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Co-existence of gas hydrate, free gas, and brine within the regional gas hydrate stability zone at Hydrate Ridge (Oregon margin): evidence from prolonged degassing of a pressurized core

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Abstract

Standard scientific operations on Ocean Drilling Program (ODP) Leg 204 documented a horizon of massive gas hydrate and highly saline pore water ~0–20 m below the southern summit of Hydrate Ridge offshore Oregon. The sediment zone lies near active seafloor gas venting, raising the possibility that free gas co-exists with gas hydrate in shallow subsurface layers where pore waters have become too saline to precipitate additional gas hydrate. Here we discuss a unique experiment that addresses this important concept. A 1-m-long pressurized core was retrieved from ~14 m below sea floor at Site 1249 and slowly degassed at ~0 °C in the laboratory over ~178 h to determine in situ salinity and gas concentrations in the interval of massive gas hydrate. The core released ~95 l of gas (predominantly methane), by far the greatest gas volume ever measured for a 1 m core at ambient shipboard pressure and temperature conditions. Geochemical mass-balance calculations and the pressure of initial gas release (4.2 MPa) both imply that pore waters had an in situ salinity approaching or exceeding 105 g kg^{-1}, the approximate salinity required for a gas hydrate–free gas–brine system. Relatively high concentrations of propane and higher hydrocarbon gases at the start of core degassing also suggest the presence of in situ free gas. Gas hydrate, free gas and brine likely co-exist in shallow sediment of Hydrate Ridge. Near-seafloor brines, produced when rapid gas hydrate crystallization

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extracts large quantities of water, impact the distribution and cycling of gas and gas hydrate in this region and perhaps elsewhere.
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Keywords: methane; gas hydrate; free gas; brine; hydrocarbons; pressure core; Leg 204; Site 1249; Hydrate Ridge

1. Introduction

Gas hydrate and free gas bubbles can form in the pore space of deep marine sediment when concentrations of low molecular weight gases, typically methane (CH_4), surpass saturation. These naturally occurring phases command our attention because they may constitute a future energy resource [1] and a significant component of the global carbon cycle [2].

Crucial to many investigations are the vertical distributions of gas hydrate and free gas in marine sediment sequences. From a thermodynamic perspective, these distributions should primarily depend on gas concentrations and three environmental conditions: pressure, temperature, and the activity of water (a_w), the latter a parameter measuring the effective concentration of water and inversely related to salinity [3]. Most descriptions of marine gas hydrate systems have assumed steady increases in subsurface pressure and temperature, and pore water salinity close to that of seawater. This has led to the widely accepted concept that natural gas hydrate systems are stratified [4–7], with an upper gas hydrate stability zone (GHSZ) and a lower free gas zone (FGZ) separated at a depth where pressures and temperatures on the geotherm intersect those on a dissolved gas–gas hydrate–free gas equi-

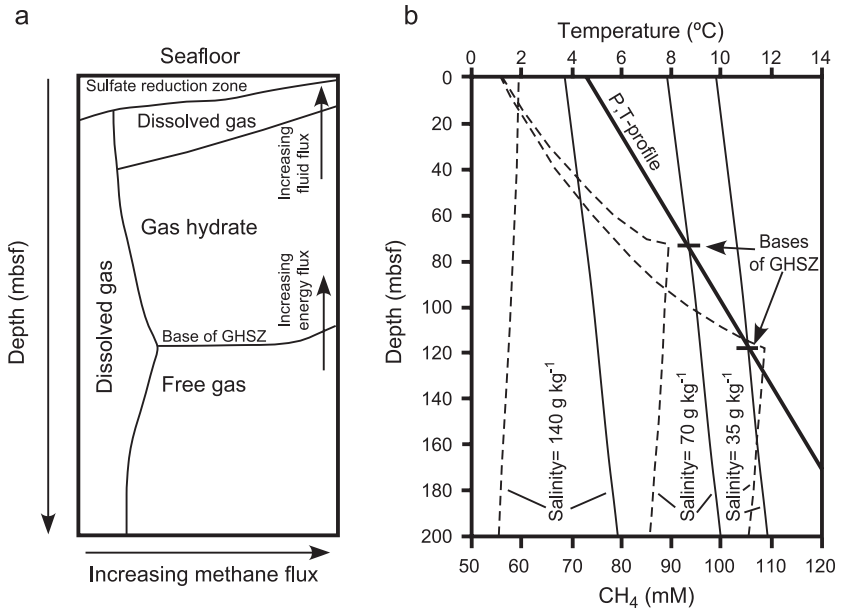

Fig. 1. Diagrams illustrating the widely accepted concept of stratified natural gas hydrate systems and how pore water salinity may modify these systems. (a) Occurrence and boundaries of various gas phases (dissolved, free, and gas hydrate) depend on the variations of energy, fluid, and methane fluxes [7,42]. Methane concentration in pore water defines the occurring phase. When methane concentration in pore water exceeds the solubility of methane, gas hydrate is present above the base of the GHSZ and free gas is present below the base of the GHSZ. Only dissolved gas is present in the system when methane concentration in pore water is below solubility. (b) The salinity of pore water significantly affects gas hydrate stability conditions [21] (thin solid lines) and the solubility of methane [36] (thin dashed line). The calculations are made for pressure (assumed to be hydrostatic) and temperature (based on the geothermal gradient 55 °C km^{-1}) at Site 1249 (thick line). Note that the phase distribution as presented in (a) occurs only at salinity 35 g kg^{-1}. The GHSZ thins when the salinity of pore water increases to 70 g kg^{-1}, and is not present at salinity 140 g kg^{-1}.

librium curve for seawater (Fig. 1). Depth intervals within these zones may not contain their respective phases because of insufficient gas concentration [5–7]. However, this simple view does preclude free gas above gas hydrate (i.e., in the GHSZ) without invoking kinetic arguments and multi-phase fluid flow [4,7,8].

Several recent studies have suggested significant amounts of free gas within the GHSZ. This idea has received its strongest push from investigations along the Cascadia margin off western North America (Fig. 2). Here, free gas within the GHSZ has been inferred from gas bubble trains emanating above the seafloor [9–12], "globular" fabrics within recovered gas hydrate specimens [13], and acoustic "wipe-outs" on seismic profiles [14,15]. Apparently, either: (1) kinetic effects prevent the precipitation of gas hydrate at favorable stability conditions despite excess gas, or (2) environmental conditions vary over short distances so that the GHSZ has a complicated volume. For example, the upward migration of warm fluids could allow free gas to exist much shallower than expected from regional geotherms [15,16], or free gas could be separated from water along channels [10].

Ocean Drilling Program (ODP) Leg 204 drilled a series of boreholes through the GHSZ of southern Hydrate Ridge on the Cascadia Margin (Fig. 2) [17,18]. One intriguing finding was abundant gas hydrate (>30–40% of porosity) and high salinity (S>60 g kg^{-1}; Cl>1000 mM) pore water at shallow depths (<20 m) below the summit of Hydrate Ridge (Fig. 3) [17,18]. Because relatively small increases in salinity can dramatically decrease the stability of gas hydrate [3,19–21], it is possible that free gas could occur with gas hydrate and brine in horizons within the regional GHSZ (Figs. 1 and 3). Co-existence of gas hydrate, free gas and brine does happen in laboratory experiments [3,19], and has been suggested as a means to move free gas through the GHSZ [8]. Evaluating such co-existence in nature is difficult, however, because in situ salinity and gas concentrations are hard to quantify in gas hydrate bearing sediment using standard techniques. Dissociation of gas hydrate during conventional core retrieval releases gas, which escapes [5,22], and fresh water, which decreases pore water salinity [23,24].

In this paper, we present and discuss data acquired from a pressurized core that was retrieved during Leg 204 from the high salinity horizon at Hydrate Ridge. The core was collected and examined because, in theory, in situ salinity and gas concentrations can be determined through slow, controlled degassing of pressurized cores [25]. Our data suggests that gas hydrate, free gas and brine indeed co-exist near the seafloor. Depth intervals containing hypersaline pore waters, perhaps produced during gas hydrate formation, can

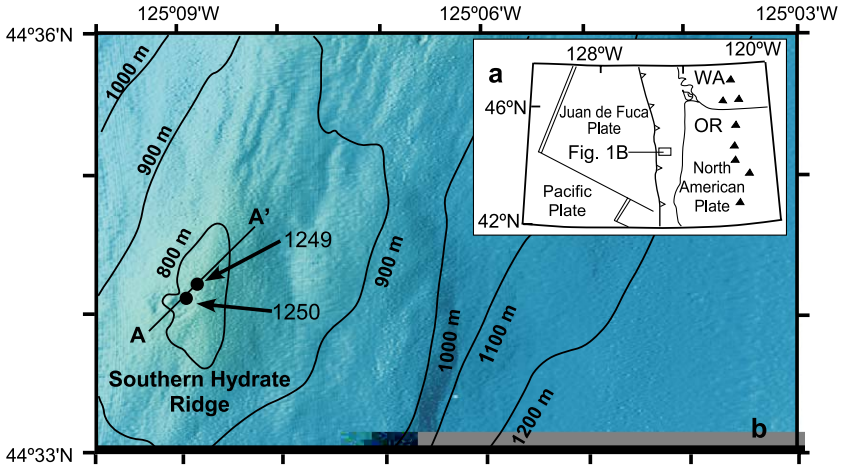

Fig. 2. ODP Sites 1249 and 1250 on Hydrate Ridge, offshore of Oregon (OR), northwest United States. (a) Tectonic setting of Hydrate Ridge showing the ridge located within the Cascadia accretionary complex where the Juan de Fuca plate subducts beneath North American plate. (b) Bathymetric map [43] showing detailed location of ODP Sites 1249 and 1250, and cross-section of Fig. 9.

(C_4) and pentane (C_5) were minor components, although their concentrations generally decreased with degassing. During the second stage, when the next ~61 l of gas were released, gas composition stayed remarkably stable (mean concentrations C_1 = 997,100 ppm, C_2 = 1490 ppm, C_3 = 29 ppm, and CO_2 = 1390 ppm). As the last ~15 l of gas were released, the concentration of CO_2 consistently increased to ~15,000 ppm. Concentrations of C_2 and C_3 also increased to 2180 and 47 ppm, respectively, whereas the concentration of C_1 decreased to 982,600 ppm.

Water in the outer chamber after complete degassing had a Cl^- concentration of 678 mM (SO_4^{2-} was not measured). The inner core barrel contained a slurry of water and sediment. The water had Cl^- and SO_4^{2-} concentrations of 825 and 14.2 mM, respectively, and the sediment appeared similar to that in surrounding cores collected by other conventional coring. The dry weight of sediment in this slurry was 620 g, which corresponds to a volume of 230 ml assuming an appropriate sediment density of 2.7 g cm^{-3}. Given a full 1.00 m recovery, this implies that gas hydrate, water, and gas filled 1235 ml (or ~85% porosity) of the core at in situ conditions. This is consistent with porosity estimates for this interval based on Site 1249 well-log data [17]. However, although many PCS cores recovered during Leg 204 were full or nearly full (after accounting for volume loss from dissociated gas hydrate), we cannot be sure that Core 204-1249F-4P was indeed 1.00 m long at in situ conditions. We discuss the ramifications of an incomplete core below.

5. Estimates of in situ methane abundance and gas hydrate content

Using established PVT relationships for gases, ~3.9 mol CH_4 degassed from Core 204-1249F-4P. Theoretical methane solubility between dissolved gas and gas hydrate is ~58 mM at in situ pressure (~7.9 MPa), in situ temperature (~6 °C), and measured pore water salinity (66 g kg^{-1}) for the depth of this core [36]. This solubility is relatively insensitive to salinity [36], and limits the maximum amount of dissolved CH_4 in the core to ~0.07 mol (the quantity if water occupied all available space). Gas hydrate and free gas collectively held >3.8 mol CH_4 within 1235 ml at in situ conditions.

The volume of gas hydrate within the core can be readily estimated from CH_4 abundance given an assumption of no free gas, and knowledge of gas hydrate density (ρ_{GH}) and crystal structure [5,25,34]. Applying this reasoning, Core 204-1249F-4P contained 520 ml of gas hydrate (~42% porosity) if it occurred as a "typical" structure I hydrate (ρ_{GH} = 0.91 g/cm^3; stoichiometry of $CH_4 \cdot 6H_2O$). However, average ρ_{GH} of gas hydrate specimens from Hydrate Ridge has been measured at 0.79 g/cm^3 [9], and the small but significant amounts of propane released from Core 204-1249F-4P (Fig. 7) may suggest that gas hydrate occurred as structure II. If the CH_4 resided only in dissolved gas and low-density structure II gas hydrate (stoichiometry of $CH_4 \cdot 5.67H_2O$), 570 ml of gas hydrate existed at in situ conditions (~46% porosity). However, these gas hydrate abundances are too high if free gas co-existed at depth.

6. Estimates of in situ salinity

Numerous experiments have shown that the outer chamber of the PCS contains only borehole water (i.e., surface seawater; ~559 mM Cl^-) when pressurized cores are first recovered [25,33]. The measured 678 mM Cl^- concentration in outer chamber water, therefore, implies incursion of high salinity water from the inner core barrel during degassing and disassembling of the PCS. Simple mixing of 2000 ml seawater and 1235 ml of inner core barrel fluid with an initial Cl^- concentration of 1020 mM would give the measured Cl^- concentrations for both the outer and inner chambers at the end of degassing. However, pore space within the inner core barrel must have contained gas hydrate, so in situ pore water must be more saline than 1020 mM.

Chloride within the inner chamber after complete degassing reflects a mixture of borehole water, initial pore water of high Cl^- concentration, and water originally in gas hydrate and presumably lacking Cl^- [23,24]. Assuming no free gas, in situ pore water Cl^- can be readily estimated from the measured Cl^- concentrations, the total available space, and the original amount of gas hydrate. Core 204-1249F-4P had ~715 ml of pore water with 1630 mM Cl^- and 412 ml of fresh water bound in gas hydrate at in situ conditions if it began with 520 ml of structure I gas

hydrate. Alternatively, the core had ~665 ml of pore water with 1665 mM Cl^- and 389 ml of fresh water bound in gas hydrate at in situ conditions if it began with 570 ml of low density structure II gas hydrate. In either case, in situ Cl^- greatly exceeds Cl^- measured by conventional techniques (Fig. 3). Note also that consideration of a free gas component at in situ conditions would increase the inferred in situ pore water Cl^- because it would occupy space and therefore decrease the amount of available water.

High pore water Cl^- concentration should signify pore water with low a_w and high salinity [3]. Indeed, assuming a conservative relationship between the three variables (and other caveats above), original pore water within Core 204-1249F-4P must have had a salinity >102 g kg^{-1}. The degassing curve (Fig. 6) provides an important, independent means to assess this interpretation. At 0 °C, the temperature of degassing, gas hydrate should begin to dissociate and release large volumes of gas at ~3 MPa if surrounding pore water has a salinity of 35 g kg^{-1} [25]. However, Core 204-1249F-4P began releasing significant quantities of gas at ~4.2 MPa (Fig. 6), which suggests a starting pore water salinity ~105 g kg^{-1}, in good agreement with the chloride mass-balance calculations.

Initial pore water salinity may, in fact, have been >105 g kg^{-1} for three reasons (beyond consideration of free gas). First, we assumed that Core 204-1249F-4P recovered a full 1-m-long core. Previous PCS operations indicate that this is not always the case [25,34]. Second, a small amount of sediment may have been lost during PCS disassembly. Third, it was observed that water escaped from the PCS during each gas release. Although the volume and chemical composition of the released water was not measured, we infer that some dissolved ions escaped from the PCS during the degassing and was not accounted for in mass-balance calculations. Any of these factors would result in underestimated in situ salinity. For example, if only a 0.95 m core was recovered, in situ salinity may have approached 120 g kg^{-1}.

An in situ pore water salinity at or above 105 g kg^{-1} has fundamental implications toward our understanding of gas hydrate and free gas in shallow sediment of Hydrate Ridge. At the in situ pressure and temperature conditions of Core 204-1249F-4P, a

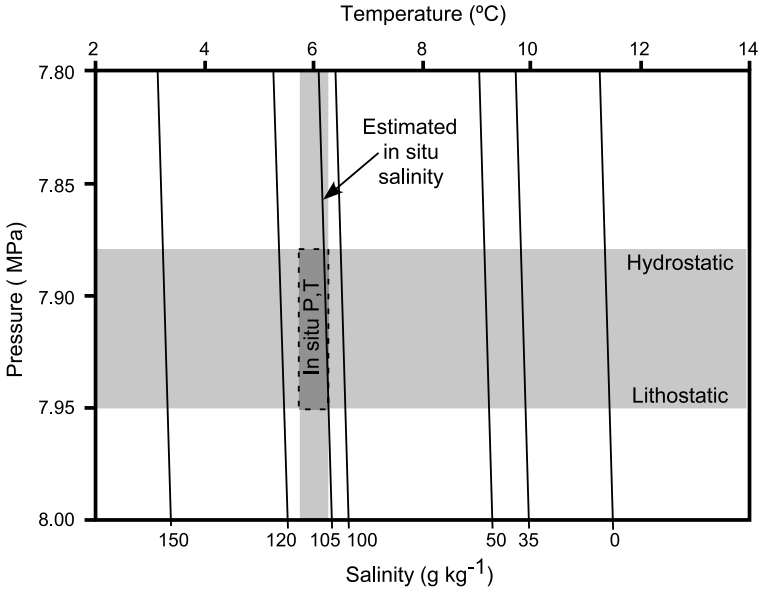

Fig. 8. In situ temperature and pressure at 14 mbsf at Site 1249 compared to the hydrate stability boundaries for pore water salinities 0–150 g kg^{-1} (calculated using CSMHYD [21] and consistent with experimental results [37] for a salinity of 100 g kg^{-1}). Temperature was measured during Leg 204 at 16.5 mbsf, and the range shown here includes uncertainties in this measurement and extrapolation based on the regional temperature gradient. Pressure is assumed to lie between hydrostatic and lithostatic, with the density of the overlying sediment constrained by measurements made during Leg 204 [17]. Gas hydrate and free gas are predicted to co-exist at these conditions for salinity of 105–115 g kg^{-1}.

methane hydrate–free methane gas–brine mixture should occur between 105 and 115 g kg^{-1} [21,37] (Fig. 8). This is the point where gas hydrate can no longer incorporate excess methane because surrounding waters are too saline.

Core 204-1249F-4P presumably lacked SO_4^{2-} before degassing because it came from below the sulfate reduction zone where pore water SO_4^{2-} is zero. The SO_4^{2-} concentration of the inner core barrel after degassing thus reflects borehole water contamination of the original, collective volume of pore water and hydrate water. For the two cases stated above, where all excess gas resides in gas hydrate, there would have been 1127 and 1054 ml of total SO_4^{2-} depleted water within the tool before degassing. A specific, partial mixing of these volumes and 2000 ml of borehole water renders the observed Cl^- concentrations (above), but necessitates inner core barrel dissolved SO_4^{2-} concentrations of 12.8 and 13.2 mM after degassing, rather than the measured 14.2 mM. The simplest explanation is that the inner core barrel contained 50–150 ml less water than expected from gas and Cl^- mass balance calculations alone because free gas occupied space at depth.

7. Evidence of free gas

The first increment of gas collected from the PCS usually contains air trapped during deployment [25,33], and this was observed for Core 204-1249F-4P (Fig. 7). Following this, gas composition should not vary significantly during degassing if only gas hydrate and dissolved gas are present in the core. Only toward the end of the experiment, when all gas hydrate has dissociated, should gas composition change as various gases come out of solution according to their solubility.

The second and third stages of degassing (Fig. 7) generally conform to expectations for a core with abundant gas hydrate and dissolved gas. During the second stage of degassing, the core released ~61 l (~2.5 mol) of gas. This gas was predominantly CH_4 (>99.7%) and had a very uniform overall gas composition. Moreover, during this degassing stage, pressure only decreased slightly (Fig. 6). These observations are consistent with steady dissociation of 340 to 380 ml of methane hydrate (depending on ρ_{GH}), with the drop in pressure over time (and volume) resulting from freshening of pore water within the inner chamber (Fig. 5). Gas increments collected during the third stage of degassing are relatively enriched in CO_2, C_2, and C_3, and relatively depleted in C_1 (Fig. 7). This observation is consistent with gas release from water because CO_2, C_2, and C_3 are more soluble than C_1 at low temperature and pressure [38]. It should be recognized that the 15 ml (~0.6 mol) of gas released during stage 3 exceeds the amount that can be dissolved in 2900 to 3100 ml of water (the total quantity within the tool including pore water, hydrate water and borehole water) at in situ or laboratory conditions. At low pressure, Core 204-1249F-4P undoubtedly contained a large headspace (100–270 ml), which formed after evacuation of free gas at high pressure and dissociation of gas hydrate.

In contrast, gas composition varied systematically as the first 18.5 l of gas were released from Core 204-1249F-4P (Fig. 7). Of particular interest, gas released during this first stage is initially depleted in C_2 and CO_2, and enriched in C_1, C_3, C_4, and iC_5 relative to gas released during stage 2. Indeed, C_{4+} components were not detected during the second stage of degassing (Fig. 7). These changes in gas composition are significant given the analytical precision, and are best explained by mixing of gases from two distinct sources, most likely decomposed gas hydrate and free gas. Although small amounts of gas can be desorbed from sediment [39], the sheer volume of gas precludes this as a plausible source.

Propane (C_3) concentrations decrease nearly linearly ($r^2 = 0.86$) during the first stage of degassing (Fig. 7). A simple mixing model based on C_3 variation was therefore used to estimate the contribution of gas from the two sources during stage 1 degassing. For one source, we assumed a C_3 concentration of 29 ppm, the average composition of gas evolved during stage 2 degassing and presumably from gas hydrate. For the other source, we assumed a C_3 concentration of 69 ppm, the composition of the second gas increment. Based on this mixing model, we estimate that 10.7 l (~0.44 mol) of gas came from decomposed gas hydrate during stage 1 degassing, while 7.8 l (~0.32 mol) of gas was derived from the other source. Assuming this source was free gas, it would occupy ~76 ml at in situ pressure and temperature, after accounting for methane compressibility. This is within the amount predicted from pore water mass balance considerations.

8. Mechanism for co-existence of shallow gas hydrate and free gas

Gas hydrate, free gas and dissolved gas likely co-exist with hypersaline pore water in shallow sediment at Site 1249. Considering all information gathered from Core 204-1249F-4P, sediment pore space between 13.5 and 14.5 mbsf had about 40% gas hydrate, 50% pore water of >105 g kg^{-1} salinity, and 10% free gas.

We propose a straightforward mechanism for this finding (Fig. 9). Gas hydrate formation extracts methane and water, but excludes dissolved ions to surrounding pore water [23,24]. Thus, pore water salinity rises with gas hydrate precipitation [24]. Unless diffusion or advection remove dissolved ions, gas hydrate formation will continue with a supply of gas until pore water salinity is so high that the fugacity of gas in water equals the fugacity of free gas [20]. At this point, a gas hydrate–free gas–brine equilibrium is reached [20], and excess gas enters free gas rather than gas hydrate. This is probably the situation at Site 1249, although its exact cause remains unclear. Co-existence of gas hydrate, free gas and brine could occur when high gas flux drives rapid gas hydrate formation, when excessive gas hydrate precipitation decreases permeability of sediment and removal of dissolved ions, or when both processes operate together.

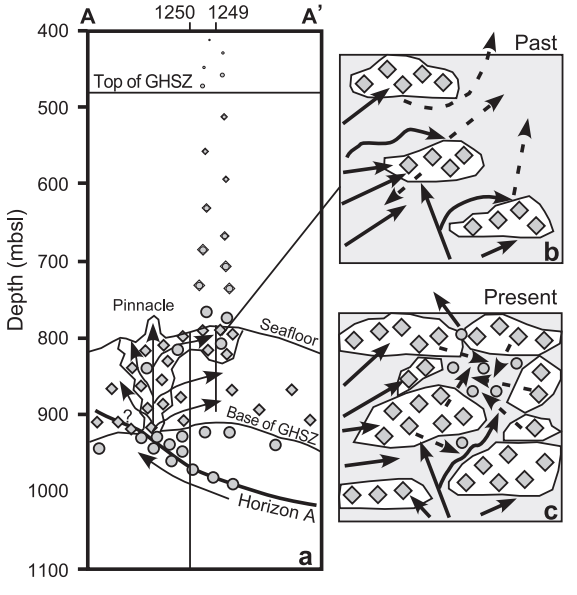

Fig. 9. Possible mechanism for co-existence of gas hydrate, free gas and brine in shallow sediment at Hydrate Ridge as viewed at large and small scales. (a) Schematic of cross-section A–A′ (Fig. 2) showing an inferred distribution of gas hydrate (diamonds) and free gas (circles), and the inferred rapid upward transport of free gas from depth along Horizon A [17], through the regional gas hydrate stability zone (GHSZ), to the seafloor and the water column. (b) The high gas flux (solid arrows) induces rapid gas hydrate formation, which fills pore space and initiates the flow of dissolved ions (broken arrows) away from gas hydrate. (c) The filling of pore space also decreases sediment permeability, which decreases the removal of dissolved ions. If gas hydrate formation is faster than removal of dissolved ions, pore waters eventually become too saline for further gas hydrate formation. Free gas can now co-exist with gas hydrate and brine.

9. Conclusions and implications

Core 204-1249F-4P was retrieved from a shallow interval of massive gas hydrate and high salinity pore water on the southern summit of Hydrate Ridge. This core offers a unique opportunity to assess the natural co-existence of gas hydrate, free gas and hypersaline pore water, a phenomenon only known previously from laboratory experiments [19]. All information obtained from Core 204-1249F-4P indicates that it indeed held gas hydrate, free gas and brine together at in situ conditions. Such co-existence may occur in shallow sediment elsewhere on Hydrate Ridge, and in other regions of high upward methane flux [40]. This has several implications toward our general understanding of marine gas hydrate systems.

First, gas hydrate, free gas and salinity each affect physical properties of bulk sediment (e.g., electrical resistivity and acoustic velocity). Thus, in regions where gas hydrate, free gas and brine co-exist, the combined affects of multiple variables need consideration when applying certain proxy methods to quantify gas hydrate abundance. For example, electrical resistivity logs have been used to estimate the amount of water and gas hydrate within the GHSZ, invariably assuming an Archie relationship, an absence of free gas, and moderate to low salinity [41]. This approach would overestimate the amount of gas hydrate if free gas was present. Preliminary shipboard interpretations of electrical resistivity logs at Site 1249, based on the aforementioned assumptions, suggest that sedi-

ment pore space at 14 mbsf holds ~65% gas hydrate and ~35% water [17]. This is much different than suggested above, arguably because the initial resistivity log interpretation did not include the appropriate amount of free gas and dissolved ions.

Second, high-salinity brines may provide a means to transport free gas through water-bearing shallow sediment. A growing body of evidence suggests that free gas moves through the GHSZ on Hydrate Ridge [9–13] and elsewhere [8,14–16,40]. Where this phenomenon has been discussed for Hydrate Ridge, various authors have typically invoked a special circumstance of gas–water segregation during gas transport [9,10]. For example, Suess et al. [10] suggest that free methane moves through shallow sediment of northern Hydrate Ridge along channels lined with gas hydrate that has incorporated all surrounding water. We cannot dismiss these ideas, but note that they are inconsistent with macroscopic observations indicating abundant water in shallow sediment of Hydrate Ridge. Even the thin sediment intervals with the highest gas hydrate content at Site 1249 have large amounts of water according to well logs [17] and our information from Core 204-1249F-4P. Rather than arguing for segregation of free gas and water within the GHSZ, we hypothesize that free gas can move through the regional GHSZ in association with high salinity water (Fig. 9).

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