

GAS HYDRATES

IN MARINE SEDIMENTS

LESSONS FROM SCIENTIFIC OCEAN DRILLING

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Certain low-molecular-weight gases, such as methane, ethane, and carbon dioxide, can combine with water to form ice-like substances at high pressure or low temperature. These compounds, commonly called gas hydrates, concentrate gas in solid form and occur

naturally in sediment beneath the Arctic permafrost and in the sediments of the continental slope. A decomposing piece of gas hydrate can be ignited and will sustain a flame as the methane is released, producing the phenomenon of “burning ice.”

Ocean drilling has proven to be an important tool for the study of marine gas hydrate systems, which have been increasingly recognized as important to society. In some places, methane hydrate may be concentrated enough to be an economically viable fossil fuel resource. However, geohazards may be associated with gas hydrates as well, through large-scale slope destabilization (e.g., Maslin et al., 2004) and release of methane, a potent greenhouse gas. Indeed, evidence collected from deep-sea sediments suggests that major global warming episodes in the past were associated with massive methane releases from gas hydrate deposits (e.g., Dickens et al., 1995; Hesslebo et al., 2000), although this hypothesis remains controversial (e.g., Bowen et al., 2006). Climate changes over the late Quaternary have also been linked to re-

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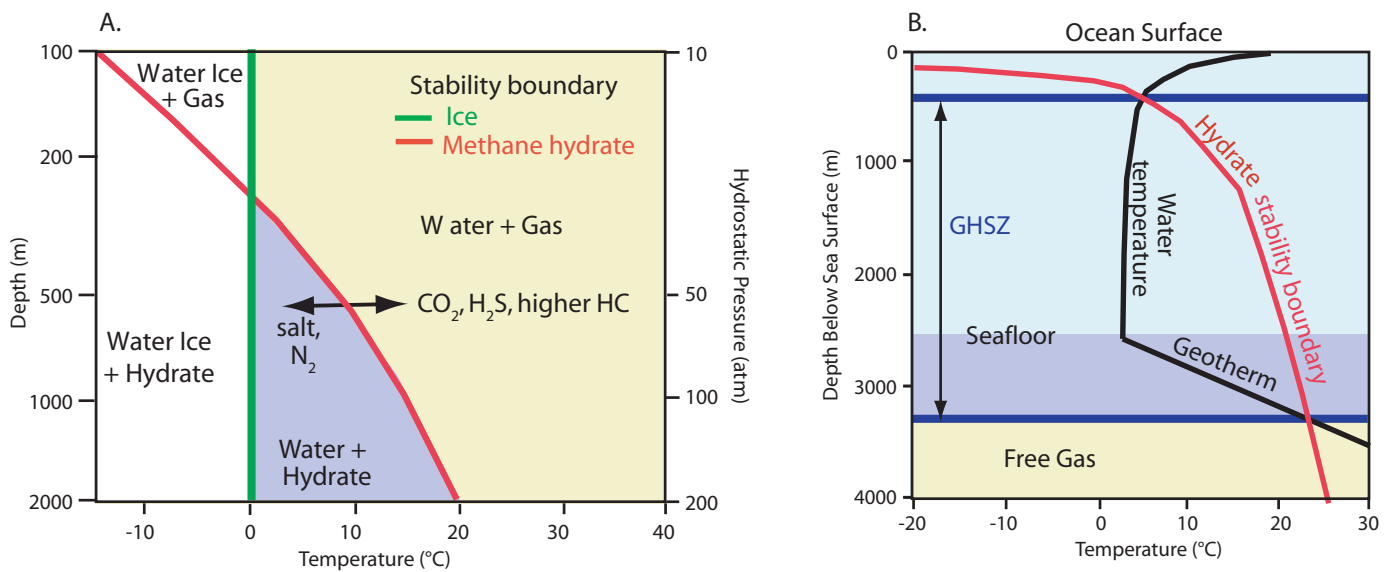


Figure 1. (A) The methane hydrate stability boundary compared to water ice stability for fresh water. The stability boundary moves to the right if gas contains CO₂, H₂S, or higher-order hydrocarbons and to the left as pore-water salinity increases or if the gas contains N₂. For quantitative analysis of the effects of these parameters on gas hydrate stability, see Sloan (1998). (B) Gas hydrate stability in the marine environment. The gas hydrate stability zone (GHSZ) extends from the depth within the ocean at which gas hydrate becomes stable (which depends on local water temperature) to a depth beneath the seafloor that is determined by the local geothermal gradient. Much of the seafloor is within the GHSZ. The thickness of the GHSZ below the seafloor increases as water depth increases if the geothermal gradient is constant.

lease of methane from submarine gas hydrates (Kennett et al., 2003). However, isotopic studies of methane in ice cores (e.g. Sowers, 2006) and budget calculations for the global carbon cycle suggest that the impact of gas hydrates must have been minor (Maslin and Thomas, 2003). Methane hydrate deposits and the associated sediments have also become an important focus for biogeochemical studies of the deep biosphere to elucidate the function and community structure of microbes that produce and consume methane (e.g., Wellsbury et al., 2000).

In this paper, we summarize the principal lessons learned about marine gas hydrate deposits through scientific ocean drilling, focusing on results of recent expeditions conducted by the Ocean Drilling Program (ODP), the Integrated Ocean Drilling Program (IODP), and

the U.S. Department of Energy (DOE)/ChevronTexaco Joint Industry Program (JIP). Gas-hydrate-bearing marine sediments were first cored during Leg 11 of the Deep Sea Drilling Project (DSDP) in 1970 at Blake Ridge (southeast U.S. continental margin), and the first deep-sea gas hydrate specimens were observed in sediments recovered from the accretionary complex of the Middle America trench during DSDP Legs 66 and 67 in 1979. Since that time, gas hydrates have been inferred or observed in numerous scientific boreholes. Here we focus on examples from recent expeditions in three major gas hydrate provinces. Blake Ridge is a passive margin sediment drift deposit located on the southeastern United States margin, which was drilled during ODP Leg 164 (1995). The Cascadia margin offshore the Pacific North-

west coast is an accretionary complex drilled during ODP Legs 146 (1992) and 204 (2002), and IODP Expedition 311 (2005). The Gulf of Mexico represents a passive margin petroleum province that has been strongly affected by salt tectonics and has been the subject of IODP site surveys and drilling by the DOE/ChevronTexaco JIP.

GAS HYDRATES IN MARINE SEDIMENTS

The stability of gas hydrate depends most fundamentally on temperature, pressure, gas composition and saturation, and pore-water composition (Figure 1A). Gas hydrate nucleation and growth also depend on sediment grain size, shape, and composition (Clennell et al., 1999). These parameters, which control gas hydrate formation and per-

sistence, are affected by a wide range of processes in the ocean, leading to multiple possible dynamic feedbacks on various timescales (e.g., Kvenvolden, 1988; Paull et al., 1991; Dickens et al., 1995; Kennett et al., 2003; Buffett and Archer, 2004).

Because methane is the dominant gas contained in submarine gas hydrates (Kvenvolden, 1993), we use the stability curve calculated for pure methane Structure-I hydrate in this discussion. At atmospheric pressure, methane hydrate is stable only at temperatures below $\sim -80^{\circ}\text{C}$. Thus, when a sample containing gas hydrate is recovered through

deep-ocean drilling, gas hydrate is lost as the core experiences decreased pressure and increased temperature during recovery. Sampling gas hydrate, preserving it for further study, and using observations in recovered cores to infer its concentration and distribution *in situ* present unique challenges to the ocean drilling community.

Temperature and pressure conditions consistent with methane hydrate stability are found at the seafloor nearly everywhere at water depths exceeding 300–800 m, depending on regional seawater temperature (Figure 1B). Temperatures below the seafloor increase with

depth following the regional geothermal gradient, which can be overprinted by local thermal perturbations caused by fluid flow and heat focusing (e.g., near salt diapirs). At a depth of a few to several hundred meters below the seafloor, the temperature profile in the sediments crosses the pressure-temperature curve that defines methane stability conditions (Figure 1B). Based on these criteria, gas hydrate could potentially form almost everywhere beneath the continental slope and ocean basins. In most of the deep ocean basin, however, methane concentrations in pore water are below saturation (Claypool and Kaplan, 1974).

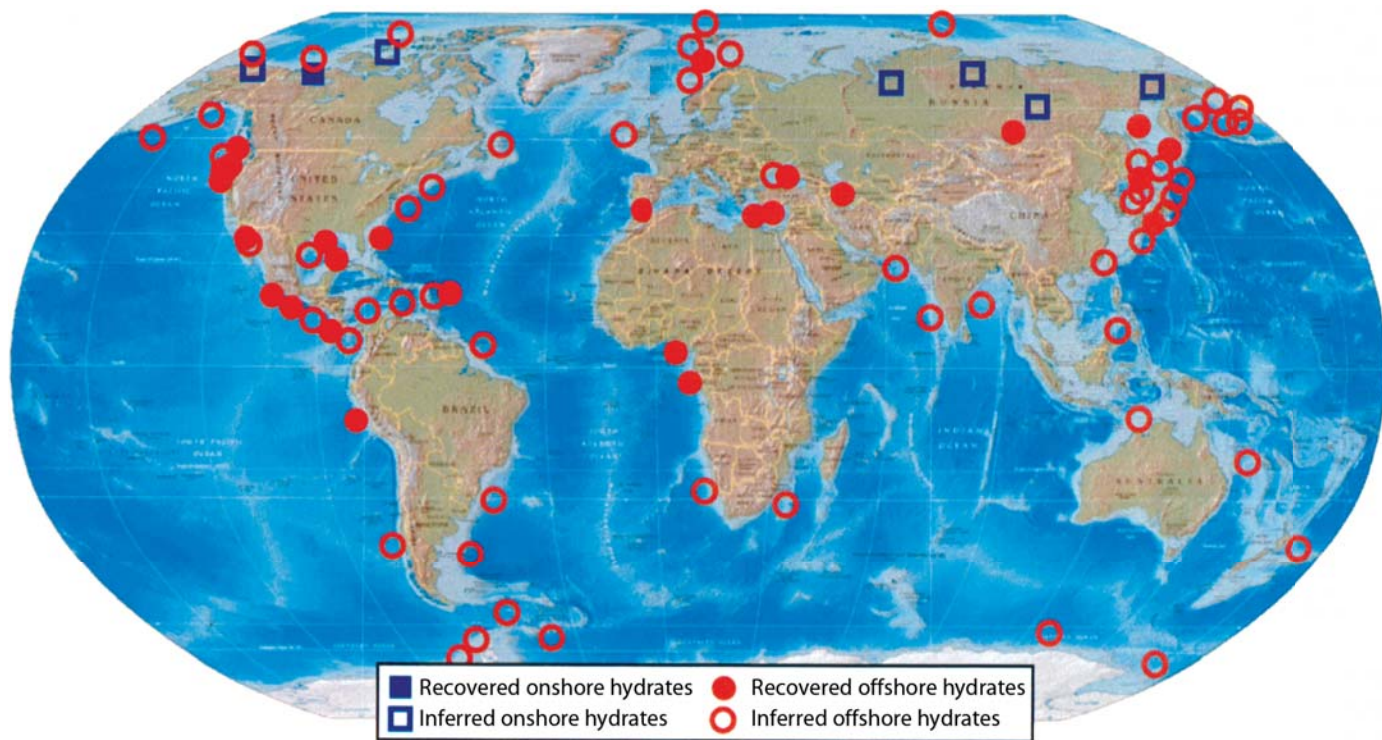


Figure 2. World map with documented and inferred gas hydrate occurrences. Inferred gas hydrate occurrences are based primarily on the presence of a seismic reflection known as the Bottom-Simulating Reflection (BSR), velocity amplitude peculiarities on seismic records, well-log signatures indicative of the presence of gas hydrate, and freshening of pore waters in cores. Samples were recovered using research submersibles, remotely operated vehicles (ROVs), grab samplers, dredges, piston coring, and coring during DSDP, ODP, and IODP operations. Data from Kvenvolden and Lorenson (2001) and updated by Milkov (2005). Reprinted from Doyle et al. (2004).

This condition means that gas hydrate is, generally, restricted to continental margins and enclosed seas (Figure 2), where organic matter accumulates rapidly enough to support methane production by bacteria or where existing free or dissolved gas is transported into the gas hydrate stability zone (GHSZ).

Temperature and pressure are not static parameters. They are affected by *tectonic activity, sedimentation, changes in sea level, and changes in ocean temperature*. As one example, Figure 3 demonstrates how uplift or changes in sea level will affect the GHSZ (Pecher et al., 1998, 2001). Similarly, an increase in the temperature of deep-ocean water will thin the GHSZ, although such temperature changes require thousands of years to propagate into sediments (Xu, 2004; Mienert et al., 2005; Bangs et al., 2005).

Short-term changes in bottom water temperature and pressure due to tides, currents, or deep eddies can also affect gas hydrate deposits (e.g., Ruppel, 2000; MacDonald et al., 1994, 2005).

Both *biogenic and thermogenic sources* produce hydrocarbons that are incorporated into gas hydrate deposits. Biogenic methane can originate wherever organic matter occurs in the presence of a suitable microbial consortium (Davie and Buffett, 2001). Offsetting methane production are microbial processes that consume methane (e.g., Boetius et al., 2000; Orphan et al., 2001a, 2001b; Luff et al., 2005). Within marine sediments, anaerobic oxidation of methane (AOM) by sulfate is largely responsible for the methane-free zone found from the seafloor to subsurface depths as great as hundreds of meters in some

settings. The thickness of this methane-depleted zone, the base of which coincides with depletion in sulfate, is a valuable proxy for methane flux in diffusion-dominated systems (e.g., Borowski et al., 1996). However, gas hydrate deposits have been observed at and near the seafloor (e.g., Brooks et al., 1984; Suess et al., 2001; Chapman et al., 2004). Formation and maintenance of these deposits require rapid methane flux and many of these deposits show geochemical indicators of thermogenic gas that has migrated from subsurface depths greater than 2 km.

A critical factor in formation of gas hydrates is the concentration of methane with respect to *methane solubility* in the sediment pore water, which is a function of temperature and pressure (Claypool and Kaplan, 1974). Methane

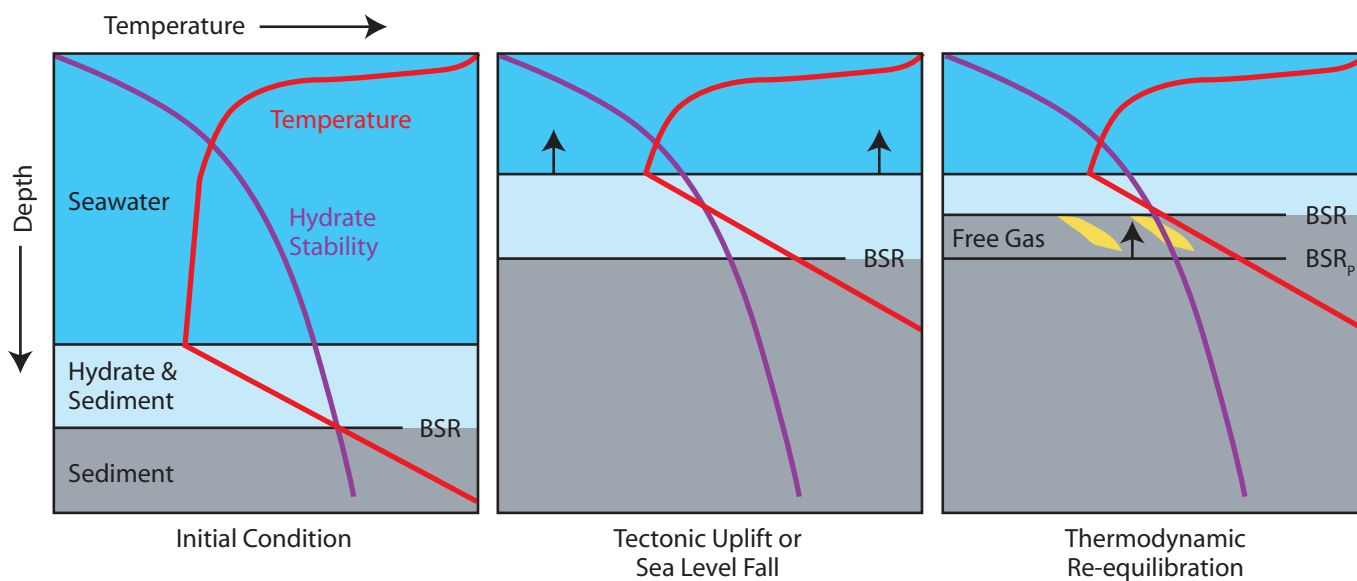


Figure 3. Effect on gas hydrate stability of tectonic uplift or sea level fall. The resultant decrease in pressure will, in either case, result in destabilization of any gas hydrate present near the base of the former gas hydrate stability zone. If the gas hydrate content in this zone is high enough, this may result in large pore pressures and induce slope instability or initiation of “gas chimneys.” In some cases, this gas hydrate dissociation leaves a “paleoBSR” (BSR_p) in the geologic record. After Bangs et al. (2005).

solubility varies with depth as shown in Figure 4. Methane hydrate will form only where the concentration of methane in the pore water exceeds solubility. In most environments, no gas hydrate is present near the top of the GHSZ because the concentration of methane is low, due to AOM and to diffusion of methane into the ocean, where the concentration of dissolved methane is very low (Claypool and Kaplan, 1974). Because solubility generally decreases as water depth decreases (Figure 4B), gas hydrate formation can result from tectonic uplift of sediment and depressurization of pore water as it migrates through the sedi-

ment to a more shallow depth.

Pore fluid composition is another dynamic parameter that affects gas hydrate (Handa, 1990). Briny fluids originating with salt deposits inhibit gas hydrate stability in some settings (e.g., Gulf of Mexico, Ruppel et al., 2005). In other cases, the process of forming gas hydrate, whose clathrate structure excludes salts, may increase the salinity of pore waters (Milkov et al., 2004a; Torres et al., 2004a, 2005; Milkov and Xu, 2005; Liu and Flemings, 2006). Another complication may arise in low-permeability sediments, where gas hydrate formation may stall as all available water is consumed

(Tréhu et al., 2004a; Claypool et al., in press). These feedbacks—between pore-water composition and availability, and gas hydrate formation and stability—are most important where methane flux is rapid and probably do not significantly affect gas hydrate dynamics on a global scale. Locally, though, these factors may be important in permitting the migration of free gas through the GHSZ (Liu and Flemings, 2006).

Ocean drilling results have highlighted the importance of *lithology* (the composition, grain size, and shape of sediment particles) in controlling where and how gas hydrate precipitates (e.g., Ginsberg et

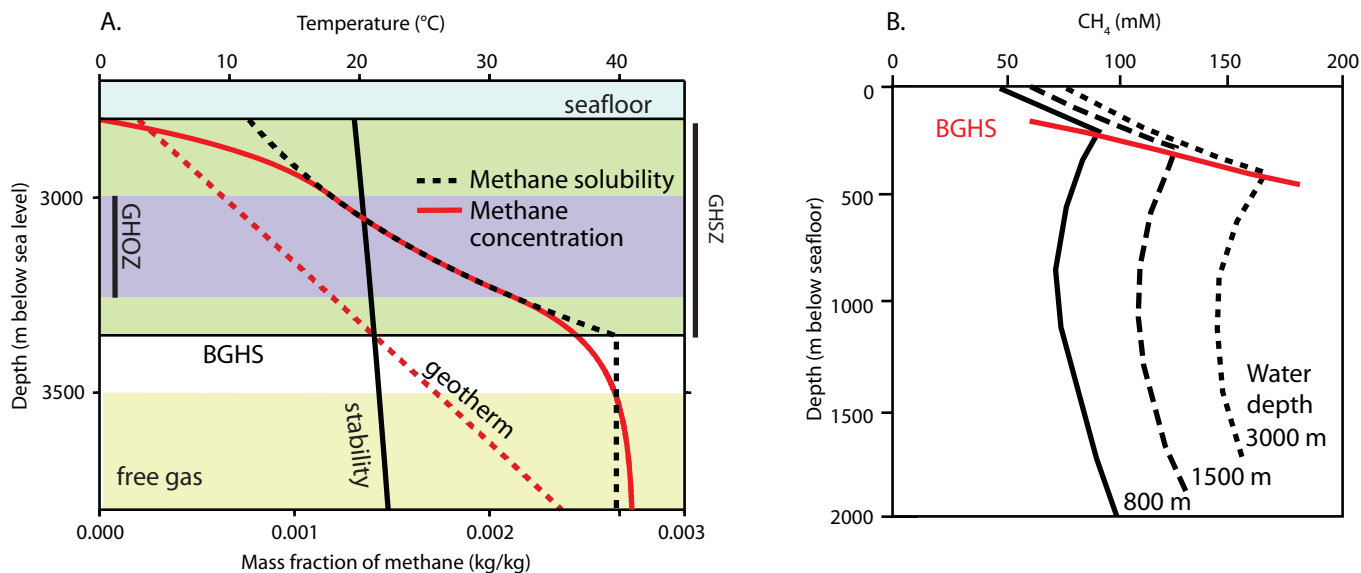


Figure 4. (A) The relationship among the gas hydrate stability zone (GHSZ), the zone in which gas hydrate actually occurs (GHOZ), the free gas zone, and the base of the gas hydrate stability zone (BGHS) calculated for a case in which methane is supplied from below in sediments of uniform permeability (after Xu and Ruppel, 1999). Methane concentration depends on the model and will be different for models with local biogenic generation of methane (Davie and Buffett, 2001). The geotherm (dashed red line) intersects the theoretical methane hydrate stability curve (black line) at the BGHS. In the case shown here, the methane concentration is below solubility at the base of the stability zone, where solubility is largest, and near the seafloor, where methane is typically consumed through sulfate reduction and AOM. As the methane flux increases to a critical value, the gas hydrate and free gas zones will expand downward and upward, respectively. (B) Effect of water depth on methane solubility. As a parcel of sediment is uplifted from 3000 to 800 meters below seafloor in an accretionary complex, methane solubility decreases by a factor of two (G. Claypool, U.S. Geological Survey, retired, personal communication, 2000). Similarly, solubility will decrease as pore water is expelled upwards as a result of sediment compaction.

al., 2000; Weinberger et al., 2005; Expedition 311 Scientists, 2005), as predicted based on models of capillary forces (e.g., Clennell et al., 1999; Henry et al., 1999) and laboratory studies of gas hydrate formation in different sediments (Santamarina et al., 2004). In natural systems, gas hydrate preferentially forms in coarse-grained sediments (Figure 5A). In fine-grained sediments, gas hydrate tends to form discrete veins and lenses (Figure 5B) and often concentrates in zones with slightly enhanced permeability (e.g., diatom-rich layers; Kraemer et al., 2000).

In summary, it is clear that many processes affect migration of free gas and

aqueous fluids through the GHSZ (Figure 6). The geologic setting controls rates of fluid flow and the amount of methane available for gas hydrate formation. Rich, shallow gas hydrate deposits form near the seafloor only where geologic structure focuses methane. Lithology, fracture distribution and pore-space geometry also impact fluid flow and gas hydrate nucleation and growth, and thus control the fine-scale gas hydrate distribution.

REMOTE SENSING

Geophysical surveys are a primary tool for detecting the presence of gas hydrate in marine sediments and represent an

essential precursor for drilling expeditions. The geophysical data are used to identify suitable drill sites and provide the supporting geological context for the sites. Drilling data, in turn, are used to calibrate and validate models for gas hydrate distribution derived from remote-sensing data.

The most widely used geophysical indicator for gas hydrate is a distinctive seismic reflection known as the *Bottom-Simulating Reflection (BSR)* because it roughly follows the shape of the seafloor and cross-cuts reflections from dipping sedimentary strata (Figure 7). This reflection occurs close to the predicted

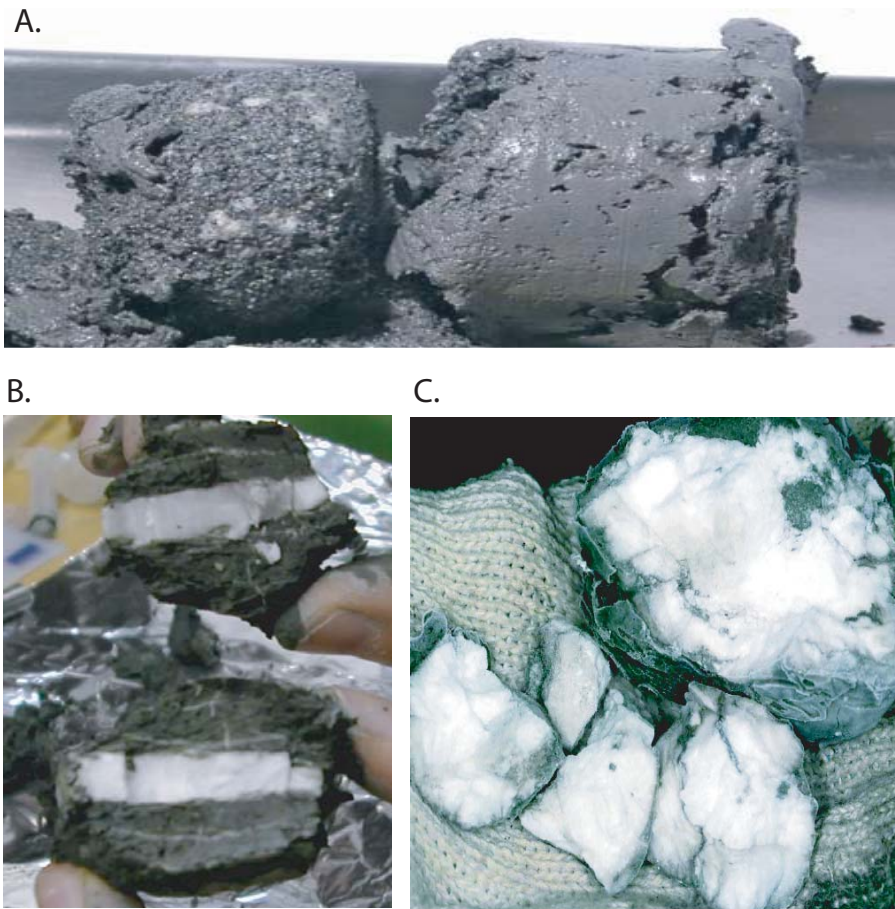


Figure 5. Examples of gas hydrate recovered by ODP and IODP drilling. (A) Gas hydrate recovered during Expedition 311, cementing sand adjacent to hydrate-free clay from 44.85 mbsf. (B) A 1-cm-thick gas hydrate lens with thin gas hydrate veins recovered during Leg 204, Site 1248, from 7.37 mbsf. This sample contained an anomalous amount of propane (Shipboard Scientific Party, 2003). (C) Massive gas hydrate from Leg 204, from 1.20 mbsf.

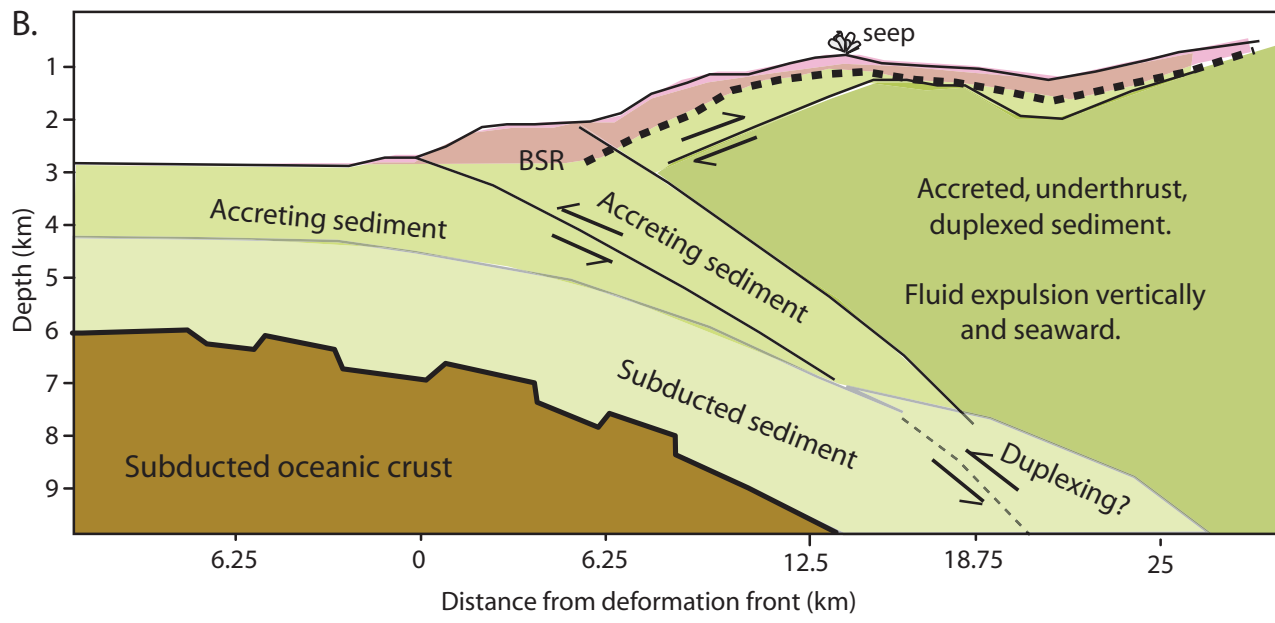
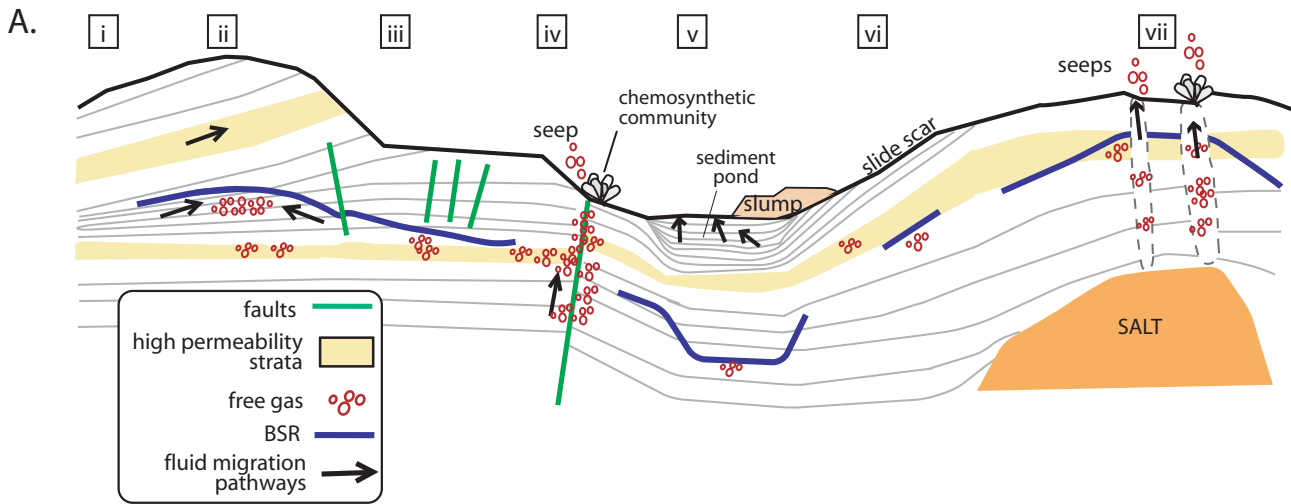


Figure 6. (A) Schematic of gas hydrate dynamics on continental margins; particular features at different locations in the cross section are keyed to the letters at the top of the diagram (Figure after Ge et al. [2002] and Nimblett and Ruppel [2003]). (i) Lack of BSR due to subcritical methane flux (Xu and Ruppel, 1999). (ii) Focused flow in high-permeability layers and trapping of gas beneath the BSR at a bathymetric high. The BSR may trap underlying free gas due to permeability sealing by gas hydrate or free gas. (iii) Faults that cut the BSR and perturb fluid flow enough to slightly affect the BSR or that are merely pervasive and located entirely within the GHSZ are often observed in marine gas hydrate provinces and serve as the loci of concentrated hydrate deposits, particularly when the surrounding sediments have very low permeability (e.g., Tréhu et al., 2004a; Wilson and Ruppel, 2005). (iv) Major faults that tap into deeper free gas deposits can produce seafloor cold seeps and are sometimes associated with seafloor chemosynthetic communities that are sustained by methane emission. The BSR can be upwarped (e.g., Zwart et al., 1996) or completely absent (e.g., Wood et al., 2002) immediately adjacent to these seeps, which are found on both active and passive continental margins. (v) Very rapid sedimentation or erosion can alter the hydrate stability field. In this example, very rapid sedimentation has stranded the BSR at anomalously great depth because thermal equilibration did not keep pace with sedimentation. (vi) Some submarine slides have a temporal association with sea-level variations and a spatial association with gas hydrates. (vii) Salt diapirs are often accommodated by large faults and typically perturb both sediment thermal structure and pore-water chemistry, which in turn affect gas hydrate stability and the position of the BSR. Chimneys tapping into deep levels within the sediments can feed chemosynthetic communities at these locations. (B) Schematic illustration of mechanisms for delivering methane to the GHSZ in an accretionary complex. Sediments that are deposited on the abyssal plain are tectonically thickened by sediment subduction and accretion, leading to dewatering in excess of the amount induced by normal sedimentation, increasing the volume of sediment available for generation of methane that can migrate into the GHSZ. This environment also results in many anticlines and faults that serve as gas traps and conduits, respectively. Slumping and rapid sedimentation in slope basins overlying the accretionary complex are also common in this tectonic setting.

base of the GHSZ and has characteristics consistent with layering of higher-velocity over lower-velocity material. The BSR is thus interpreted to result from the velocity contrast between gas-hydrate-bearing strata and strata containing free gas (Tucholke et al., 1977; Shipley et al., 1979). Gas hydrate has, however, been documented where no BSR is observed (e.g., Mathews and von Huene, 1985; Paull et al., 1996), so although the presence of a BSR is a strong indicator that at least a small amount of gas hydrate is present, the lack of a BSR does not imply that gas hydrate is absent.

Although many attempts have been made to determine the amount of gas hydrate and underlying free gas by modeling BSR waveforms (e.g., Singh et al., 1993; Korenaga et al., 1997; Yuan et al., 1999; Tinivella and Accaino, 2000), these efforts contain large uncertainties. Even a small amount of free gas has a large effect on seismic velocity (e.g., Ostrander, 1984), whereas the effect of gas hydrate on seismic velocity depends strongly on the microscale distribution of gas hydrate and its relationship to the sediment grains (e.g., Dvorkin and Nur, 1993; Helgerud, 1999). Calibration of estimates of gas hydrate and free gas amounts derived from seismic data is restricted to a few places where downhole logging data and coincident samples constrain the heterogeneity of gas distribution in marine sediments. Laboratory studies of gas hydrate formation in marine sediments also provide important information for calibrating remote-sensing efforts (e.g., Yun et al., 2005).

Other techniques that have the potential to identify and quantify the gas hydrate and free-gas content of sedi-

ments over large regions include controlled-source electromagnetic sounding (e.g., Edwards, 1997; Yuan and Edwards, 2000; Weitemeyer et al., 2005), seafloor compliance (Willoughby and Edwards, 1997; Willoughby et al., 2005), and ocean-bottom seismology, which permits analysis of seismic shear waves as well as pressure waves (e.g., Hobro et al., 2005; Spence et al., 1995; Westbrook et al., 2005; Backus et al., 2006).

Near-seafloor deposits of gas hydrate present particular challenges for widely spaced, regional geophysical survey techniques. These deposits require specific geologic structures to generate the required rapid methane flux and are often of limited spatial extent. An important exploratory mapping tool for these deposits, which appear as highly reflective patches when they breach the seafloor, is surface or deep-towed *side-scan reflectivity* (e.g., Carson et al., 1994; Johnson et al., 2003; Roberts et al., 2006). This technique rapidly images large patches of seafloor. Interpreting such data requires distinguishing “brightness anomalies” representing gas hydrate deposits from those associated with seafloor topography, changes in sediment type, and seafloor mineral deposits, features that may or may not be related to the presence of gas hydrates (Roberts and Carney, 1997).

LOGGING AND CORING

Direct information about the abundance and distribution of gas hydrate in marine sediments can only be obtained by drilling. Coring allows for recovery and analysis of subsurface samples, while logging techniques permit measurement of *in situ* geophysical and geochemical parameters along the length of the borehole.

Gas hydrate is subject to rapid dissociation when recovered from the seafloor in conventional (non-pressurized) cores. Estimates of gas hydrate abundance and distribution in the subsurface must therefore often rely on proxies of varying accuracy and resolution. Proxies for gas hydrate include: total gas volumes from pressure-core samples; geochemical measurements such as pore-water–dissolved chloride (Cl⁻) concentration; core temperatures measured with scanning infrared (IR) cameras; geophysical logs; and vertical seismic profiles. The first two techniques provide accurate but incomplete estimates of the gas hydrate content of the subsurface because they represent only a small fraction of the sediment within the GHSZ. The latter three approaches provide good spatial coverage, but algorithms for quantifying gas hydrate from the observations must be calibrated and verified by other techniques. Geophysical logs provide the only means of obtaining high-resolution data at *in situ* conditions from the entire borehole, including those intervals for which sediment is not recovered. Moreover, many geophysical parameters (e.g., seismic velocity, electrical resistivity, density) depend on the sediment fabric, which changes as pressure is released.

Pressure Cores

Pressure cores provide the only means of recovering all of the gas present at *in situ* conditions, including gas dissolved in the pore water, free gas bubbles, and gas trapped in gas hydrate. Assuming that various gas phases (gas hydrate, free gas, and dissolved gas) are at equilibrium conditions prior to core recovery, the

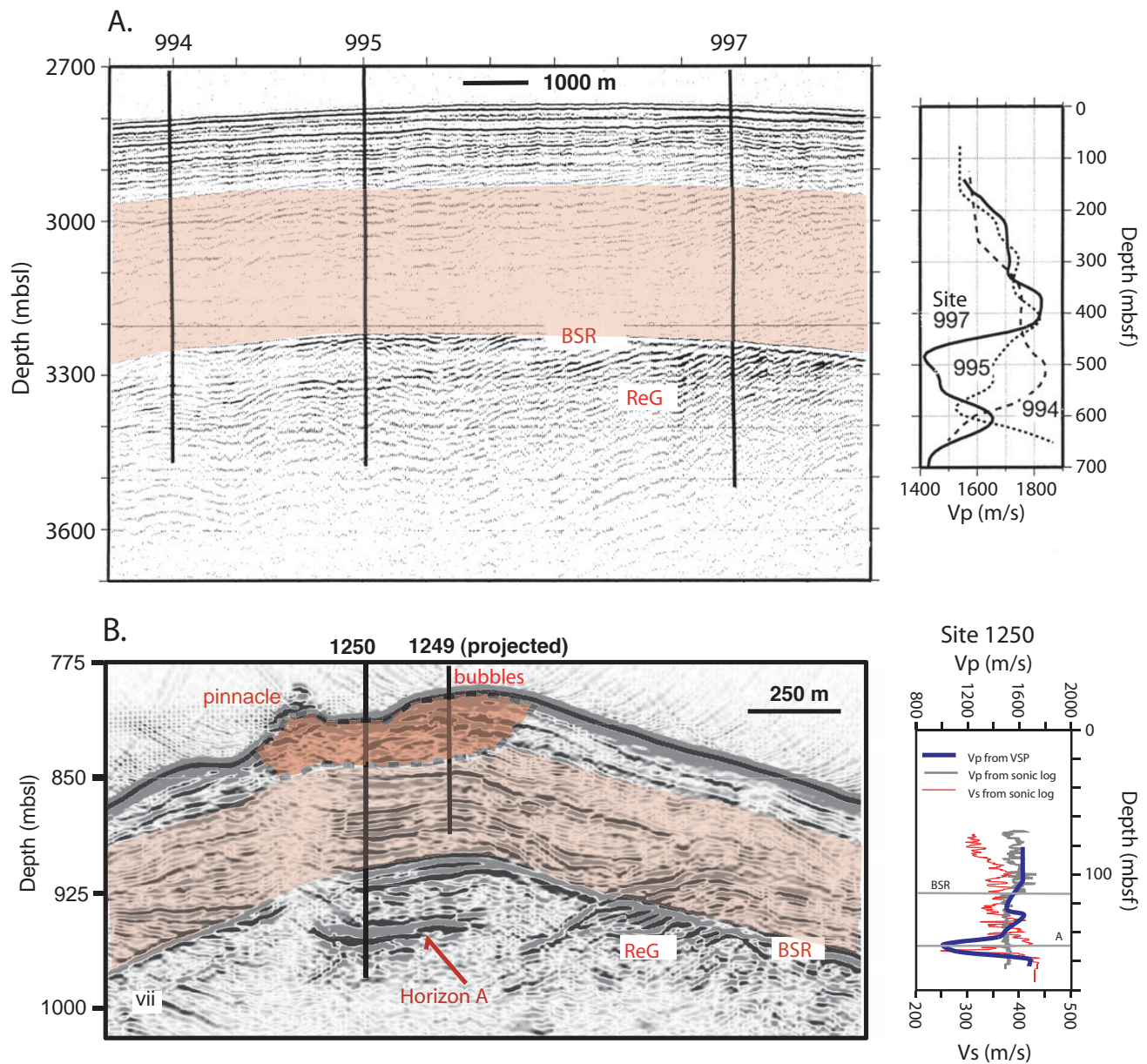


Figure 7. (A) Single channel seismic profile across the crest of the Blake Ridge showing locations of Sites 994, 995, and 997, drilled during ODP Leg 164. Seismic velocity profiles at the three sites from vertical seismic profiles are shown on the right (from Holbrook et al., 1996). Note the absence of a BSR at Site 994. Here, the methane flux is such that the base of gas hydrate and the top of free gas are separated by a depth range in which the methane concentration is too low to allow gas hydrate formation near the base of the GHSZ as defined by *in situ* temperature and pressure. ReG – reflectivity enhanced by the presence of free gas; mbsl – meters below sea level; mbsf – meters below seafloor; Vp – velocity of seismic P-waves. (B) Vertical slice extracted from a three-dimensional (3D) seismic survey of southern Hydrate Ridge in the Cascadia accretionary complex. Sites 1249 and 1250, near the summit of the structure, are shown on this slice. The velocity of seismic P and S waves determined by sonic logs (red and grey lines) and a vertical seismic profile (blue line) at Site 1250 is shown on the right. A BSR is apparent on both seismic profiles at a depth of ~ 475 mbsf beneath Blake Ridge and ~ 120 mbsf beneath southern Hydrate Ridge. The light pink shading on both profiles delimits DLF deposits in which gas hydrate occupies 2–8 percent of the pore space, on average (Dickens et al., 1997; Holbrook et al., 1996; Tréhu et al., 2004b), with locally greater gas hydrate content controlled by lithology (e.g., Ginsberg et al., 2000; Kraemer et al., 2000; Tréhu et al., 2004b; Weinberger et al., 2005). At southern Hydrate Ridge, a FHF deposit is superimposed on the regional DLF deposit (dark pink shading). The gas hydrate content of this deposit appears to be ~ 25 percent of the total sediment volume (Tréhu et al., 2004b). Modeling suggests that an abundant supply of free gas is needed to form this deposit (Torres et al., 2004a). A decrease in P-wave velocity to ~ 1400 m/s below the BSR at all the sites shown in this figure indicates the presence of free gas (Holbrook et al., 1996; Tréhu et al., 2006). Extremely low P- and S-wave velocities associated with Horizon A support the conclusion that it contains enough free gas to result in high gas pressures, which can drive free gas into and through the GHSZ (Tréhu et al., 2004a).

amount of gas hydrate present within the core can be determined by measuring the total amount of gas released from the core as pressure is released and comparing the *in situ* gas concentration to the *in situ* gas saturation assuming that *in situ* porosity is known (Dickens et al., 1997). The first *in situ* gas-concentration measurements were collected at Blake Ridge during ODP Leg 164 (Dickens et al., 1997) using the Pressure Core Sampler (PCS) developed by ODP. Similar data have now been generated from boreholes in other regions using the same first-generation tool (e.g., Milkov et al., 2003). As the only direct measurement of the amount of gas in a core, these measurements provide critical information to test estimates of gas hydrate content obtained by other means, but provide little information on length scales shorter than a core length (generally 1 m). Because information on the fine-scale distribution is critical for development of models to interpret downhole geophysical logs and remote sensing data (e.g. Dvorkin and Nur, 1993; Helgerud et al., 1999), considerable effort has been expended in recent years to develop new pressure coring systems that permit detailed analysis of physical properties at *in situ* conditions (Box 1; Figure 8A).

Existing pressure coring tools consume considerable time and labor to deploy and de-gas. Consequently, only a small percentage of the sediment column can be sampled using these tools.

Geochemical Proxies

Several geochemical proxies have been developed to estimate the *in situ* gas hydrate content of sediment cores. The most widely used is based on measure-

BOX 1: RECENT ADVANCES IN PRESSURE CORING

Pressure cores are critical for understanding the fine-scale structure of gas-hydrate-bearing sediments and the physical and chemical conditions within these sediments. In the past few years, new pressure coring systems have been developed and field tested to provide this information and to constrain the total amount of gas present *in situ*. These new systems include the HYACINTH pressure corers (HYACE rotary corer and Fugro pressure core) that have been used on several ODP and IODP expeditions (Shipboard Scientific Party, 2003; Expedition 311 Scientists, 2005; Schultheiss et al., 2006) and during JIP Gulf of Mexico drilling, and the PTCS (Pressure-Temperature Coring System), a three-meter-long pressure corer developed by the Japanese National Oil Corporation (JNOC) for use drilling gas hydrates in the Nankai accretionary complex offshore Japan (Takahashi and Tsuji, 2005). The HYACINTH pressure coring systems have the unique ability to transfer the core under pressure to shipboard or shore-based analysis equipment for further study at *in situ* hydrostatic pressure.

A pressurized Multi-Sensor Core Logger has been developed specifically to make noninvasive, continuous measurements of physical properties (Shipboard Scientific Party, 2003) on cores recovered and maintained at *in situ* hydrostatic pressure. Current instrument capabilities include acoustic velocity (V_p), gamma density, and X-ray imaging (Expedition 311 Scientists, 2005). The addition of X-ray and gamma-density analysis to traditional pressure coring system (PCS) cores has improved quantitative estimates of gas hydrate in these cores by better constraining sediment volume and sediment density, and by providing a temporal history of gas void creation during and after depressurization (Figure 8A). Combined with the X-rays, these analyses provide unique information on fine-scale gas hydrate structures (Abegg et al., in press; Expedition 311 Scientists, 2005).

Discrete point measurements, collected by placing sensors in direct contact with the sediment through holes drilled into the core liner without ever releasing the pressure on the cores were first conducted on the JIP Gulf of Mexico drilling expedition in 2005 (Yun et al., 2006). The first generation of measurements included seismic velocities (V_p and V_s), electrical properties, and shear strength. Mechanical properties in particular cannot be accurately measured on conventional cores at atmospheric pressure due to the substantial disruption of sediment fabric by the coring and depressurization process. This problem is exacerbated in hydrate-bearing sediments by the release of gas and water during dissociation of the hydrate. Pressure cores maintain the hydrostatic, but not effective, stress on the sediments, and future physical properties measurements on pressure cores will be most valuable if effective stress can be restored (Yun et al., 2006). In the meantime, even the data on cores held at *in situ* hydrostatic pressures are critically important for calibrating estimates of gas hydrate concentrations obtained from analysis of remote sensing data.

While gas hydrate investigations are the primary driver for the development of these pressure coring and analysis techniques, other scientists can benefit from techniques that preserve hydrostatic pressure and the geochemistry of the solid and fluid sediment phases. Microbial growth experiments are being conducted using deep sediments that have never been depressurized, but instead have been retrieved, subsampled, and transferred into enrichment vessels under *in situ* pressure (R.J. Parkes, Cardiff University, personal communication, 2006). As pressure coring tools mature, more disciplines will be able to take advantage of samples returned at *in situ* conditions.

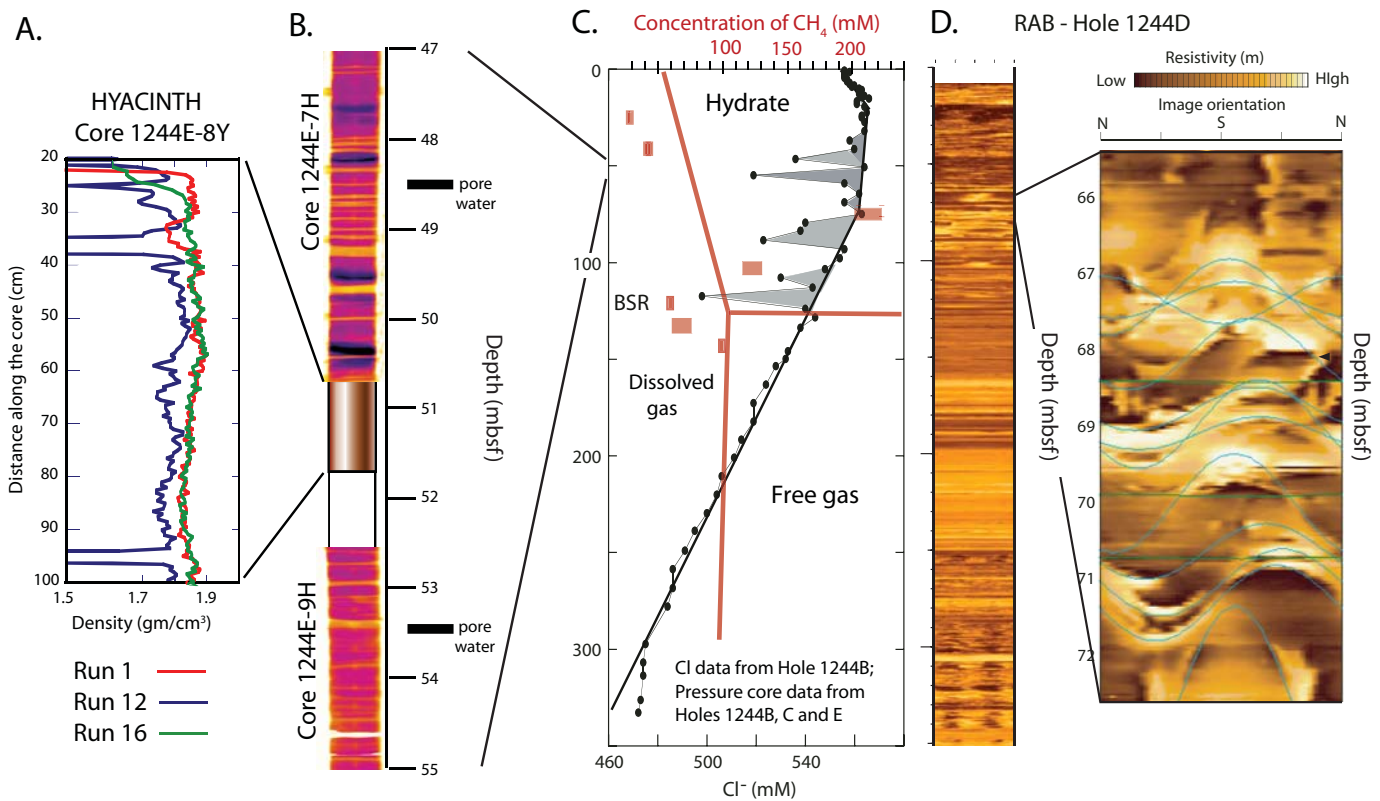


Figure 8. (A) Gamma density profiles of a HYACINTH pressure core for ODP Leg 204 as pressure was released (Shipboard Scientific Party, 2003). Layers of very low density develop with time as gas hydrate lenses decompose in response to decreasing pressure. (B) Infrared image of several m of core on either side of the HYACINTH pressure core. Dark horizontal lines represent cold anomalies (6–8°C) resulting from gas hydrate decomposition; yellow lines represent warm anomalies (12–14°C) resulting from voids due to gas expansion. The approximate thickness and spacing of pore-water samples illustrates the relationship between the scale length of heterogeneities in the apparent gas hydrate distribution relative to pressure core and pore-water samples. (C) Cl⁻ concentration measured in ODP Hole 1244C. If the envelope of the data is assumed to represent the background Cl⁻ concentration (smooth black line), the low Cl⁻ anomalies imply that the pore space contained up to 9 percent gas hydrate in the anomalous samples. Methane concentration from pressure-core data (red squares) is overlain on the Cl⁻ data along with the hydrate phase diagram (red lines). Two pressure cores at this site likely contained gas hydrate. The amount of gas hydrate at this site, averaged over the thickness of the gas hydrate occurrence zone, is 2–8 percent (Tréhu et al., 2004b). (D) Resistivity-at-bit (RAB) data from LWD operations in ODP Hole 1244D. A detail from 66–73 mbsf is shown, as well as an image of the entire hole. Bright regions (high resistivity) are indicative of gas hydrate when they also correspond to low-density zones. The detail shows considerable azimuthal variation in gas hydrate distribution, suggesting that the gas hydrate forms in steeply dipping faults and fractures in this interval (Janik et al., 2003; Weinberger and Brown, 2006).

ment of dissolved Cl⁻ in pore fluids squeezed from sediment (e.g., Hesse and Harrison, 1981; Paull et al., 1996; Shipboard Scientific Party, 2003; Expedition 311 Scientists, 2005). Like ice, gas hydrate incorporates water but excludes dissolved ions during formation. With time, excess dissolved ions will advect or diffuse away from the location of gas hy-

drate precipitation. When cores are recovered from depth, however, gas hydrate will dissociate, adding fresh water to pore space and diluting dissolved ions, including Cl⁻. One limitation of this technique is the time required to extract pore water from the sediment and accurately measure pore water Cl⁻ concentration, which has limited routine sampling to ~ 5-m

intervals along the core (Figure 8B, C), with finer sampling in regions of special interest (e.g., Tréhu et al., 2004b; Expedition 311 Scientists, 2005). Another limitation is uncertainty about the background chloride content of the pore water, which can be affected by many different processes (e.g., Egeberg and Dickens, 1999; Davie and Buffett, 2001; Torres

et al., 2004b). For example, alteration of volcanogenic sediments may increase background chloride (Martin et al., 1995; Riedel et al., 2005), whereas clay dehydration, opal formation, and dissociation of gas hydrate left beneath the base of the GHSZ during upward migration of the stability zone can freshen pore waters (e.g., Egeberg and Dickens, 1999; Davie and Buffett, 2001; Ussler and Paull, 2001; Torres et al., 2004b).

The methane-ethane ratio of gas exsolved from pore water is another proxy that shows some promise for quantifying the amount of gas hydrate present *in situ* and for understanding gas hydrate dynamics (Milkov et al., 2004b). Ethane fractionation effects that distinguish ethane-enriched Structure-I gas hydrate solids from ethane-depleted dissolved gas may also be useful to reconstruct upward migration of the base of the gas hydrate stability field in the past (Claypool et al., in press).

Infrared Cameras

Infrared cameras were first introduced during ODP Leg 201 (Ford et al., 2003) and have been used since ODP Leg 204 to image all core recovered from within or near the GHSZ. Gas hydrate dissociation is strongly endothermic, producing temperature anomalies in cores that can be several degrees colder than adjacent sediments. These cold spots were detected using individual temperature probes on ODP Leg 164 (e.g., Paull et al., 1996), but track-mounted infrared cameras now permit rapid, systematic scanning of all cores to identify gas-hydrate-bearing intervals and estimate gas hydrate distribution and concentration (Tréhu et al., 2004b; Long et al., 2004;

Weinberger et al., 2005; Expedition 311 Scientists, 2005). The resulting thermal images (e.g., Figure 8B) guide shipboard sampling of sediment intervals for detailed studies of pore waters and lithologies associated with gas-hydrate-bearing intervals or for storage in liquid nitrogen or in pressure vessels (for later analysis of gas hydrate structures).

Downhole Geophysical Logs

Downhole geophysical logs have been used to record data on the ephemeral properties of methane hydrates since DSDP Leg 84 (Mathews, 1986) and have been acquired at all sites where gas hydrates have been detected during ODP and IODP. The use of logging-while-drilling (LWD) technology, which obtains logs immediately after drilling and before the sediments are affected by thermal perturbations associated with coring, is especially important for methane hydrate and gas-bearing sediments (Goldberg, 1997) where core recovery may be poor. LWD has recently been used as a reconnaissance tool to identify thin hydrate-bearing layers to be targeted by subsequent coring and sampling (e.g., Shipboard Scientific Party, 2003, Expedition 311 Scientists, 2005). The most robust logging indicators of *in situ* methane hydrate are elevated electrical resistivity (Figure 8D) and acoustic velocities (Figure 7) that coincide with low gamma ray density values (e.g., Mathews, 1986; Collett, 1993; Guerin et al., 1999; Guerin and Goldberg, 2002; Goldberg et al., 2004). As for other remote-sensing techniques, quantitative estimates of gas hydrate concentrations from log data require assumptions about the microstructural arrangement of gas hydrate

and sediment grains (e.g., Helgerud et al., 1999; Yun et al., 2005) or the use of empirical Archie parameters (e.g., Collett and Ladd, 2000). Spatial resolution of these techniques is such that they provide unique information on the heterogeneous distribution of hydrate through comparison of data obtained in closely spaced, laterally offset holes (Collett et al., 2004) and through acquisition of 360-degree images of variation in physical parameters around the circumference of single borehole (e.g., Collett and Ladd, 2000; Janik et al., 2003).

Vertical Seismic Profiles

Vertical seismic profiles (VSPs) link data obtained by drilling to regional seismic reflection data, thus calibrating algorithms to quantify gas hydrate volume using remote-sensing techniques. VSP data have been important for constraining the amount of free gas present beneath the GHSZ (e.g., MacKay et al., 1994; Holbrook et al., 1996; Tréhu et al., in press) and for defining patterns of velocity anisotropy that can be related to mechanisms for gas migration (e.g., Haacke, 2005). Seismic impedance inversion based on core and logging data has also been used to determine regional gas hydrate concentrations away from boreholes (e.g., Dai et al., 2004; Bellefleur et al., 2006). Although impedance inversion must be carefully calibrated, it is a powerful tool for regional gas hydrate concentration estimates and resource assessments.

In Situ Temperature Measurements

In situ temperature measurements acquired with special downhole tools that measure equilibrium formation tem-

perature provide an important direct constraint on the state of the gas hydrate reservoir (Ruppel, 2000). The first complete set of relatively closely spaced *in situ* temperature measurements within a GHSZ was acquired to depths of ~ 385 mbsf (meters below seafloor) on Blake Ridge (Ruppel, 1997). The results revealed a thermal gradient up to 30 percent lower than that predicted based on conventional heat-flow data and a BSR temperature lower than the theoretical base of gas hydrate stability by 0.5 to 2.9°C. In the Cascadia accretionary complex, the observed BSR depth is consistent with the base of GHSZ predicted for methane in seawater at hydrostatic pressure within the uncertainty of *in situ* temperature and BSR depth estimates (Tréhu, in press; Expedition 311 Scientists, 2005).

DISTRIBUTION AND DYNAMICS

Gas hydrate deposits can be classified into end-member regimes based on the mechanisms that control gas transport into the GHSZ, although both regimes operate simultaneously in many regions. In *focused, high-flux (FHF)* gas hydrate systems, methane from a large volume of sediment is concentrated through focused fluid flow in well-defined conduits. In *distributed, low-flux (DLF)* systems, most of the methane available for gas hydrate formation is generated near where the gas hydrate is formed, and fluid flow is pervasive. FHF systems are associated with rich, localized hydrate deposits near the seafloor, whereas DLF systems result in the broadly distributed gas hydrates that are widespread in marine sediments on continental margins. In this section, we discuss the

characteristics of FHF and DLF gas hydrate systems based on lessons learned from recent drilling expeditions to three contrasting continental margin environments: (1) Blake Ridge, which is dominantly a DLF system with secondary salt and focused venting; (2) the Gulf of Mexico, which is dominated by FHF deposits influenced by the presence of deep hydrocarbon and evaporite deposits; and (3) Cascadia, where both regimes coexist but evaporite deposits are absent, highlighting dynamic effects of ion accumulation in the pore water during rapid gas hydrate formation.

Focused, High-Flux Gas Hydrate Deposits

Mounds of gas hydrates have been directly observed at the seafloor during submersible dives and by using deep-towed cameras and remotely operated vehicles (ROV) at many sites around the world, including the Gulf of Mexico (e.g., MacDonald et al., 1994; Roberts and Carney, 1997), Cascadia (e.g., Suess et al., 2001; Spence et al., 2001; Torres et al., 2002; Tryon et al., 2002; Chapman et al., 2004), the Blake Ridge Diapir (Van Dover et al., 2003), Central America (e.g., Grevemeyer et al., 2004), the Black Sea (e.g., Klaucke et al., 2006), and the Arctic Ocean (Vogt et al., 1997). Vigorous expulsion of gas bubbles into the ocean is often observed above the seafloor hydrate mounds, even when the mound lies within the thermodynamic gas hydrate stability field (e.g., MacDonald et al., 1994, 2005; Heeschen et al., 2003). The gas discharge, which is often episodic, provides evidence for the dynamic processes that lead to the formation of massive hydrate near the seafloor.

Although many of these gas hydrate occurrences were originally identified by seafloor imaging, some have been found by serendipity. For example, massive gas hydrate mounds offshore Vancouver Island, Canada, were first discovered when fishermen trawling for ground fish accidentally dredged up some in their nets (Spence et al., 2001).

Although these seafloor gas hydrate deposits may constitute only a small percentage of the total amount of gas hydrate present in marine sediments, they represent the most accessible and best-studied deposits and are usually accompanied by complex fauna (e.g., Kulm et al., 1986; MacDonald et al., 1989; Fisher et al., 2000; Van Dover et al., 2003) that depend on a food chain based on symbiotic microorganisms similar to those found at hydrothermal vents. In most cases that have been studied in detail, the gas within these near-seafloor deposits contains a mixture of biogenic and thermogenic gas, indicating that the gas has been transported from depths of several kilometers below seafloor through geological structures that focus gas from a large volume of deeply buried sediments. The presence of longer-chain hydrocarbons, such as propane, can also result in the formation of rare forms of Structure-II or even Structure-H gas hydrate (e.g., Sassen et al., 2001; Pohlman et al., 2005) as well as the more common Structure-I hydrate (Sloan, 1998).

FHF deposits that extend to tens of meters below the seafloor have been drilled at the Blake Ridge Diapir (Site 996 of ODP Leg 164), in Cascadia during ODP Legs 146 (Site 892 at North Hydrate Ridge) and 204 (Sites 1248–1250 at South Hydrate Ridge), and IODP

Expedition 311 (Site 1328 at the “Bullseye” vent; Expedition 311 Scientists, 2005), and in the Gulf of Mexico (Atwater Valley vents, GoM-JIP; Kastner et al., 2005). At South Hydrate Ridge, gas that supplies seafloor vents is focused towards the crest of an anticline by an anomalously coarse-grained, volcanic-ash-rich stratigraphic horizon in which free gas saturation reaches 90 percent, leading to high gas pressures immediately beneath the GHSZ (Tréhu et al., 2004a). Here, methane appears to migrate in the free gas phase, and the aqueous fluid flux is low as constrained by *in situ* temperature data (Torres et al., 2004a; Tréhu, in press). In northern Cascadia (IODP Expedition 311), localized vertical flow of warm aqueous pore fluid has been suggested (Wood et al., 2002). However, the upwarping of the BSR predicted by this model is not observed in seismic data and *in situ* temperature measurements do not reveal perturbation of the GHSZ beneath the shallow hydrate deposit (Riedel et al., 2002; Expedition 311 Scientists, 2005), suggesting that the near-seafloor hydrate may be a relict of an earlier episode of fluid flow. In the Gulf of Mexico and at the Blake Ridge diapir, lateral changes in thermal regimes or pore-water salinity, particularly near dissolving, high-thermal-conductivity, buried salt structures, can lead to complex flow patterns (e.g., Ruppel et al., 2005) and focusing of fluids in chimneys beneath near-seafloor hydrate deposits (e.g., Hornbach et al., 2005). Numerical modeling studies (Wilson and Ruppel, 2005) show that faults in such systems are the locus of very rapid flux relative to the surrounding sediment, precisely the condition required to produce localized,

transport-dominated hydrate deposits. Overpressures due to topography and rapid sedimentation (Dugan and Flemings, 2000) certainly also contribute to flow at many sites.

Distributed Low-Flux Gas Hydrate Deposits and Effects of Lithology

Gas hydrate deposits generated by distributed low-flux methane transport and *in situ* microbial methane production are generally characterized by relatively low concentrations (a few percent of pore space) of gas hydrate averaged over the GHSZ (e.g., Lorensen et al., 2000; Tréhu et al., 2004b). Even in regions dominated by DLF, however, fluid advection is still critical for the delivery of methane-bearing fluids to the GHSZ. As demonstrated by Xu and Ruppel (1999), the diffusion of such fluids is simply too slow to permit the formation of substantial thicknesses of gas hydrate over reasonable geologic timescales unless rates of *in situ* microbial methane production are higher than is generally thought to be likely (Davie and Buffett, 2001).

Blake Ridge, with its relatively low-permeability, homogeneous sediments and tectonically quiescent setting, represents an end-member DLF system for homogeneous, fine-grained sediments. The pervasive BSR observed in the Cascadia accretionary complex also results from distributed low-flux fluid flow. In recent years, it has become clear that some of the undisturbed sedimentary sections in salt-withdrawal basins of the northern Gulf of Mexico probably also host low concentrations of gas hydrate with methane of entirely biogenic origin (Hutchinson et al., 2004). Thus, despite its overall thermogenic character and the

occurrence of transport-dominated gas hydrate deposits at seafloor mounds, the Gulf of Mexico also has elements that lie firmly within the DLF end member of gas hydrate deposits.

Models of DLF gas hydrate provinces predict that gas hydrate concentrations are maximal near the base of the GHSZ (Hyndman and Davis, 1992; Rempel and Buffett, 1998; Xu and Ruppel, 1999). This result may in part reflect the assumption of upward fluid advection in these models and the form of the methane solubility curve (Nimblett and Ruppel, 2003), which has an inflection at the hydrate-free gas phase boundary (Figure 4). Although logging and VSP results for Blake Ridge suggest higher concentrations of gas hydrate near the BSR, the inferred concentration of gas hydrate within the stability zone is far from uniform. Even within the relatively homogeneous sediments of Blake Ridge, small variations in permeability induced by variations in grain size (Ginsberg et al., 2000) and local concentration of diatom tests (Kraemer et al., 2000), lead to greater gas hydrate concentrations in some thin horizons at relatively shallow depths within the GHSZ. In addition to such lithologically induced permeability variations, the permeability regime is modulated by very fine scale, steeply dipping faults (e.g., Rowe and Gettrust, 1993), which appear to concentrate gas hydrate within this DLF hydrate province (Wood and Ruppel, 2000).

In Cascadia, where the sediments hosting gas hydrates include highly deformed accretionary complex sediments and turbidite-filled slope basins, lithologic variation is greater than on Blake Ridge and gas hydrate distribu-

tion is strongly influenced by permeability variations induced by lithologic variations (Weinberger et al., 2005) and fractures controlled by the local effective stress (Weinberger and Brown, 2006). Infrared thermal imagery and high-resolution chloride measurements document many examples in which gas hydrate is confined to sandy layers but absent from the adjacent clay- and silt-rich sediments (Expedition 311 Scientists, 2005). Where silty and sandy layers are absent, gas hydrate forms discrete veins and lenses of nearly pure gas hydrate that are millimeters to centimeters thick, rather than occupying sediment pore space (Shipboard Scientific Party, 2003; Abegg et al., in press; Expedition 311 Scientists, 2005).


SUMMARY

The last decade has seen tremendous advances in understanding marine gas hydrate reservoirs, due principally to the success of ocean drilling expeditions designed particularly to advance gas hydrate objectives. Key lessons have emerged from scientific drilling of marine gas hydrate systems:

- Gas hydrate is distributed heterogeneously at all spatial scales, with permeability variations resulting from faults or variations in lithology exercising primary control over the locus of gas hydrate concentration, even in seemingly homogeneous sediments.
- Lithology plays an important role in controlling where gas hydrate forms and whether it fills pore space between sediment grains or displaces grains to form lenses and nodules. In heterogeneous sediments, gas hydrate forms preferentially in coarse-grained horizons.

- Gas hydrate occurs even in locations where no BSR can be recognized. Remote-sensing techniques under development may hold promise for identifying gas-hydrate-bearing sediments without relying exclusively on the presence of a BSR.
- Multiple proxies are required to constrain the distribution and concentration of gas hydrate in natural systems. New tools under development will continue to enhance our capacity to study *in situ* gas hydrate deposits and recovered cores. Of particular note are new advances in laboratory imaging (infrared, computerized tomography and X-ray scanning), LWD, pressure coring, and the physical testing of recovered cores under *in situ* pressure.
- Fluid flow that focuses methane from a large volume of sediment and results in transport of methane over large distances results in locally high methane flux and represents one end-member process that forms massive gas hydrate deposits near the seafloor (focused high flux, FHF). Diffuse fluid flow, or *in situ* microbial methane production results in a low methane flux and generates gas hydrate deposits with distinctly different patterns of the distribution and concentration (distributed low flux, DLF). Most gas hydrate provinces contain gas hydrates formed by both of these end-member processes.
- Just as for conventional hydrocarbon provinces, predicting where gas hydrate deposits will occur and how they will respond to environmental change requires integration of high-quality regional geophysical, sedimentological, and geochemical data.

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