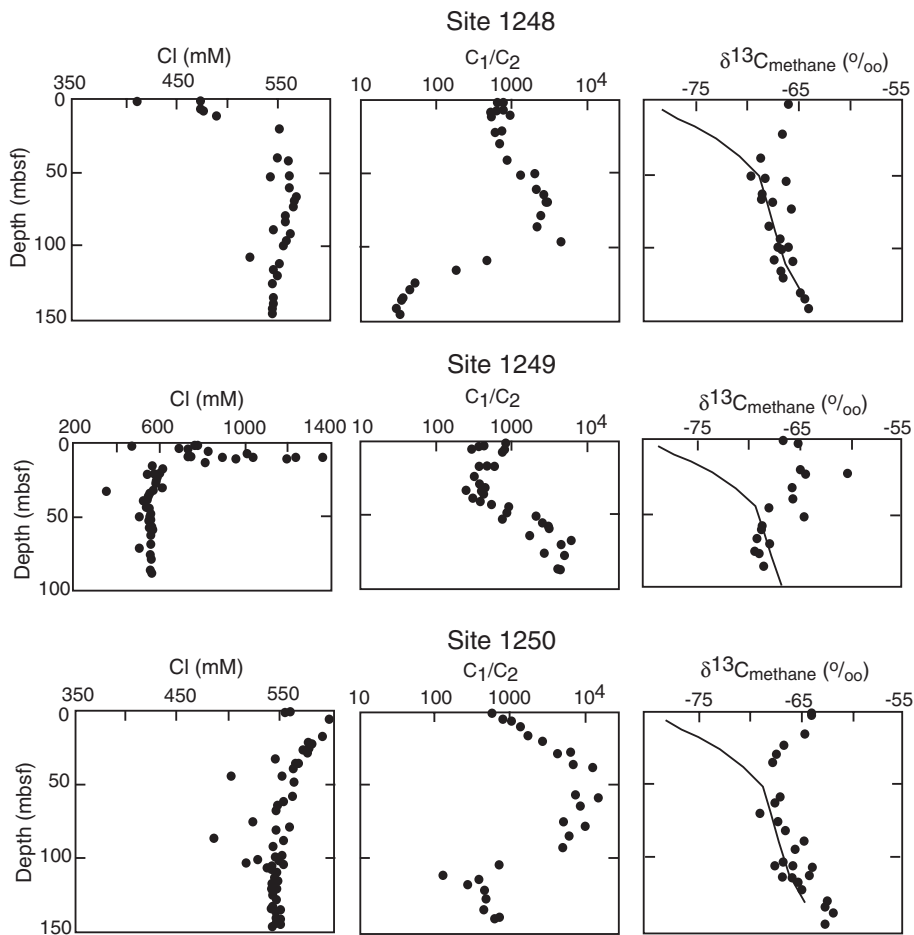


Fig. 2. Dissolved chloride [1] and hydrocarbon [6,12] data for the summit Sites 1248 to 1250. Solid lines in the $\delta^{13}C$ graphs demark the isotopic distribution observed at non-summit sites (e.g. 1245–1247), as shown in [4].

2.2. Presence of free gas

Milkov and Xu [4] state that the gas concentration beneath the BSR at Sites 1249 and 1250 estimated from the PCS data (0–4% of porosity) is not enough to support a critically pressured gas column. The authors

limit their interpretations to sparse PCS data, which are clearly insufficient to adequately constrain the heterogeneous gas distribution beneath the GHSZ (Fig. 3). We note that drilling at Site 1249 did not penetrate the BSR; therefore there are no PCS data below the GHSZ at this site.

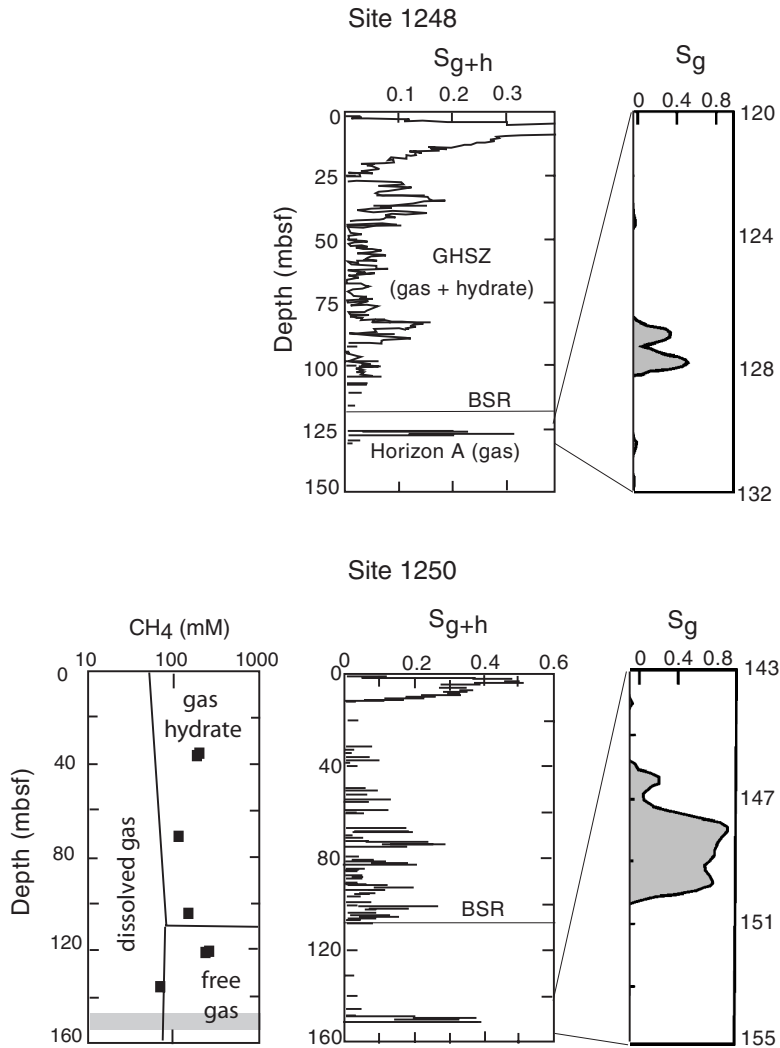


Fig. 3. Comparison of estimates of the fraction of pore space occupied by gas hydrate and gas (S_{g+h}) at Sites 1248 (upper panel) and 1250 (lower panel) from logging and coring data, with methane concentrations measured in PCS. The bottom of the gas hydrate stability zone at these sites (shown in the stability diagram in the lower left panel) corresponds to the depth of the bottom-simulating reflector (BSR). Center panels show estimates of S_{g+h} from resistivity data collected as part of the logging program during Leg 204 [6]; note that beneath the GHSZ, the saturation values reflect only gas occupancy, since there is no hydrate present at these depths. Right panels illustrate S_g values for the Horizon A region estimated from the difference between the in situ bulk density as measured by logging while drilling and the bulk density of core samples, from Trehu et al. [7]. The uncertainties in these estimates is discussed in [7], but the values agree with those obtained by resistivity data and both estimates of S_g are high enough to support migration of gas through the GHSZ. Lower left panel [modified from 19] illustrates data collected with PCS at Site 1250 (no PCS data were collected at Site 1248). Approximate phase boundaries are shown between fields where dissolved gas, gas hydrate and free gas are predicted based on thermodynamic estimates. Comparison of the PCS data (solid squares) with the high-resolution estimates of gas concentration (right panels) shows that these two data sets are not inconsistent, rather the PCS deployments beneath the GHSZ collected samples from areas of lower gas content and simply missed the region of maximum S_g values, which is demarked with a gray box in the phase diagram.

Resistivity data collected beneath the BSR at Sites 1248 and 1250 indicates gas saturations (S_g) of 30–40% (Fig. 3; [6]). A separate analysis of density data from log and core records from these sites yields gas saturation values larger than 40% (Fig. 3) [7]. Such saturations and the depth range over which these saturations occur generate enough pressure to force gas migration through the GHSZ [7]. A gas transport mechanism suggested by Trehu et al. [7], is based on the invasion/percolation model of Impey et al. [8], which can generate a random pathways of upwardly moving gas stringers. The estimates of gas saturation and gas effective stress (Fig. 1A) in [6] and [7] are based on integrated analyses of seismic, logging and core data and provide a more robust estimate of gas content than those values extrapolated from analyses of sporadic PCS sampling, superimposed on assumptions for the gas hydrate stability curves in this system. PCS data are extremely valuable but must be used in ways consistent with its strengths. Fig. 3 illustrates that the PCS data are indeed consistent with the gas saturation estimates from high-resolution core and log data but at Site 1250 simply miss the location of significant gas concentration. No PCS data were collected at Site 1248.

2.3. Vertical gas pipe beneath the Pinnacle

The Milkov and Xu [4] hypothesis is linked to observations of seismic ‘wipe-out zones’ located beneath a carbonate structure known as “the Pinnacle”, located ~250 m away from the summit of HR [9] (Fig. 1). Seismic wipe-out zones associated with near-surface hydrates have been documented in northern Cascadia [10], West Angola [11], and elsewhere. However, the observed acoustic blanking beneath the Pinnacle site may be due, at least in part, to the low transmission coefficient through the overlying solid carbonate structure and not to the presence of a gas column underneath.

There are no data to support or disprove the presence of the deep-seated brine beneath the Pinnacle, but if such a localized salty fluid is present, lateral diffusion of chloride should be apparent in the samples recovered in deeper sequences at Site 1250, located only ~100 m from the postulated deep pore water brine (Fig. 1E).

Milkov and Xu [4] present $\delta^{13}\text{C}$ data of methane to support their postulate that “gas migrates to shallow sediments at Sites 1249 and 1250 mostly laterally from the carbonate Pinnacle area”. However, the data cannot uniquely locate the source as the Pinnacle area. The relative enrichment of C2 at Site 1250 is less than that at Site 1249 (Fig. 2) and similarly the chloride enrich-

ment at Site 1250 is not as well developed as that in Site 1249 (Fig. 2), as would be expected in the scenario proposed by Milkov and Xu [4].

3. Complexities of the hydrocarbon data

We argue here that the geochemical data [1,4,5,12] in the near-surface sediments at the summit sites (1248–1250) are not yet fully understood. Lateral migration is a possibility but, as noted above, not all the data can be explained with the model in Fig. 1E [4]. In a recent study, Tomaru et al. [13] show that the oxygen and hydrogen isotopic fractionation in the massive shallow deposits in the Hydrate Ridge summit sites departs significantly from experimental data and from the inferred isotopic fractionation in the deeper disseminated hydrate. These results hint to an atypical behavior of the fast-forming shallow hydrate. It is then not implausible that the observed elemental and isotopic composition of the hydrocarbon data collected from the area of massive hydrate deposition at Sites 1248–1250 may arise from the not-yet-fully understood behavior of gas and water during gas hydrate formation in near-surface sediment.

The arguments above support our contention that the mechanism proposed by Milkov and Xu [4] is not as solidly constrained as they claim. Nevertheless such a postulate is worth further investigation and we agree with their conclusion that a fully integrated approach in gas hydrate studies and extensive geochemical research is critical to understand gas hydrate systems.

4. Insights from the 1-D model

We agree with Milkov and Xu [4] that a 3-D model would better describe this, and probably other hydrate-bearing systems. “We recognize that our one-dimensional vertical transport model, though internally consistent, represents a simplified look at the gas transport on Hydrate Ridge and that more structure and complexity is indeed present” [1,page,237]. Our 1-D-model does demonstrate that the strong chloride enrichments can only be generated via gas transport and is consistent with fast rates of hydrate formation obtained by an independent box model.

4.1. Hydrate formation rates

If we assume that the system we observe today has reached steady state, first-order model estimates of the methane gas flux based on seafloor and water column observations [14,15] indicate that the supply rates at the bottom of the GHSZ are enough to generate the mas-

sive hydrate deposits in ~400 years (Fig. 1D). Methane hydrate is thus precipitating at extremely fast rates ($\sim 10^2$ mol CH₄ m⁻² yr⁻¹). Here we emphasize that the box model estimates illustrated in Fig. 1D [1] are independent of the transport mechanism and are based on seafloor and water column observations.

The results of the 1-D model for scenarios 2 and 3 [1] represent an additional attempt to estimate the time of formation of these deposits. There are several simplifications and assumptions in these simulations, which arise from lack of data to fully constrain the system. We recognize these as such and present solutions with varying kinetic constants, which we vary by orders of magnitude because measurements of these parameters are not yet available. Milkov and Xu [4] state that “kinetic effects of hydrate formation and methane transfer from the free gas to the dissolved phase is negligible” and cite several publications to this effect [16–20]. We agree that this is the case in unconstrained media (seawater and water/gas mixtures in laboratory experiments), but note that there are no available data to parameterize the effect that a porous medium would have on these constants. It is well established that when capillary forces are large (such as in fine, unfractured marine sediments), free gas and hydrate formation is inhibited, requiring larger supersaturation values [3 and references therein]. Whether it is conceptually correct to view the required supersaturation as analogous to a higher energy is debatable, but given the scarcity of information on hydrate formation processes in porous media, we believe that ours is a valid approach. Regardless of the validity of this assumption, the formation rates inferred from the 1-D simulations are consistent with those predicted by single box model calculations and thus our conclusion that the massive hydrates are very young does not depend solely on the modeling approach and assumptions therein. Nevertheless, we recognize the limitations of our approach and thus state that the rates of hydrate formation are “first-order estimates” [1, page 237].

4.2. Validity of a 1-D approach

Modeling aqueous flow with a 1-D approach [1] is adequate to demonstrate that not enough methane can be supplied by water transport to sustain the observed methane hydrate deposits and chloride enrichment in the pore fluids. Brines, such as those based on pore water measurements (minimum values) and those based on pressure core sample (PCS) estimates, cannot be generated by water transport regardless of whether the flow is vertical or horizontal. Due to the low

methane solubility, not enough methane can be delivered by the fluids to account for the massive accumulation of gas hydrate and the high (>1300 mM) chloride concentrations.

4.3. Transport of free gas

Milkov and Xu [4] raise the issue that our “numerical results are not accurate” because we did not consider the transport of free gas in our differential equations. Our approach represents an end-member scenario in which we assume that enough free gas is present throughout the sediment column and introduce a rate term (R_G) defining the dissolution of free gas in the ascending pore fluids. Hence, our numerical results are correct if there is always enough methane in the system to maintain saturation. Methane gas is likely to occur in localized high-porosity horizons that lead to amplitude changes in the seismic records (Fig. 1B and C).

We do not require, nor do we assume, a “continuous gas pipe” anywhere on Hydrate Ridge. Instead, we postulate a mechanism of capillary inhibition and catenary transport of methane through a media of highly heterogeneous porosity, as a *possibility* to explain the methane supply rates derived from the box model and numerical simulations. Such a mechanism has been widely used in the literature to explain gas transport in sedimentary environments [3 and references therein]. These studies show that in deep sedimentary formations, gas exsolution is limited by the size of the pore spaces so that gas is preferentially sequestered in high-permeability horizons where capillary pressures are lower [e.g. 2,3]. Thus methane migration is likely to be driven by catenary transport [3] and pressure-dependent flow within hydrofractures and lithologically controlled paths [7,21]. Within the bulk of the unfractured, fine-grained sediment, capillary pressures drive the methane to solution above saturation values. The highly saturated fluids can move through inter-particle throats that would block transport of methane in the gas form. When these supersaturated fluids encounter horizons of higher permeability, gas exsolution will occur. We note that our postulated mechanism is consistent with the observed strong correlation between the sites of hydrate deposition (identified by continuous infrared scanning of the cores) and high-permeability horizons in the sediment [22].

We disagree with Milkov and Xu’s [4] statement that “the modeling framework in Torres et al. is inconsistent with gas concentrations in the pore space measured by PCS [23] and inferred resistivity profiles [6].” Given the

lithostratigraphy of the region, high-porosity layers that may be hosting gas can be as thin as 3–10 cm [6]. PCS samples are, by necessity, retrieved sporadically (lower left panel in Fig. 3) and thus provide a low-resolution record of the sediment column. Trehu et al. [24] has illustrated the power of using multiple proxies that incorporate high-resolution data in constraining such heterogeneous systems. More significantly, methane data collected by degassing PCS from the GHSZ cannot differentiate between methane in free gas and hydrate phases. If gas is present within the GHSZ, the total methane concentration will plot in the gas hydrate field (Fig. 3). Resistivity data, although continuous and in this regard better than the PCS to discern the heterogeneity of the system, cannot easily resolve gas vs. hydrate signals within the GHSZ as they both lead to higher resistivity values.

5. Summary and outstanding questions

In summary, Milkov and Xu [4] do not disagree with the two main conclusions of the Torres et al. [1] paper. They do not dispute that methane needs to be transported in the gas phase and have presented no evidence to challenge the rapid rates of formation we propose. We also know that on Hydrate Ridge massive deposits are limited to the upper 25 mbsf at all sites drilled on the ridge summit (consistent with the depth at which internal hydrate and bubble pressures exceed the local effective overburden stress) and that the hydrocarbon geochemical signals are similar at all three sites (1248 to 1250). Furthermore, we are confident that there is enough evidence to support the presence of critically pressured gas at the base of the GHSZ to drive gas transport through the GHSZ to the seafloor [6,7]. The main argument of [4] focuses on the mechanisms of gas transport and we contend that we do not yet fully understand how methane migrates through the hydrate stability zone as a gaseous phase on Hydrate Ridge. Several issues are still unresolved:

- What do the wipe-out zones beneath the Pinnacle and Site 1248 reflect (surface acoustic impedance vs. continuous gas column)?
- What inhibits gas hydrate formation to support gas transport within the GHSZ (salinity barrier vs. capillary inhibition effects)?
- What does the zone of massive hydrate and brine formation indicate (lateral migration of a gas-bearing salty fluid vs. depth at which internal pressures of gas and gas hydrate phases can overcome the effective overburden stress)?
- What do the geochemical anomalies in the hydrocarbon data represent (lateral migration or the result of in situ formation of shallow hydrate at fast rates)?
- What are the pathways of gas transport (column of gas beneath the Pinnacle vs. random pathways controlled by porosity changes in the lithostratigraphy following invasion, percolation and catenary transport models)?

Hydrate Ridge is perhaps the first locality in which shallow gas hydrate deposits not associated with diapir/mud volcano systems have been intensively studied. However, it is not unlikely that such sites may be more common than thus far recognized because the lack of obvious topography and dedicated seafloor imaging efforts has not been sufficient to identify these shallow hydrate sites in a larger regional area. Understanding gas transport processes in these systems is important as this migration sustains formation of massive hydrate at the seafloor, feeds gas plumes, and provides the forcing that modulates the episodicity of flow. Further study of such systems is planned for the upcoming ODP Leg 311 to northern Cascadia, which may help answer some of the outstanding questions on Hydrate Ridge.

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