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## Gas Hydrates: Greenhouse Nightmare? Energy Panacea or Pipe Dream?

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### ABSTRACT

Recent interest in methane hydrates has resulted from the recognition that they may play important roles in the global carbon cycle and rapid climate change through emissions of methane from marine sediments and permafrost into the atmosphere, and in causing mass failure of sediments and structural changes on the continental slope. Their presumed large volumes are also considered to be a potential source for future exploitation of methane as a resource.

Natural gas hydrates occur widely on continental slope and rise, stabilized in place by high hydrostatic pressure and frigid bottom-temperature conditions. Change in these conditions, either through lowering of sea level or increase in bottom-water temperature, may trigger the following sequence of events: dissociation of the hydrate at its base, weakening of sediment strength, major slumping, and release of significant quantities of methane in the atmosphere to affect enhanced greenhouse warming. Thus, gas-hydrate breakdown has been invoked to explain the abrupt nature of glacial terminations, pronounced  $^{12}\text{C}$  enrichments of the global carbon reservoir such as that during the latest Paleocene thermal maximum, and the presence of major slides and slumps in the stratigraphic record associated with periods of sea-level lowstands. The role of gas hydrates in controlling climate change and slope stability cannot be assessed accurately without a better understanding of the hydrate reservoir and meaningful estimates of the amount of methane it contains. Lack of knowledge also hampers the evaluation of the resource potential of gas hydrates, underscoring the need for a concerted research effort on this issue of significant scientific importance and societal relevance.

### INTRODUCTION

Recently, politicians have joined scientists and engineers in their interest in gas hydrates. The 105th Congress of the

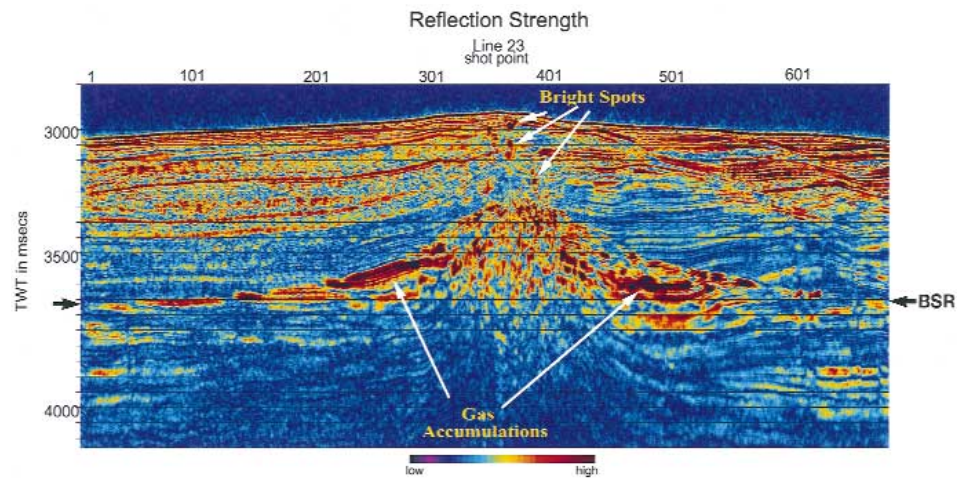


Figure 1. This seismic profile, over the landward side of Blake Ridge, crosses a salt diapir; the profile has been processed to show reflection strength. The prominent bottom-simulating reflector (BSR) swings upward over the diapir because of the higher conductivity of the salt. Note the very strong reflections of gas accumulations below the gas-hydrate stability zone and the "blanking" of energy above it. Bright Spots along near-vertical faults above the diapir represent conduits for gas venting. (After Taylor et al., 1997. Courtesy of W. P. Dillon, USGS.)

United States is on the verge of enacting a bill to promote gas-hydrate research under the aegis of the Department of Energy. Scientists view gas hydrates (also known as clathrates) as potential *agents provocateurs* for global climate change and continental margin tectonics. Politicians' interest is predicated on the premise that gas hydrates may represent a huge untapped source of energy for their constituents.

Natural gas hydrates (crystalline solids composed mostly of methane and water) are present in marine sediments on the continental slope and rise (Fig. 1) under the dual conditions of high hydrostatic pressure (>50 bar) and low ambient temperature at the sediment-water interface (<7 °C). They also occur associated with permafrost and at shallower submarine depths in the high latitudes of the Arctic. The hydrate consists of a lattice of water molecules enclosing gas molecules (usually methane, but also higher-order hydrocarbons), and at least three structures have been identified (e.g., Sloan, 1998). Methane in hydrates is commonly of biogenic origin, but thermogenic

methane also occurs in hydrates, vented to shallower depths through subsurface conduits (e.g., MacDonald et al., 1994). Estimates of total hydrate volumes vary widely, but even the relatively conservative estimate of Kvenvolden (1988),  $10^4$  Gt (gigaton) of methane carbon (1 Gt =  $10^{15}$  g), exceeds estimates of organic carbon from all other sources, with the exception of dispersed carbon in the lithosphere, and is approximately double the estimate of carbon from known fossil-fuel sources (Kvenvolden, 1988). Whether or not these estimates of large amounts can be translated into a viable energy source is a crucial question that has been the focus of researchers in many countries. The petroleum industry to date has largely ignored methane hydrates because of the difficulties in estimating and extracting the resource and distributing it to consumers.

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### Gas Hydrates *continued from p. 1*

#### DISTRIBUTION AND ESTIMATES OF GAS HYDRATES

The requirements for the stability of gas hydrate (low bottom water and thus low sediment temperature, as well as high pressure [Fig. 2]; see also, Ruppel, 1997) are theoretically met over a high percentage of the seafloor of the continental slope and rise where water depth exceeds 530 m in the low latitudes and 250 m in high latitudes. Rapidly deposited sediments with high biogenic content are well suited for the genesis of large quantities of methane by bacterial alteration of the buried organic matter. Relatively high gas content in pore waters (i.e., amount of methane dissolved in pore waters is in excess of local solubility of methane) is considered to be a prerequisite for the formation of hydrate (Kvenvolden and Barnard, 1983; Zatsepina and Buffett, 1997).

Gas hydrates in marine sediments have been detected since the 1970s (e.g., Markl et al., 1970; Shipley et al., 1979) by the presence of the so-called bottom simulating reflectors (BSRs). BSRs usually delineate the top of the free-gas zone that may occur at or below the base of the gas-hydrate stability zone (GHSZ) (Fig. 1). A significant quantity of free gas must be present below the hydrate to provide the velocity contrast for a BSR, as revealed by Ocean Drilling Program (ODP) drilling on the Blake Plateau, off the southeast coast of the United States. There, hydrate also exists with no discernible BSRs at its base when a significant amount of free gas is lacking below the base of the GHSZ (Paull et al., 1996b).

BSRs have been observed on many continental margins of the world (e.g., Kvenvolden, 1993), but hydrates have been sampled only rarely. In spite of the new data from recent ODP drilling in hydrate fields (e.g., Legs 141, 146, 164),

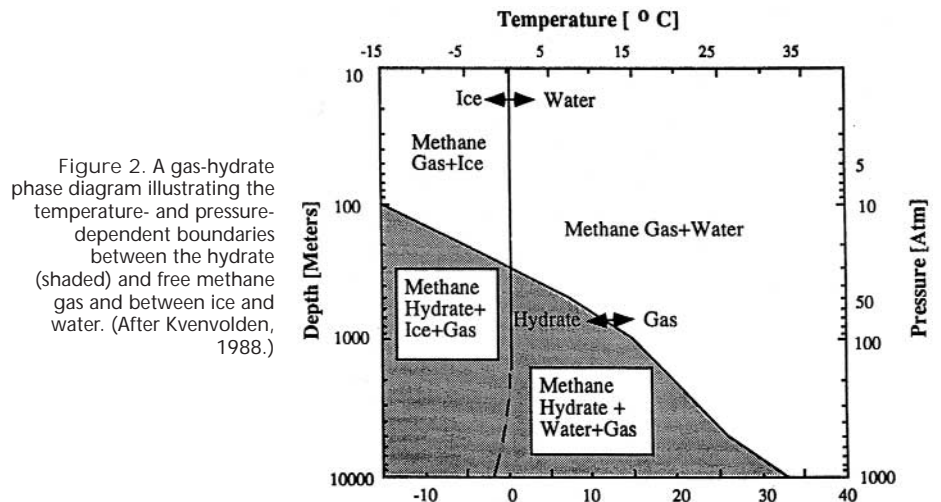


Figure 2. A gas-hydrate phase diagram illustrating the temperature- and pressure-dependent boundaries between the hydrate (shaded) and free methane gas and between ice and water. (After Kvenvolden, 1988.)

the general lack of ground-truthing means that the volumes of methane trapped in hydrates, or in associated free gas, remain largely speculative. Blake Ridge remains the only hydrate field where multiple estimates of the volume of hydrate are available from seismic reflection profiling, vertical seismic profiling, and direct measurements on cores obtained from the GHSZ and below (Paull et al., 1996b; Holbrook et al., 1996; Dickens et al., 1997). The in situ measurements indicate that as much as 35 Gt of methane carbon may be tied up in the Blake Ridge clathrates, equal to about 7% of the carbon in total terrestrial biota (Dickens et al., 1997).

Gas hydrates can also be detected through well-log response; high electrical resistivity, high acoustic (P-wave) velocity, and significant release of gas during drilling are known to characterize the presence of gas hydrate (Collett et al., 1988; Bangs et al., 1993). Reduction in pore-water chlorinity during drilling can also indicate dissociation of gas hydrate and therefore its recent presence (Hesse and Harrison, 1981). Chloride anomalies occur when the hydrate molecule crystallizes and expels salts, causing surrounding pore water to become more saline initially. Subsequently, advection and diffusion homogenize the salinity gradient, and later dissociation of gas hydrate will lead to apparent freshening of pore water. Such chloride anomalies within the GHSZ depths have been observed in the sites drilled by ODP on the Blake Ridge and elsewhere (Dickens et al., 1997). Other indications of the presence of gas hydrates at depth may include gas-escape features such as mud volcanoes and other diapirs. On some areas of the continental slope of the Gulf of Mexico with high gas flux, hydrates crop out on the seafloor. There, they are commonly associated with a diverse and specialized biota, with gas-hydrate-associated chemosynthetic bacteria at the base of the food chain (MacDonald et al., 1994) (see Fig. 3).

Global estimates of the total methane trapped in and beneath gas-hydrate reservoirs vary widely. Guesstimates of amounts trapped in marine sediments range from 1700 to 4,100,000 Gt of methane carbon (Kvenvolden, 1993), variations reflecting effects of many simplifying assumptions. For example, one estimate includes only areas characterized by >1% organic matter, a 0.5 km gas hydrate zone, and a porosity of 50%, hydrate occupying 10% of pore space (Kvenvolden and Claypool, 1988). In contrast, another estimate is based on porosity of 2% to 4%, with clathrate in only 1% of the pore space (MacDonald, 1990). Application of disparate assumptions over large but potentially heterogeneous areas is problematic, and lack of

information on the amount of free gas trapped underneath the gas hydrates only compounds the uncertainty in estimating the total gas reservoir.

## SCENARIOS OF RAPID CLIMATE CHANGE

The pressure and temperature conditions necessary for the stability of the gas hydrate (see Fig. 2) imply that any major change in these controlling factors will tend to alter the zone of gas-hydrate stability. For example, a significant drop in sea level will reduce hydrostatic pressure on the slope and rise. This will cause the GHSZ to thin by dissociation of the hydrate at its base. Dillon and Paull (1983) suggested that the sea-level drop of about 120 m during the last glacial maximum reduced hydrostatic pressure sufficiently to raise the base of the GHSZ by about 20 m. The basal destabilization would have created a zone of weakness where sedimentary failure could take place. This may have led to major slumping, documented by the presence of common Pleistocene slumps worldwide—e.g., the North Sea, the Bering Sea, offshore West Africa, U.S. Atlantic margin, Gulf of Mexico, and elsewhere (Bugge et al., 1987; Collett et al., 1990; Kayen and Lee, 1991; Kvenvolden, 1993; Booth et al., 1994; Paull et al., 1996a).

Submarine slumping related to gas-hydrate dissociation may cause rapid terminations of glacial events (Paull et al., 1991). At some stage during the glaciation, slumping may liberate significant amounts of methane, causing greenhouse warming. As the frequency of slumping and methane release increases, a threshold eventually may be reached above which added methane could cause glacial melting. Paull et al. (1991) attributed the abrupt terminations of Pleistocene glacial events to such a process.

During glaciation, more methane would be released at lower latitudes than at higher latitudes, where glacially induced freezing would inhibit hydrate dissociation. However, once deglaciation begins, a small increase in atmospheric temperature at higher latitudes could cause significant methane release (and warming). For example, a small triggering event leading to liberation of one or more Arctic gas pools could initiate massive release of methane from the permafrost, ushering in accelerated warming. This mechanism has been invoked to explain the abruptness of the end of the Younger Dryas (~10,000 yr ago), and it has been suggested that gas hydrates may play a dominant role in recharging the biosphere with carbon dioxide (the main oxidation product of methane) near a glacial termination (Nisbet, 1990).

It is conceivable that a combined effect of sea-level-lowstand-induced

slumping and methane release in low latitudes triggers a negative feedback to glaciation as suggested by Paull et al. (1991), and the ensuing degassing of carbon dioxide from the ocean and eventual warming in the higher latitudes leads to further release of methane from near-surface sources, as envisioned by Nisbet (1990). In this feedback-loop scenario, the former would help force a reversal of the glacial episode, and the latter could reinforce the trend, resulting in apparent rapid warming observed at the end of the glacial cycles (Haq, 1993).

Kennett et al. (1996) found evidence in Santa Barbara Basin for rapid warming episodes in the late Quaternary that are synchronous with warming associated with Dansgaard-Oeschger (D-O) events in the Greenland ice record. The ice cores indicate that the D-O events were commonly characterized by rapid warming, transitions from glacial to interglacial modes lasting only a few decades. In the Santa Barbara Basin cores, relatively large excursions of  $\delta^{13}\text{C}$  (up to 5‰) in benthic foraminifera are associated with the D-O events. During several brief intervals the planktonics also show large negative shifts in  $\delta^{13}\text{C}$  (up to 2.5‰), implying that the entire water column may have experienced rapid  $^{12}\text{C}$  enrichment. One plausible mechanism for these changes may be the liberation of methane from clathrates during the interstadials. Thus, abrupt warmings at the onset of D-O events may have been forced by dissociation of gas hydrates, modulated by temperature changes in overlying intermediate waters.

At least one modeling study has played down the role of methane release from hydrate sources as a major climate modulator. Harvey and Huang (1995) modeled heat transfer and methane destabilization processes in oceanic sediments in a coupled atmosphere-ocean model and found hydrate dissociation effects to be less important than the effects of increased carbon dioxide emissions resulting from anthropogenic activity. In a worst-case scenario, global warming increased by 10%–25% more with gas-hydrate destabilization than without. These models, however, did not take into account the associated free gas beneath the hydrate zone that may play an additional and significant role as well.

Several unresolved problems remain with the rapid-climate-change models. The feedback scenario assumes a time lag between events as they shift from lower to higher latitudes, but the duration of the lag remains unknown. A short duration (tens to hundreds of years) is implied by the ice-core records, but fine-scale time resolution (50 years or better) needed to clarify the leads and lags is not available. Another large uncertainty is

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## Gas Hydrates *continued from p. 3*

the fate of methane released from hydrate sources in the water column. How much of this is dissolved in the water and what proportion is emitted to the atmosphere?

Changes in  $\delta^{13}\text{C}$  composition of the carbon reservoir may provide a signature preserved in the longer-term geological record of significant methane release into the ocean. The  $\delta^{13}\text{C}$  of methane in gas hydrates averages about  $-60\text{‰}$  (PDB) (Kvenvolden, 1993), perhaps the lightest (most enriched in  $^{12}\text{C}$ ) carbon anywhere in the Earth system. Dickens et al. (1995) argued that massive methane release from gas-hydrate sources is the most likely mechanism for the pronounced input of carbon enriched in  $^{12}\text{C}$  during a period of rapid bottom-water warming.

In the latest Paleocene, bottom-water temperature increased rapidly (in  $<10,000$  yr) by as much as  $4^\circ\text{C}$ , with a coincident excursion of up to  $-3\text{‰}$  in  $\delta^{13}\text{C}$  of all carbon reservoirs worldwide (Kennett and Stott, 1991). Dickens et al. (1995) maintained that this rapid excursion cannot be explained by the usual suspects of increased volcanic emissions of carbon dioxide, changes in oceanic circulation, and/or increased terrestrial and marine productivity. However, the recorded rapid warming of bottom waters at this time from  $11$  to  $15^\circ\text{C}$  could have altered the sediment thermal gradients leading to methane release from gas hydrates. Increased flux of methane into the ocean-atmosphere system and its subsequent oxidation to  $\text{CO}_2$  is sufficient to explain the  $-2.5\text{‰}$  excursion in  $\delta^{13}\text{C}$  in the inorganic carbon reservoir. Adding large quantities of carbon dioxide to the ocean should also increase its acidity, leading to elevation of the lysocline and greater carbonate dissolution. Although there is some indication of increased carbonate dissolution in the late Paleocene, its extent and magnitude are unclear. Dickens et al. (1995) suggested that explosive volcanism, rapid release of carbon dioxide, and changes in the sources of bottom water during this time are plausible triggering mechanisms for the peak warming that may have led to gas-hydrate dissociation.

## SLOPE STABILITY ISSUES

Decomposition of gas hydrates and weakening of the mechanical strength of sediments that encourages failure along low-angle faults may produce more coherent slides and slumps rather than chaotic debris flows (Haq, 1998). Examples include: (1) slump features expressed as low-angle faults that sole out at or above BSR levels in the Carolina Trough area (Paull et al., 1989), and (2) a series of slumps with a composite slump scar of  $290$  km and a runoff of  $800$  km off

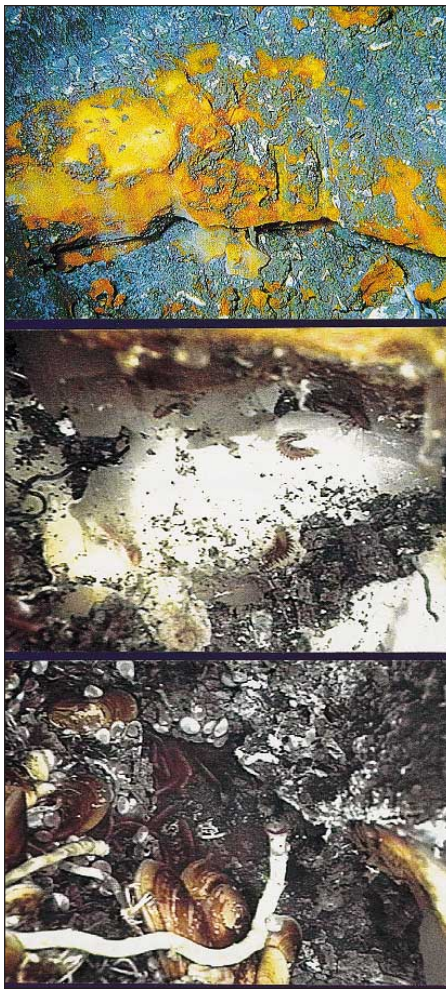


Figure 3. Outcrops of gas hydrates on the floor of the Gulf of Mexico at about  $535$  m water depth. Top: "Yellow ice" represents a hydrate formed from methane vented to the seafloor via subsurface conduits. The hydrate lens is about  $150$  cm across and  $50$  to  $75$  cm thick. Middle: "White" hydrate with the newly discovered polychaete worms on its surface. The worms, which are  $2$ – $3$  cm long, forage on the chemosynthetic bacteria associated with the gas hydrate. Bottom: Commonly, a diverse biotic assemblage is associated with outcropping hydrate; this photo shows tube-worms, mussels, orbinid polychaetes, gastropods, Alvinocaris shrimp, and Munidopsis crabs. (Photos by I. MacDonald and S. Mackovoy. Courtesy of I. R. MacDonald, Texas A&M University.)

the Norwegian continental margin (Storregga) which have been ascribed to earthquakes and gas-hydrate dissociation (Bugge et al., 1987; Jansen et al., 1987).

Is there geological evidence of increased slump frequency associated with major sea-level drops in the sedimentary record that can be ascribed to gas hydrate breakdown? In a seismic stratigraphic study, Mountain and Tucholke (1985) and Mountain (1987) documented four periods of Paleogene slumping and infilling along the New Jersey slope (at the Cretaceous-Tertiary boundary, the Paleocene-Eocene boundary, the top of the lower Eocene, and in

the middle Eocene) and a widespread unconformity near the Eocene-Oligocene boundary. Near the top of the lower Eocene, a megaslump that is compositionally similar to enclosing sediments seems to have traveled several kilometers downslope to its present position. Mountain and Tucholke (1985) and Mountain (1987) suggested slope failure related to episodic collapse of the underlying Mesozoic carbonate margin as the probable cause. However, all events except the K/T boundary event documented on this margin occur close to major sea-level lowstands (see Haq et al., 1988). Some slump blocks maintain their original bedding. These features can be readily explained in terms of gas-hydrate destabilization, following sea-level falls and reduced hydrostatic pressure. This could also explain the apparent coeval shelf and slope erosion associated with some of these events, since during lowstands the subareally exposed shelf would be prone to extensive erosion while the slope will suffer from accelerated slumping caused by gas-hydrate dissociation.

These ideas, nevertheless, are largely conjectural and require testing. A reexamination of seismic and stratigraphic data for evidence of low-angle normal faults, major slumping and sliding within gas hydrate field depths along continental margins, and associated large negative  $\delta^{13}\text{C}$  excursions could point to causal linkages between gas hydrates and sedimentary tectonic processes (Haq, 1998).

## EXPLOITATION OF GAS HYDRATE AS A RESOURCE

Methane is a clean-burning fuel, and clathrate concentrates  $>160$  times more methane in the same space as free gas at atmospheric pressure. Thus, natural gas hydrates are considered by many to represent a viable, though as yet unproven, resource of methane.

Direct measurements of methane in hydrated sediments and the free gas below have been made only during ODP Leg 164 (Paull et al., 1996b; Dickens et al., 1997). These results indicate that large quantities of methane are stored in gas hydrates on the Blake Ridge, and even more as free gas below the hydrate. In the GHSZ (between  $200$  and  $450$  m below seafloor) the volume of the gas hydrate, on the basis of direct measurements, was estimated to be up to  $9\%$  of the pore space (Dickens et al., 1997), and between  $5\%$  and  $7\%$  on the basis of vertical seismic profile velocity data (Holbrook et al., 1996). Though the clathrate is mostly finely disseminated in the sediment, there are also intermittent hydrate bodies up to  $30$  cm thick. Below the GHSZ, pore spaces are saturated with free gas. Thus, the total

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## GSA Field Guide Editor Named

David R. Lageson has been appointed editor of the new GSA Field Guide series by the GSA Council. Lageson, a professor of geology at Montana State University (Bozeman), will initiate the series with the 1999 GSA Annual Meeting in Denver. His appointment is effective through 2001.

Previously, Tommy Thompson of Colorado State University edited some field guides for GSA meetings, and these were published through the Society of Economic Geologists (SEG) guidebook series. Lageson plans to incorporate Thompson's high standards and consistent format into the new GSA series.

### Plan for the New Series

The GSA Field Guide series will reflect the Society's mission in several ways. The series will foster understanding of the earth by documenting important field localities and relationships in a format that is accessible to a broad spectrum of people, extending beyond the community of professional earth scientists.

As the first editor of the GSA Field Guide series, Lageson says he hopes that the publications will be much more than a collection of road logs and field reports, "which admittedly have had their place in the spectrum of professional literature, but are often too limited in substance and readership appeal." Lageson's plan includes the following goals:

- To develop a series that disseminates field guide data in an exciting, readable format that appeals to professional earth scientists, educators, and non-geologists;
- To avoid the conventional road log format;

- To develop a parallel series of field guides for K-16 educators with "active" learning modules for students and teachers;
- To set a standard for consistently high-quality, refereed field guide products;
- To publish only the highest quality maps, diagrams, photographs, computer-generated illustrations, and other graphics;
- To explore new, innovative ways to translate geologic field guides into educational, interactive products that have wide appeal to the scientifically literate public;
- To encourage field trips and guides for national meetings that capture the excitement and appeal of field-based geologic inquiry.

"This is a wonderful opportunity for the Society to launch a new publication series, at a turning point when many changes are taking place in how science is being conducted in the public eye and how information is made accessible," Lageson said. "As professional earth scientists we hold a responsibility to promote public outreach and education, to address those geological issues that affect the greater good of society, and to disseminate information about the earth in formats that do the greatest good to the greatest number. Field geology is the historical essence of our discipline, and it will surely remain a vital component of future research and dis-



New GSA Field Guide series Editor Dave Lageson leads a field trip in the Bridger Range, southwest Montana.

coveries that shape the way we view the earth. The new field guide series will comprise important publications that will, I hope, not only serve our profession well, but also serve the needs of field-based public education and outreach."

### In the Field

Lageson, a GSA Fellow, has been a professor of geology at Montana State University for 18 years; he was department head for 5 years. He earned a Ph.D. in structural geology at the University of Wyoming in 1980. His areas of interest are structural geology and tectonic evolution of the northern Rocky Mountain region with emphasis on neotectonics and active tectonics surrounding the contemporary Yellowstone hotspot. He has led structural field trips for regional and national meetings of various geological societies, oil and gas companies, and minerals exploration companies, as well as numerous academic field trips at Montana State University. ■

### Gas Hydrates *continued from p. 4*

volume of methane on the Blake Ridge may be significantly larger than that inferred from seismic data and may be as large as 12% (Dickens et al., 1997).

From the point of view of recoverability, the free gas below the GHSZ, if it is present in sufficient quantities, could be recovered first. Eventually, the gas hydrate may itself be dissociated artificially and recovered through injection of hot water or through depressurization.

Although the hydrocarbon industry has had a long-standing interest in clathrates (largely because of their nuisance value in clogging up gas pipelines in colder high latitudes and in seafloor instability for rig structures), their reluctance to give whole-hearted support to gas-hydrate research as an energy

resource stems from several factors. Many in the industry believe that the widely cited large estimates of methane in gas hydrates on the continental margins may be grossly overstated (e.g., Hovland and Lysne, 1998). Moreover, if the hydrate is mostly thinly dispersed in the sediment rather than concentrated, it may not be easily recoverable, and thus not cost-effective to exploit. One suggested scenario for exploitation of such dispersed resources is excavation (open-pit style) rather than through drilling, which is environmentally a least acceptable option. Finally, if recovering methane from hydrate ever becomes feasible, it may have important implications for slope stability. Because most hydrates are on the continental slope, extracting the hydrate or recovering the free gas below the GHSZ could cause slope instabilities

of major proportions, which may not be acceptable to coastal communities. Producing gas from gas hydrates locked up in the permafrost may also be difficult, as the unsuccessful Russian efforts to do so in the 1960s and 1970s imply. The present low price of oil is another impediment to a wider industry interest in developing an alternative resource such as gas hydrate.

### THE FUTURE

It is obvious that much of the uncertainty concerning the value of gas hydrates as a resource is a result of lack of information on the nature of the gas-hydrate reservoir. Understanding the characteristics of the reservoir and find-

Gas Hydrates *continued on p. 6*

ing ways to image and evaluate its contents remotely may be the two most important challenges in gas-hydrate research and development. Research plans that target this goal are in the offing in many countries. With the promise of funding as a result of the U.S. Congress initiative, starting in the year 2000, the Department of Energy has begun to plan an ambitious program of gas hydrate R&D for the next 10 to 15 years. The plan includes focused efforts in five major components of gas-hydrate research (resource characterization, production, global climate change, safety, and seafloor stability) and is being conceived as a combined industry, academia, and government effort aimed at determining the efficacy of methane hydrate as a resource by the year 2010.

Some of the scenarios concerning the role of gas hydrate in rapid climate change and slope instability have been touched upon here, but many major questions remain unanswered. Whether clathrates will prove to be an enormous untapped source of energy for the future, as many hope, can only be resolved after a better knowledge of the gas hydrate reservoir and more meaningful global estimates have been acquired. This underscores the need for more focused and accelerated research on this issue of fundamental importance to sedimentary geology.

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