

GAS METHANE HYDRATES – RESEARCH STATUS, ANNOTATED BIBLIOGRAPHY, AND ENERGY IMPLICATIONS

Final Report

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TASK 1.4 – GAS METHANE HYDRATES FOR SMALL POWER SYSTEMS

1.0 INTRODUCTION

1.1 Background

Methane hydrate deposits worldwide in permafrost regions and on the sea floor off continental margins are estimated to be two orders of magnitude greater than recoverable conventional methane resources, and the carbon associated with these methane hydrates may account for twice that associated with all other fossil fuel resources combined. The occurrence of these gas hydrates in both the permafrost and deep-sea sedimentary deposits and their influence on the physical properties of related sediments have, in the past, been considered by the oil industry more as a nuisance complicating drilling operations and geotechnical stability of offshore constructions than as a resource. Also, methane is 10 times by weight more effective as a greenhouse gas than carbon dioxide; thus, any large accidental release from gas hydrate deposits could have a profound climatic impact on a global scale. However, the utilization of methane as a fuel produces less carbon dioxide than other fossil fuels because of its higher ratio of hydrogen to carbon. Therefore, while methane hydrate may have important advantages as a resource, its recovery will involve a multitude of technical and environmental challenges.

1.2 Project Goals and Objectives

The objective of this task as originally conceived was to compile an assessment of methane hydrate deposits in Alaska from available sources and to make a very preliminary evaluation of the technical and economic feasibility of producing methane from these deposits for remote power generation. Gas hydrates have recently become a target of increased scientific investigation both from the standpoint of their resource potential to the natural gas and oil industries and of their positive and negative implications for the global environment

After we performed an extensive literature review and consulted with representatives of the U.S. Geological Survey (USGS), Canadian Geological Survey, and several oil companies, it became evident that, at the current stage of gas hydrate research, the available information on methane hydrates in Alaska does not provide sufficient grounds for reaching conclusions concerning their use for energy production. Hence, the original goals of this task could not be met, and the focus was changed to the compilation and review of published documents to serve as a baseline for possible future research at the Energy & Environmental Research Center (EERC). An extensive annotated bibliography of gas hydrate publications has been completed. The EERC will reassess its future research opportunities on methane hydrates to determine where significant initial contributions could be made within the scope of limited available resources.

2.0 GAS HYDRATES

2.1 Definition

Gas hydrates are water clathrates of natural gas. A clathrate is a solid mixture in which small molecules of an element or compound are trapped in holes in the crystal lattice of another substance. In the case of the gas hydrates, hydrocarbon gas molecules, such as methane, are encased in the crystal lattice of water ice which has crystallized in the isometric crystallographic system rather than the hexagonal system of normal ice. Gas hydrates form one of two basic crystal structures: Structure I and Structure II.

A unit cell of Structure I gas hydrate includes 46 water molecules that form two small dodecahedral voids and six large tetradecehedral voids. Structure I gas hydrates can only hold gas molecules whose diameters do not exceed 5.2 angstroms, such as methane and ethane. Most of the naturally occurring natural gas hydrate formations are Structure I hydrates. Structure II gas hydrate unit cells consist of 16 small dodecahedral and eight large hexakaidecahedral voids formed by 136 water molecules. Structure II gas hydrates may contain gases with molecular dimensions ranging from 5.9–6.9 angstroms, such as propane and isobutane (Collett and Kuns kraa, 1998).

From a macroscopic point of view, gas hydrate looks like ice. Because it contains a minimum of 85% water on a molecular basis, many of its mechanical properties resemble those of ice, although when it melts (dissociates) it releases both gas and water. Another important property of Structure I hydrates is that at standard temperature and pressure (STP), one volume of saturated methane hydrate may contain as much as 164 volumes of methane. Because of this large gas storage capacity, gas hydrates are an important storage site for gas (Collett and Kuns kraa, 1998).

The source of hydrate methane is buried organic matter that is altered microbially or thermally to produce methane. Most of the methane is thought to be generated by microbial activity, although at some sites in the Gulf of Mexico and the Caspian Sea, geochemical evidence indicates that thermogenic processes were the primary mechanism generating methane. The amount and quality of organic matter present is critical to the methane generation process.

2.2 Occurrence

Gas hydrates are stable at moderately high pressure and low temperature and, therefore, are primarily confined to two geological settings: permafrost regions and beneath the ocean floor sediments of outer continental margins where water depths are greater than 500 m. Seismic reflectance data indicate that oceanic hydrate stability zones range from depths of 100–1100 m below the sea floor. In permafrost regions, gas hydrates may exist at subsurface depths ranging from about 130–2000 m below surface level.

Geographically, natural gas hydrates have been documented at numerous locations throughout the world. Oceanic locations where gas hydrates are known to occur include the Gulf

of Mexico, the Black Sea, the Caspian Sea, the Okhotsk Sea, the Pacific Ocean (offshore from Chile, Peru, Costa Rica, Japan, Oregon, and northern California), and the Atlantic Ocean (offshore from Guatemala, Mexico, Norway, and the eastern United States from New Jersey to Georgia). Two of the most studied oceanic locations include Hydrate Ridge on the Juan de Fuca plate off the coast of Oregon and Blake Ridge off the coast of South Carolina.

Onshore natural gas hydrates are exclusively located in permafrost regions. In Asia, gas hydrate deposits have been identified in the West Siberian basin, Timan-Pechora province, eastern Siberian craton, and the northeastern Siberia and Kamchatka area. In North America, natural gas hydrates are known to occur on the Alaska North Slope, including the areas of the Prudhoe Bay and Kuparuk River oil fields; the Mackenzie River delta of Canada; and the Arctic Islands.

2.3 Volumes/Resources

According to Kvenvolden (1993), the worldwide estimates for the amount of gas, most of which is methane, in natural gas hydrates ranges from 1.1×10^5 to 2.7×10^8 tcf for oceanic deposits and from 5.0×10^2 to 1.2×10^6 tcf for permafrost formations. The estimates are based primarily on the theoretical conditions of hydrate stability rather than direct measurements of the presence and concentrations of hydrate deposits. USGS has estimated that for the entire United States, the mean in-place volume of gas associated with natural gas hydrates is 320,000 tcf. For example, based on the recovery of gas hydrates in pressurized core barrels at the Arco-Exxon N.W. Eileen State No. 2 wildcat well on the North Slope of Alaska, it has been estimated that about 1.1×10^2 m³ of methane is present in gas hydrates in the region of the Prudhoe Bay and Kuparuk River oil fields (Collett, 1993).

According to the USGS (1998), the worldwide amount of methane carbon in gas hydrate may be equivalent to about twice the amount of carbon that resides in all fossil fuels on Earth (including coal) and also represents an amount of methane that could be as much as 3000 times the amount in the present atmosphere.

2.4 Properties and Stability Fields

As with normal water ice, natural gas hydrates are able to fill sediment pore space and reduce permeability, which enables hydrate-cemented sediments to act as seals for gas traps. There are essentially two ways in which hydrate formations can provide deposits of energy gases: 1) the hydrates themselves bind gas within sediments and 2) hydrate-cemented sediments act as a seal, thereby creating a gas trap.

A variety of geological settings can create gas traps. Hydrate-cemented layers parallel the sea floor bottom, so that in areas where the sea floor forms a dome, the hydrate layer also forms a dome which can act as a gas trap. Traps above salt diapirs form where the greater thermal conductivity of the salt creates a warm spot and salt ions act as antifreeze, thereby liberating methane gas from the base of the hydrate layers. Traps can also form at locations where strata dip relative to the sea floor and the updip regions of porous strata are sealed by the gas hydrate-

cemented layer. In such situations, the gas in the hydrate-sealed trap, as well as the gas that forms the hydrate, may become a resource (Dillon et al., 1999).

3.0 STATUS OF CURRENT KNOWLEDGE

3.1 Resource Characterization

The presence of gas hydrates in oceanic settings has been inferred largely from seismic reflectors that coincide with the predicted temperature–pressure–phase boundary at the base of the gas hydrate stability zone. This reflector is referred to as a bottom-simulating reflector (BSR). A seismic reflection phenomenon in which a reduction in amplitude of reflections (otherwise known as “blanking”) within the hydrate-cemented zone is observed may also provide information on the presence and character of gas hydrate deposits.

3.2 Geotechnical Stability

The geotechnical stability of sediments with high concentrations of gas hydrates is dependent on temperature and pressure. An increase in temperature and/or decrease in pressure can cause gas hydrate formations to dissociate, thereby substantially reducing the stability of the matrix sediments. Dissociation of the gas hydrate crystals can convert a strong, gas hydrate-cemented sediment to a weaker, gas–water-rich sediment. Dissociation of the hydrates can also generate gas overpressures (pressures greater than the load of water and sediment above) in the seafloor sediments. The gas overpressures coupled with the loss of structural integrity within the sediments can cause seafloor slides and collapses. The geologic record indicates that seafloor slides related to gas hydrate dissociation may have occurred on a massive scale during and shortly after the end of the last ice age (15,000 years ago). The presence of thick polar ice caps and continental glaciers during the last glaciation (Pleistocene age) caused a lowering of sea level and a corresponding reduction in pressure on the seafloor in nonglaciated regions (such as the U.S. States Atlantic coast). Seismic profiles and sidescan sonar images taken of the seafloor on the U.S. Atlantic continental margin reveal major, Pleistocene age, sediment collapse features on low slopes that would be expected to be stable. The tops of landslide scars are concentrated at depths near the top of the range of hydrate stability (500–700 m) which, along with the timing of the slides, suggests that the slides were induced by the dissociation of gas hydrates (USGS, 1998).

A very large seafloor collapse event that may be related to the decomposition of gas hydrates occurred off the west coast of Norway about 8000 years ago. The Storrega submarine landslide was composed of approximately 5600 km³ (1343 miles³) of sediments, which slid a distance of 800 km from the upper edge of the western Norwegian continental slope into the basin of the Norwegian Sea. The presence of methane hydrate fields in the same vicinity as the slide implies that unstable hydrates triggered the event as they rapidly decomposed because of a change in the pressure and/or temperature after the last ice age. Pressure on the seafloor caused by the enormous weight of glacial ice was released as the glaciers receded. The removal of the ice not only decreased pressure on the seafloor sediments, but allowed the earth’s crust in that region to rebound. As the crust rebounded, the overlying sea became shallower and warmer, which further

moved the hydrates out of their zone of stability. The massive landslide that ensued caused tsunamis that appear to have pounded the east coast of the United States (Suess et al., 1999).

The relatively tenuous geotechnical stability of gas hydrates also pose a serious hazard for deep-water petroleum exploration and production (E&P) activities. Oil and associated waters produced from great depths are hot. Pumping hot fluids through drill pipes or transmission pipelines can cause a warming of the sediments and a corresponding dissociation of hydrate, thereby setting the stage for seafloor movement as described above. Though on a smaller scale, dissociation of hydrates related to E&P activities could lead to gas blowouts, loss of support for pipes, and minor slides that can damage and disrupt seafloor installations.

3.3 Resource Recovery

Reports of gas hydrate formations being used as a source of energy in Siberia are largely anecdotal with little or no technical evidence available to substantiate the claims. However, developments in technology, increased understanding of the chemical and physical characteristics of gas hydrates, and an increasing need for energy resources will likely make such formations viable sources of methane fuel in the future. Unfortunately, today the recovery of methane from gas hydrate formations for use as an energy source faces many significant technical and market-related obstacles.

Initially, sustained production would likely be conducted on the Alaskan North Slope where the industrial infrastructure for handling gas is already in place. Even in this case, the lack of a nearby energy market for the gas means that it will most likely be used for repressurization of older oil fields rather than as a source of fuel. If gas hydrates are to make significant contributions to the world energy market, then production will have to be developed from the oceanic formations whose locations are relatively close to the market (i.e., the eastern and western seaboard of the United States and off the coast of Japan). Unfortunately, because of their submarine location, production from oceanic formations will be even more problematic than that from permafrost. The largest obstacle may be related to the role that hydrates play in the stability of the seafloor. Since gas hydrates appear to provide significant stability to the seafloor sediments in which they occur, production of the hydrates may decrease stability, thereby increasing the risk of submarine landslides which could damage or destroy expensive production equipment and infrastructure. Such problems have already been encountered during conventional offshore oil and gas E&P activities. Hot petroleum flowing through drill pipes or transmission pipelines can warm the surrounding sediments and cause dissociation of the hydrates, thus decreasing the geotechnical stability of the sediments. The dissociation of the hydrates may also generate gas at high pressures. This has led to a variety of engineering obstacles for conventional deep-water drilling including gas blowouts, loss of support for pipes, seafloor failure, and slides. The inherent instability of gas hydrate deposits also makes the establishment and maintenance of reservoir flow paths a substantial problem in developing sustainable production from a hydrate reservoir.

The potential methods for recovering gas from hydrates that have been most commonly discussed in recent years involve releasing the methane from in situ hydrate formations by

- 1) raising the temperature of the hydrate reservoir above hydrate formation temperatures;

2) decreasing the pressure on the reservoir, thereby allowing the gas hydrate to dissociate; and
3) injecting an inhibitor such as methanol or glycol, which will depress the temperature of hydrate formation, thereby decreasing the stability of the hydrate reservoir and enhancing dissociation of the gas. Hydraulic mining systems and the use of electromagnetic stimulation techniques have also been discussed, but such ideas are only in the theoretical stage at this point of time.

3.4 Environmental Aspects

The large volumes of methane hydrates that exist in the seafloors and permafrost regions around the world not only have the potential to be a tremendous future resource for the energy industry, but also appear to have the potential to affect the environment on a global scale, particularly with regard to global warming.

Global warming is widely regarded as being driven by increased atmospheric concentrations of gases that enhance the greenhouse effect. Carbon dioxide is the most common greenhouse gas in the atmosphere. However, methane is ten times by weight more effective as a greenhouse gas than carbon dioxide. If large volumes of gas hydrate formations become unstable and decompose, then large volumes of methane will be released to the atmosphere. Increased levels of methane gas in the atmosphere will enhance the greenhouse effect, thereby leading to an increase in global warming. Theoretically, it appears possible that a single explosive methane release, such as may occur with a large seafloor collapse event, could cause a significant climate change over a short time period. For instance, catastrophic releases of methane could have triggered the notable increase in temperature that occurred over the last few decades of the most recent ice age (approximately 15,000 years ago) (Suess et al., 1999). In theory, increased global atmospheric temperatures caused by the decomposition of methane hydrates could launch a vicious circle of more dissolution of hydrates, leading to further increases in global warming.

4.0 POTENTIAL FUTURE RESEARCH TOPICS

Future research efforts related to natural gas hydrates will likely be grouped into two broad categories: 1) environmental issues related to hydrate dissociation and 2) development of hydrate formations as sources of energy.

From an environmental perspective, methane gas released to the atmosphere because of hydrate dissociation may enhance the greenhouse effect, thereby contributing to global warming. The enormous volume of methane locked up in gas hydrate formations means that hydrate-related contributions to global warming could be significant. With global warming being arguably the foremost environmental issue facing the world today, research focused on the environmental aspects of hydrate dissociation will probably take precedence over energy production. Questions related to the environmental effects of hydrate dissociation include, but are certainly not limited to:

- Do the recent observed trends in increasing global temperatures mean we can expect increases in the natural dissociation of hydrates?

- What sort of environmental effects (i.e., tsunamis and accelerated global warming) can we expect from increased natural dissociation of hydrates because of recent and/or future global warming?
- What effects, both locally and globally, can be expected from artificial dissociation of hydrates for methane production purposes?
- Is natural dissociation occurring today? If so, where and why is it occurring?
- What sort of remote sensing methods can be used to evaluate natural dissociation of hydrates?
- How close to natural dissociation is the bulk of the methane hydrate formations today?
- What sort of changes in permafrost and seafloor temperature and/or pressure regimes would have to occur to move hydrate formations out of their stability zones?

With regard to the utilization of gas hydrate formations as sources of energy, there are several factors that will likely push such efforts farther out into the future. First of all, the known conventional gas resources are sufficient to meet current and projected near-term (next decade) demands. Secondly, since tremendous capital expenditures would be required to develop economically and technically feasible technologies and construct the types of infrastructure and facilities (most notably the underwater components) necessary for large-scale production of methane from hydrate formations, it is not likely that such activities would be commenced until conventional sources were nearly exhausted or the price of natural gas was significantly higher. It is possible that gas production from hydrates may be more economically attractive for a nation such as Japan, which is resource-deficient, economically healthy, and located relatively close to large subsea gas hydrate fields. In any event, several technical obstacles would have to be overcome in order to turn the concept of large-scale methane production from hydrates into reality. The technical questions facing the development of such technologies include:

- How can we safely and efficiently dissociate methane hydrate formations?
- Will innovative mining methods be more effective than variations of “conventional” drilling and production methods?
- Are there ways that the pressure and/or temperature of the hydrate formations can be maintained or quickly restored (thus maintaining structural integrity) while still removing the methane?
- What specifically are the local and large scale environmental problems associated with methane production from hydrates? In permafrost regions? In seafloor settings?
- What types of innovative infrastructure designs will be required for seafloor production?

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APPENDIX A

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APPENDIX B

ABSTRACTS

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Abrajano, T.A.; Struchio, N.C.; Bohlke, J.K.; Lyon, G.L.; Poreda, R.J., and Ctevens, C.M., 1988, Methane-Hydrogen Gas Seeps, Zambales Ophiolite, Philippines: Deep or Shallow Origin?, *Chemical Geology*, v. 71, p. 211–222.

Isotopically anomalous CH₄-rich gas escapes at low flow rate and ambient temperature from seeps in serpentinized ultramafic rock in the Zambales Ophiolite, Philippines. The major components of the gas are CH₄ (55 mole%) and H₂ (42 mole%); the CH₄/CO₂ ratio is >1800 and the CH₄/He ratio is $9.2 \cdot 10^4$. The d¹³C-value of the CH₄ is $7.0 \pm 0.4\text{‰}$ (PDB), ~8‰ higher than the highest published values for CH₄ in other natural gases and hot springs, but similar to values commonly attributed to mantle carbon. The ³He/⁴He ratio is $5.70 \cdot 10^{-6}$, 4.1 times the atmospheric ratio, indicative of a substantial mantle He component. The dD-values of CH₄ and H₂ are 136 and –590‰, respectively, consistent with equilibration temperatures of 110–125°C. Carbon and He isotopic data could be consistent with derivation of the Zambales gas directly from a reduced mantle. However, phase equilibria and H isotope data indicate that the gas also could have been produced by reduction of water and carbon during low-temperature serpentinization of the ophiolite.

Bangs, N.L.B.; Sawyer, D.S., and Golovchenko, X., 1993, Free gas at the base of the gas hydrate zone in the vicinity of the Chile triple junction, *Geology*, v. 21, p. 905-908.

At Ocean Drilling Program Site 859 in the vicinity of the Chile triple junction, the source of the bottom simulating reflection (BSR) at the base of the gas hydrate layer has, for the first time, been logged to reveal the nature of the impedance contrasts producing the reflection. We estimate from the P-wave velocity (VP) that hydrate occupies no more than 18% of the pore space just above the BSR and is not concentrated enough to cause the reflections. The BSR is caused by a sharp drop in VP, and presumably density, from ~1950 to 1600 m/s (on average) within an 8 m interval. Seismic modeling of wave form and amplitude vs. offset of the BSR at Site 860 indicates that the BSR is produced by a 12 m interval with low VP and shear-wave velocities that are consistent with small quantities of free gas (~1% of pore space) in the interval.

Brooks, J.M.; Jeffrey, A.W.A.; McDonald, T.J.; Pflaum, R.C., and Kvenvolden, K.A., 1985, Geochemistry of hydrate gas and water from site 570, Initial Reports of the Deep Sea Drilling Project, v. 84, p. 699–703.

Molecular and isotopic measurements of gas and water obtained from a gas hydrate at Site 570, DSDP Leg 84, are reported. The hydrate appeared to be Structure I and was composed of a solid framework of water molecules enclosing methane and small amounts of

ethane and carbon dioxide. Carbon isotopic values for the hydrate-bound methane, ethane, and carbon dioxide were -41 to about -44, -27, and -2.9‰, respectively. The $d^{13}C_{C_1}$ values are consistent with void gas values that were determined to have a biogenic source. A significant thermogenic source was discounted because of high C_1/C_2 ratios and because the $d^{13}C_{CO_2}$ values in these sections were also anomalously heavy (or more positive) isotopically, suggesting that the methane was formed biogenically by reduction of heavy CO_2 . The isotopically heavy hydrate $d^{13}C_{C_2}$ is also similar to void gas isotopic compositions and is either a result of low-temperature diagenesis producing heavy C_2 in these immature sediment sections or upward migration of deeper thermogenic gas. The salinity of the hydrate water was 2.6‰ with dD_{H_2O} and $d^{18}O_{H_2O}$ values of +1 and +2.2‰, respectively.

Brooks, J.M.; Field, M.E., and Kennicutt, M.C., 1991, Observations of gas hydrates in marine sediments, offshore northern California, *Marine Geology*, v. 96, p. 103–109.

Biogenic gas hydrates were recovered in shallow cores (<6 m deep) from the Eel River basin in offshore northern California between 40°38' and 40°56'N. The gas hydrates contained primarily methane ($d^{13}C = -57.6$ to -69.1 ‰) and occurred as dispersed crystals, small (2–20 mm) nodules, and layered bands within the sediment. These hydrates, recovered in sediment at water depths between 510 and 642 m, coincide nearly, but not exactly, with areas showing bottom-simulating reflectors (BSRs) on seismic-reflection records. This study confirms indirect geophysical and geologic observations that gas hydrates are present north of the Mendocino Fracture Zone in sediment of the Eel River basin but probably are absent to the south in the Point Arena basin. This discovery extends the confirmed sites of gas hydrates in the eastern Pacific region beyond the Peruvian and Central American margins to the northern California margin.

Cha, S.B.; Ouar, H.; Wildejman, T.R., and Sloan, E.D., 1988, A Third-Surface Effect on Hydrate Formation, *Journal of Physical Chemistry*, v. 92, p. 6492–6494.

Natural gas hydrate studies have shown that formation is strongly dependent on pressure, temperature, phase compositions, and interfacial contact area. We have recently investigated the effect of third surfaces on the formation variables. Our research suggests that large areas of interactive surface and possible surface ordering have an effect on the thermodynamic and kinetic characteristics of natural gas hydrate formation. The findings of this work may provide useful insight into gas-water-surface interactions.

Christian, H.A. and Cranston, R.E., 1997, A methodology for detecting free gas in marine sediments, *Canadian Geotech Journal*, v. 34, p. 293–304.

The existence of occluded or continuous-phase pore gas at shallow depths beneath the seabed can lead to acoustic turbidity or blanking, resulting in poor definition of seismo-stratigraphic features. Shallow gas can dramatically affect the engineering behavior of marine sediment by increasing the bulk compressibility and the rate of settlement can alter the undrained shear strength mobilized at failure, can reduce permeability, and can delay the pore pressure response to cyclic loading, giving rise to residual pore pressures. A method is

presented that overcomes previous uncertainties in seabed gas detection, facilitating calculation of the in situ degree of saturation. Gaseous and dissolved molar concentrations are evaluated under atmospheric conditions using gas chromatography and are corrected for in situ pressure and temperature and compared to dissolved limit (gas solubility) curves. The volumes of gases existing at concentrations in excess of their dissolved limits are determined to evaluate the overall in situ degree of saturation.

Clark, I.D.; Matsumoto, R.; Dallimore, S.R.; Lowe, B., and Loop, J., 1999, Isotope constraints on the origin of pore waters and salinity in the permafrost and gas hydrate core intervals of the JAPEX/JNOC/GSC Mallik 2L-38 gas hydrate research well, *in* Scientific Results from JAPEX/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, Northwest Territories, Canada, Geological Survey of Canada, Ontario, Canada v. 544, p. 177–188.

Pore waters have been extracted from sediments in the permafrost interval (110–176 m) and the gas hydrate interval (886–952 m) of the JAPEX/JNOC/GSC Mallik 2L-38 drill core and analyzed for $d^{18}O$, d^2H , and geochemistry. Pore waters from the permafrost interval have $d^{18}O$ values of $-19.5 \pm 0.5\text{‰}$ (upper permafrost) and $-23.1 \pm 1.0\text{‰}$ (lower permafrost) indicating the likely origin to be local, contemporary meteoric waters infiltrating these sediments during a period of subaerial exposure.

Pore waters in the subpermafrost gas hydrate zone are isotopically depleted from seawater values, with $d^{18}O$ ranging between 14‰ and 8‰. A weak correlation between $d^{18}O$ and Cl^- exists in the gas-hydrate-bearing sands, consistent with the combined effect of isotopic depletion during gas hydrate formation, and enrichment associated with gas hydrate decomposition. The upper silt and deeper clayey silt sections also retain a minor correlation between isotopes and Cl^- , and show strong variability in both $d^{18}O$ and Cl^- with depth, suggesting a history of gas hydrate formation, decomposition, and fluid migration. The Cl^- - $d^{18}O$ relationships demonstrate that the original pore waters are a mixture of seawater with greater than 50% meteoric water.

Claypool, G.E.; Threlkeld, C.N.; Mankiewicz, P.N.; Arthur, M.A., and Anderson, T.F., 1985, Isotopic Composition of Interstitial Fluids and Origin of Methane in Slope Sediments of the Middle America Trench, Initial Reports of the Deep Sea Drilling Project, v. 84, p. 683–691.

CH_4 and CO_2 species in pore fluids from slope sediments off Guatemala show extreme ^{13}C -enrichment ($d^{13}C$ of -41 and $+38\text{‰}$, respectively) compared with the typical degree of ^{13}C -enrichment in pore fluids of DSDP sediments ($d^{13}C$ of -60 and $+10\text{‰}$). These unusual isotopic compositions are believed to result from microbial decomposition of organic matter, and possibly from additional isotopic fractionation associated with the formation of gas hydrates. In addition to the isotopic fractionation displayed by CH_4 and CO_2 , the pore water exhibits a systematic increase in $d^{18}O$ with decrease in chlorinity. As against seawater $d^{18}O$ values of 0 and chlorinity of 19‰, the water collected from decomposed gas hydrate from Hole 570 had a $d^{18}O$ of $+3.0\text{‰}$ and chlorinity of 9.5‰. The isotopic compositions of

pore-fluid constituents change gradually with depth in Hole 368 and discontinuously with depth in Hole 570.

Collett, T.S., 199, Gas hydrate resources of northern Alaska, *Bulletin of Canadian Petroleum Geology*, v. 45(3), p. 317–338.

Large amounts of natural gas, composed mainly of methane, can occur in arctic sedimentary basins in the form of gas hydrates under appropriate temperature and pressure conditions. Gas hydrates are solids, composed of rigid cages of water molecules that trap molecules of gas. These substances are regarded as a potential unconventional source of natural gas because of their enormous gas-storage capacity. Most published gas hydrate resource estimates are highly simplified and based on limited geological data. The gas hydrate resource assessment for northern Alaska presented in this paper is based on a “play analysis” scheme, in which geological factors controlling the accumulation and preservation of gas hydrates are individually evaluated and risked for each hydrate play. This resource assessment identified two gas hydrate plays; the in-place gas resources within the gas hydrates of northern Alaska are estimated to range from 6.7 to 66.8 trillion cubic metres of gas (236 to 2,357 trillion cubic feet of gas), at the 0.50 and 0.05 probability levels respectively. The mean in-place hydrate resource estimate for northern Alaska is calculated to be 16.7 trillion cubic metres of gas (590 trillion cubic feet of gas). If this assessment is valid, the amount of natural gas stored as gas hydrates in northern Alaska could be almost seven times larger than the estimated total remaining recoverable conventional natural gas resources in the entire United States.

Collett, T.S., 1983, Detection and Evaluation of Natural Gas Hydrates From Well, Logs, Prudhoe Bay, Alaska, *Proceedings of the 4th International Conference on Permafrost*, Fairbanks, Alaska, p. 169–174.

The purpose of this study is to develop techniques for the detection and evaluation of in-situ gas hydrates from well log data and to determine possible geologic controls on the occurrence of hydrates in the North Slope region of Alaska. Several new methods of evaluation for subsurface gas hydrate were developed and incorporated with existing techniques. For each of 125 wells examined as part of this study the geothermal gradient was determined and the theoretical stability zone for methane hydrate was calculated. Among these, there was 102 apparent hydrate occurrences in 32 wells. A subsurface structural-stratigraphic framework was established to a depth of 1,000 meters. This sediment package is characterized by three deltaic depositional sequences. The high frequency of hydrate occurrences in the structurally up-dip region of the Kuparuk Oil Field suggests that upward migration of free gas preceded hydrate development in the zone of hydrate stability.

Collett, T.S.; Goodbole, S.P., and Ecomides, C., 1984, Quantification of In-Situ Gas Hydrates with Well Logs, *Papers Presented at the 35th Annual Technical Meeting of the Petroleum Society of CIM*, p. 571–582.

The purpose of this study is to evaluate a series of well log responses within an in-situ natural gas hydrate interval, specifically to develop a method by which formation characteristics such as porosity and hydrate saturation can be determined within a suspected hydrate zone.

Efforts have been undertaken to analyze the use of neutron log for quantification of hydrate deposits. Neutron porosity logs respond primarily to the amount of hydrogen present in the formation. With an increase in hydrogen content there will be an increase in the apparent neutron porosity. Theoretically, a hydrate zone should have a higher neutron porosity compared to gas zones. The increased neutron porosity reflects the higher concentration of hydrogen atoms in the hydrate state. The stoichiometric hydrogen content within a unit pore volume of methane gas, free water, hydrate and ice have been calculated. Hydrate contains volumetrically the greatest amount of hydrogen atoms in comparison to free water, ice, and methane gas. A zone saturated with methane gas would contain the smallest number of hydrogen atoms representing the other extreme, with free water and ice existing as intermediates.

The sonic velocity log has also been examined in detail in order to evaluate the effect of hydrate on porosity calculations undertaken with data from the transit time device. A detailed examination of a series of Pickett crossplots used to evaluate hydrate saturation have been included.

This paper concludes with an examination of one stratigraphically controlled hydrate occurrence in the Kuparuk Oil Field. The newly developed techniques have been used to calculate hydrate saturation and porosity within the hydrate interval in order to evaluate the new procedures. In addition, a procedure for estimation of natural gas in the form of hydrate deposits is included.

Collett, T.S., 1988, Freezing-Point Depression at the Base of Ice-Bearing Permafrost on the North Slope of Alaska, Proceedings of the 5th International Conference on Permafrost, Trondheim, Norway, p. 50–55.

Ice-bearing sediments, common in Arctic regions, exhibit physical characteristics that can be detected with bore-hole logging devices. Properties such as anomalously high electrical resistivity and short acoustic transit-times have been used to detect qualitatively the presence of ice within sediments. Correlation of measured near-equilibrium, formation temperatures with the log-determined base of ice-bearing sediments (ice-bearing permafrost) in North Slope wells shows temperatures lower than 0°C at the ice/water interface, ranging generally from –1.0°C to as low as –4.8°C. Near Prudhoe Bay, the temperature at the base of the ice-bearing permafrost is approximately –1.0°C, whereas 50 km or more to the west in the National Petroleum Reserve in Alaska (NPR), the temperature ranges from –3.0 to –4.8°C.

Temperatures at the base of ice-bearing permafrost may be influenced by pore-fluid salinity, pore-pressures, and sediment grain-size; these factors collectively depress the freezing point

of water (freezing-point depression). Theoretical calculations coupled with analysis of North Slope subsurface data indicates that the maximum cumulative effect of pore-water salinity and pore-pressure accounts for only about 1.5°C of the freezing-point depression. Freezing-point depression greater than 1.5°C may be caused by the presence of fine-grained (clayey) moderately compacted sediments, as well as the limitations of well logs to detect relatively small or finely disseminated amounts of ice in fine-grained sediments.

Collett, T.S.; Bird, K.J.; Kvenvolden, K.A., and Magoon, L.B., 1988, Geologic interrelations relative to gas hydrates within the North Slope of Alaska, U.S. Geological Survey, Menlo Park, CA v. 88-389, p. 1–150.

The five primary objectives of the U.S. Geological Survey North Slope Gas Hydrate Project were to: (1) Determine possible geologic controls on the occurrence of gas hydrate; (2) locate and evaluate possible gas-hydrate-bearing reservoirs; (3) estimate the volume of gas within gas hydrates; (4) develop a model for gas-hydrate formation, and (5) select a coring site for gas-hydrate sampling and analysis.

Our studies of the North Slope of Alaska suggest that the zone in which gas hydrates are stable is controlled primarily by subsurface temperatures and gas chemistry. Other factors, such as pore-pressure variations, pore-fluid salinity, and reservoir-rock grain size, appear to have little effect on gas hydrate stability on the North Slope. Data necessary to determine the limits of the gas hydrate stability field are difficult to obtain. On the basis of mud-log gas chromatography, core data, and cuttings data, methane is the dominant species of gas in the near-surface (0–1,500 m) sediment. Subsurface temperature information, obtained from 46 high-resolution equilibrated well-bore surveys and from estimates based on well-log identification of the base of ice-bearing permafrost in 98 other wells, indicate that the depth of the 0°C isotherm increases in an irregular way from 220 m in the south to as much as 660 m near the coastline at Prudhoe Bay in the north. Formation-water samples and well-log calculations indicate low pore-fluid salinities (fresh to brackish), ranging from 0.5 to 19.0 ppt. The maximum recorded salinity would only suppress methane hydrate stability temperatures by approximately 1.0°C. Pressure data, obtained from drill-stem testing and well log calculations, indicate a hydrostatic pore-pressure gradient within the near-surface sedimentary rocks, thus having minimal effect on gas hydrate stability. In the near-surface coarse sandstone and conglomerate of the Prudhoe Bay area, grain size has little effect on gas hydrate stability; however, in the more clay-rich sedimentary rocks near Harrison Bay the freezing point of water may be depressed by several degrees Celsius, resulting in a shallower gas hydrate stability field. Our analyses indicate that the region in which methane hydrate is stable is really extensive beneath the coastal plain province, with thicknesses greater than 1,000 m in the Prudhoe Bay area. Thermal conditions, however, preclude the occurrence of gas hydrates in the north-central part of the National Petroleum Reserve in Alaska and in the foothills east of Umiat.

Gas hydrates were identified in 34 wells utilizing well-log responses calibrated to the response of an interval in one well where gas hydrates were actually recovered in a core by an oil company. Most of the well-log identified gas hydrates occur in six laterally

continuous Upper Cretaceous and lower Tertiary sandstone and conglomerate units, and are geographically restricted to the eastern part of the Kuparuk River Unit and the western part of the Prudhoe Bay Unit. All of the mapped occurrences are stratigraphically below a regionally extensive siltstone sequence, deposited during a regional marine transgression in Eocene time. The total mapped area of these six occurrences is about 380 km². The thicknesses of the identified individual gas-hydrate-bearing sequences range from 2 to 28 m, and reservoir porosities average approximately 40 percent. Well-log analyses suggest that the identified reservoirs are about 85 percent saturated with gas hydrate. If theoretical minimum and maximum hydrate numbers are assumed, then the volume of gas within the identified gas hydrates of the North Slope is approximately 2.4×10^{11} to 2.9×10^{11} m³ (STP) [approximately 8 to 10 tcf of gas], or about one-third of the volume of conventional gas in the Prudhoe Bay field. Because of the low drilling density outside of the Prudhoe Bay-Kuparuk River area, many more gas hydrate occurrences may exist.

A possible scenario describing the origin of the inferred gas hydrates on the North Slope involves the migration of thermogenic solution- and free-gas from deeper reservoirs upward along faults into the overlying sedimentary rocks. As the gas migrated into the upper horizons it was either directly converted to gas hydrate or first concentrated in existing structural/stratigraphic traps and later converted to gas hydrate. Major climatic changes may have influenced the depth limits of the gas hydrate occurrences.

We have identified two (dedicated) core-hole sites, the Eileen and the South-End core-holes, at which there is a high probability of recovering a sample of gas hydrate. At the Eileen core-hole site, at least three stratigraphic units may contain gas hydrate. The South-End core-hole site provides an opportunity to study one specific rock unit that appears to contain both gas hydrate and oil.

Collett, T.S.; Kvenvolden, K.A., and Magoon, L.B., 1990, Characterization of hydrocarbon gas within the stratigraphic interval of gas-hydrate stability on the North Slope of Alaska, U.S.A., *Applied Geochemistry*, v. 5, p. 279–287.

In the Kuparuk River Unit 2D-15 well, on the North Slope of Alaska, a 60 m-thick stratigraphic interval that lies within the theoretical pressure-temperature field of gas-hydrate stability is inferred to contain methane hydrates. This inference is based on interpretations from well logs: (1) release of methane during drilling, as indicated by the mud log, (2) an increase in acoustic velocity on the sonic log, and (3) an increase of electrical resistivity on the electric logs. Our objective was to determine the composition and source of the gas within the shallow gas-hydrate-bearing interval based on analyses of cuttings gas. Headspace gas from canned drill cuttings collected from within the gas-hydrate-bearing interval of this well has an average methane to ethane plus propane [$C_1/(C_2 + C_3)$] ratio of about 7000 and an average methane $\delta^{13}C$ value of -46% (relative to the PDB standard). These compositions are compared with those obtained at one well located to the north of 2D-15 along depositional strike and one down-dip well to the northeast. In the well located on depositional strike (Kuparuk River Unit 3K-9), gas compositions are similar to those found at 2D-15. At the down-dip well (Prudhoe Bay Unit

R-1), the $C_1/(C_2 + C_3)$ ratios are lower (700) and the methane $d^{13}C$ is heavier (-33‰). We conclude that the methane within the stratigraphic interval of gas hydrate stability comes from two sources – *in situ* microbial gas and migrated thermogenic gas. The thermal component is greatest at Prudhoe Bay. Up-dip to the west, the thermogenic component decreases, and microbial gas assumes more importance.

Collett, T.S., 1993, Natural Gas Hydrates of the Prudhoe Bay and Kuparuk River Area, North Slope, Alaska, The American Association of Petroleum Geologists Bulletin, v. 77(5), p. 793–812.

Gas hydrates are crystalline substances composed of water and gas, mainly methane, in which a solid-water lattice accommodates gas molecules in a cage-like structure, or clathrate. These substances commonly have been regarded as a potential unconventional source of natural gas because of their enormous gas storage capacity. Significant quantities of naturally occurring gas hydrates have been detected in many regions of the Arctic, including Siberia, the Mackenzie River Delta, and the North Slope of Alaska. On the North Slope, the methane-hydrate stability zone is areally extensive beneath most of the coastal plain province and has thicknesses greater than 1000 m in the Prudhoe Bay area.

Gas hydrates have been inferred to occur in 50 North Slope exploratory and production wells on the basis of well-log responses calibrated to the response of an interval in a well where gas hydrates were recovered in a core by ARCO and Exxon. Most North Slope gas hydrates occur in six laterally continuous lower Tertiary sandstones and conglomerates; all these gas hydrates are geographically restricted to the area overlying the eastern part of the Kuparuk River oil field and the western part of the Prudhoe Bay oil field. The volume of gas within these gas hydrates is estimated to be about 1.0×10^{12} to 1.2×10^{12} m³ (37 to 44 tcf), or about twice the volume of conventional gas in the Prudhoe Bay field.

Geochemical analyses of well samples suggest that the inferred hydrates probably contain a mixture of deep-source thermogenic gas and shallow, microbial gas that was either directly converted to gas hydrate or first concentrated in existing traps and later converted to gas hydrate. The thermogenic gas probably migrated from deeper reservoirs along the same faults thought to have been migration pathways for the large volumes of heavy oil that occur in the shallow reservoirs of this area.

Collett, T.S.; Bird, K.J., and Magoon, L.B., 1993, Subsurface temperatures and geothermal gradients on the North Slope of Alaska, Cold Regions Science and Technology, v. 21, p. 275–293.

On the North Slope of Alaska, geothermal gradient data are available from high-resolution, equilibrated well-bore surveys and from estimates based on well-log identification of the base of ice-bearing permafrost. A total of 46 North Slope wells, considered to be in or near thermal equilibrium, have been surveyed with high-resolution temperatures devices and geothermal gradients can be interpreted directly from these recorded temperature profiles. To augment the limited North Slope temperature data base, a new method of evaluating

local geothermal gradients has been developed. In this method, a series of well-log picks for the base of the ice-bearing permafrost from 102 wells have been used, along with regional temperature constants derived from the high-resolution stabilized well-bore temperature surveys, to project geothermal gradients. Geothermal gradients calculated from the high-resolution temperature surveys generally agree with those projected from known ice-bearing permafrost depths over most of the North Slope. Values in the ice-bearing permafrost range from $\sim 1.5^{\circ}\text{C}/100\text{ m}$ in the Prudhoe Bay area to $\sim 4.5^{\circ}\text{C}/100\text{ m}$ in the east-central portion of the National Petroleum Reserve in Alaska. Geothermal gradients below the ice-bearing permafrost sequence range from $\sim 1.6^{\circ}\text{C}/100\text{ m}$ to $\sim 5.2^{\circ}\text{C}/100\text{ m}$.

Collett, T.S. and Kvenvolden, K.A., 1993, Significance of natural-gas hydrates at the Mackenzie Delta drill site, *The Nasen Ice Breaker*, v. 4, p. 1–8

Collett, T.S., 1993, Natural Gas Production from Arctic Gas Hydrates, United States Government Printing Office, Washington *The Future of Energy Gases*, U.S. Geological Survey Professional Paper 1570, p. 299–311.

The natural-gas hydrates of the Messoyakha field in the West Siberian basin of Russia and those of the Prudhoe Bay-Kuparuk River area on the North Slope of Alaska occur within a similar series of interbedded Cretaceous and Tertiary sandstone and siltstone reservoirs. Geochemical analyses of gaseous well-cuttings and production gases suggest that these two hydrate accumulations contain a mixture of thermogenic methane migrated from a deep source and shallow, microbial methane that was either directly converted to gas hydrate or was first concentrated in existing traps and later converted to gas hydrate. Studies of well logs and seismic data have documented a large free-gas accumulation trapped stratigraphically down-dip of the gas hydrates in the Prudhoe Bay-Kuparuk River area. The presence of a gas-hydrate/free-gas contact in the Prudhoe Bay-Kuparuk River area is analogous to that in the Messoyakha gas-hydrate/free-gas accumulation, from which approximately 5.17×10^9 cubic meters (183 billion cubic feet) of gas have been produced from the hydrates alone. The apparent geologic similarities between these two accumulations suggest that the gas-hydrate-depressurization production method used in the Messoyakha field may have direct application in northern Alaska.

Collett, T.S., 1994, Permafrost-Associated Gas Hydrate Accumulations, International Conference on Natural Gas Hydrates, v. 715, p. 247–269

Collett, T.S. and Cunningham, K.I., 1994, Near-Surface Expression of Hydrocarbon Migration, Vancouver, British Columbia, Canada

Collett, T.S., 1995, Distribution of Permafrost-Associated Natural Gas Hydrate Accumulations Within the Circum-arctic of the Northern Hemisphere, 1995 International Gas Research Conference, p. 9–20.

Natural gas hydrates are known to be present in the West Siberian Basin and are believed to occur in other permafrost areas of northern Russia, including the Lena-Tunguska province.

Permafrost-associated gas hydrates are also present in the North American Arctic. Direct evidence for gas hydrates on the North Slope of Alaska comes from a core-test, and indirect evidence comes from drilling and open-hole industry well logs which suggest the presence of numerous gas hydrate layers in the area of the Prudhoe Bay and Kuparuk River oil fields. Well-log responses attributed to the presence of gas hydrates have been obtained in about one-fifth of the wells drilled in the Mackenzie Delta of Canada, and more than half of the wells in the Sverdrup Basin are inferred to contain gas hydrates. The combined information from Arctic gas-hydrate studies shows that, in permafrost regions, gas hydrates may exist at subsurface depths ranging from about 130 to 2,000 m.

Collett, T.S. and Ginsburg, G.D., 1997, Gas Hydrates in the Messoyakha Gas Field of the West Siberian Basin – A Re-Examination of the Geological Evidence, Proceedings of the Seventh International Offshore and Polar Engineering Conference, p. 96–103.

The amount of natural gas within the gas hydrate accumulations of the world is believed to greatly exceed the volume of known conventional natural gas reserves. The hydrocarbon production history of the Russian Messoyakha field, located in the West Siberian Basin, has been used as evidence that gas hydrates are an immediate source of natural gas that can be produced by conventional means. Re-examination of available geologic, geochemical, and hydrocarbon production data suggests, however, that gas hydrates may not have contributed to gas production in the Messoyakha field. More field and laboratory studies are needed to assess the historical contribution of gas hydrate production in the Messoyakha field.

Collett, T.S. and Kuuskraa, V.A., 1998, Hydrates contain vast store of world gas resources, Oil and Gas Journal, p. 90–95

Collett, T.S., 1998, Well Log Characterization of Sediment Porosities in Gas-Hydrate-Bearing Reservoirs, 1998 SPE Annual Technical Conference and Exhibition in New Orleans, Louisiana, p. 765–776.

With growing interest in natural gas hydrates, it is becoming increasingly important to be able to determine the volume of gas hydrate and included gas within natural gas hydrate accumulations. Gas volumes that may be attributed to gas hydrates are dependent on a number of reservoir parameters, one of the most difficult reservoir parameters to determine is porosity. Well logs often serve as a source of porosity data; however, well-log calculations within gas-hydrate-bearing intervals are subject to error. The well-logging devices that show the greatest promise of yielding gas hydrate reservoir porosities are the gamma-gamma density and neutron porosity logs. Well log response modeling has revealed that under most conditions, the bulk-density of a water-bearing sedimentary section is almost identical to the bulk-density of a gas-hydrate-bearing sedimentary section as measured by a gamma-gamma density logging tool. At relatively high porosities ($\phi > 40\%$) and gas-hydrate saturations ($Sh > 50\%$), however, the downhole log derived bulk-density porosities need to be corrected for the presence of gas hydrate. A neutron well-log response computer simulator, SNUPAR, has been used to calculate nuclear transport and capture

parameters for various gas-hydrate-bearing reservoirs. The calculated thermal neutron capture cross section of various hypothetical gas-hydrate-bearing reservoirs indicates that methane hydrate has little effect on neutron porosity measurements within “normal” reservoir conditions ($\phi < 40\%$) and low gas-hydrate saturations ($S_h < 50\%$). Within this study, density porosity and neutron porosity nomographs have been developed with which it is possible to correct for the effect of high gas-hydrate saturations on the log derived porosities. In the field verification phase of this study, downhole density and neutron porosity log data (in some cases corrected for the presence of gas hydrate) have yielded accurate porosities for gas-hydrate-bearing reservoirs on the North Slope of Alaska.

Collett, T.S. and Ginsburg, G.D., 1998, Gas Hydrates in the Messoyakha Gas Field of the West Siberian Basin—A Re-Examination of the Geologic Evidence, *International Journal of Offshore and Polar Engineering*, v. 8(1).

The amount of natural gas within the gas hydrate accumulations of the world is believed to greatly exceed the volume of known conventional natural gas reserves. The hydrocarbon production history of the Russian Messoyakha field, located in the West Siberian Basin, has been used as evidence that gas hydrates are an immediate source of natural gas that can be produced by conventional means. Re-examination of available geologic, geochemical and hydrocarbon production data suggests, however, that gas hydrates may not have contributed to gas production in the Messoyakha field. More field and laboratory studies are needed to assess the historical contribution of gas hydrate production in the Messoyakha field.

Collett, T.S., 1998, Gas Hydrates of Northern Alaska—A Potential Energy Resource or Just a Nuisance?, *Alaska Geology*, v. 28(1), p. 1–5

Collett, T.S. and Kvenvolden, K.A., 1999, Interrelations Between Gas Hydrates of Northern Alaska and Atmospheric Methane, *Proceedings of the U.S. Geological Survey Global Change Forum*, p. 77–78

Collett, T.S.; Lewis, R.E.; Dallimore, S.R.; Lee, M.W.; Mroz, T.H., and Uchida, T., 1999, Detailed evaluation of gas hydrate reservoir properties using JAPEx/JNOC/GSC Mallik 2L-38 gas hydrate research well downhole well-log displays, *in* Scientific Results from JAPEx/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, Northwest Territories, Canada, Geological Survey of Canada, Ontario, Canada, v. 544, p. 295–311.

The JAPEx/JNOC/GSC Mallik 2L-38 gas hydrate research well project was designed to investigate the occurrence of in situ natural gas hydrate in the Mallik area of the Mackenzie Delta of Canada. Because gas hydrate is unstable at surface pressure and temperature conditions, a major emphasis was placed on the downhole logging program to determine the in situ physical properties of the gas-hydrate-bearing sediments. Downhole logging tool strings deployed in the Mallik 2L-38 well included the Schlumberger Platform Express with

a high resolution laterolog, Array Induction Imager Tool, Dipole Shear Sonic Imager, and a Fullbore Formation MicroImager.

The downhole log data obtained from the log- and core-inferred gas-hydrate-bearing sedimentary interval (897.25–1109.5 m log depth) in the Mallik 2L-38 well is depicted in a series of well displays. Also shown are numerous reservoir parameters, including gas hydrate saturation and sediment porosity log traces, calculated from available downhole well-log and core data. The gas hydrate accumulation delineated by the Mallik 2L-38 well has been determined to contain as much as $4.15 \times 10^9 \text{ m}^3$ of gas in the 1 km^2 area surrounding the drill site.

Collett, T.S.; Lee, M.W.; Dallimore, S.R., and Avena, W.F., 1999, Seismic- and well-log-inferred gas hydrate accumulations on Richards Island, *in* Scientific Results from JAPEx/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, Northwest Territories, Canada, Geological Survey of Canada, Ontario, Canada, v. 544, p. 357–376.

The gas hydrate stability zone is areally extensive beneath most of the Mackenzie Delta-Beaufort Sea region, with the base of the gas hydrate stability zone more than 1000 m deep on Richards Island. In this study, gas hydrate has been inferred to occur in nine Richards Island exploratory wells on the basis of well-log responses calibrated to the response of the logs within the cored gas-hydrate-bearing intervals of the JAPEx/JNOC/GSC Mallik 2L-38 gas hydrate research well. The integration of the available well-log data with more than 240 km of industry-acquired reflection seismic data have allowed us to map the occurrence of four significant gas hydrate and associated free-gas accumulations in the Iviq-Mallik-Taglu area on Richards Island. The occurrence of gas hydrate on Richards Island is mostly restricted to the crest of large anticlinal features that cut across the base of the gas hydrate stability zone. Combined seismic and well-log data analysis indicate that the known and inferred gas hydrate accumulations on Richards Island may contain as much as $187\,178 \times 10^6 \text{ m}^3$ of gas.

Colwell, F.S.; Delwiche, M.E.; Blackwelder, D.; Wilson, M.S.; Lehman, R.M., and Uchida, T., 1999, Microbial communities from core intervals, JAPEx/JNOC/GSC Mallik 2L-38 gas hydrate research well, *in* Scientific Results from JAPEx/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, Northwest Territories, Canada, Geological Survey of Canada, Ontario, Canada, v. 544, p. 189–195.

Microbial cell distribution in sediment core samples from the JAPEx/JNOC/GSC Mallik 2L-38 gas hydrate research well on the Mackenzie Delta (Canada) was studied using acridine orange direct counts of stained cells for total cell estimation, and by most probable number statistical enumeration for culturable methanogens. The purpose was to characterize the microbial communities in gas-hydrate-bearing sediments. Results indicated that the total cell count values were in the range of 1.1×10^5 cells/g to 2.8×10^6 cells/g with culturable methanogens present at $1 \times 10^{-4}\%$ to 1.0% of those values. These results also indicated that culturable methanogens may be more numerous in the porous sandy strata of the Mackenzie

Bay Sequence than in clay and silt units of the Kugmallit Sequence. These data expand the known distribution of methanogens in deep sediments and establish the presence of microbial communities in subpermafrost environments.

Cranston, R.E., 1999, Pore-water geochemistry, JAPEX/JNOC/GSC Mallik 2L-38 gas hydrate research well, *in* Scientific Results from JAPEX/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, Northwest Territories, Canada, Geological Survey of Canada, Ontario, Canada, v. 544, p. 165–175.

A pore-water research program was designed to measure dissolved components in interstitial water from sediment core samples collected during the JAPEX/JNOC/GSC Mallik 2L-38 gas hydrate research-well project. Pore waters from the gas-hydrate-bearing samples had an average salinity of 8 ppt compared to 34 ppt for non-gas-hydrate-bearing samples. The difference in salinities suggests that 80-90% of the pore space in the gas-hydrate-bearing sediment was filled with gas hydrate, which dissociated during recovery. Potassium concentration was also measured in pore water, to estimate the amount of drill-mud contamination in pore-water samples, since the drill mud contained brine solution made from potassium chloride. On average, pore-water salinities were estimated to be enhanced by 2 ppt due to drill-mud contamination.

Dallimore, S.R. and Collett, T.S., 1995, Intrapermafrost gas hydrates from a deep core hole in the Mackenzie Delta, Northwest Territories, Canada, *Geology*, v. 23(6), p. 527–530.

Visible gas hydrate and possible pore-space hydrate samples have been recovered for the first time in North America from within ice-bonded permafrost in a 451-m-deep core hole in the Mackenzie Delta, Northwest Territories, Canada. The visible hydrate was found as thin icelike layers that released methane gas initially upon retrieval, but stabilized for up to 4 h at atmospheric pressure conditions and subfreezing temperatures. The temporary stabilization of hydrate samples is attributed to the self-preservation phenomenon described by others on the basis of laboratory studies. High methane concentrations in well-ice-bonded sediments and gas releases suggest that pore-space hydrate may be found at depths as shallow as 119 m. Geochemical and isotopic determinations suggest that the methane hydrate observed in the core hole is biogenic (microbial) in origin.

Dallimore, S.R. and Collett, T.S., 1999, Regional gas hydrate occurrences, permafrost conditions, and Cenozoic geology, Mackenzie Delta area, *in* Scientific Results from JAPEX/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, Northwest Territories, Canada, Geological Survey of Canada, Ontario, Canada, v. 544, p. 31–43.

The occurrence of natural gas hydrate within Cenozoic sediments of the Mackenzie Delta-Beaufort Sea region has been well documented. In preparation for the JAPEX/JNOC/GSC Mallik 2L-38 gas hydrate research well, a detailed evaluation of terrestrial gas hydrate occurrences was undertaken to assess the geological setting, sediment associations, pressure and temperature conditions, and the presence of free gas in the Mackenzie Delta-Beaufort

Sea region. After an exhaustive review, it was determined that the Mallik L-38 site, drilled by Imperial Oil in 1972, offered the highest probability of encountering a thick gas hydrate occurrence with high gas hydrate concentrations. On the basis of open-hole well-log evaluation, it was estimated that about 111 m of gas-hydrate-bearing strata occur at this location from 810.1 to 1102.3 m, within the zone of predicted methane hydrate stability and below the base of ice-bearing permafrost, estimated to be at 640 m.

Dallimore, S.R.; Collett, T.S., and Uchida, T., 1999, Overview of science program, JAPEX/JNOC/GSC Mallik 2L-38 gas hydrate research well, *in* Scientific Results from JAPEX/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, Northwest Territories, Canada, Geological Survey of Canada, Ontario, Canada, v. 544, p. 11–17.

The JAPEX/JNOC/GSC Mallik 2L-38 gas hydrate research well was drilled in February and March, 1998, in the Mackenzie Delta, Northwest Territories, Canada, to a depth of 1150 m. The scientific program was conducted through a collaborative agreement between the Japan National Oil Corporation and the Geological Survey of Canada with key participation by the Japan Petroleum Exploration Company and the United States Geological Survey. A primary objective of the well was to undertake a comprehensive scientific research program to study an arctic gas hydrate accumulation. Field research conducted as part of the Mallik 2L-38 program included collection of permafrost and gas-hydrate-bearing core samples, downhole geophysical logging, and a vertical seismic profile survey. Laboratory and modelling studies undertaken during the field program, and subsequently as part of a post-field research program, documented the sedimentology, biostratigraphy, physical/petrophysical properties, pore-water and gas geochemistry, geophysics, and reservoir characteristics of the Mallik field gas hydrate accumulation.

De Roo, J.L.; Peters, C.J.; Lichtenthaler, R.N., and Diepen, G.A.M., 1983, Occurrence of Methane Hydrate in Saturated and Unsaturated Solutions of Sodium Chloride and Water in Dependence of Temperature and Pressure, *AIChE Journal*, v. 29(4), p. 651–657.

Experimental results of the formation of methane hydrate in dependence of temperature and pressure in unsaturated solutions of NaCl in water will be presented in a temperature range from 261.85 to 285.98 K and pressure up to 11.0 MPa. Furthermore the four-phase equilibrium $\text{NaCl}\cdot 2\text{H}_2\text{O}_s\text{-CH}_4\text{-nH}_2\text{O}_s\text{-L-G}$ has been calculated from the experimental results. Also the heats of transformation of several other equilibria in the ternary system $\text{CH}_4\text{-H}_2\text{O-NaCl}$ are obtained.

Dholabhai, P.D.; Englezos, P.; Kalogerakis, N., and Bishnoi, P.R., 1991, Equilibrium Conditions for Methane Hydrate Formation in Aqueous Mixed Electrolyte Solution, *The Canadian Journal of Chemical Engineering*, v. 69, p. 800–805.

Equilibrium data on the formation of methane hydrate in six mixtures of NaCl and KCl, six mixtures of NaCl and CaCl, and a mixture of eight electrolytes found in sea water were experimentally obtained. The ionic strength (in molarity units) of the NaCl and KCl

mixtures ranged from 0.97 to 4.72 and that of the NaCl and CaCl₂ mixtures from 1.27 to 3.90. The experimental temperatures ranged from 264 to 284 K and the pressures from 2.5 to 9.7 MPa. Equilibrium pressures predicted using a recently proposed method (Englezos and Bishnoi, 1988) have been compared with the data obtained and it was found that the predictions match the data very well. The standard errors for the mixtures of NaCl and KCl, NaCl and CaCl₂, and the synthetic sea water were 5.54, 3.5 and 1.4%, respectively. The largest prediction error for an experimental data point was 10.1%.

Dickens, G.R. and Quinby-Hunt, M.S., 1994, Methane hydrate stability in seawater, *Geophysical Research Letters*, v. 21(19), p. 2115–2118.

Experimental data are presented for methane hydrate stability conditions in seawater (S ~ 33.5‰). For the pressure range of 2.75–10.0 MPa, at any given pressure, the dissociation temperature of methane hydrate is depressed by approximately –1.1 °C relative to the pure methane-pure water system. These experimental results are consistent with previously reported thermodynamic predictions and experimental results obtained with artificial seawater. Collectively these results provide a minimum constraint concerning depth ranges over which methane hydrate is stable in the oceanic environment.

Dickens, G.R. and Quinby-Hunt, M.S., 1997, Methane Hydrate Stability in Pore Water: A Simple Theoretical Approach for Geophysical Applications, *Journal of Geophysical Research*, v. 102, p. 773–783.

Geophysicists have recently expressed an interest in understanding how pore water composition affects CH₄ hydrate stability conditions in the marine environment. It has previously been shown in the chemical engineering literature that CH₄ hydrate stability conditions in electrolyte solutions are related to the activity of water (a_w). Here we present additional experimental data in support of this relationship and then use the relationship to address issues relevant to geophysicists. Pressure and temperature conditions of CH₄ hydrate dissociation were determined for 10 solutions containing variable concentrations of Cl[–], SO₄^{2–}, Br[–], Na⁺, K⁺, Mg²⁺, NH₄⁺, and Cu²⁺. The reciprocal temperature offset of CH₄ hydrate dissociation between the CH₄-pure water system and each of these solutions (and for other electrolyte solutions in literature) is directly related to the logarithm of the activity of water ($\ln a_w$). Stability conditions for CH₄ hydrate in any pore water system therefore can be predicted simply and accurately by calculating $\ln a_w$. The effect of salinity variation and chemical diagenesis on CH₄ hydrate stability conditions in the marine environment can be evaluated by determining how these processes affect $\ln a_w$ of pore water.

Dillon, W.P.; Myung, W.L.; Fehllhaber, K., and Coleman, D.F., 1999, Gas Hydrates on the Atlantic Continental Margin of the United States—Controls on Concentration, The Future of Energy Gases, U.S. Geological Survey Professional Paper 1570, p. 313–330.

Large volumes of gas hydrates exist within ocean-floor deposits at water depths exceeding about 300 to 500 m. They cement a surface layer of sediments as much as about 1,000 m thick, limited at its base by increasing temperature. Gas hydrates are identified by drilled

samples and by their characteristic responses in seismic reflection profiles. These seismic responses include, at the base of the hydrate-cemented surface layer, a marked velocity decrease and a sea-floor-parallel reflection (known as the bottom-simulating reflection, or BSR) and, within the hydrate-cemented layer, a reduction in amplitude of seismic reflections (known as blanking), which is apparently caused by cementation of strata. By using seismic-reflection data we have mapped the volume of hydrate and thickness of the hydrate-cemented layer off the U.S. East Coast. Concentrations of gas hydrate are located at sites of present or past rapid deposition of sediments and at a linear group of diapirs and associated faults. The sources of gas at these concentrations are probably bacterial generation of methane at the locations of rapid deposition, and possibly the migration of deep, thermogenic gas up faults near diapirs. The thickness of the gas-hydrate layer decreases markedly at landslide scars, possibly due to breakdown of hydrate resulting from pressure reduction caused by removal of sediment by the slide. Gas traps appear to exist where a seal is formed by the gas-hydrate-cemented layer. Such traps are observed (1) where the sea floor forms a dome, and therefore the bottom-parallel, hydrate-cemented layer also forms a dome; (2) above diapirs, where the greater thermal conductivity of salt creates a warm spot and salt ions act as antifreeze, both effects resulting in a local shallowing of the base of the hydrate; and (3) at locations where strata dip relative to the sea floor, and the updip regions of porous strata are sealed by the gas-hydrate-cemented layer to form a trap. In such situations the gas in the hydrate-sealed trap, as well as the gas that forms the hydrate, may become a resource.

Dvorkin, J. and Nur, A., 1999, Rock Physics for Characterization of Gas Hydrates, The Future of Energy Gases, U.S. Geological Survey Professional Paper 1570, p. 293–298.

Our theoretical and experimental results indicate that even small amounts of intergranular cementation can dramatically increase the stiffness of a granular material if the cement is placed around grain-to-grain contacts. This finding can explain the seismically discovered phenomenon of bottom-simulating-reflectors (BSR's): the gas-hydrate cementation above a reflector acts to strongly increase the elastic moduli of the rock, an effect that results in strong reflections at the base of a hydrated zone, and muted reflections at natural lithological boundaries within the zone.

Englezos, P. and Bishnoi, P.R., 1988, Prediction of Gas Hydrate Formation Conditions in Aqueous Electrolyte Solutions, *AIChE Journal*, v. 34, p. 1718–1721

Englezos, P. and Hall, S., 1994, Phase Equilibrium Data on Carbon Dioxide Hydrate in the Presence of Electrolytes, Water Soluble Polymers and Montmorillonite, *The Canadian Journal of Chemical Engineering*, v. 72, p. 887–893.

Equilibrium formation conditions for carbon dioxide hydrate were measured in pure water and in aqueous polymer and electrolyte solutions. The solutions that were used include: polyethylene oxide, partially (10 and 90 percent) hydrolyzed polyacrylamide, sodium chloride and calcium chloride. Experiments with solutions containing both electrolyte and polymers were also performed. It was found that the electrolytes exhibited a substantial

inhibiting effect whereas the polymers only slightly altered the equilibrium hydrate formation conditions. The measured equilibrium formation pressures were compared with the predictions from existing hydrate equilibria methods and were found to be in good agreement. The effect of montmorillonite was also studied and it was found that it did not affect the equilibrium hydrate formation conditions. A total of 101 experimental measurements are reported.

Field, M.E. and Kvenvolden, K.A., 1985, Gas hydrates on the northern California continental margin, *Geology*, v. 13, p. 517–520.

The inner continental margin of northern California is underlain by a well-defined and extensive acoustic reflector that crosses other reflectors and mimics the surface of the sea floor. This bottom-simulating reflector (BSR) lies at a typical subsurface depth of about 250 m and has been mapped continuously beneath the Klamath plateau and upper slope (water depths of 800 to 1200 m) for a distance of more than 130 km; it covers an area of at least 3000 km². Limited data show that the BSR extends northward into Oregon and seaward at least to the base of the slope (3000 m).

The water depths, subsurface depths, and pervasive nature of the BSR all suggest that it represents the base of a natural-gas hydrate. Using standard phase boundary diagrams for hydrate stability, we estimate the local geothermal gradient within the gas hydrate to be about 55°C/km. This value is higher than that of most subduction margins and may be a result of the youthfulness of the subducting oceanic crust. This acoustically inferred gas hydrate is the first to be mapped on the western conterminous United States continental margin.

Galimov, E.M. and Shabaeva, I.J., 1993, Carbon Isotope Composition of CH₄ and CO₂ in Sediments of the Middle American Trench, *The Future of Energy Gases*, U.S. Geological Survey Professional Paper 1570, v. 84, p. 693–694

Handa, Y.P. and Stupin, D., 1992, Thermodynamic Properties and Dissociation Characteristics of Methane and Propane Hydrates in 70-Å-Radius Silica Gel Pores, *Journal of Physical Chemistry*, v. 96, p. 8599–8603.

The pressure-temperature profiles for the hydrate-ice-gas and hydrate-liquid water-gas equilibria were measured for methane and propane hydrates in 70-Å-radius silica gel pores. In both cases, the equilibrium pressures were 20–100% higher than those for the bulk hydrates. The dissociation characteristics of the gas hydrates in pores were also studied calorimetrically by heating the hydrates under about zero pressure from 100 K to room temperature. It was found that after the initial dissociation into ice and gas the hydrate became totally encapsulated among the pore walls and the ice caps formed at the pore openings. The hydrate thus trapped in the interior of the pore remained stable up to the melting point of pore ice. These results are similar to those obtained in our previous studies on the bulk hydrates which are also stabilized by a shielding layer of ice. However, the apparent increase in the stability of the pore hydrates was found to be much larger than that

of the bulk hydrates. The composition of methane hydrate in 70-Å pores was determined to be $\text{CH}_4 \cdot 5.94\text{H}_2\text{O}$, and its heat of dissociation into pore water and gas, obtained calorimetrically, was $45.92 \text{ kJ mol}^{-1}$; the corresponding values in the bulk phase are 6.00 and $54.19 \text{ kJ mol}^{-1}$, respectively.

Haq, B.U., 1998, Gas Hydrates: Greenhouse Nightmare? Energy Panacea or Pipe Dream?, *GSA Today*, v. 8, p. 2–6.

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}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 low-stands. 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.

Hesse, R. and Harrison, W.E., 1981, Gas hydrates (clathrates) causing pore-water freshening and oxygen isotope fractionation in deep-water sedimentary sections of terrigenous continental margins, *Earth and Planetary Science Letters*, v. 55, p. 453–462.

The occurrence of gas hydrates in deep-water sections of the continental margins predicted from anomalous acoustic reflectors on seismic profiles has been confirmed by recent deep-sea drilling results. On the Pacific continental slope off Guatemala gas hydrates were brought up for the first time from two holes (497, 498A) drilled during Leg 67 of the DSDP in water depths of 2360 and 5500 m, respectively. The hydrates occur in organic matter-rich Pleistocene to Miocene terrigenous sediments. In the hydrate-bearing zone a marked decrease in interstitial water chlorinities was observed starting at about 10–20 m subbottom depth. Pore waters at the bottom of the holes (near 400 m subbottom) have as little as half the chlorinity of seawater (i.e. 9‰). Similar, but less pronounced, trends were observed during previous legs of the DSDP in other hydrate-prone segments of the continental margins where recharge of fresh water from the continent can be excluded (e.g. Leg 11). The crystallization of hydrates, like ice, excludes salt ions from the crystal structure. During

burial the dissolved salts are separated from the solids. Subsidence results in a downward motion of the solids (including hydrates) relative to the pore fluids. Thawing of hydrates during recovery releases fresh water which is remixed with the pore fluid not involved in hydrate formation. The volume of the latter decreases downhole thus causing downward decreasing salinity (chlorinity). Hydrate formation is responsible for oxygen isotope fractionation with ^{18}O -enrichment in the hydrate explaining increasingly more positive $\delta^{18}\text{O}$ values in the pore fluids recovered (after hydrate dissociation) with depth.

Jenner, K.A.; Dallimore, S.R.; Clark, I.D.; Pare, D., and Medioli, B.E., 1999, Sedimentology of gas hydrate host strata from the JAPEX/JNOC/GSC Mallik 2L-38 gas hydrate research well, *in* Scientific Results from JAPEX/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, Northwest Territories, Canada, Geological Survey of Canada, Ontario, Canada v. 544, p. 57–68.

A detailed sedimentological program has been conducted on gas-hydrate-bearing core samples from the JAPEX/JNOC/GSC Mallik 2L-38 gas hydrate research well. Three structurally and texturally distinct sedimentary facies are identified. Facies Csc (952.2–926.5 m) is a weakly bioturbated, clayey silt interbedded with fissile coal and silty sand. Facies Sg (926.5–908.5 m) is comprised of interbedded, fining-upward successions of matrix-supported gravel to pebbly sand and fine sand. A dolomite-cemented sandstone (926.5–925 m) forms a distinct basal subfacies (Sst). Facies Ss (908.5–886.2 m) is a fine-to medium-grained sand interbedded with gravel which fines upward to fine-grained sand with a gradational increase in silt content. The Kugmallit-Mackenzie Bay sequence boundary is interpreted to occur at the base of facies Sg. In situ and self-preserved gas hydrate occurred mainly in the sands and gravels of the Sg and Ss facies. The dolomite-cemented sandstone (subfacies Sst) may be related to complementary geochemical environments resulting from the formation of authigenic pyrite and solute exclusion related to gas hydrate growth within facies Sg.

Judd, A.G. and Hovland, M., 1992, The evidence of shallow gas in marine sediments, *Continental Shelf Research*, v. 12(10), p. 1081–1095.

Evidence of the presence of shallow gas is considered here under the following categories: seismic sub-bottom signatures, geochemical signatures and indirect features on and above the seabed. The various forms of evidence indicate that gas has migrated and may still be migrating through the seabed, and therefore implies that gas within sediments is mobile.

Katsube, T.J.; Dallimore, S.R.; Uchida, T.; Jenner, K.A.; Collett, T.S., and Connell, S., 1999, Petrophysical environment of sediments hosting gas hydrate, JAPEX/JNOC/GSC Mallik 2L-38 gas hydrate research well, *in* Scientific Results from JAPEX/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, Northwest Territories, Canada, Geological Survey of Canada, Ontario, Canada v. 544, p. 109–124.

A petrophysical study has been performed on mudstone and sandstone samples from depths of 880–950 m to determine the petrophysical controls on gas hydrate distribution in the

sedimentary sequence at the JAPEx/JNOC/GSC Mallik 2L-38 well site, Northwest Territories, Canada. Within the cored interval of the Mallik 2L-38 well gas hydrate is hosted in two sandstone horizons with overlying and underlying mudstone horizons, with minor gas hydrate concentrations within some mudstone formations.

Results indicate that, although the interbedded mudstone units have relatively high porosities (24–30%) and are at relatively shallow depths, they have a well developed framework-supported texture, probably due to high silt and sand content (56–78 weight per cent), and a maximum burial depth greater than present. Regardless of this, the minor matrix content (13–25 weight per cent) controls the fluid transport characteristics, resulting in extremely low mudstone permeability sections (2×10^{-21} m to 2×10^{-19} m²). There are indications that these low permeabilities and the storage pore sizes contribute to the gas hydrate distribution.

Kayen, R.E. and Lee, H.J., 1993, Slope Stability in Regions of Sea-Floor Gas Hydrate: Beaufort Sea Continental Slope, USGS Bulletin 2002, p. 97–103

Khairkhah, D.; Pooladi-Darvish, M.; Bishnoi, P.R.; Collett, T.S., and Dallimore, S.R., 1999, Production potential of the Mallik field reservoir, *in* Scientific Results from JAPEx/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, Northwest Territories, Canada, Geological Survey of Canada, Ontario, Canada v. 544, p. 377–390.

Immense volumes of naturally occurring gas hydrate in different parts of the world, onshore and offshore, have encouraged the belief that gas hydrate in the next century may become a viable energy resource. Various issues need to be resolved to convert gas hydrate from an energy resource to an energy reserve of real commercial value. The production capability of a gas hydrate reservoir and the gas production technique that could be utilized should be addressed through geological and petrophysical studies, well-production tests and reservoir simulation. To make the simulation of practical value, the controlling mechanisms of fluid flow, kinetics, and heat transfer should be incorporated in the model.

The Mallik gas hydrate accumulation in the Mackenzie Delta has exhibited promising potential to be considered a gas reserve through the assessments made of the Mallik L-38 and 2L-38 wells. The data available from both wells and the results of production tests in JAPEx/JNOC/GSC Mallik L-38 gas hydrate research well accommodate basic requirements for comprehensive modelling of the reservoir and production of gas from the in situ gas hydrate through various methods.

Kurita, H. and Uchida, T., 1999, Dinoflagellate cysts from the JAPEx/JNOC/GSC Mallik 2L-38 gas hydrate research well, *in* Scientific Results from JAPEx/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, Northwest Territories, Canada, Geological Survey of Canada, Ontario, Canada v. 544, p. 77–80.

Sparse occurrences of organic-walled dinoflagellate cysts were recorded from the JAPEX/JNOC/GSC Mallik 2L-38 gas hydrate research well, Mackenzie Delta area, Northwest Territories, Canada. Some of the recorded taxa are indicative of a Paleocene-Eocene age, while others are considered to be of Cretaceous origin. Because the deepest parts of the section are correlated to the Oligocene Kugmallit Sequence, all the dinoflagellate cysts are interpreted to be reworked. According to this interpretation, the total absence of in situ marine dinoflagellate cysts suggests that the studied samples were deposited under nonmarine conditions, most likely within a fluvial system.

Kvenvolden, K.A.; Claypool, G.E.; Thirekeld, C.N., and Sloan, E.D., 1984, Geochemistry of a natural occurring massive marine gas hydrate, *Org. Geochemistry*, v. 6, p. 703–713.

During Deep Sea Drilling Project (DSDP) Leg 84 a core 1 m long and 6 cm in diameter of massive gas hydrate was unexpectedly recovered at Site 570 in upper slope sediment of the Middle America Trench offshore of Guatemala. This core contained only 5–7% sediment, the remainder being the solid hydrate composed of gas and water. Samples of the gas hydrate were decomposed under controlled conditions in a closed container maintained at 4°C. Gas pressure increases and asymptotically approached the equilibrium decomposition pressure for an ideal methane hydrate, $\text{CH}_4 \cdot 5\text{--}3/4\text{H}_2\text{O}$, of 3930 kPa and approached to this pressure after each time gas was released, until the gas hydrate was completely decomposed.

The gas evolved during hydrate decomposition was 99.4% methane, ~0.2% ethane, and ~0.4% CO_2 . Hydrocarbons from propane to heptane were also present, but in concentrations of less than 100 p.p.m. The carbon-isotopic composition of methane was 41 to 44 permil (‰), relative to PDB standard. The observed volumetric methane/water ratio was 64 or 67, which indicates that before it was stored and analyzed, the gas hydrate probably had lost methane. The sample material used in the experiments was likely a mixture of methane hydrate and water ice.

Formation of this massive gas hydrate probably involved the following processes: (i) upward migration of gas and its accumulation in a zone where conditions favored the growth of gas hydrates, (ii) continued, unusually rapid biological generation of methane, and (iii) release of gas from water solution as pressure decreased due to sea level lowering and tectonic uplift.

Kvenvolden, K.A.; McDonald, T.J., and Thomas, J., 1985, Gas Hydrates of the Middle America Trench, *Initial Reports of the Deep Sea Drilling Project*, v. 84, p. 667–682.

On DSDP Leg 84, gas hydrates were found at three sites (565, 568, and 570) and were inferred, on the basis of inorganic and organic geochemical evidence, to be present at two sites (566 and 569); no evidence for gas hydrates was observed at Site 567. Recovered gas hydrates appeared as solid pieces of white, icelike material occupying fractures in mudstone or as coarse-grained sediment in which the pore space exhibited rapid outgassing. Also a 1.05-m-long core of massive gas hydrate was obtained at Site 570. Downhole logging

indicated that this hydrate was actually 3 to 4 m thick. Measurements of the amount of methane released during the decomposition of these recovered samples clearly showed that gas hydrates had been found. The distribution of evolved hydrocarbon gases indicated that Structure I gas hydrates were present because of the apparent inclusion of methane and ethane and exclusion of propane and higher molecular weight gases. The water composing the gas hydrates was fresh, having chlorinities ranging from 0.5 to 3.2‰. At Sites 565, 568, and 570, where gas hydrates were observed, the chlorinity of pore water squeezed from the sediment decreased with sediment depth. The chlorinity profiles may indicate that gas hydrates can often occur finely dispersed in sediments but that these gas hydrates are not recovered because they do not survive the drilling and recovery process. Methane in the gas hydrates found on Leg 84 was mainly derived *in situ* by biogenic processes, whereas the accompanying small amounts of ethane likely resulted from low-temperature diagenetic processes. Finding gas hydrates on Leg 84 expands observations made earlier on Leg 66 and particularly Leg 67. The results of all of these legs show that gas hydrates are common in landward slope sediments of the Middle American Trench from Mexico to Costa Rica.

Kvenvolden, K.A., 1988, Methane Hydrate—A Major Reservoir of Carbon in the Shallow Geosphere?, *Chemical Geology*, v. 71, p. 41–51.

Methane hydrates are solids composed of rigid cages of water molecules that enclose methane. Sediment containing methane hydrates is found within specific pressure-temperature conditions that occur in regions of permafrost and beneath the sea in outer continental margins. Because methane hydrates are globally widespread and concentrate methane within the gas-hydrate structure, the potential amount of methane present in the shallow geosphere at subsurface depths of $< \sim 2000$ m is very large. However, estimates of the amount are speculative and range over about three orders of magnitude, from $2 \cdot 10^3$ to $4 \cdot 10^6$ Gt (gigatons = 10^{15} g) of carbon, depending on the assumptions made. The estimate I favor is $\sim 1 \cdot 10^4$ Gt of carbon.

The estimated amount of organic carbon in the methane-hydrate reservoir greatly exceeds that in many other reservoirs of the global carbon cycle - for example, the atmosphere (3.6 Gt); terrestrial biota (830 Gt); terrestrial soil, detritus and peat (1960 Gt); marine biota (3 Gt); and marine dissolved materials (980 Gt). In fact, the amount of carbon may exceed that in all fossil fuel deposits ($5 \cdot 10^3$ Gt). Because methane hydrates contain so much methane and occur in the shallow geosphere, they are of interest as a potential resource of natural gas and as a possible source of atmospheric methane released by global warming. As a potential resource, methane hydrates pose both engineering and production problems. As a contributor to a changing global climate, destabilized methane hydrates, particularly those in shallow, nearshore regions of the Arctic Ocean, may have some effect, but this effect will probably be minimal, at least during the next 100 years.

Kvenvolden, K.A. and Grantz, A., 1990, Gas hydrates of the Arctic Ocean region, *The Geology of North America*, v. 1(28), p. 539–549.

Sediments of the Arctic Ocean region may trap enormous quantities of natural gas in and beneath gas hydrates. These solid, ice-like substances, composed mainly of methane and water, are found in two distinct environments: (1) offshore, in sediment of the outer continental margin, and (2) onshore, in and below areas of thick permafrost. Most offshore gas-hydrate occurrences have been inferred from marine seismic-reflection records where an anomalous acoustic reflector correlates with the base of the gas-hydrate zone. Onshore, most gas-hydrate occurrences have been inferred from well-log responses. In only a few cases have gas hydrates actually been sampled. This chapter focuses on the known and inferred gas hydrates of the North American Arctic and estimates the amount of methane that may be associated with sediments in the Arctic Basin.

Kvenvolden, K.A., 1993, A Primer on Gas Hydrates, The Future of Energy Gases, U.S. Geological Survey Professional Paper 1570, p. 279–291.

Natural-gas hydrates are ice-like mixtures of gas and water in which the gas molecules, mainly methane, are trapped within a framework of cages, that is within a clathrate, of water molecules. Gas hydrates are stable under pressure and temperature conditions that occur worldwide in two distinct locations: (1) in polar regions, where temperatures are cold enough for onshore and offshore permafrost to be present, and (2) in offshore sediment of outer continental and insular margins, where there are cold bottom-water temperatures and deep waters, exceeding 300 to 500 m. Samples of gas hydrates have been recovered in 14 areas of the world, and geophysical and geochemical evidence for them has been found in about 30 other areas. Many oceanic occurrences of gas hydrates are inferred, mainly on the basis of the appearance on marine seismic-reflection profiles of a pronounced bottom-simulating reflection, commonly called a BSR. This reflection is inferred to coincide with the base of the gas-hydrate stability field. BSR's indicating gas hydrates are useful in estimating geothermal gradients and heat flow in oceanic sediments and, in conjunction with other seismic information, in assessing the amount of methane within and below the gas-hydrate interval. Wire-line well logs also provide a basis for estimating the quantity of methane. Most methane in gas hydrates is microbial in origin, determined on the basis of molecular and isotopic compositions; however, thermogenic methane hydrates are known from the Gulf of Mexico and the Caspian Sea. During gas-hydrate formation, salt ions are excluded from the crystal structure; therefore pore-water freshening is observed with gas-hydrate occurrence. The total amount of methane in gas hydrates around the world likely exceeds 10^{19} g of methane carbon ($\sim 20 \times 10^{15}$ m³ of methane gas = $\sim 7 \times 10^5$ trillion cubic feet (Tcf)). Because gas hydrates represent a large amount of methane within 2,000 m of the Earth's surface, they are considered to be an unconventional, potential source of fossil fuel. Because of unsolved technological problems in producing methane from gas hydrates, however, wide-scale recovery of methane from these substances probably will not take place until sometime in the 21st century.

Kvenvolden, K.A. and Collett, T.S., 1999, Permafrost and Gas Hydrates as Possible Sources of Atmospheric Methane at High Latitudes, Proceedings of the U.S. Geological Survey Global Change Forum, p. 92–93

Lee, M.W. and Collett, T.S., 1999, Amount of gas hydrate estimated from compressional- and shear-wave velocities at the JAPEx/JNOC/GSC Mallik 2L-38 gas hydrate research well, *in* Scientific Results from JAPEx/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, Northwest Territories, Canada, Geological Survey of Canada, Ontario, Canada v. 544, p. 313–322.

The amount of in situ gas hydrate concentrated in the sediment pore space at the JAPEx/JNOC/GSC Mallik 2L-38 gas hydrate research well was estimated by using compressional-wave (P-wave) and shear-wave (S-wave) downhole log measurements. A weighted equation developed for relating the amount of gas hydrate concentrated in the pore space of unconsolidated sediments to the increase of seismic velocities was applied to the acoustic logs with porosities derived from the formation density log. A weight of 1.56 ($W = 1.56$) and the exponent of 1 ($n = 1$) provided consistent estimates of gas hydrate concentration from the S-wave and the P-wave logs. Gas hydrate concentration is as much as 80% in the pore spaces, and the average gas hydrate concentration within the gas-hydrate-bearing section from 897 m to 1110 m (excluding zones where there is no gas hydrate) was calculated at 39.0% when using P-wave data and 37.8% when using S-wave data.

Lorenson, T.D. and Kvenvolden, K.A., 1998, Methane in coastal sea water, sea ice, and bottom sediments, Beaufort Sea, Alaska, Internet:
http://geochange.er.usgs.gov/pub/gas_hydrates/OFR_95-70/Core/meta/report.html v. 95-70, p. 1–13.

This report summarizes data acquired from 1990 to 1994 for the gas-hydrate portion of the USGS project “Permafrost and gas hydrate as possible sources of methane” of the USGS Global Change and Climate History program. The objective of this project has been to test the hypothesis that gas hydrate deposits of the Beaufort Sea continental shelf are destabilized by the $\sim 10^{\circ}\text{C}$ temperature increase that has resulted from the Holocene transgression of the Arctic Ocean. To test this idea we have selected an area off the north coast of Alaska centered on Harrison Bay. We have measured the concentration of methane in surficial sediments, in the water column when ice is present and absent, and in seasonal sea ice. Our results show that more methane is present in the water when ice is present than when ice is absent, and that methane is also present within the ice itself, often at higher concentrations than in the water. Thus the Beaufort Sea shelf of Alaska is a seasonal source of methane. The primary source of this methane has not yet been defined, but gas hydrate is a reasonable candidate.

Lorenson, T.D.; Whiticar, M.J.; Waseda, A.; Dallimore, S.R., and Collett, T.S., 1999, Gas composition and isotopic geochemistry of cuttings, core, and gas hydrate from the JAPEx/JNOC/GSC Mallik 2L-38 gas hydrate research well, *in* Scientific Results from JAPEx/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, Northwest Territories, Canada, Geological Survey of Canada, Ontario, Canada v. 544, p. 143–163.

Molecular and isotopic composition of gases from the JAPEx/JNOC/GSC Mallik 2L-38 gas hydrate research well demonstrate that the in situ gases can be divided into three zones composed of mixtures of microbial and thermogenic gases. Sediments penetrated by the well are thermally immature; thus the sediments are probably not a source of thermogenic gas. Thermogenic gas likely migrated from depths below 5000 m. Higher concentrations of gas within and beneath the gas hydrate zone suggest that gas hydrate is a partial barrier to gas migration. Gas hydrate accumulations occur wholly within zone 3, below the base of permafrost. The gas in gas hydrate resembles, in part, the thermogenic gas in surrounding sediments and gas desorbed from lignite. Gas hydrate composition implies that the primary gas hydrate form is Structure I. However, Structure II stabilizing gases are more concentrated and isotopically partitioned in gas hydrate relative to the sediment hosting the gas hydrate, implying that Structure II gas hydrate may be present in small quantities.

MacDonald, G.J., 1990, Role of Methane Clathrates in Past and Future Climates, *Climatic Change*, v. 16, p. 247–281.

Methane clathrates are stable at depths greater than about 200 m in permafrost regions and in ocean sediments at water depths greater than about 250 m, provided bottom waters are sufficiently cold. The thickness of the clathrate stability zone depends on surface temperature and geothermal gradient. Average stability zone thickness is about 400 m in cold regions where average surface temperatures are below freezing, 500 m in ocean sediments, and up to 1,500 m in regions of very cold surface temperature ($< -15^{\circ}\text{C}$) or in the deep ocean. The concentration of methane relative to water within the zone of stability determines whether or not clathrate will actually occur. The geologic setting of clathrate occurrences, the isotopic composition of the methane, and the methane to ethane plus propane ratio in both the clathrates and the associated pore fluids indicate that methane in clathrates is produced chiefly by anaerobic bacteria. Methane occurrences and the organic carbon content of sediments are the bases used to estimate the amount of carbon currently stored as clathrates. The estimate of about 11,000 Gt of carbon for ocean sediments, and about 400 Gt for sediments under permafrost regions is in rough accord with an independent estimate by Kvenvolden of 10,000 Gt.

The shallowness of the clathrate zone of stability makes clathrates vulnerable to surface disturbances. Warming by ocean flooding of exposed continental shelf, and changes in pressure at depth, caused, for example, by sea-level drop, destabilize clathrates under the ocean, while ice-cap growth stabilizes clathrates under the ice cap. The time scale for thermal destabilization is set by the thermal properties of sediments and is on the order of thousands of years. The time required to fix methane in clathrates as a result of surface cooling is much longer, requiring several tens of thousands of years. The sensitivity of clathrates to surface change, the time scales involved, and the large quantities of carbon stored as clathrate indicate that clathrates may have played a significant role in modifying the composition of the atmosphere during the ice ages. The release of methane and its subsequent oxidation to carbon dioxide may be responsible for the observed swings in atmospheric methane and carbon dioxide concentrations during glacial times. Because methane and carbon dioxide are strong infrared absorbers, the release and trapping of

methane by clathrates contribute strong feedback mechanisms to the radiative forcing of climate that results from earth's orbital variations.

Majorowicz, J.A. and Smith, S.L., 1999, Review of ground temperatures in the Mallik field area: a constraint to the methane hydrate stability, *in* Scientific Results from JAPEx/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, Northwest Territories, Canada, Geological Survey of Canada, Ontario, Canada v. 544, p. 45–56.

Analysis of data from 32 industrial exploration wells in the Mallik field and surrounding area in the Mackenzie Delta-Beaufort Sea region allowed construction of temperature-depth profiles using regional heat-flow values, temperature at the base of ice-bearing permafrost, and models of thermal conductivity with depth. An analysis of the stability conditions for methane hydrate showed that it is stable in the Mallik field area and that the depth to the base of the methane hydrate stability zone can be as deep as 1500 ± 100 m in areas of thick permafrost. The depth to the base of the methane hydrate stability zone, calculated in this study using reconstructed temperature-depth profiles, was found in a majority of the wells to be 50–150 m deeper than that previously determined using linear temperature profiles and a constant thermal conductivity with depth.

Makogon, Y.F., 1988, Gas-Hydrate Accumulations and Permafrost Development, Proceedings of the 5th International Conference on Permafrost, Trondheim, Norway, p. 95–101.

The existence of natural gas-hydrate accumulation is related not only to a considerable increase in hydrocarbon resources but also to the necessity of serious study of “dangerous” properties of hydrates and hydrate-saturated rocks and their close control during the engineering development of HFZ both on land and in oceans.

The processes of phase transition of gas-water systems under natural conditions are accompanied by a considerable change in thermoregime of section and specific volume of gas and water during hydrate formation and degradation. The value of change in phase specific volume leads, on the one hand, to a sharp increase in stresses in engineering constructions which exceed the critical stresses and, on the other hand, to a sharp decrease in load capacity of hydrate-containing rocks. These features should be kept in mind while developing the hydrate distribution regions both on land and, especially, in ocean.

Mason, R.; Bloom, N.; Capellino, S.; Gill, G.; Benoit, J., and Dobbs, C., 1998, Investigation of Porewater Sampling Methods for Mercury and Methylmercury, Environmental Science Technology, v. 32, p. 4031–4040

Matsumoto, R.; Paull, C.; Wallace, P.; Fox, P.; Baldauf, J., and Francis, T., 1996, Gas Hydrate Sampling on the Blake Ridge and Carolina Rise, Ocean Drilling Program Leg 164 Preliminary Report: Texas A&M University Research Park.

Leg 164 was devoted to refining our understanding of the amounts and in situ characteristics of natural gas hydrate stored in marine sediments. Drilling on the Blake

Ridge at Sites 994, 995, and 997 documented that finely disseminated gas hydrate occupies a minimum of 1% of the sedimentary section between 200 and 450 m below seafloor (mbsf). Some solid gas hydrate nodules also occur. Free gas is dispersed throughout a zone a few hundred meters thick below the gas hydrate-bearing zone. Coupled with geophysical data indicating that sedimentary gas hydrate occurs throughout a laterally extensive portion of the Blake Ridge, the results of Leg 164 confirm that enormous amounts of methane are contained in these sediments.

Sites 994, 995, and 997 were drilled to 700-750 mbsf on the Blake Ridge and penetrated through the predicted depth of the bottom-simulating reflector (BSR) into the sediments below. The Blake Ridge sediments consist largely of a monotonous sequence of nanofossil-rich clays that were deposited from contour currents at rates varying from 40 m/m.y. in the Pleistocene to 150–350 m/m.y. for the Miocene-Pliocene sequences. Minimal compositional or facies changes occur near the depth of the BSR (~450 m). Cores from all three sites are very gassy and underwent vigorous expansion, which resulted in low recovery. Some nodules of hydrate and one massive gas hydrate zone greater than 30 cm thick were recovered. Decomposition experiments on gas hydrate samples yielded volumetric ratios of gas to water of 130–160, and demonstrated that the gas filling the hydrates was ~99% methane. As anticipated, the ephemeral nature of gas hydrate under surface conditions made sampling difficult. Therefore, emphasis was placed on proxy sampling and downhole tool measurements that allow the in situ conditions of the gas hydrate to be reconstructed.

Closely spaced pore-water samples were taken because interstitial water chloride concentrations can be used to make quantitative estimates of the amount of gas hydrate present in the sediment before coring. During gas hydrate formation, water and methane are taken out of the pore waters, leaving the residual pore waters increasingly saline. Over time, locally elevated chloride concentrations associated with gas hydrate formation diffuse away. When gas hydrate in sediments decomposes during drilling and core recovery, water and gas are released back into the pore space, freshening the pore waters. Pore-water profiles from Sites 994, 995, and 997 are very similar and indicate three distinct chloride concentration zones: (1) a zone of progressive freshening with depth to ~200 mbsf, (2) a zone that extends to the approximate depth of the BSR (~450 mbsf) of highly variable chloride values characterized by local anomalously fresh values, and (3) a zone of nearly constant chloride beneath the BSR. These anomalies are interpreted to indicate that a minimum of 1% of the sedimentary section within the zone from 200 to 450 mbsf is filled with gas hydrate.

An unprecedented level of success was achieved using the pressure core sampler (PCS), a device that returns a short core to the surface at formation pressures so that gases are not lost. Gas volumes captured by the PCS indicate that gas concentrations are grossly in excess of gas saturation, thus demonstrating that free gas exists beneath the BSR. Gases also occur throughout the sedimentary section below.

Vertical seismic profiles were used to locate the precise depth of the BSR and indicated no significant lateral changes in velocity above the BSR. However, velocities as low as 1400 m/s were measured beneath the BSR at Site 997. Well-logs disclosed distinct zones of higher electrical resistivity and velocity that coincided with chloride anomaly zones indicative of gas hydrates. Preliminary well-log analysis of the resistivity data indicate that gas hydrate occupies 3%–5% of sediment volume throughout this zone. A minimum of 13 in situ temperature measurements were made in each hole to establish temperature gradients. Extrapolation of these thermal gradients to depth makes it possible to estimate the maximum depth at which gas hydrate is stable, based on experimentally-determined phase boundaries. The results indicate that the base of gas hydrate stability is ~30 m (Site 997) to ~100 m (Site 994) below the observed BSR depth.

Max, M.D. and Lowrie, A., 1996, Oceanic Methane Hydrates: A “Frontier” Gas Resource, *Journal of Petroleum Geology*, v. 19(1), p. 41–56.

Methane hydrates are ice-like compounds consisting of natural gas (mainly methane) and water, whose crystal structure effectively compresses the methane: each cubic meter of hydrate can yield over 150 cu. m of methane. Hydrates “cement” sediments and impart considerable mechanical strength; they fill porosity and restrict permeability. Both biogenic and thermogenic methane have been recovered from hydrates.

Hydrates occur in permafrost regions (including continental shelves), and are stable in ocean-floor sediments below water depths of about 400 m in the “Hydrate Stability Zone” (HSZ). This is a surface-parallel zone of thermodynamic equilibrium that extends down from the sediment surface to a depth determined by temperature, pressure and local heat flow. Methane and water are stable below the HSZ.

Although the economic recovery of hydrates has taken place in arctic regions, oceanic hydrates offer far greater potential as an energy resource. A variety of traps for methane gas can be formed by oceanic hydrates. In addition to the gas within the hydrates themselves, simple gas traps in closures beneath the HSZ in the vicinity of bathymetric highs, and complex traps involving both hydrate and structural/stratigraphic components, have been observed.

It has been estimated that at least twice as much combustible carbon occurs associated with methane hydrates as in all other fossil fuels on Earth. The evaluation of methane in, and associated with, oceanic hydrates therefore constitutes a major energy exploration frontier.

McNeil, D.H., 1999, Micropaleontology of the JAPEX/JNOC/GSC Mallik 2L-38 gas hydrate research well, *in* Scientific Results from JAPEX/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, Northwest Territories, Canada, Geological Survey of Canada, Ontario, Canada v. 544, p. 69–75.

Core and cuttings samples from the JAPEX/JNOC/GSC Mallik 2L-38 gas hydrate research well in the Mackenzie Delta have yielded sparse terrestrial microfossils and abundant

reworked Cretaceous foraminifers (silicified) and plant microfossils. No definitely in situ marine microfossils were recovered in the borehole (total depth 1150 m; gas hydrate at 896–1110 m). Cores from 110–118 m and 173–175 m contained terrestrial microfossils including fungi, seeds, insect fragments, and abundant macerated plant fragments typical of the Pliocene-Pleistocene Iperk Sequence in the Mackenzie-Beaufort Basin. Core from 886–951 m and cuttings samples from 670–870 and 960–1140 m yielded reworked algal cysts, seed casings, and megaspores. In addition, cuttings contained reworked Cretaceous agglutinated foraminifers. Core and cuttings samples were also characterized by quartz, chert, brownish-black lignite, coaly fragments, and rare amber. The lithology of the section below 670 m is characteristic of the Oligocene Kugmallit Sequence in the Mackenzie-Beaufort Basin.

Miyairi, M.; Akihisa, K.; Uchida, T.; Collett, T.S., and Dallimore, S.R., 1999, Well-log interpretation of gas-hydrate-bearing formations in the JAPEx/JNOC/GSC Mallik 2L-38 gas hydrate research well, *in* Scientific Results from JAPEx/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, Northwest Territories, Canada, Geological Survey of Canada, Ontario, Canada v. 544, p. 281–293.

Techniques for evaluating subsurface natural gas hydrate were part of the JNOC/GSC/JAPEx joint research project. The physical properties of pure methane hydrate, related to well-log responses, were directly measured and/or calculated based on its physico-chemical properties. A petrophysical model of the pore-filling gas hydrate was built considering the existence of thermally dissociated free gas in the pores of the formation. Tool sensitivity to gas hydrate content was analyzed, and formation resistivity and acoustic transit time were found to show distinct sensitivity. Three practical methods for evaluating gas hydrate content were proposed and were tested to confirm their applicability: 1) the resistivity method, 2) the acoustic-velocity method, and 3) the statistical-inversion-analysis method. The porosity and gas hydrate saturation results calculated from these methods agreed quite well. Thus, reasonable interpretations can be achieved using these methods if the drilling and log measurements are carefully designed, and the zoning and parameter settings are made properly in pore-filling-type gas hydrate occurrences similar to those found in the JAPEx/JNOC/GSC Mallik 2L-38 gas hydrate research well.

Ohara, T.; Dallimore, S.R., and Fercho, E., 1999, Drilling operations, JAPEx/JNOC/GSC Mallik 2L-38 gas hydrate research well, *in* Scientific Results from JAPEx/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, Northwest Territories, Canada, Geological Survey of Canada, Ontario, Canada v. 544, p. 19–29.

The JAPEx/JNOC/GSC Mallik 2L-38 gas hydrate research well, located in the Mackenzie Delta, Northwest Territories, Canada, was completed to 1150 m on March 30, 1998, after 39 days. Operations were undertaken through a collaborative agreement between the Japan National Oil Corporation and the Geological Survey of Canada. Research goals included evaluation of engineering technologies used to drill and core gas-hydrate-bearing strata. Eight coring runs were conducted within the permafrost interval (0–640 m) in a surface hole drilled to 687 m. Subsequently, a 340 mm surface casing was installed and the main hole

was advanced to a depth of 1150 m with 16 coring runs. A cooled ($\sim 2^{\circ}\text{C}$) KCl/polymer drilling mud and Driltreat, a chemical mud additive, successfully stabilized gas hydrate within cores and formation sediments. No serious hole problems, accidents, or mishaps occurred; however, delays caused by adverse weather and mechanical problems caused cancellation of planned production testing. Coring in the main hole was successful, allowing the evaluation of four different core barrels. Gas-hydrate-bearing cores were collected in a variety of sediments between 896 and 952 m.

Premchitt, J.; Rad, N.S.; To, P.; Shaw, R., and James, J.W.C., 1992, A study of gas in marine sediments in Hong Kong, *Continental Shelf Research*, v. 12(10), p. 1251–1264.

During the course of an offshore investigation for sand sources in Hong Kong, seismic reflection profiles revealed areas of acoustic turbidity in Holocene marine sediments. These areas assumed particular significance during a subsequent comprehensive planning study for Hong Kong's new airport. Acoustic turbidity is generally regarded as a possible indicator of gas within sediments, which may have an important effect on the engineering properties of the sediments. To investigate the presence of the gas and to assess its significance, an extensive in situ testing program was initiated. The test utilized the offshore BAT system developed at the Norwegian Geotechnical Institute (NGI) in cooperation with the BAT company in Sweden. This system was considered to be the most direct and reliable means of determining the presence of pore gas. A total of 96 BAT tests were carried out at 11 test sites, at about nine different depths at each site. Test results indicated that some occluded gas bubbles exist in the areas of acoustic turbidity. The free gas was shown to be mainly composed of nitrogen and methane, while carbon dioxide was the dominant dissolved gas. These constituents were considered to have been generated by biogenic degradation of organic matter. No free gas was detected at the control stations where acoustic turbidity had not been observed on seismic records.

Rempel, A.W. and Buffett, B.A., 1997, Formation and accumulation of gas hydrate in porous media, *Journal of Geophysical Research*, v. 102(B5), p. 10151–10164.

Vast quantities of clathrate hydrate are found in the Arctic and in marine sediments along continental margins. The clathrate structure traps enormous volumes of methane gas, which is both a possible source of global climate change and a potential energy resource. The growth rate and spatial distribution of gas hydrate in the shallow sediments are influenced by a variety of interacting physical processes. In order to quantify these processes, we develop mathematical models for hydrate formation in porous media. An analytical model is derived for the idealized problem of hydrate growth in a porous half-space which is cooled on its boundary. Our calculations predict the growth rate of a hydrate layer for a given rate of cooling and show that the volume of hydrate is strongly dependent on the two-phase equilibrium between hydrate and seawater. For a representative phase diagram we find that the volume of hydrate in the layer is less than 1% of the pore volume. Larger volumes of hydrate observed in some locations demand a sustained supply of gas and a long accumulation time. Numerical calculations are used to investigate situations that are more representative of conditions in marine sediments. A simple theoretical expression is derived

for the rate of hydrate accumulation due to advection of methane gas from depth. Using typical estimates of fluid velocities in accretionary environments, we obtain an accumulation rate of 1% of the pore volume in 105 years. The predicted vertical distribution of hydrate is consistent with geophysical inferences from observed hydrate occurrences along the Cascadia margin. Similar distributions can arise from the combined effects of in situ methane production and warming due to ongoing sedimentation. Predicted differences between these two formation models may be detectable in geophysical and geochemical measurements.

Roberston, A., 1996, Mud Volcanism on the Mediterranean Ridge: Initial Results of Ocean Drilling Program Leg 160, *Geology*, v. 24(3), p. 239–424.

Drilling during Ocean Drilling Program Leg 160 (April–May, 1995) revealed important new evidence concerning the internal composition, depositional processes, and age of two mud volcanoes within the Mediterranean Ridge accretionary complex. Holes were drilled at ca. 2000 m water depth on the crest areas, across the flanks of the mud volcanoes, and onto adjacent deep-sea sediments. The main depositional units forming the flanks of both mud volcanoes are debris flows (“mud breccias”) composed of a volumetrically dominant mud matrix, containing clasts of mainly clay, mudstone, siltstone, sandstone, and limestone. More variable muddy, silty, and sandy sediments were recovered from the crestal areas of both volcanoes. The lowest mud-volcano units drilled include well-sorted medium- to coarse-grained sediments, mainly composed of clay, that were deposited partly by turbidity currents. The mud-volcano sediments are associated with background deep-sea sediments that allow dating by using microfossils. The Milano mud volcano is at least 1.75 Ma, and is apparently now dormant, and the Napoli mud volcano started prior to, or during, 1.5–1.2 Ma and is currently active. Pore fluids at Napoli, and to a lesser extent at Milano, indicate the presence of halite of presumed latest Miocene age beneath the volcanoes. Hydrocarbon gas is venting from the crest of the Napoli mud volcano, and gas was also detected on the crest of the Milano mud volcano. Methane hydrates (clathrates) are also inferred to exist beneath the crest of the Milano mud volcano. The mud volcanoes are located above a shallowly dipping subduction zone in an area where the accretionary complex is apparently being thrust northward over a backstop of continental crust, related to initial collision of the African and Eurasian plates. Mud volcanism may have begun when backthrusting punctured a seal of latest Miocene evaporates, allowing the escape of over-pressured materials.

Rowe, M.M. and Gettrust, J.F., 1993, Fine Structure of Methane Hydrate-Bearing Sediments on the Blake Outer Ridge as Determined From Deep-Tow Multichannel Seismic Data, *Journal of Geophysical Research*, v. 98(B1), p. 463–473.

High-resolution, deep-tow multichannel seismic data are used to investigate the detailed structure of sediments containing methane hydrate. These data support thick, laterally extensive layers of methane hydrate-bearing sediment underlain by a bottom simulating reflector (BSR) and spatially discontinuous zones of hydrate within the sediments above the BSR depth where no BSR is present. These data resolve normal faults which extend from the surface through the BSR with apparent offsets of up to 20 m. A phase inversion

identified at the top of the BSR shows that the material immediately beneath the BSR has anomalously low velocity, consistent with a layer of sediment containing free methane gas. The fault offsets along the BSR are consistent with a pressure change of ~200 kPa (~2 bars) across the fault zone.

Ruppel, C., 1997, Anomalously cold temperatures observed at the base of the gas hydrate stability zone on the U.S. Atlantic passive margin, *Geology*, v. 25(8), p. 699–702.

In situ measurements to depths of ~415 m below sea floor in methane hydrate-bearing sediments on the U.S. Atlantic passive margin indicate that temperatures at the bottom simulating reflector (BSR) are anomalously low by 0.5–2.9°C if the BSR marks the base of gas hydrate stability (BGHS). Several hypotheses may explain the occurrence of the BSR at inappropriate pressure-temperature (P-T) conditions. (1) If the BSR does not mark the BGHS, then P-T conditions need not be sufficient to dissociate gas hydrate at this depth. (2) The BSR may lie at non-equilibrium P-T conditions due to incomplete readjustment in response to upper Pleistocene-Holocene climate change. However, the occurrence of the Blake Ridge BSR at an overly shallow depth cannot be easily explained by realistic combinations of pressure-driven deepening (sea-level rise) and temperature-driven shoaling (bottom water temperature changes). (3) The properties of sediments or pore fluids may inhibit the stability of gas hydrate. In particular, capillary forces arising in the fine-grained, montmorillonite-rich sediments of the Blake Ridge may lead to shoaling of the BSR in this setting.

Sakai, A., 1999, Velocity analysis of vertical seismic profile (VSP) survey at JAPEx/JNOC/GSC Mallik 2L-38 gas hydrate research well, and related problems for estimating gas hydrate concentration, *in* Scientific Results from JAPEx/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, Northwest Territories, Canada, Geological Survey of Canada, Ontario, Canada v. 544, p. 323–340.

A VSP survey was conducted at the JAPEx/JNOC/GSC Mallik 2L-38 gas hydrate research well to determine elastic-wave velocities that were estimated by travel time inversion of zero-offset VSP and wavefield inversion of offset VSP data. Shear-wave velocity is estimated to be slower from VSP data than from wireline DSI measurements in the depth interval from 677 in to 889 m. The compressional-wave velocity difference between the VSP- and DSI-derived velocities are comparatively small. Synthetic seismograms from the drift-corrected DSI velocity log correlate well with VSP sections, especially for compressional waves. Azimuthal anisotropy is suggested in VSP shear-source data and the mode of anisotropy appears to change around the base of permafrost.

By comparing computed elastic velocities with drift-corrected DSI velocity logs, two opposing gas hydrate saturation models are examined. Shear wave velocity proved to be the key data to select the correct model. The observed elastic velocity fits the computed elastic velocity for the model of gas hydrate disseminated in pore-space with little cementation at the grain boundaries.

Schoell, M., 1988, Multiple Origins of Methane in the Earth, *Chemical Geology*, v. 71, p. 1–10.

Methane occurrences in the Earth's crust are predominantly of biogenic origin, i.e. their ultimate source is biologically formed organic matter. Methane can also form through inorganic reactions and is consequently termed abiogenic. Biogenic methanes can either form through bacterial or thermogenic processes. Bacterial processes follow a CO₂ reduction and/or fermentation pathway. The fermentation processes are quantitatively more important in recent fresh sediments and swamps. Methane formed by CO₂ reduction, however, is most common in older sediments and commercial gasfields. Temperature, organic substrate and age may be the major factors controlling the relative importance of the two pathways. Stable-isotope concentrations in thermogenic methanes seem to be controlled by the extent of conversion of organic matter, the timing of gas expulsion, and trapping. The different character of methane in individual sedimentary basins may be a result of the geologic history. Geothermal methanes are most likely derived from pyrolysis of organic matter. Abiogenic methane occurs in hydrothermal vents and ophiolite complexes. Inorganic reactions, either surficial or deep-seated, are the likely source of such methanes. A uniform mantle origin of methane is not supported by the observed isotope variations in naturally occurring methanes.

Scholl, D.W. and Hart, P.E., 1999, Velocity and Amplitude Structures on Seismic-Reflection Profiles-Possible Massive Gas-Hydrate Deposits and Underlying Gas Accumulations in the Bering Sea Basin, *The Future of Energy Gases*, U.S. Geological Survey Professional Paper 1570, p. 331–351.

Regional geologic and geophysical data imply that large areas of the deep-water (3,700–4,000 m) floor of the Bering Sea Basin are underlain by pore-filling deposits of methane gas hydrate. Hydrate deposits are hypothesized to occur in diatomaceous turbidite beds of middle Pliocene and younger age that cap the basin's 2- to 12-km-thick sedimentary fill. Methane hydrate deposits can theoretically occur only within the uppermost ~450 m of surficial sediment, which thus constitutes the basin's hydrate layer (HDL).

Distinctive acoustic velocity and amplitude anomalies are recorded widely within the HDL. VAMP's are displayed on seismic reflection records as vertical columns (1–2 km wide) of downflexed horizons commonly stacked directly beneath the crestal region of a series of arched or domed horizons. VAMP structures are most commonly recorded within flat-lying beds and in nonstructural settings. A prominent bottom simulating reflector (BSR) of negative polarity separates the upward arch from the underlying columns of downflexed horizons. The BSR is recorded at a subsurface depth closely matching that of the theoretical base of the HDL. These observations are interpreted to mean that VAMP's are compound-velocity pseudostructures (a pullup over a pushdown) recording a localized body of massive gas hydrate of high acoustic velocity overlying a column of low-velocity sediment containing free interstitial gas. Within the HDL, hydrate deposits are thus inferred to occur in two principal modes: (1) disseminated deposits occupying probably less than <10–20 percent of available pore space, and (2) massive accumulations (>10–20 percent) localized at VAMP structures and mainly concentrated in the basal beds of the HDL.

VAMP's occur over an area of approximately 400,000 km², roughly equivalent to that of the states of Nevada and Utah combined. At VAMP'S, a basinwide inferred average pullup effect of 10 ms is acoustically equivalent to at least a 12.5-m-thick column of solid methane hydrate, and a measured average underlying pushdown of 23 ms is acoustically equivalent to a 77-m-thick column of sediment with pore space charged with at least 2 or more percent free gas. If VAMP's are discrete bodies of massive hydrate and free gas, then a conservatively estimated 12,000 VAMP's occur in the Bering Sea Basin. The corresponding total volume of methane occurring at them is approximately 1,100 trillion cubic feet (Tcf)-about 900 Tcf in the form of massive hydrate and about 200 Tcf as free gas. This basinwide volume is a minimum or low-end estimate of the methane potentially available in the Bering Sea Basin. The volume potentially available at a single large VAMP structure is about 0.3 Tcf. The methane is thought to be chiefly of thermogenic origin. A major advance in information is needed to accurately map and model VAMP structures, to confirm their inferred relation to massive hydrate deposits, and to resolve the special geologic history that favors the widespread formation of VAMP's in the Bering Sea Basin.

Sherwood, B.; Fritz, P.; Frape, S.K.; Macko, S.A.; Weise, S.M., and Welhan, J.A., 1988, Methane Occurrence in the Canadian Shield, *Geology*, v. 71, p. 223–236.

Methane is ubiquitous and discharging freely from numerous exploration boreholes in the Canadian Shield. Methane concentrations in the free gas phase vary from a few % to over 80%. The gas occurs in association with He (up to 20%), Ar (up to 4%) and H₂ (up to 30%), as well as with N (up to 80%) and minor amounts of noble gases and higher hydrocarbons. The d¹³C-values of the methane vary between ~ -56 and ~ -25‰ PDB, whereas deuterium contents range from dD = -130‰ to values as low as -450‰. No equilibration with associated fluids (usually Ca-Na-Cl brines) or known carbon compounds has occurred.

Chemical and isotopic analyses tentatively indicate an abiogenic origin for these gases. In each mining district the observed isotopic compositions are unique, and tightly grouped, suggesting local gas production under specific environmental conditions. A positive correlation between d¹³C and dD in each mining district is not readily explainable in terms of carbon sources and formation mechanisms, or in terms of migration and mixing of gases from more than one source. He isotope results typical of crustal He indicate that a mantle origin for methane is unlikely; but as yet there are no definitive indications of the role of secondary processes such as diffusion and bacterial oxidation in establishing the observed isotopic signatures.

The occurrence of high levels of free hydrogen gas in certain mining districts indicates that hydrogen may be involved in kinetically controlled, inorganic processes of methane formation. Reactions involving light hydrogen typical of that generated in the Canadian Shield and in other ultramafic-mafic environments could explain the deuterium-depleted nature of the Canadian Shield methanes. However, no specific generating mechanism has yet been identified.

Sloan, E.D., 1985, Shore-Based Laboratory Experimental Measurements on a Gas Hydrate Sample Recovered at Site 570, Initial Reports of the Deep Sea Drilling Project, v. 84, p. 695–698.

Initial and proposed efforts to determine some of the physical characteristics of the massive gas hydrate recovered from Site 570 are described. Sample chamber fabrication and preservation techniques are detailed from the time of shipboard sampling until the sample distribution to various investigators.

The properties considered are heat capacity; heat of dissociation; thermal conductivity; dissociation rate; thermal expansion; acoustic velocity; electrical resistivity; hardness; elastic wave velocity; isotopes of carbon deuterium, and oxygen; chlorinity of hydrated waters; gas composition; ratio of water to methane; pressure changes on gas decomposition; ratio of hydrogen in guest molecules to water; dynamic viscosity and elastic modulus; mineral content of sediment; and liquid water content and location. Participants in the shore-based experiments include the following institutions: U.C. Geological Survey; University of California, Los Angeles; Texas A&M University; Standard Oil of Ohio; National Bureau of Standards (Boulder); Department of Energy (METC); and the Colorado School of Mines.

Snowdon, L.R., 1999, Methane and carbon dioxide gas-generation kinetics, JAPEX/JNOC/GSC Mallik 2L-38 gas hydrate research well, *in* Scientific Results from JAPEX/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, Northwest Territories, Canada, Geological Survey of Canada, Ontario, Canada v. 544, p. 125–141.

Optimized, first-order, discrete Arrhenius kinetic parameters have been determined for the thermogenic generation of methane and carbon dioxide for several low-maturity, organic-rich core samples from the JAPEX/JNOC/GSC Mallik 2L-38 gas hydrate research well. Pyrolysis was carried out using a thermo-gravimetric analyzer heated at 10, 25, and 50°C/min. The specific products were detected using a directly coupled Fourier Transform Infrared spectrometer. Results indicated that at typical geological heating rates of 3°C/Ma, significant (about 10% of the total) thermogenic carbon dioxide was released at very low temperatures (<60°C) and would be coproduced with microbiologically mediated, diagenetic carbon dioxide. At the same geological heating rate, the first 10% of thermogenic methane was determined to have been released between about 110° and 140°C while significant methane generation from the kerogen continued beyond 250°C. The absolute kinetic parameters for methane indicate that below about 60°C essentially no thermogenic methane should be expected. Thus no in situ thermogenic methane should be expected in the Mallik 2L-38 well.

Stevens, C.M., 1999, Atmospheric Methane, Chemical Geology, v. 71, p. 11–21.

A brief review of atmospheric methane is presented with emphasis on the isotopic composition of $^{13}\text{CH}_4$ - $^{12}\text{CH}_4$. A tentative budget of the fluxes from natural and anthropogenic sources based on isotopic data is given. The trends of $\delta^{13}\text{C}$ for atmospheric CH_4 in the southern and northern hemisphere since 1978 are discussed with the following

conclusions: (1) in the southern hemisphere an increasing $d^{13}C$ trend is attributed to increasing fluxes of isotopically heavy CH_4 from biomass burning; and (2) in the northern hemisphere the average $d^{13}C$ of the source fluxes decreased from 1978 to 1983 at a rate much greater than can be reasonably accounted for by increasing fluxes of isotopically light CH_4 from anthropogenic sources and therefore is attributed to increasing fluxes from natural sources. After 1982–1983 the $d^{13}C$ increased at a greater rate in both hemispheres, which is attributed most plausibly to a decrease in the flux of isotopically light CH_4 from natural sources.

Suess, E.; Bohrmann, G.; Greinert, J., and Lausch, E., 1999, Flammable Ice, *Scientific American*, v. 281(5), p. 76–83

Taylor, A.E., 1999, Modelling the thermal regime of permafrost and gas hydrate deposits to determine the impact of climate warming, Mallik field area, *in* Scientific Results from JAPEX/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, Northwest Territories, Canada, Geological Survey of Canada, Ontario, Canada v. 544, p. 391–401.

We apply a two-dimensional geothermal model to predict the permafrost and natural gas hydrate structure in the Mallik field area, based on two paleoenvironmental scenarios deduced at other wells in the Mackenzie Delta area. Scenario A indicated a subaerial history throughout the Holocene, and scenario B documented a several thousand year, subaqueous episode during the Holocene followed by recent subaerial exposure. The effects of these histories is limited largely to the 600 m thick permafrost zone, with scenario B predicting a substantial talik. The most defensible scenario can be resolved with ground temperatures or independent paleoenvironmental indicators. The effect of climate warming will be apparent in a warming of the permafrost and, with marine transgression, creation of an underlying talik. Terrestrial methane hydrate deposits remain stable with increasing surface temperatures over several centuries, but the base of gas hydrate stability rises about 2 m after 300 years.

The Society of Professional Well Log Analysts, I., 1998, Transactions of the SPWLA Thirty-Ninth Annual Logging Symposium, The Keystone Conference Center, Keystone, CO, p. 1–14.

The amount of gas sequestered in gas hydrates is probably enormous, but estimates are highly speculative due to the lack of previous quantitative studies. Gas volumes that may be attributed to a gas hydrate accumulation within a given geologic setting are dependent on a number of reservoir parameters; one of which, gas-hydrate saturation, can be assessed with data obtained from downhole well logging devices. The primary objective of this study was to develop quantitative well-log evaluation techniques which will permit the calculation of gas-hydrate saturations in gas-hydrate-bearing sedimentary units.

The “standard” and “quick look” Archie relations (resistivity log data) yielded accurate gas-hydrate and free-gas saturations within all of the gas hydrate accumulations assessed in the

field verification phase of the study. Compressional wave acoustic log data have been used along with the Timur, modified Wood, and the Lee weighted average acoustic equations to calculate accurate gas-hydrate saturations in all of the gas hydrate accumulations assessed in this study. The well log derived gas-hydrate saturations calculated in the field verification phase of this study, which range from as low as 2% to as high as 97%, confirm that gas hydrates represent a potentially important source of natural gas.

Tulk, C.A.; Ratcliffe, C.I., and Ripmeester, J.A., 1999, Chemical and physical analysis of natural gas hydrate from the JAPEX/JNOC/GSC Mallik 2L-38 gas hydrate research well, *in* Scientific Results from JAPEX/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, Northwest Territories, Canada, Geological Survey of Canada, Ontario, Canada v. 544, p. 251–262.

Gas hydrate samples from the JAPEX/JNOC/GSC Mallik 2L-38 gas hydrate research well were analyzed on both macroscopic and molecular scales using several complementary experimental techniques. These included gas volume analysis, thermogravimetric analysis, precision gas analysis, powder X-ray diffraction, differential scanning calorimetry, Fourier transform infrared spectroscopy, and Raman Spectroscopy. Powder X-ray diffraction indicated that the samples were Structure I gas hydrate. Enclathrated gas species were identified to be mostly methane (98–100%); however, some samples contained significant amounts of heterogeneously dispersed propane and carbon dioxide (at least 1.5–2.0%). These samples were found to be significantly more stable than samples containing methane only. In addition, Raman spectra indicate subtle variations in the cage occupancies of the mixed gas hydrate as compared to those in pure methane hydrate.

Tulk, C.A.; Wright, J.F.; Ratcliffe, C.I., and Ripmeester, J.A., 1999, Storage and handling of natural gas hydrate, *in* Scientific Results from JAPEX/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, Northwest Territories, Canada, Geological Survey of Canada, Ontario, Canada v. 544, p. 263–267.

Gas hydrate samples that are recovered from natural deposits usually need to be preserved for subsequent analysis in a laboratory setting remote from the recovery site. The preservation of integrity of the gas hydrate and the quality of the subsequent sample analysis will depend on the details of sample storage and handling. Previously, massive gas hydrate samples, both natural and synthetic, have been stored in liquid nitrogen without apparent ill effects. We propose this method also for sediment-rich natural samples that are recovered for the analysis of fundamental gas hydrate properties; liquid nitrogen storage is safe and convenient as long as some care is taken with the detailed handling procedure. This is rationalized in terms of the current state of knowledge of the dynamics and reactivity of gas hydrate and ice.

Uchida, T.; Dallimore, S.R.; Mikami, J., and Nixon, F.M., 1999, Occurrences and X-ray computerized tomography (CT) observations of natural gas hydrate, JAPEX/JNOC/GSC Mallik 2L-38 gas hydrate research well, *in* Scientific Results from JAPEX/JNOC/GSC

Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, Northwest Territories, Canada, Geological Survey of Canada, Ontario, Canada v. 544, p. 197–204.

The JAPEx/JNOC/GSC Mallik 2L-38 gas hydrate research well was drilled through a thick interbedded sequence of gas-hydrate-bearing sediments between 896 and 1106 m. In total, 37.3 m of core were collected between 886 and 952.6 m, using a variety of coring systems. Visual observations at the drill site identified a predominance of pore-space gas hydrate in varying concentrations within framework-supported sands and pebbly sands. Gas hydrate was mainly fine grained (<2 mm), filling the intergranular pores and/or coating mineral grains. Although rare, thin veins (1–2 mm) and clasts or nodules of gas hydrate (up to 0.5 mm) were also observed. The largest gas hydrate occurrence (2 cm in diameter) formed the matrix of a granular sand at 913 m.

X-ray CT imagery, carried out in Japan, has identified eight well constrained signatures of the constituent components of the gas-hydrate-bearing sands and granular sands. These images have been used to establish textural characteristics and the relationship between sediment grains and gas hydrate.

Uchida, T.; Matsumoto, R.; Waseda, A.; Okui, T.; Yamada, K.; Okada, S., and Takano, O., 1999, Summary of physicochemical properties of natural gas hydrate and associated gas-hydrate-bearing sediments, JAPEx/JNOC/GSC Mallik 2L-38 gas hydrate research well, by the Japanese research consortium, *in* Scientific Results from JAPEx/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, Northwest Territories, Canada, Geological Survey of Canada, Ontario, Canada v. 544, p. 205–228.

The JAPEx/JNOC/GSC Mallik 2L-38 gas hydrate research well was drilled to a depth of 1150 m in the Mackenzie Delta, Northwest Territories, Canada, in February and March, 1998. A highlight of the project was the successful retrieval of natural gas hydrate samples in a variety of sediments. A summary is presented of research conducted by the Japanese research consortium led by the Japan National Oil Corporation with participation by ten Japanese companies and institutes. Fingerprints of the gas hydrate crystal structure and the molar ratio of water to guest-gas molecules occupying lattice sites are described for gas-hydrate-bearing samples as obtained by NMR and Raman spectroscopy. X-Ray CT imagery is used to describe the texture and gas hydrate/sediment characteristics of recovered samples during controlled dissociation testing. In addition, inorganic and organic chemical, thermal geophysical, and physical properties are described for key core horizons. Results are also presented documenting the rate of gas hydrate dissociation in drilling fluids with different chemistry including lecithin.

Uchida, T.; Mikami, J.; Masuda, Y., and Satoh, T., 1999, Dissociation properties of natural gas hydrate from the JAPEx/JNOC/GSC Mallik 2L-38 gas hydrate research well by X-ray computerized tomography (CT) experiments, *in* Scientific Results from JAPEx/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, Northwest Territories, Canada, Geological Survey of Canada, Ontario, Canada v. 544, p. 269–279.

Core samples from the JAPEx/JNOC/GSC Mallik 2L-38 gas hydrate research well contained a variety of forms of gas hydrate within sands and granular sands in the interval from 896 to 926 m. A number of these samples were placed inside pressure vessels charged with nitrogen gas and subsequently transported to Japan for specialized dissociation experiments. X-Ray CT images were acquired, at constant intervals, from a granular sand (collected from 913.76 m) containing pore-space gas hydrate during warming from -35° to 4°C , and subsequently during stepped decreases in cell pressures (0.1 MPa) below assumed threshold stability conditions. Dissociated gas flow and sample temperatures were monitored continuously.

Changes in CT values indicated that gas hydrate dissociated simultaneously, both on the exposed surfaces and within the pore spaces of the sample, in response to pressure changes. This suggested that pressure reductions were effectively transmitted through the sample, most likely because the samples were not fully saturated with gas hydrate. Gas-flow measurements indicated that a larger pressure drawdown caused a higher dissociation rate.

USGS, 1998, Gas Hydrate in Ocean Sediments-A Curiosity? An Energy Resource? A Hazard?, USGS Information Sheet

USGS, 1998, Gas hydrate laboratory research: the GHASTLI experiments, USGS Information Sheet

Vogt, P.R.; Crane, K.; Sundvor, E.; Max, M.D., and Pfirman, S.L., 1994, Methane-generated(?) pockmarks on young, thickly sedimented oceanic crust in the Arctic: Vestnesa ridge, Fram strait, *Geology*, v. 22, p. 255–258.

Acoustic backscatter imagery in the Fram strait (between Greenland and Spitzbergen) reveals a 1–3-km-wide, 50-km-long belt of ~50 pointlike backscatter objects decorating the ~1300-m-deep crest of Vestnesa Ridge, a 1–>2 km thick sediment drift possibly underlain by a transform-parallel oceanic basement ridge (crustal ages ~3–14 Ma). A 3.5 kHz seismic-reflection profile indicates that at least some objects are pockmarks ~100–200 m in diameter and 10–20 m deep. The pockmarks (possibly also mud diapirs) may have been formed by evolution of methane generated by the decomposition of marine organic matter in the Vestnesa ridge sediment drift. The ridge may be underlain by an anticlinal carapace of methane-hydrate calculated to be 200–300 m thick, comparable to the hydrate thickness measured just to the south. The rising methane would collect in the ridge-crest trap, intermittently escaping to the sea floor. This hypothesis is supported by multichannel evidence for bright spots and bottom-simulating reflectors in the area. The pockmark belt may also be located above a transcurrent fault. Sediment slumps on the flanks of Vestnesa ridge and northeast of Molloy ridge may have been triggered by plate-boundary earthquakes and facilitated by methane hydrates.

Walia, R.; Mi, Y.; Hyndman, R.D., and Sakai, A., 1999, Vertical seismic profile (VSP) in the JAPEx/JNOC/GSC Mallik 2L-38 gas hydrate research well, *in* Scientific Results from JAPEx/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta,

Northwest Territories, Canada, Geological Survey of Canada, Ontario, Canada v. 544, p. 341–355.

As part of the JAPEX/JNOC/GSC Mallik 2L-38 field program, a vertical seismic profiling (VSP) survey was carried out at zero and offset-source positions with multicomponent receiver tools and multipolarized vibrators. The results will be integrated with downhole logs and regional seismic data to evaluate the effect of gas hydrate on seismic velocity and to estimate gas hydrate concentrations. The excellent data quality allows accurate compressional- and shear-velocity depth profiles. There are down-going and up-going waves from numerous reflectors, and corridor stacks provide comparison with surface multi-channel data. Velocities in the permafrost zone above 600 m are enhanced, to more than 2500 m/s. In the largely unfrozen section from 600 m to 850 m, the velocities are lower, about 2000 m/s. The gas hydrate zone is well defined below about 900 m, with velocities of 2500–2700 m/s. Poisson's Ratio is ~0.39 in both the permafrost and gas hydrate sections, compared to ~0.44 in the unfrozen sections.

Warnke, D.A., 1986, Comment and Reply on “Gas hydrates on the northern California continental margin”, *Geology*, p. 536–539

White, J.M., 1999, Palynology, age, and paleoenvironmental interpretations from the JAPEX/JNOC/GSC Mallik 2L-38 gas hydrate research well, *in* Scientific Results from JAPEX/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, Northwest Territories, Canada, Geological Survey of Canada, Ontario, Canada v. 544, p. 81–93.

The JAPEX/JNOC/GSC Mallik 2L-38 gas hydrate research well was drilled in 1998 to investigate the geological, geochemical, geophysical, and engineering properties of a gas hydrate accumulation previously identified in the Mallik L-38 well. Palynological analysis of core and cuttings from 670 m to 1150 m (TD) are reported here. Detailed quantitative analysis has been done on the 886–952 m cored interval that hosts the main gas hydrate accumulation. The pollen and spore evidence suggests the following biostratigraphic subdivisions for the 670–1150 m succession: 670–785 m, Late Miocene or older; 775–897 m within the range of Early Miocene to Late Eocene; 897–930 m, probably Late Eocene; 930–995 m, Late Eocene; and 995–1151 m within the range Early to Middle Eocene. Below 930 m the rocks are best assigned to the Richards and upper Taglu sequences. A dominantly continental succession is indicated, with a marginal marine and/or estuarine episode between about 945 m and 948 m, in the Late Eocene. The dinoflagellates in this interval are considered to be indigenous to the sampled rock. There is evidence of two episodes of edaphic-climatic dryness in the Late Eocene and probable Late Eocene.

Winters, W.J.; Dallimore, S.R.; Collett, T.S.; Katsube, T.J.; Jenner, K.A.; Cranston, R.E.; Wright, J.F.; Nixon, F.M., and Uchida, T., 1999, Physical properties of sediments from the JAPEX/JNOC/GSC Mallik 2L-38 gas hydrate research well, *in* Scientific Results from JAPEX/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta,

Northwest Territories, Canada, Geological Survey of Canada, Ontario, Canada v. 544, p. 95–100.

A 1150 m deep gas hydrate research well was drilled in the Canadian Arctic in February and March 1998 to investigate the interaction between the presence of gas hydrate and the natural conditions presented by the host sediments. Profiles of the following, measured and derived properties are presented from that investigation: water content, sediment wet bulk density, grain size, porosity, gas hydrate quantity, and salinity. These data indicate that the greatest concentration of gas hydrate is located within sand and gravel deposits between 897 m and 922 m.

Winters, W.J.; Pecher, I.A.; Booth, J.S.; Mason, D.H.; Relle, M.K., and Dillon, W.P., 1999, Properties of samples containing natural gas hydrate from the JAPEX/JNOC/GSC Mallik 2L-38 gas hydrate research well, determined using Gas Hydrate And Sediment Test Laboratory Instrument (GHASTLI), *in* Scientific Results from JAPEX/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, Northwest Territories, Canada, Geological Survey of Canada, Ontario, Canada v. 544, p. 241–250.

As part of an ongoing laboratory study, preliminary acoustic, strength, and hydraulic conductivity results are presented from a suite of tests conducted on four natural-gas-hydrate-containing samples from the Mackenzie Delta JAPEX/JNOC/GSC Mallik 2L-38 gas hydrate research well. The gas hydrate samples were preserved in pressure vessels during transport from the Northwest Territories to Woods Hole, Massachusetts, where multistep tests were performed using GHASTLI (Gas Hydrate And Sediment Test Laboratory Instrument), which recreates pressure and temperature conditions that are stable for gas hydrate. Properties and changes in sediment behaviour were measured before, during, and after controlled gas hydrate dissociation. Significant amounts of gas hydrate occupied the sample pores and substantially increased acoustic velocity and shear strength.

Wright, J.F.; Taylor, A.E.; Dallimore, S.R., and Nixon, F.M., 1999, Estimating in situ gas hydrate saturation from core temperature observations, JAPEX/JNOC/GSC Mallik 2L-38 gas hydrate research well, *in* Scientific Results from JAPEX/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, Northwest Territories, Canada, Geological Survey of Canada, Ontario, Canada v. 544, p. 101–108.

During drilling of the JAPEX/JNOC/GSC Mallik 2L-38 gas hydrate research well, core temperatures were measured immediately upon recovery in the core-logging trailer. Gas-hydrate-bearing cores were typically frozen, with temperatures as much as 6°C lower than cores containing no gas hydrate. This temperature depression is attributed to the endothermic dissociation of gas hydrate during uphole tripping, and can be used to estimate minimum in situ gas hydrate saturation.

Numerical modelling of heat exchange between core and circulating mud during tripping demonstrates that cores cool to mud temperature before leaving the methane hydrate P-T stability field. Simple arguments support the hypothesis that the endothermic heat of gas hydrate dissociation is supplied largely by the release of latent heat during coincident

freezing of pore waters. Assuming minimal heat exchange with circulating mud, energy-balance calculations yield estimates of the quantity of gas hydrate lost to dissociation during recovery. These estimates are comparable to the in situ gas hydrate concentrations inferred from downhole geophysical logs.

Wright, J.F.; Dallimore, S.R., and Nixon, F.M., 1999, Influences of grain size and salinity on pressure-temperature thresholds for methane hydrate stability in JAPEX/JNOC/GSC Mallik 2L-38 gas hydrate research-well sediments, *in* Scientific Results from JAPEX/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, Northwest Territories, Canada, Geological Survey of Canada, Ontario, Canada v. 544, p. 229–240.

This paper summarizes laboratory determinations of the pressure-temperature (P-T) phase equilibrium conditions for methane hydrate stability in sediments recovered from the gas-hydrate-bearing interval at JAPEX/JNOC/GSC Mallik 2L-38 gas hydrate research well. Three test samples consisted of quartz-rich sand with in situ pore-water salinities of 4 ppt (parts per thousand), 20 ppt, and 40 ppt. A fourth sample was dominated by silt, with a salinity of 31 ppt. Initially, methane hydrate was regrown in the sediments, followed by the determination of P-T stability thresholds between 0° and 12°C. Comparisons with published data for methane hydrate stability in pure gas-water systems indicate no appreciable shift in P-T stability conditions in sand with salinity of 4 ppt, but suggest a progressively increasing shift towards the higher pressure, lower temperature region for sand samples with elevated salinity. Test results for the saline silt sample indicate an additional shift in the stability threshold attributed to the effect of the porous medium in fine-grained sediments.

Youslf, M.H.; Abass, H.H., and Sloan, E.D., 1998, Experimental and Theoretical Investigation of Methane-Gas-Hydrate Dissociation in Porous Media, Proceedings of the 63rd Annual Technical Conference and Exhibition of the Society of Petroleum Engineers, Houston, Texas, p. 571–583.

Vast quantities of natural gas deposits exist in the form of solid hydrates. Methane gas hydrate was formed and dissociated for the first time in Berea core samples. A three-phase 1D model was developed to simulate the process of gas production from Berea sandstone samples containing methane hydrate by means of a depressurization mechanism. The model closely matched the experimental data of gas and water production, the progress of the dissociation front, and the pressure and saturation profiles.

Zakrzewski, M. and Handa, Y.P., 1993, Thermodynamic properties of ice and of tetrahydrofuran hydrate in confined geometries, *Journal of Chemical Thermodynamics*, v. 25, p. 631–637.

The formation of structure II clathrate hydrate of tetrahydrofuran (THF) in 4.2 nm radius pores in Vycor glass was confirmed by X-ray diffraction studies. Heat capacities of ice and THF hydrate in the 4.2 nm pores were found to be smaller below T ~180 K and larger above this temperature than the corresponding values of the materials in the bulk phase. The melting temperature of pore hydrate was found to be depressed by 8.7 K and the enthalpy

of melting by 36.9 per cent relative to the corresponding values for the bulk phase. The changes in the thermal properties due to confinement in pores were of the same magnitude for ice and THF hydrate.