

Clathrate Hydrates in Nature

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Key Words

gas hydrates, methane, unconventional energy resource, climate change, geohazard

Abstract

Scientific knowledge of natural clathrate hydrates has grown enormously over the past decade, with spectacular new findings of large exposures of complex hydrates on the sea floor, the development of new tools for examining the solid phase in situ, significant progress in modeling natural hydrate systems, and the discovery of exotic hydrates associated with sea floor venting of liquid CO₂. Major unresolved questions remain about the role of hydrates in response to climate change today, and correlations between the hydrate reservoir of Earth and the stable isotopic evidence of massive hydrate dissociation in the geologic past. The examination of hydrates as a possible energy resource is proceeding apace for the subpermafrost accumulations in the Arctic, but serious questions remain about the viability of marine hydrates as an economic resource. New and energetic explorations by nations such as India and China are quickly uncovering large hydrate findings on their continental shelves.

Clathrate hydrates: inclusion compounds comprised of water cages that trap guest molecules; also known as methane hydrates, gas hydrates, or simply hydrates or clathrates

Geological or geophysical hazard (geohazard): a geological state with the potential for damage or uncontrolled risk

INTRODUCTION

The literature on clathrate hydrates is now so large that some real effort at selectivity must be made for any review to be useful. The recent publication by Sloan & Koh (2007) of the third edition of the standard textbook in this field provides a comprehensive look at the entire field of clathrate hydrate research from fundamental issues to applications. The review by Buffett (2000) provides key information on hydrates in Earth systems, with a particular emphasis on physical processes and models in deep-Earth sediments. Here we have chosen to examine the most recent information on natural hydrates.

Clathrate hydrates are crystalline compounds formed from water cages stabilized by guest molecules through van der Waals-type interactions. The discovery of clathrate hydrates occurred near the end of the eighteenth century. A cold winter night in Birmingham, England, allowed Sir Joseph Priestly to conduct freezing experiments with water in contact with various gases (Priestley 1790, pp. 359). Unlike other gases he experimented with, sulfur dioxide promoted “ice” formation, which was likely clathrate hydrate. Priestly did not repeat these experiments but remarked that “the further prosecution of this experiment, and a proper attention to it, will probably throw great light on the nature of freezing.” The work by Sir Humphry Davy in 1810 with chlorine showed definitively the existence of this curious form of solid water (Davy 1811).

Starting with Faraday’s work on the composition of chlorine hydrate (Faraday 1823), interest in clathrate hydrates over the next 120 years focused mainly on identifying hydrate guests and corresponding compositions. In 1934, the potential of clathrate hydrates to block oil and gas flow lines sparked increased research on preventing their growth (Hammerschmidt 1934). Although hydrates are a hindrance to maintaining flow in oil and gas pipelines, various beneficial applications of clathrate hydrates have also been explored, from water desalination (Max 2006) to gas storage and transportation of methane (Gudmundsson et al. 2000) and hydrogen (Florusse et al. 2004, Mao et al. 2002).

Not until the 1960s was it recognized that methane-rich clathrate hydrates existed in nature, and existed in large quantities (Makogon 1965). To date, as shown in **Figure 1**, more than 90 sites have been directly or indirectly identified to contain natural gas hydrates. Current estimates show hydrates could contain from 10^{15} to more than 10^{17} m³ of methane at standard temperature and pressure (STP) conditions (Klauda & Sandler 2005, Milkov 2004). The need for energy is driving much of the current natural hydrate research, and hydrate exploration programs are underway in countries worldwide (Pooladi-Darvish 2004). Conversely, the vast quantities of hydrates in marine sediments pose a risk as a geohazard and have been implicated in past climate change events (e.g., Kennett et al. 2003). To address these important issues, a wide range of geochemical and geophysical methods are needed to understand natural hydrate occurrences and their role in the past, present, and future Earth.

Hundreds of molecules are known to form clathrate hydrates and present a plethora of possible applications. Fascination with hydrates even extends outside the scientific community: Hydrates play a fanciful role in popular books, movies, and mysteries (e.g., ship disappearances in the Bermuda Triangle) (Ratcliffe & Ripmeester 2004). This review focuses on estimates and models of hydrate abundance on continental margins, the degree to which hydrate accumulations may be predicted, the debate over hydrate stability and changing climate, the progress made in examining in situ the nature of the solid phase, and the recent findings of complex and exotic hydrates in nature.

THERMODYNAMICS: STRUCTURE AND STABILITY

Numerous excellent reviews are available on fundamental hydrate science, including Jeffrey (1984), Davidson (1979), Koh (2002), and Sloan & Koh (2007). Three common crystal types (Structure I,

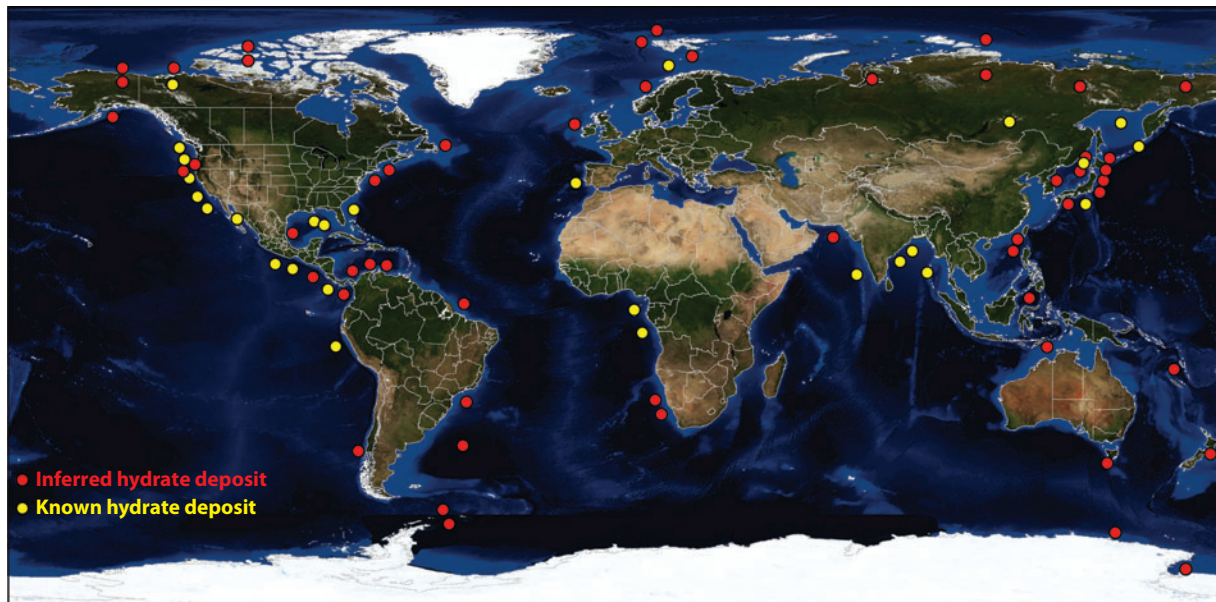


Figure 1

Worldwide map of more than 90 documented hydrate occurrences. Data from Kvenvolden & Lorenson (2001) and Milkov (2005). Inferred hydrate deposits were identified with indirect hydrate markers, mainly from seismic reflectors and pore-water freshening in core samples. Known hydrate deposits are areas where hydrates have been directly sampled from ocean drilling and remote-operated vehicle expeditions.

II, and H) form on the basis of the guest molecules present and pressure and temperature conditions. **Figure 2** shows the building blocks that combine to grow each crystal type. Each structure contains the small, nearly spherical 5^{12} cage combined with larger cages in various ratios to form a repeating unit cell. The water cages are described using the notation X^Y , where X is the number of sides per cage face and Y is the number of those face types that make up a particular cage.

Although a wide range of molecules from H_2 to tetrahydrofuran (Davidson 1979, Sloan & Koh 2007) are known hydrate guests, for this discussion on natural hydrates we focus on the most prevalent guest types. The dominant guest molecule found in natural hydrates is methane, along with smaller quantities of other hydrocarbons, carbon dioxide, and hydrogen sulfide (Milkov 2005).

Clathrate hydrates are generally classified on the basis of crystal structure. The relationship between the guest molecule, the cage sizes, and their ratios in the lattice largely determine which structure will form, especially for simple (single guest) hydrate systems (Ripmeester 2000). Structure I (sI) hydrate contains large $5^{12}6^2$ and small 5^{12} cages in a ratio of 3:1. Methane, carbon dioxide, and ethane crystallize in the sI lattice. Structure II (sII) contains the larger $5^{12}6^4$ cages, as well as 5^{12} cages, in a ratio of 1:2. Molecules too large to fit in the $5^{12}6^2$ cage, such as propane and isobutane, are examples of sII guests (Davidson 1979). Structure H (sH) contains three cage types: large $5^{12}6^8$, medium $4^35^66^3$, and small 5^{12} cages in a ratio of 1:2:3 (Ripmeester et al. 1987). Two guests are required to form sH, where one guest stabilizes the small and medium cages, such as methane, and a larger guest stabilizes the $5^{12}6^8$ cages, such as methylcyclohexane. All three structures have been identified in nature, including multiple structures coexisting in the same area (Hester et al. 2007a, Kida et al. 2006, Lu et al. 2007).

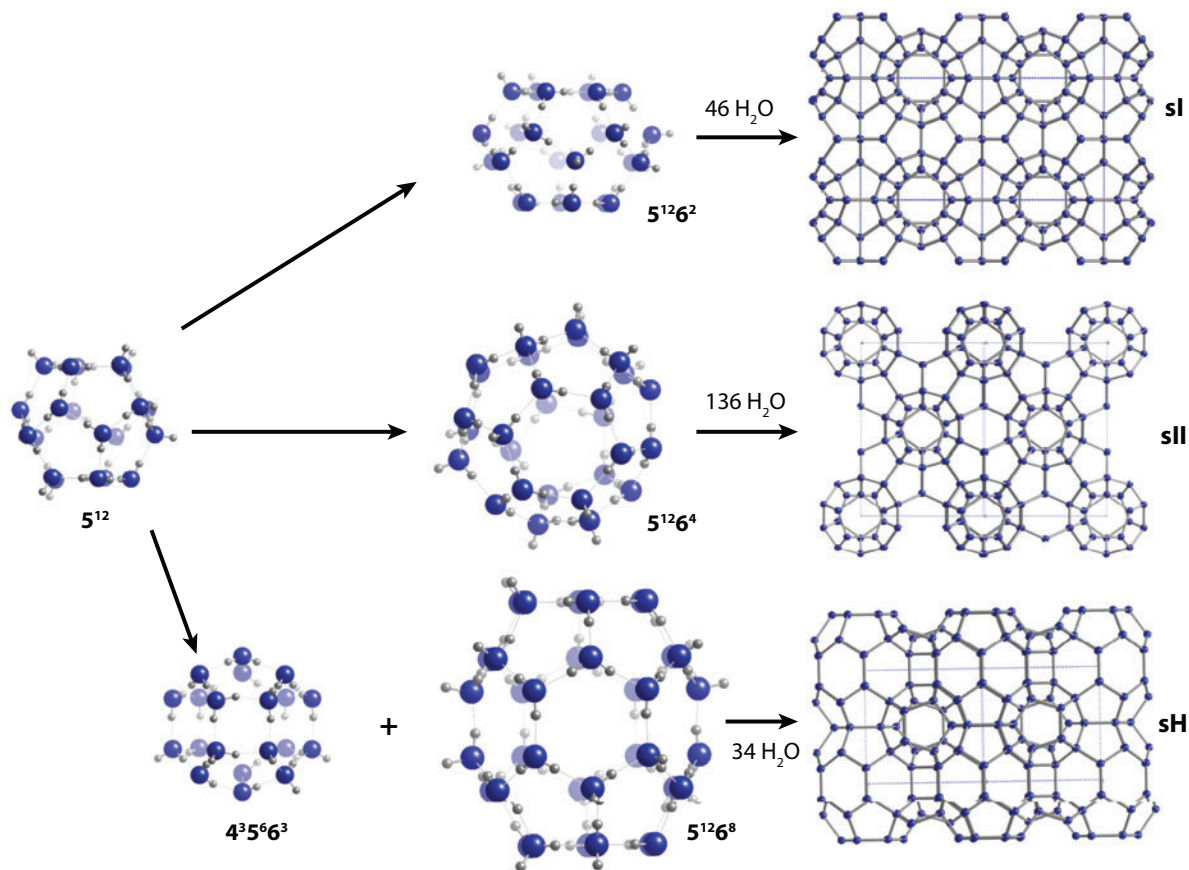


Figure 2

Three hydrate structures known in nature and the cage building blocks for each. Crystal structures were drawn using Crystallmaker[®].

When multiple guests are present, the concentration of the various guests, as well as size, become important for structural determination of the mixed hydrate (Hester & Sloan 2005, Ripmeester 2000). Whereas methane and ethane form sI as simple hydrates, a mixed methane + ethane hydrate can form either sI or sII depending on their relative concentrations (Subramanian et al. 1999). This effect is likely related to the cage ratios in the two structures and how the guest molecules stabilize the lattice (Hendriks et al. 1996, Ripmeester 2000, van der Waals & Platteeuw 1959).

Hydrates are nonstoichiometric solid solutions known to concentrate many gases. For pure methane hydrate over a wide range of conditions, the hydration number was found to remain relatively constant at 5.99 ± 0.07 (Circone et al. 2005). Recently the first single crystal X-ray measurements on a natural hydrate sample showed the $5^{12}6^2$ fully occupied and 89.8% of the 5^{12} cages filled, resulting in a hydration number of 5.90 (Udachin et al. 2007). This means that more than 97% of the cages were occupied with methane, concentrated more than 160 times versus STP conditions. For comparison, at 298 K, the methane density in the hydrate is equivalent to gaseous methane at more than 145 atmospheres.

Hydrate formation is bound by temperature and pressure. Favorable hydrate formation conditions (high pressure, low temperature) exist over much of the oceanic and permafrost sediments.

Mixed hydrate:

clathrate hydrate that contains multiple guest molecule types

Simple hydrate:

clathrate hydrate containing only one guest type

Hydration number:

molar ratio of water to hydrate guests

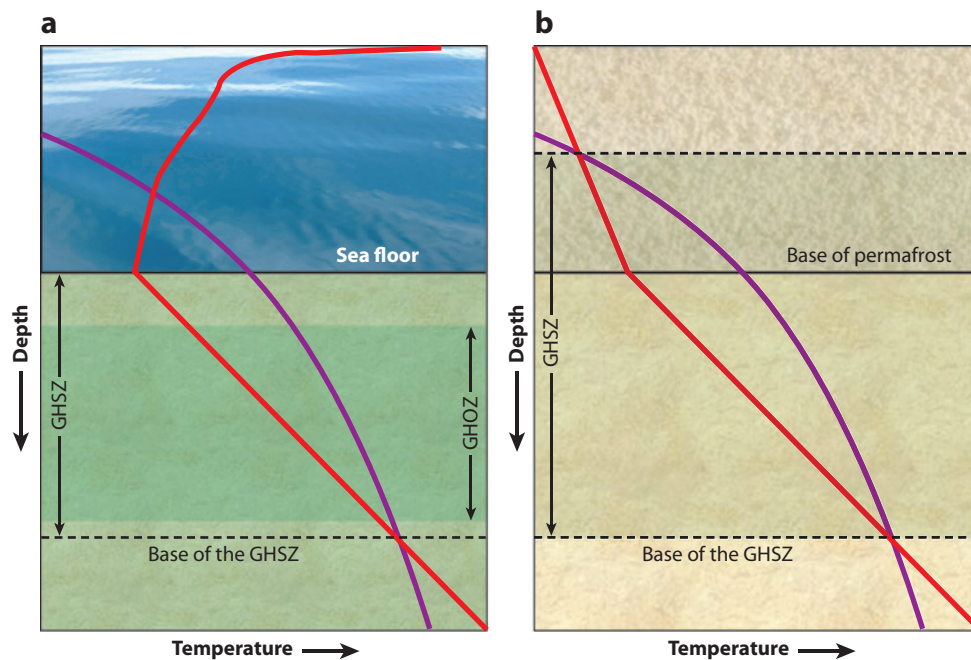


Figure 3

Gas hydrate stability zone (GHSZ) for (a) marine and (b) permafrost settings. Shown are the ambient temperature profile (*red*) and the hydrate stability curve (*purple*). For marine systems, the GHSZ typically begins below 300–600 m of water depth and can extend hundreds of meters below the sea floor, with a general temperature range from 2 to 20°C; hydrate formation is limited to the gas hydrate occurrence zone (GHZOZ) owing to availability of methane. For permafrost systems, the GHSZ typically occurs around 100–300 m depth and can extend hundreds of meters based on the base of permafrost; the general temperature range is from –10 to 20°C.

In fact, the earliest estimates of hydrate extent in nature included all areas with sufficient pressure and temperature (Milkov 2004). However, the availability of guest molecules is most often the limiting factor in natural hydrate formation. Thermodynamic equilibrium requires sufficient guest concentrations to precipitate hydrate. Therefore, researchers must explicitly account for the concentration of the hydrate guest in the bathing fluid and the activity of the water (e.g., salinity).

Figure 3 shows a representative gas hydrate stability zone (GHSZ) as a function of depth for marine and permafrost systems. Just below the sea floor, sulfate reduction and anaerobic oxidation of methane (AOM) lower methane concentration to levels below saturation, limiting hydrate formation to the gas hydrate occurrence zone (GHZOZ) (Borowski et al. 1996). The GHZOZ can also be found to terminate shallower than the base of the GHSZ. This area has the highest methane solubility and gas supply can be insufficient to reach saturation (Xu & Ruppel 1999). In permafrost settings, an ice + gas 2-phase equilibrium exists until pressures are great enough to allow for hydrate formation. The GHSZ extends through the base of permafrost until temperatures exceed hydrate stability, resulting in a gas + liquid two-phase region.

TYPES OF NATURAL HYDRATE ACCUMULATIONS

Worldwide, methane hydrate is stable below around 300–600 meters of water depth for typical ocean waters. Hydrate accumulations can be classified in two end-member categories on the basis

GHSZ: gas hydrate stability zone

Sulfate reduction: bacterial process where sulfate is reduced to sulfide

Anaerobic oxidation of methane (AOM): oxidation of methane in the presence of sulfate; occurs mainly in anoxic sediments

GHZOZ: gas hydrate occurrence zone

Structural hydrate accumulations: occur in HGF systems where features such as faults allow rapid fluid transport

HGF: high gas flux

Allochthonous: materials formed there elsewhere than their current location

Stratigraphic hydrate accumulations: occur in LGF systems where hydrate forms from gas supplied by in situ microbial production or slow fluxes from depth

LGF: low gas flux

Biogenic: formed from anaerobic bacterial decomposition of organic matter

Thermogenic: formed from thermal cracking of organic material

of how the source gas was supplied: structural-type high gas flux (HGF) systems supplied by deep migrating allochthonous gas and stratigraphic-type low gas flux (LGF) systems from in situ gas production (Milkov & Sassen 2002). A listing and review of known hydrate accumulations worldwide can be found in Milkov (2005) and Sloan & Koh (2007).

In both HGF and LGF systems, the surrounding host sediment plays an important role in the nature of the hydrate accumulation (Tréhu et al. 2006b). The two end-member sediment types are fine-grained clays and coarse-grained sands. Compared with sands, clay sediments have much lower porosity and permeability, especially after hydrate formation. The vast majority of naturally occurring hydrate either fills pore space or exists in thin fractures, resulting in a low average fillings (on the order of 1 vol%). Recent X-ray CT results on pressurized cores from Ocean Drilling Project (ODP) Leg 204 show that, in a clay-dominated system, the bulk of hydrate present forms primarily in fractures and veins at high dip angles, whereas massive hydrate sections intercalated with sediment are limited to shallow depths (Abegg et al. 2007).

With the exception of these shallow accumulations in clays, highly concentrated hydrate accumulations have been found only in coarse-grained sediments (Riedel et al. 2006) owing to the higher porosity and permeability in sands compared with in clays (Yin et al. 2002). Laboratory experiments agree very well with field observations. Over a period of one month, hydrate saturations in a sand sample were between 79–100% of the available pore space, whereas this value was only 2–6% in a sandy clay sample (Lu et al. 2004).

Hydrate Formed from High Gas Flux

HGF hydrate accumulations occur when allochthonous gases migrate through fractures into the GHSZ. Compared with the GHOZ shown in **Figure 3** for LGF sites, hydrate exists throughout the entire GHSZ at some HGF sites. HGF sites offer the easiest access to marine hydrates because massive hydrates are often found as shallow accumulations or mounds on the sea floor.

The source of gas can be biogenic and/or thermogenic. In cold vent sites such as Hydrate Ridge off the coast of Oregon (site of ODP Leg 204), the gas is primarily methane, either from mainly biogenic or mixed sources (Milkov 2005). Along with small amounts of other gases such as ethane and CO₂, H₂S has also been measured at these HGF sites. Unlike LGF systems, where AOM reduces the methane concentration below solubility (Kvenvolden 1995, Paull et al. 2000), hydrate near gas venting is prevalent. Sulfate reduction leads to the coexistence of H₂S with CH₄ near the sea floor in sufficient concentrations to form a mixed hydrate. Near-sea floor hydrates from both ODP Leg 204 and Integrated Ocean Drilling Project (IODP) Leg 311 on the Cascadia Margin off the coast of Vancouver Island, Canada, have been shown to contain small amounts (on the order of 1%) of H₂S (Hester et al. 2007b, 2008; Milkov 2005).

One of the most well-studied HGF sites and the focus of ODP Leg 204 is at the summit of Southern Hydrate Ridge, offshore Oregon (Suess et al. 2001, Tréhu et al. 2006a). As with other cold vent sites, episodic venting is observed with transport of gas to the sea floor through complex temporal variable pathways. Researchers have observed variations in the number, location, and venting rate of cold seep vents at Southern Hydrate Ridge over periods as short as hours (Brewer et al. 2002, Hester et al. 2007b, Tryon et al. 1999). Near active venting locations, disturbing the sea floor sediment caused the release of free gas and gas hydrate. However, probing where the gas flow has stopped, equilibration with the bottom water led to hydrate dissolution and the absence of these shallow hydrate accumulations.

Gas bubbles in the gas hydrate stability zone. One feature of HGF sites is the presence of free gas in the GHSZ. This is quite different from the LGF systems where free gas exists only below the

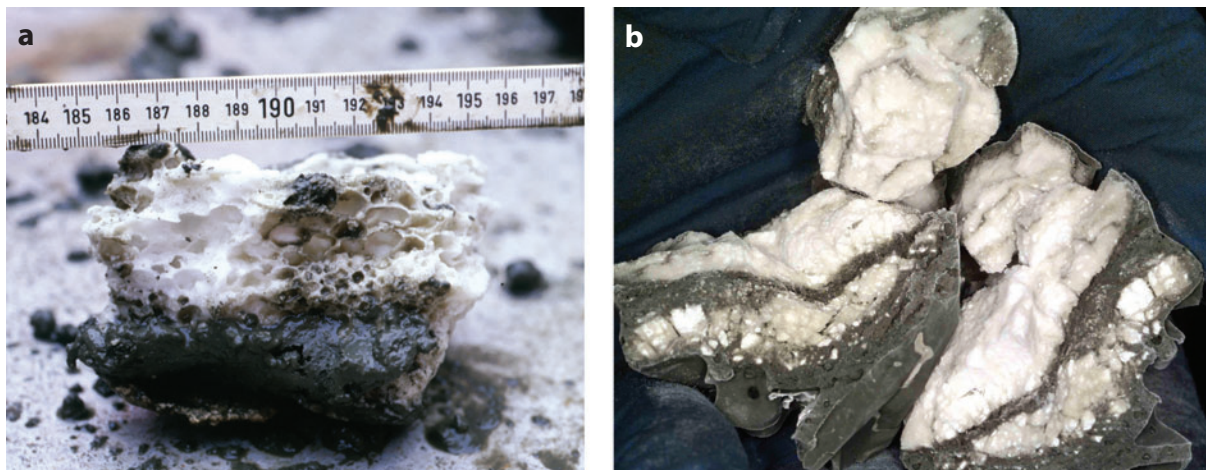


Figure 4

Near-sea floor hydrates recovered from southern Hydrate Ridge with (a) a bubble-type fabric and (b) a massive-type fabric (Reprinted with permission from Torres et al. 2004).

base of the GHSZ. Much of the evidence for this is taken from multiple expeditions to southern Hydrate Ridge. The coexistence of free gas presents a conundrum because a two-phase stability region is expected on the basis of ambient conditions. The GHSZ for Hydrate Ridge is predicted to be in a gas-limited water-hydrate (L_W -H) equilibrium or in water-limited hydrate-vapor (H-V) equilibrium depending on the relative phase amounts present. The sea floor sediments are highly porous, leading to an assumed sufficient supply of water and a gas-limited situation. However, along with the sea floor venting, seismic surveys attributed wipeout zones, or zones with no organized reflection horizons, similar to gas chimneys, to free gas directed up through the GHSZ (Rehder et al. 2002, Wood et al. 2002). A mass balance on a pressure-cored sample collected at ODP Leg 204 site 1249 led researchers to conclude that free gas must have been present along with dissolved methane and gas hydrate (Milkov et al. 2004). As shown from television-guided grabs, near-sea floor hydrate fabrics varied from a massive type to a bubble fabric shown in **Figure 4** (Bohrmann et al. 2002, Suess et al. 2001, Torres et al. 2004). Researchers hypothesized that the bubble fabric forms when hydrate-coated gas bubbles collect during ascent through the sediment. Pure methane hydrate is much stronger than ice (Durham et al. 2003); however, a bubble fabric likely has a very different geomechanical response. Although the presence of free gas has a solid foundation, the reason for it is still debatable.

Two possibilities exist if the thermodynamic predictions are accurate: (a) The system is not in equilibrium because of kinetic and/or transport limitations (Haeckel et al. 2004, Torres et al. 2004) or (b) the ambient conditions are not being described correctly, including advection of warm fluid (Wood et al. 2002) and pore water hypersalinity (Liu & Flemings 2006, 2007; Milkov et al. 2004).

In understanding free gas in the GHSZ, a key question is whether thermodynamic equilibrium is reached. Models (with essential ground truthing to field data) can give valuable insight into the hydrate formation mechanism and the coexistence of gas in the GHSZ. Salinity profiles from ODP 204 Site 1249 and 1250 show Cl^- enrichments near the sea floor of more than 1200 mM (Tréhu et al. 2006a). Various models have led researchers to conclude that nonequilibrium formation from gas bubbles, versus only dissolved methane, was required to obtain the measured enrichment (Haeckel et al. 2004, Torres et al. 2004). Both the Haeckel et al. (2004) and Torres et al. (2004) models used some form of a fitted hydrate formation kinetic constant. Haeckel et al. (2004)

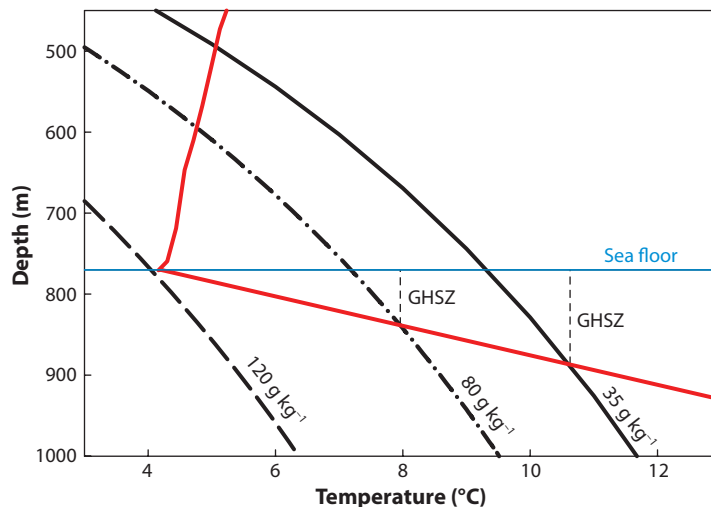


Figure 5

Hydrate phase boundary at southern Hydrate Ridge as a function of salinity. The red line is a representative temperature profile for southern Hydrate Ridge. The gas hydrate stability zone (GHSZ) (*dashed line*) extends from the sea floor (*blue line*) to the intersection with the red temperature line for each line of constant salinity. Changing the salinity from 35 to 120 g kg⁻¹ completely shifts the hydrate stability field, eliminating the GHSZ.

determined that 30 to 40 cm of hydrate would have accumulated over 4 to 10 weeks, requiring a free gas source. Torres et al. (2004) adjusted the fitted rate constant as a function of depth to match field data. This group argued that this variable rate constant was justified on the basis of changes in geomechanical forces. In both of these models, the bubble fabric is referenced, showing transport-limited free gas in the GHSZ. However, because those samples were recovered without pressure compensation, the question remains whether this is a true in situ texture or a product of recovery. Indeed, synthetic ocean experiments have shown hydrate formation on bubbles (Brewer et al. 1997, Hester et al. 2007a). Bubbling methane into clay sediment similar to that found at Hydrate Ridge showed that fractures formed and methane hydrate appeared to coat the channels (Brewer et al. 1997). Coating of the gas channels and the gas bubbles would provide a transport limitation to allow free gas in the GHSZ. In situ Raman measurements on the sea floor at Hydrate Ridge detected a free gas phase in what appeared to be solid hydrate, consistent with a thin hydrate film coating a gas bubble (Hester et al. 2007b). X-ray CT analysis of pressure cored samples also revealed bubbles present in shallow hydrates but researchers attributed this finding to an artifact of recovery (Abegg et al. 2007).

As suggested by Milkov (2004), Liu & Flemings (2006) proposed that hydrate formation from dissolved gas continues until a hypersaline pore water condition is achieved. Small changes in salinity can shift the local three-phase equilibrium curve and allow free gas to coexist with water and hydrate. As shown in **Figure 5**, on the basis of conditions at southern Hydrate Ridge, increasing salinity has a significant effect on the GHSZ. The hydrate phase boundary shifts to completely eliminate the GHSZ at a salinity above approximately 120 g kg⁻¹. Liu and Flemings' (LF) equilibrium model showed salt buildup was limiting, allowing free gas to be present at the three-phase boundary throughout the sediment. This model eliminated a fitted constant and was successfully matched to field data. The equilibrium model was later extended to include heat and mass transfer in two dimensions (Liu & Flemings 2007) and showed that in fine clay sediments, the formation of hydrate significantly reduces permeability, causing pressure to build, opening

fractures. These fracture pathways build up with salt, which causes much of the free gas to bypass the reservoir and be rapidly expelled into the ocean (Liu & Flemings 2007).

Thermogenic high gas flux sites. Thermogenic hydrates primarily contain enhanced quantities of hydrocarbons. Thermogenic gas, strongly enriched in ^{13}C , travels through fractures from a deep petroleum reservoir to feed thermogenic HGF systems. Thermogenic hydrates have been found in several places worldwide, including the Gulf of Mexico, the Caspian Sea, the Black Sea, and the Sea of Japan (Diaconescu et al. 2001, Matsumoto et al. 2005, Sassen & MacDonald 1994, Woodside et al. 2003). The relatively few known locations could be due to our current detection ability of these accumulations and difficulties in predicting where they will occur. As an example, hydrates at Barkley Canyon were discovered only when a fishing trawler pulled up tons of hydrate on deck (Spence et al. 2001).

These accumulations focus an upward flow of fluids, often leading to gas venting and hydrate exposure on the sea floor. Hydrate mounds on the sea floor, stained with oil, have been observed in the Gulf of Mexico and Barkley Canyon. In the Gulf of Mexico, the geology shows that petroleum seepage is common; vent sites are found at the rims of salt minibasins (Sassen et al. 2001). In Barkley Canyon, the only known thermogenic hydrate site on a convergent margin, the current proposed mechanism is vertical migration of fluids deep within the basin. These fluids continue to concentrate in Barkley Canyon and support the sea floor hydrates (Pohlman et al. 2005).

These hydrate mounds can extend several meters above the sea floor, partially veiled in a thin sediment cover, such as at Barkley Canyon (**Figure 6**). Although bacterial mat and vesicomid

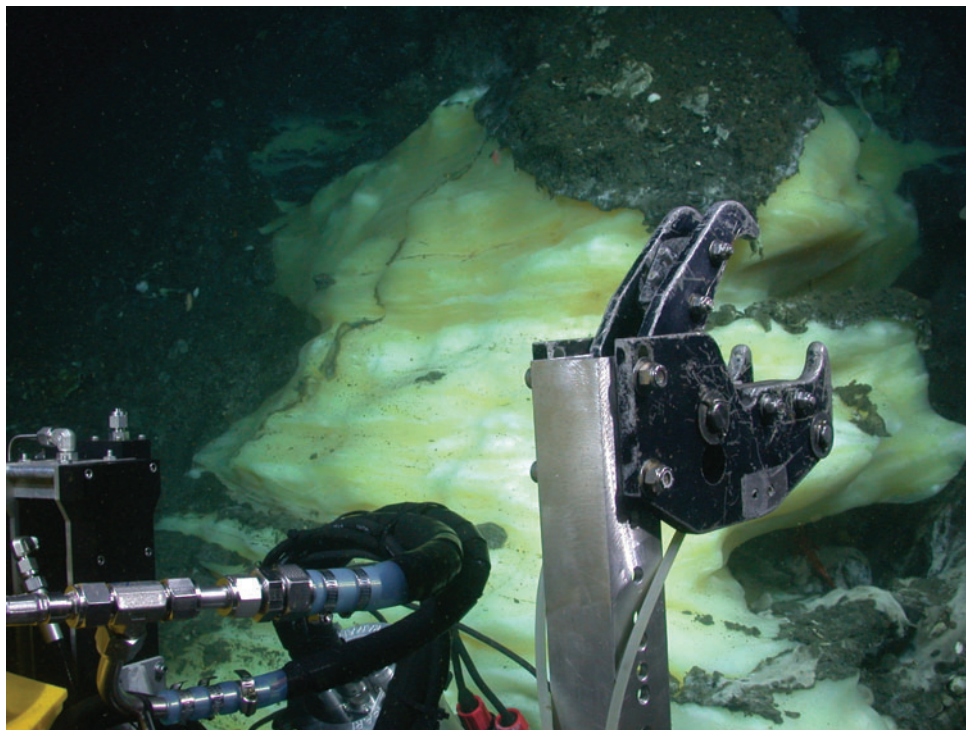


Figure 6

Hydrate mound at Barkley Canyon at a water depth of approximately 850 m. Thinly veiled sediment and bacterial mat cover part of the mound and oil-stained hydrate is exposed to the ambient seawater.

clams were present, no tube worms were found as in the Gulf of Mexico (Chapman et al. 2004, Sassen et al. 1999). These exposed hydrates are dynamic systems that respond to changes in the benthic environment. Changes in currents, temperature, and venting rates are expected to affect the stability of these mounds. Some of these mounds are surprisingly stable. A long-term time-lapse monitoring (July 2001 to July 2002) of a hydrate mound at Bush Hill Site GC-185 in the Gulf of Mexico showed no major change in the shape or size of the mound (Vardaro et al. 2006).

Thermogenic hydrate accumulations can be highly heterogeneous and vary in composition and structure in the subcentimeter length scale. This heterogeneity occurs in gas-limited systems as the heavier hydrocarbons are selectively concentrated in the hydrate phase (Hester et al. 2007a, Uchida et al. 2004). Although this phenomenon increases the challenge of characterizing these accumulations, unlike pure methane systems, gas fractionation provides insights into their growth pathways and system dynamics.

Two examples using measured hydrate compositions to infer growth pathways are measured ethane/propane ratios and the presence of isopentane. Using thermodynamic predictions with vent gas compositions, natural hydrates are expected to contain significantly more propane than ethane. However, the relative amounts of ethane and propane reported for natural thermogenic systems are often similar or even enriched in ethane (Milkov 2005). Possible reasons for this observation include changes in vent gas composition over time (Chen & Cathles 2003) or small inclusions of gas bubbles during formation (Hester et al. 2007a). Occluded gas trapped during formation will reduce the observed ethane/propane fractionation.

Isopentane has been identified as a possible marker for massive sII hydrate crystallization (Sassen et al. 2004, Sassen et al. 2000). Although present in vent gas, isopentane does not fit in the sII lattice. Isopentane is therefore excluded during formation and has been shown to accumulate in the surrounding sediments. Isopentane does form a sH hydrate in the presence of a smaller molecule such as methane; however, this is not predicted to occur unless most of the sII-forming molecules are consumed (Hester et al. 2007a).

In addition to compositional variations, the coexistence of multiple structures in hydrate accumulations has only recently been measured directly and provides more clues about the system dynamics. The coexistence of sI and sII has been observed at Lake Baikal and Barkley Canyon (Hester et al. 2007a, Kida et al. 2006). Bulk measurements at Lake Baikal indicated a mixed biogenic/thermogenic source. Three distinct hydrate layers containing methane and ethane were measured: a pure sI layer, a pure sII layer, and a mixed sI/sII layer. Suggested explanations for this coexistence of structures include fractionation or possible metastability (Kida et al. 2006). In situ Raman measurements of undisturbed hydrates at Barkley Canyon (**Figure 7**) showed small-scale heterogeneity and intermixed sI/sII phases that contain hydrocarbons up to butane (Hester et al. 2007a). On the basis of a previous field experiment, researchers hypothesized that hydrate-coated gas bubbles acted as individual hydrate reactors. As the heavier sII-forming hydrocarbons were exhausted, sI became the stable phase. Also from Barkley Canyon, Lu et al. (2007) and Hester (2007) showed oil-stained yellow hydrate was mainly sII with small amounts of sH. Although sH was long suggested to exist, these were the first direct measurements of sH in a natural hydrate system.

Hydrate Formed from Low Gas Flux

LGF systems form by slow hydrate precipitation from dissolved methane owing to changes in solubility during upward fluid flow. A thorough review of these systems was given by Buffett (2000). These systems are the primary known hydrate accumulations and the basis for hydrate reserve estimates, and are estimated to contain greater than 99% CH₄, mainly from microbial origins. Diagenesis of organic carbon results in methane production, which builds and transports through

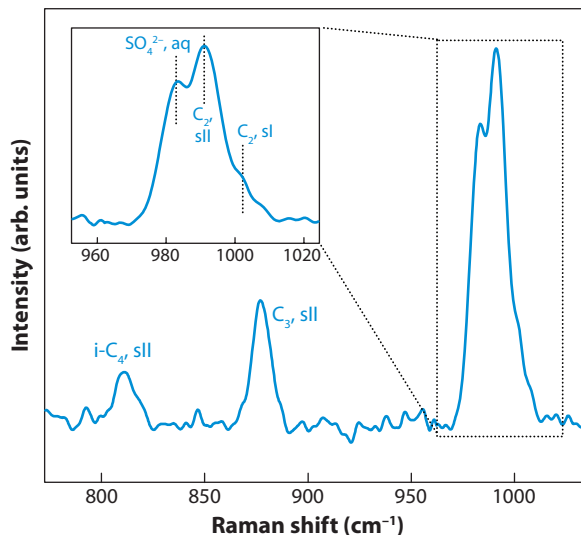
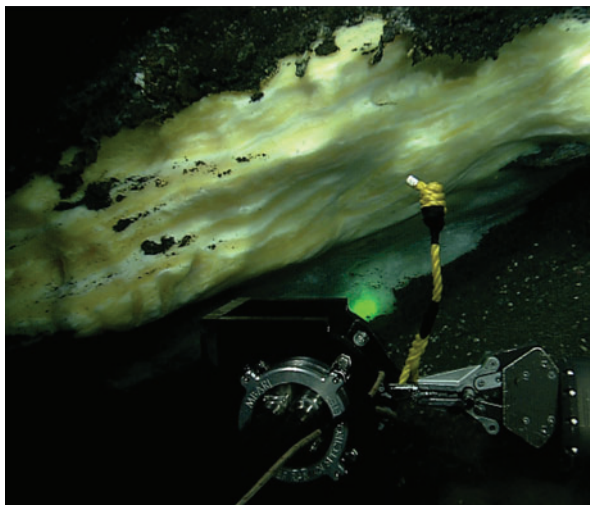


Figure 7

In situ Raman measurement of undisturbed hydrate at Barkley Canyon. The resulting spectrum shows that the hydrate is mainly sII intermixed with a small amount of sI. Adapted with permission from Hester et al. (2007a).

the sediment on the basis of diffusion and upward migration from sedimentation and compaction. When the solubility reaches hydrate equilibrium based on ambient conditions, hydrate precipitation occurs. Extensive modeling of such systems has been performed (e.g., Davie & Buffett 2001, Rempel & Buffett 1997, Xu & Ruppel 1999). Bhatnagar et al. (2007) recently proposed a 1-D unified modeling approach for both HGF and LGF systems. Through the creation and scaling of dimensionless groups, researchers determined steady-state hydrate saturations as well as sensitivity to site-specific conditions (e.g., sea floor temperature and geothermal gradient).

ESTIMATES OF WORLDWIDE HYDRATE DEPOSITS

To date, as shown in **Figure 1**, more than 90 sites have been directly or indirectly identified to contain natural gas hydrates. In-place methane estimates have been made primarily with empirical calculations based on field observations and recently with mechanistic models. A thorough review of empirical hydrate estimates and methodologies is given by Milkov (2004). Over time, estimated reserves have decreased from 530×10^{15} g of carbon (530,000 Gt C) (Trofimuk et al. 1973) to a minimal possible estimate of 0.1×10^{15} g of carbon (100 Gt C) (Soloviev 2002). Widely cited current estimates still range from 500 to 63,400 Gt C. Field and laboratory studies of natural hydrate systems have led directly to these refined estimates. **Table 1** highlights the most recent in-place estimates.

Hydrate resource estimates have focused on stratigraphic-type hydrate deposits (Milkov & Sassen 2002) typical for LGF systems. Modeling structural-type gas hydrate accumulations (Milkov & Sassen 2002) would require much more extensive knowledge of their worldwide distribution and underlying petroleum systems and it is estimated that up to 10^7 of these structural deposits would be needed to have a significant global contribution (Milkov 2004, Milkov et al. 2003).

Of the empirical estimates, arguably the “consensus” value of 10,000 Gt C (Kvenvolden 2002) obtained independently by Kvenvolden (1988) and MacDonald (1990) is still the most widely quoted. These estimates required a total organic carbon (TOC) content of >0.5–1% for hydrate

TOC: total organic carbon

Table 1 Current estimates of carbon contained in worldwide methane accumulations

Source	Estimate (Gt C)	Model type	Approach ¹
Milkov et al. 2004	500–2500	Empirical	Hydrate formation limited to continental margins GHOZ between 10–30% of GHSZ Average hydrate saturations of 2% in the GHOZ
Buffett & Archer 2004	3000	Mechanistic	Constant geothermal gradient (0.04 K m ⁻¹ for passive and 0.06 K m ⁻¹ for active margins) Depth-dependent TOC Carbon burial using sediment diagenesis model Accounted for methane transport from below GHSZ
Klauda & Sandler 2005	63,400	Mechanistic	Thermodynamic model with pore size effects Sea floor T and geothermal gradient with greater than 1° × 1° spatial resolution Current sea floor TOC and average sedimentation rate based on body of water Correctly identified 68 of 71 known hydrate locations

¹Abbreviations: GHOZ, gas hydrate occurrence zone; GHSZ, gas hydrate stability zone; TOC, total organic carbon.

formation. However, Milkov (2004) indicates that the use of TOC from shallow sediments may not be representative of the deeper hydrate-bearing sediments. Because of limited field data, pore saturations were poorly constrained and ranged from 10% to 100% (Kvenvolden 1988, MacDonald 1990). Recent seismic and drilling field data were combined to better constrain the extent and saturations in hydrate deposits. The GHOZ was estimated to be between 10–30% of the GHSZ (Borowski et al. 1999, Dickens 2001), with hydrate formation limited to the continental margins. At Blake Ridge (Dickens et al. 1997) and Hydrate Ridge (Milkov et al. 2003), hydrate saturations were approximately 2% of the GHOZ. By incorporating constraints from direct ocean drilling measurements, Milkov (2004) gave a more conservative assessment of 500–2500 Gt C.

Buffett & Archer (2004) and Klauda & Sandler (2005) have provided estimates via the use of a mechanistic modeling approach. However, as with the empirical volume estimates, these mechanistic estimates differ widely from 3000 (Buffett & Archer 2004) to 63,400 Gt C (Klauda & Sandler 2005). Both the Buffett and Archer (BA) model and the Klauda and Sandler (KS) model use thermodynamics to determine the GHSZ and methanogenesis kinetics/mass transfer to determine the hydrate saturation in the GHOZ, matching hydrate pore saturations from Blake Ridge for validation. In addition, Klauda & Sandler (2005) reported a spatial distribution of hydrate locations and correctly identified 68 of 71 known hydrate locations.

In calculating the worldwide GHSZ, both models predicted the GHSZ assuming constant salinity. The KS model took a more rigorous approach by accounting for pore size effect. Without accounting for pore effects in clay-dominated systems (e.g., Blake Ridge, ODP Site 995), the depth of hydrate stability was overpredicted by 100 m (Klauda & Sandler 2005). On the basis of available ODP hydrate depth data, adding pore effects leads to a reduction in absolute average error from 12% to 5%. However, the addition of the pore effects lowers the total volume of the GHSZ. Therefore, the discrepancy between the KS and BA models is likely based on assumptions for methanogenesis kinetics/mass transfer.

Both the BA and the KS models use a mass transfer model similar to Davie & Buffett (2001), with steady state reached after approximately 1 Ma. The BA approach is more rigorous and includes depth-dependent regressions for TOC accumulation, carbon burial with a sediment diagenesis model, and transport of methane gas from deeper sediments. The KS model used an average sedimentation rate based on the body of water, which Archer (2007) points out is high by an order

of magnitude. This accounts for predicted hydrate accumulations in abyssal sediments by the KS model. However, even considering only the continental margins, the KS model still estimates that more than 23,000 Gt C is trapped in hydrates.

ENERGY PRODUCTION FROM HYDRATE DEPOSITS

The amount of methane trapped in natural hydrates is comparable with a conservative worldwide fossil fuel estimate of 5000 Gt C (Kvenvolden 2002). However, although the overall estimate of hydrated methane is possibly as high as twelve times that of conventional fossil fuels, a distinction is needed between in-place, technically recoverable, and economically producible resources when considering energy production from hydrates. A thorough review of the economic geology of gas hydrates as an energy resource can be found in Max et al. (2006).

The need for energy has created a strong international interest in the exploitation of natural hydrates, including national hydrate programs in Canada, China, India, Japan, Taiwan, and the United States. Technical feasibility and economics will determine future production of gas from hydrate deposits that, to this point, has only been shown in the permafrost. Whereas the hydrate contribution at the Messoyakha field is still disputed (Collett & Ginsburg 1998, Makogon et al. 2005), the 2002 Mallik program, an international consortium of countries and energy companies, showed definitively that production from hydrates is technically feasible. A five-day production test (Figure 8) combined depressurization with thermal stimulation on a 17-m-thick section of highly concentrated hydrate. A test well at the Mallik 2L-38 site was established in April 2007 in



Figure 8

The Mallik 5L-38 well supported a flare during a five-day production test from March 5–11, 2002 (Photograph courtesy of T. Collett).

Table 2 Classification system for the production of hydrate reservoirs

Deposit type	Zones present	Mobile phases	Confining strata
Class 1	Two zones: hydrate-bearing layer (HBL) above two-phase zone	Free gas, water	Yes
Class 2	Two zones: HBL above one-phase zone	Water	Yes
Class 3	One zone: HBL	None	Yes
Class 4	One zone: HBL	None	No

preparation for longer production tests planned in the near future (Yamamoto et al. 2007). The recent Indian Natural Gas Hydrate Project (NGHP) Expedition 01 discovered one of the world's richest known gas hydrate deposits (Collett & Scientific Party 2007). Production testing on marine deposits is planned for as early as 2009 by the Indian NGHP, and the Japanese National Program set 2017 for commercial production from hydrate deposits in the Nankai Trough (Koh & Sloan 2007).

To evaluate energy production capability from clathrate hydrates, a classification system detailed in **Table 2** has been developed to better characterize the deposit type and includes rankings according to desired production scenarios (Moridis & Collett 2003, Moridis & Sloan 2006). Many of the permafrost hydrate accumulations, including the Mallik well, are Class 1–type wells that offer the best chance at success. However, the permafrost contains an estimated two orders of magnitude less gas than oceanic reserves (Kvenvolden 1988). Significant challenges exist when moving into the marine environment. Oceanic reserves are commonly classified as Class 4 deposits. Recent numerical simulation of production has suggested that excess water production would make Class 4 deposits unfeasible (Moridis & Sloan 2006). Therefore, much of the estimated in-place methane would not currently be considered viable as a resource.

Production of marine hydrates also requires that sea floor stability questions be addressed. Geomechanics studies are needed to assess how hydrate-bearing sediments will react to external disturbances both man-made (e.g., pipelines, production) and from nature (e.g., earthquakes). Using general principles of marine slope stability and fracture, Kleinberg (2005) showed that the presence and decomposition of hydrates in shallow marine sediments had the potential for fracturing and slope instability. Recent work has incorporated a geomechanical component in numerical simulations of hydrate reservoirs (Freij-Ayoub et al. 2007, Rutqvist & Moridis 2007). Simulations show that warming due to pipelines and production can affect the cohesion and stability of hydrate-bearing sediment, especially for unconsolidated sediments that are typical near the sea floor.

One idea under exploration in a number of laboratories is replacement of CH₄ in natural hydrates with CO₂ to combine energy recovery with CO₂ sequestration (Lee et al. 2003, Ohgaki et al. 1996, Ota et al. 2005). The approach is also advantageous in that hydrate is left in place, which reduces the risk of geomechanical failure. Thermodynamically, if the methane-saturated fluid bathing the hydrate is replaced with CO₂, a driving force exists for CO₂ to enter the hydrate phase and for methane to be released. In a closed system, the extent of this exchange is based on the relative stability of methane versus CO₂ in the hydrate phase and replacement continues until equilibrium is achieved. When considering liquid CO₂, pure CO₂ hydrate can actually be less stable than pure CH₄ hydrate. However, owing to undersaturation of the phase, exchange will still occur, but to a lesser extent than when CO₂ exists as a vapor.

Although CH₄-CO₂ exchange is thermodynamically favorable, the extent of CH₄-CO₂ exchange and transport limitations must be addressed to determine feasibility. Unless the CO₂ fluid is circulated, a certain amount of CH₄ will remain in the hydrate phase, reducing recovery. Lee et al. (2003) showed that more than 64% of the CH₄ could be recovered through exchange with

gaseous CO₂. This amount will be reduced in the case of liquid CO₂, with recovery of less than 40% of the hydrated CH₄. Transport limitations also exist with slow exchange rates even in stirred systems, with reaction times of more than 50 hours to release 20% of the CH₄ (Ota et al. 2005). Recent work has begun to address more realistic transport limitations and exchange rates using hydrate formed in porous media (Graue et al. 2006, Stevens et al. 2007, Zhou et al. 2008). Magnetic resonance imaging showed direct replacement of methane with carbon dioxide without a measured free water/gas transition, which could be important for sediment stability and the commercial viability of this technology (Graue et al. 2006, Stevens et al. 2007).

HYDRATES AND CLIMATE CHANGE

The possible connections between climate and hydrates have long been of interest to geoscientists and the debate is far from resolved today. Revelle (1983) reviewed the earliest estimates of hydrate abundance and the possibility of release of large quantities of methane from the sea floor to the atmosphere as a result of fossil fuel CO₂-induced global warming. In the quarter century since then there has been an extraordinary effort to examine this problem, often with sharply contradictory findings. The arguments include both the possibility of large-scale methane releases from climate change today (Gornitz & Fung 1994, Harvey & Huang 1995) and the geologic evidence, primarily from the carbon isotopic record of deep-sea cores, for methane releases in the past (Dickens et al. 1995, Katz et al. 1999). The mechanisms invoked for destabilizing hydrates include deep-water warming (Hesselbo et al. 2000, Norris & Rohl 1999) and mass wasting on continental slopes (Vogt & Jung 2002), but the manner in which hydrates may be destabilized, and the rate and pathways by which methane gas released from hydrates on the sea floor may be transferred to the atmosphere, are still matters of debate.

There is little or no doubt that large-scale rapid changes in Earth's methane budget in association with climate change have occurred; both the record of gases trapped in polar ice (Brook et al. 1996) and the isotopic record of deep-sea cores (Kennett et al. 2000) confirm this. But controversy has arisen over the projected source of the methane. The case for repeated loading of shallow marine sediments with large quantities of methane hydrates, which are then destabilized by climate change and release CH₄ to the atmosphere, was made in detail by Kennett et al. (2003) as "the clathrate gun hypothesis."

The arguments made in support of this hypothesis were many; for example in addition to the correlations with warming events, Kennett et al. (2003) noted that ice ages are dry periods, thus reducing the well-known land source of methane from wetlands, and thus providing additional proof for an oceanic hydrate source. But not all were convinced, and careful analyses of the timing of millennial scale climate change as recorded in ice cores (Blunier & Brook 2001, Brook et al. 1999, Severinghaus & Brook 1999, Severinghaus et al. 1998) strongly suggested an alternate source of methane. For example, careful establishment of a gas-age time scale showed that the temperature signal lead the appearance of the methane signal, thus casting doubt on a causal role for methane in the climatic warming (Severinghaus et al. 1998). The methane signals appeared only after the climate began to get warmer and wetter, thus supporting a tropical wetlands source for the methane (Severinghaus & Brook 1999). Brook et al. (1999) reported that the "hypothesis that large releases of methane from clathrates in marine sediments or permafrost" did not appear to be consistent with their ice-core data. These arguments favored a land-based wetlands source.

The details of how methane may be released from sea floor hydrates also require careful consideration. Revelle (1983) tacitly assumed in their original paper that slow warming of deep-ocean waters would liberate methane gas bubbles that would be quickly transferred to the atmosphere. This is not so; thus, this assumption led to several strong critiques.

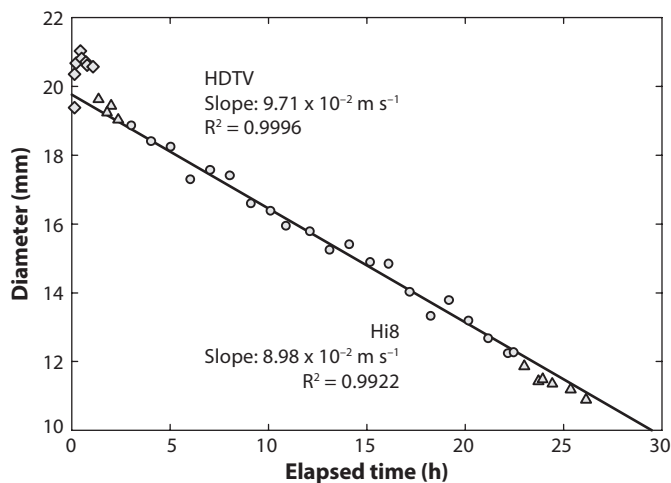
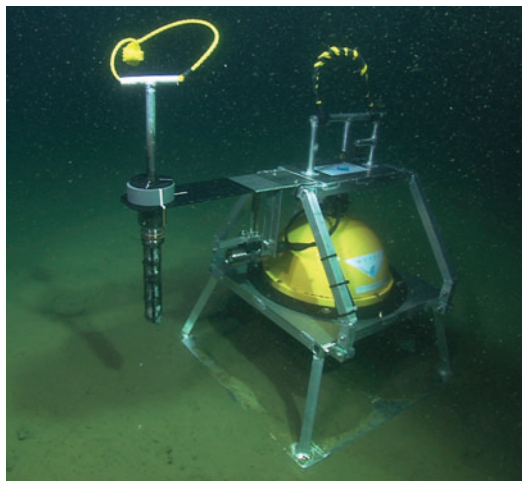


Figure 9

Experimental time-lapse camera system on the sea floor used to observe the change in size with time of two blocks of methane hydrate exposed to undersaturated sea water at a depth of 1028 m. The dissolution rate observed is $0.37 \pm 0.03 \text{ mmol CH}_4 \text{ m}^{-2} \text{ s}^{-1}$. Adapted with permission from Rehder et al. (2004).

It is interesting that accurate knowledge of the fate of methane (and other) hydrates exposed on the sea floor took so long to arrive. As recently as 1997 a report of the President's Council of Advisors on Science and Technology (PCAST 1997) recommended consideration of storage of fossil fuel CO_2 as a solid hydrate on the sea floor, under the assumption that because it would be within the required pressure and temperature field it would remain stable—thereby neglecting the requirement that the solid hydrate be in contact with an aqueous solution saturated with the hydrate molecular guest species. The experimental test of this proposal was undertaken by Rehder et al. (2004), who exposed carefully synthesized blocks of both methane and CO_2 hydrate to background sea water at a depth of 1000 m and recorded the dissolution rate with a time-lapse camera. The results (**Figure 9**) showed very clearly that rapid dissolution occurs, and that the rate may be simply described by a saturated boundary layer model.

Thus, hydrates exposed to gradually rising temperatures on the sea floor will simply dissolve without bubble formation, and the dissolved CH_4 will be oxidized by marine bacteria on a short timescale compared with ocean mixing (Rehder et al. 1999, Scranton & Brewer 1978). The question also arose as to whether methane bubbles, released from gassy and supersaturated marine sediments at depth, would be protected by a skin of hydrate long enough to survive dissolution during their upward transit through the water column, thereby providing a route to atmospheric enrichment. This concept was tested experimentally by the ingenious means of direct imaging of the changing diameter of an ascending methane bubble within the hydrate stability zone, and comparing this measurement to that of a non-hydrate-forming gas of similar diffusivity (Rehder et al. 2002). The results showed that although the formation of a hydrate skin did enhance bubble lifetime, the effect was not sufficient to lead to significant atmospheric release. Acoustic observations of large-scale natural bubble plumes and numerical modeling of the data lead to the same conclusion (McGinnis et al. 2006). It is therefore difficult to make the case that gaseous methane plumes rising from the sea floor can easily escape to the atmosphere.

This puzzle can be resolved if solid hydrate is broken loose. Brewer et al. (2002) experimentally tested this idea by observing the transit of natural hydrate pieces liberated from the sea floor, and

Paull et al. (2003) proposed that slumping of the sea floor with release of solid hydrates could indeed be a route to transfer of hydrate methane to the atmosphere.

Finally, O'Hara (2008) showed in a recent kinematic model of Quaternary ice core methane data that the ice core data could indeed be consistent with a shallow sea floor methane hydrate source, thus putting back into play the Quaternary hydrate–climate connection that had earlier been rebutted, as discussed above.

The outcome of this extended debate remains unclear. Methane hydrates were very likely associated with the large-scale climatic events of millions of years ago (e.g., the Paleocene–Eocene transition). It is quite possible, but still under debate, that a shallow marine source such as a hydrate reservoir played a role in the gaseous signals associated with the recent ice ages. But given the knowledge of the size and distribution of present-day hydrate accumulations, it appears unlikely that marine hydrates will be a major source of methane to the atmosphere from contemporary greenhouse gas warming. Methane releases associated with warming of Arctic land masses fall within a different category.

EXOTIC HYDRATES IN NATURE

Hydrates From CO₂ Sources

Although the vast majority of hydrates found in nature are methane dominated, the hydrate formation process is so fundamental that wherever the right combination of guest molecules occurs a hydrate can form. Although there has long been speculation of CO₂-dominated hydrates naturally occurring from sea floor volcanic emissions it was not until 1988 that such a site was located in the Okinawa trough at a depth of 1300–150 m and 3.8°C. Submersible investigations in 1989 by a Japanese team (Sakai et al. 1990) revealed hot (320°C) black-smoker vents, and they saw unusual bubbles emerging nearby. The team collected this material and on analysis found it to be a 86% CO₂-3% H₂S-11% (CH₄ + H₂) gas mixture. The CO₂-rich gas, upon venting into surficial sediments bathed in 3.8°C water, was condensing into the liquid state and forming a hydrate skin. This phase change gave rise to the formation of pipe-like stalks standing on the sediment surface.

Since that first discovery researchers have found a number of other oceanic CO₂ vents within the hydrate-forming regime. The NW Eifuku volcano site, discovered in 2004 in the Mariana Arc (Lupton et al. 2006) at 1600-m depth, revealed a whitish crust at the sediment surface that cracked when perturbed, releasing copious quantities of buoyant liquid CO₂ that formed a hydrate skin and adhered in large masses to the frame of the vehicle. The ability of CO₂ in the supercritical form (in which it must exist at depth) to sweep out nonpolar species is well known, and thus other gases at depth will become enriched in the CO₂ phase and then become dissolved as the liquid state forms. Thus, it is quite possible that very complex fluids and their hydrates can be created by this process.

These CO₂-rich hydrate exposures on the sea floor can exist only if they are continually fed by the source fluids. The thermodynamic requirement for formation of a saturated boundary layer (Rehder et al. 2004) and the high solubility of CO₂ in sea water (an order of magnitude more soluble than methane) means that exposed CO₂ hydrates will dissolve quickly into the undersaturated surrounding sea water.

Although CO₂ is highly soluble, liquid CO₂ as a phase is highly immiscible with water. The combination of immiscibility of phases, production of a dense saturated boundary layer, and hydrate formation with salt rejection can produce complex fluid dynamical interactions. One spectacular example of this was reported by Brewer et al. (1999) (**Figure 10**); a beaker of liquid CO₂ placed on the sea floor at 3,600-m depth showed a self-generated fluid dynamic instability: Dense hydrate and brine sank to the bottom of the beaker and expelled unreacted liquid CO₂



Figure 10

A sea floor experiment with liquid CO_2 at 3600-m depth showing hydrate formation as a crystalline slush at the bottom of the beaker and expulsion of unreacted liquid CO_2 over the lip owing to the volume expansion. The exposed liquid CO_2 surface quickly acquires a hydrate skin, and the expelled fluid thus encapsulated rolls around as a discrete blob on the sea floor. Here it is examined with curiosity by a Pacific grenadier fish (Reprinted with permission from Brewer et al. 1999).

over the lip in a series of spill-over events as the reaction proceeded. This experiment illustrates the complexity that can arise in such multiphase systems, and hints at the difficulty of describing within-sediment processes.

Hydrates Rich in Hydrogen Sulfide

Hydrogen sulfide (H_2S) forms a hydrate with great ease and is abundant in marine sediment pore waters. But the extraordinarily high solubility of H_2S makes it unlikely that any large mass of H_2S hydrate would occur in nature. Moreover, the co-occurrence of H_2S with CH_4 makes the formation of mixed CH_4 - H_2S hydrates likely and these have been found at northern Hydrate Ridge and off Southern Australia (Kastner et al. 1998, Swart et al. 2000). One intriguing prospect is hinted at by the observation of spectacular sea floor eruptions of sulfide-rich gas of such a scale that the discoloration of the sea surface is detectable from space (Weeks et al. 2004). The combination of CH_4 and H_2S reported is easily calculated to form a H_2S -rich hydrate with great ease in the marine sediments of this region at shallow depths, but so far no such finding has been reported.

SUMMARY POINTS

1. The development of in situ measurement tools and technologies to recover hydrates with minimal disturbance has led to significant advances in our understanding of natural hydrate systems.
2. Free gas can coexist in the gas hydrate stability zone (GHSZ) when gas flux is sufficiently high. Increased pore water salinity, causing the hydrate stability curve to shift, is the most likely reason for these occurrences.

- 3 Both empirical and mechanistic models predict that vast amounts of carbon are stored in natural clathrate hydrates. Field measurements have greatly improved our understanding of the spatial distributions and pore concentrations in natural hydrate accumulations.
4. The possibility of energy production from hydrates is highly dependent on the particular reservoir characteristics. Many of the known marine deposits are likely unfeasible for hydrate production.
5. Clathrate hydrates likely contributed to past climate change events millions of years ago. However, contributions in more modern times, such as in recent ice ages, are still quite debatable. Current hydrate accumulations are unlikely to be a major source in the atmospheric carbon cycle.

FUTURE ISSUES

1. A better tool is needed to assess both the presence of natural hydrate accumulations and in situ hydrate concentrations.
2. Beyond the in-place estimates of methane in natural accumulations, the technical recoverability and economics will drive the future possibility of energy production from hydrates. A rigorous economic evaluation comparing hydrate deposits with other known reserves is needed to assess the future potential for energy from clathrate hydrates.
3. More geomechanical studies are needed to understand how hydrate accumulations respond to natural and man-made disturbances. This information will help to assess the role of hydrates in climate change events and as a geohazard.

DISCLOSURE STATEMENT

The authors are not aware of any biases that might be perceived as affecting the objectivity of this review.

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