Fire in the Ice

Summer 2008 · Methane Hydrate Newsletter

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AURORA-JOGMEC-NRCAN MALLIK 2006-2008 GAS HYDRATE RESEARCH PROJECT PROGRESS

By Koji Yamamoto (Japan Oil, Gas and Metals National Corporation) and Scott Dallimore (Natural Resources Canada)

In the spring of 2002, scientists and engineers from seven participant organizations[1] from five countries celebrated the success of the world's first gas production from a methane hydrate reservoir at the JAPEX/GSC/JNOC et al. Mallik 5L-38 research well in the Mackenzie Delta, Northwest Territories, Canada. Five years later, Japanese and Canadian researchers re-united in the town of Inuvik, to pioneer a new phase of gas hydrate research. This time, the goal was to undertake a longer test and advance new research and development studies utilizing the simple depressurization technique. The two-winter research program was successfully completed in April 2008 and we believe it represents a new step forward towards realizing gas hydrate as a viable energy resource. This report summarizes the operation of the project and some progress in gas hydrate research.
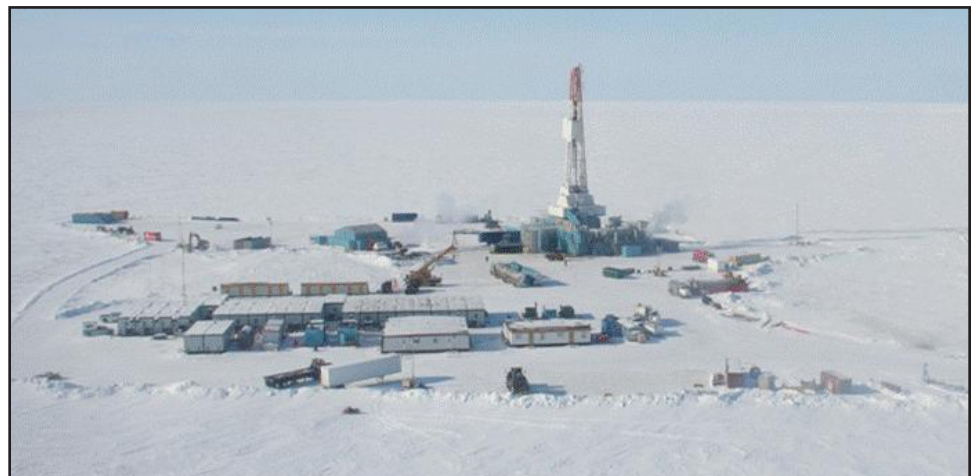

Figure 1: Landscape of the Mallik site (April 2007).

[1] Geological Survey of Canada (GSC), Japan National Oil Corporation (JNOC, former JOGMEC), GeoForschungsZentrum Potsdam (GFZ), the United States Department of Energy (DOE) , The United States Geological Survey (USGS), US, the India Ministry of Petroleum and Natural Gas (MOPNG)-Gas Authority of India (GAIL), India, and the BP-Chevron Texaco Mackenzie Delta Joint Venture

Project Objectives

As summarized in a scientific results volume published as a Geological Survey of Canada Bulletin, the Mallik 2002 program provided many significant scientific findings. One encouraging result was the 470 m^3 (surface condition) of gas production from a concentrated gas hydrate interval below thick permafrost layers by a thermal-stimulation technique employing hot fluid circulation. Besides the flaring fire of the hydrate-dissociated gas in the arctic sky, valuable data and samples were taken during the project, such as geophysical information collected by state-of-the-art logging tools, high-quality gas hydrate-bearing core samples, and MDT^2 tool derived pressure-drawdown test data. After the analysis of these data and intensive numerical modelling efforts, the 2002 research team concluded that simple reservoir depressurization techniques may be a more efficient gas hydrate production scenario than previously considered, due to relatively high permeability and an interconnected fluid phase in sand-dominated gas hydrate formations found at Mallik and in some marine settings.

After the first Mallik production test, the MH21 Gas Hydrate Research Consortium was formed to promote Japan's national gas hydrate research program. In this program, the Japan Oil, Gas, and Metals National Corporation (JOGMEC) conducted a three-dimensional seismic survey and an exploration drilling campaign in the eastern Nankai Trough area offshore Central Japan to quantify the gas hydrate resource in the area. The logging data and core samples taken in 16 locations revealed that the total gas in place in gas hydrate form in the 7000 km^2 survey area is 40 trillion cubic feet (tcf). Half of the resource (20 tcf) was found to be in "methane hydrate concentrated zones" that are characterized by sand-rich turbidite deposits that exhibit high resistivities in well logs, strong seismic reflectors, and fast *P*-wave interval velocities. Besides the surveys, the National Institute of Advanced Industrial Science and Technology (AIST) performed several modelling and laboratory studies to establish quantitative models to predict gas hydrate dissociation behavior under various conditions. Such new findings and research outcomes accelerated the effort to seek technology for effective and efficient gas production from gas hydrate deposits in geological formations.

Project Overview

In 2006, JOGMEC and Natural Resources Canada (NRCan) signed agreements for collaborative research on the second gas hydrate production test in the same location as the 2002 Program (Figure 1). This time, Aurora College/Aurora Research Institute, an educational institution and part of the Government of Northwest Territories, acted as the operator for the field program with support from Inuvialuit Oilfield Services, who were the project managers.

Japan and Canada agreed to adopt a simple depressurization technique as the gas hydrate production method to simplify the operational conditions of the test and to minimize unknown variables. The field scale verification of the technique was defined as the prime objective of the project (see Dallimore, *Fire in the Ice*, Spring/Summer 2007). In January 2007, an ice road was built on the Mackenzie River and Beaufort Sea to connect Inuvik with the Mallik site, and allow mobilization of drilling rigs and other equipment. The project was realized after more than a year of planning by a team of scientists and engineers who designed the gas production procedure and necessary downhole and surface equipment for the test.

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[2] Modular Formation Dynamics Tester - Schlumberger

Winter 2007 Operations

Field operations during the first year winter (2007) focused on installing infrastructure and undertaking a short production test. To minimize drilling waste volume, a well drilled for a 1998 research program (Japex/JNOC/GSC Mallik 2L-38) was modified to establish a production test well by reaming, casing, and cementing. After struggling with operational problems, the production test operation started on April 2. The test zone, a 12 m-thick interval near the bottom of the gas hydrate occurrence zone (GHOZ), was selected based on the logging data. Pressure and temperature conditions of the zone were considered most suitable for the depressurization method, with petrophysical conditions including fairly high gas hydrate saturation and relatively high permeabilities (Figure 2). An electrical submersible pump (ESP) was set below the perforation zone to depressurize the formation by dropping the water level of the well. For environmental protection, the well was designed to enable all produced water to be injected into aquifers below the GHOZ.

Sand production (in-flow of formation sand to the borehole with fluid) prevented continuous pumping, and the operation was terminated 60 hours after the start of pumping. However, during the most successful 12.5 hours of the test, at least 830 m^3 of gas were produced and accumulated in the borehole. This attempt was the world's first gas production by the depressurization of natural gas hydrate in geological formation, and the volume of 830 m^3 exceeded the production volume of the five-day operation of 2002. Cased-hole logging data taken before and after the test derived information about formation responses to depressurization. The test results verified the effectiveness of the depressurization method even for such a short duration, although technical challenges remained.
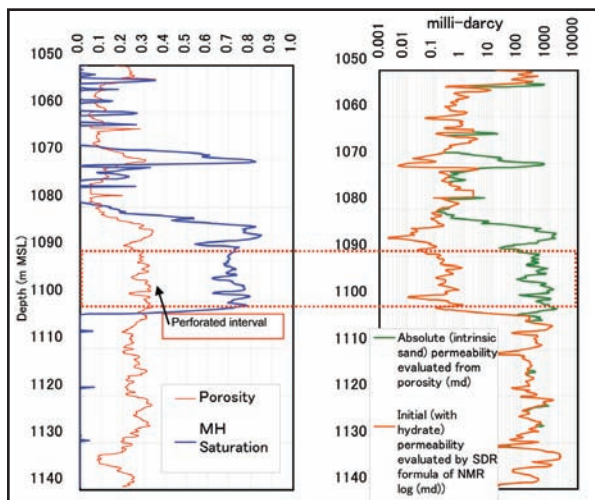

Figure 2: The perforated interval with log-derived, petrophysical parameters of the production zone.
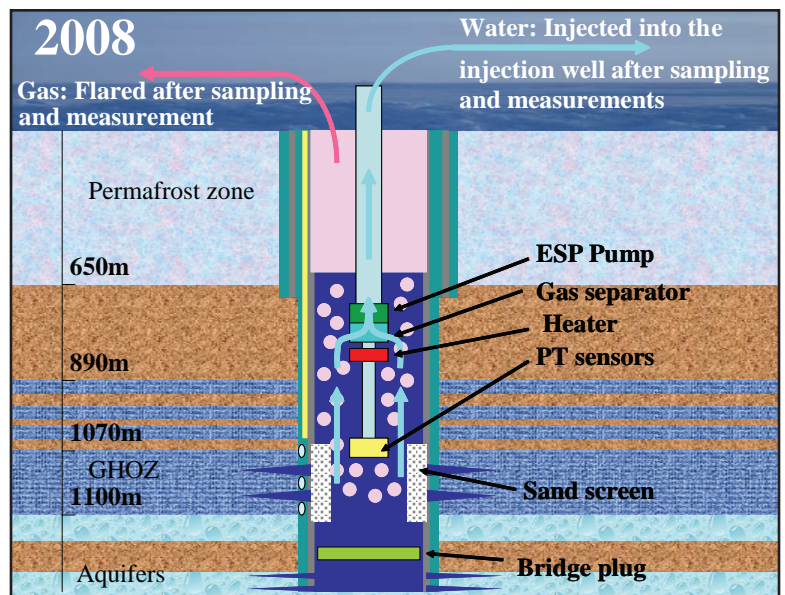

Figure 3: Schematic of the depressurization system of the 2008 completion.

Winter 2008 Operations

The goal of the winter 2008 field activities was to undertake longer term gas hydrate production testing with the implementation of countermeasures to overcome the problems encountered in 2007. After ice road and site construction, the Mallik 2L-38 production test well was re-entered, and a modified pumping system was run into the hole with sand control devices (Figure 3). The pump operation started in the afternoon of March 10 and continued until the preset test termination time of 12 noon on March 16. Six days of continuous operation of the pump established stable pressure conditions at the bottom of the hole. Stable gas flow was measured at the surface with a sustained flare of the hydrate dissociated gas (Figures 4 and 5). Pressure, temperature, and gas and liquid flow rate data were taken at the bottom of the hole and at the surface, along with gas, liquid, and solid samples. After the test, the production well was abandoned and all equipment was demobilized by early April.

Figure 4: World's first sustainable gas flare of methane from a hydrate source (March 10, 2008).

Figure 5: Methane hydrate gas still being flared six days later (March 16, 2008).

Preliminary Results

The 2008 testing program at Mallik confirmed that continuous gas flow ranging from 2000 to 4000 m^3/day was maintained throughout the course of the six-day (139-hour) test. Cumulative gas production volume was approximately 13,000 m^3. Detailed analyses of the results are ongoing, but initial data confirm that the depressurization method is the correct approach. Japanese and Canadian research teams will analyze the data and publish scientific and technical papers internationally. The analyses of the data and samples will help advance our understanding of methane hydrate dissociation behavior in formations and contribute to the development of more sophisticated production techniques. The gas rate prediction by the MH21-HYDRES gas hydrate reservoir simulation (see another by the Gas Hydrate Simulator Comparison Team, *Fire in the Ice*, Winter 2007) matches well with the observed values. By analyzing the data of the production test, we expect to make additional improvements in the model.

The Impact and Way Forward

Development of effective production techniques is the key to realizing gas hydrates as a valuable energy resource. The success of the production test in northern Canada is a meaningful step forward, and we hope it will encourage international efforts and collaboration on engineering and scientific research. Of course, more work is necessary to undertake longer term, and larger scale field tests in different geological settings and to provide additional data sets for the verification of theories and development of practical technologies. Indeed, there are many challenges to gas production from deep water marine sediments, the ultimate target of the Japanese team.

One way to achieve the desired science and engineering breakthroughs is to integrate studies of arctic and marine gas hydrate exploration and production, including basic studies in the laboratory, field demonstrations, and development and verification of numerical models. We hope that the 2006-2008 Mallik Project performed under the collaboration of Japan and Canada is not only a milestone, but also a model case of such integration (Figure 6).

Figure 6: Gas flare behind the R&D leaders of Japan (K.Yamamoto, JOGMEC) and Canada (S.R. Dallimore NRCan) - March 16, 2008.

Marine Pore Fluid Profiles of Dissolved Sulfate; Do They Reflect *In Situ* Methane Fluxes?

By Miriam Kastner[1], Marta Torres[2], Evan Solomon[1], and Arthur J. Spivack[3]

A key biogeochemical factor controlling the distribution and concentration of gas hydrates is the magnitude of the methane flux to the gas hydrate stability zone. Several complementary approaches have been used to assess this issue. Here we report on pore fluid data recovered by non-pressurized and pressurized cores from two basins in the Bengal Sea, the Krishna-Godavari (KG) and Mahanadi Basins (900-1170 m water depths) offshore southeast India, from a site in the Andaman Sea, (~1600 m water depth), and from two sites at Hydrate Ridge, Cascadia (~890 m water depth) (Figure 1). At all of these sites there is evidence of gas hydrates, even though the abundance, distribution, and texture of these deposits vary from site to site. Our data illustrate how in anoxic sediments the isotopic characterization of the dissolved inorganic carbon pool (DIC), present mainly as the HCO_3^- ion, is key to inferring carbon sources, metabolic paths of organic matter diagenesis, and sub-seafloor hydrocarbon fluxes.
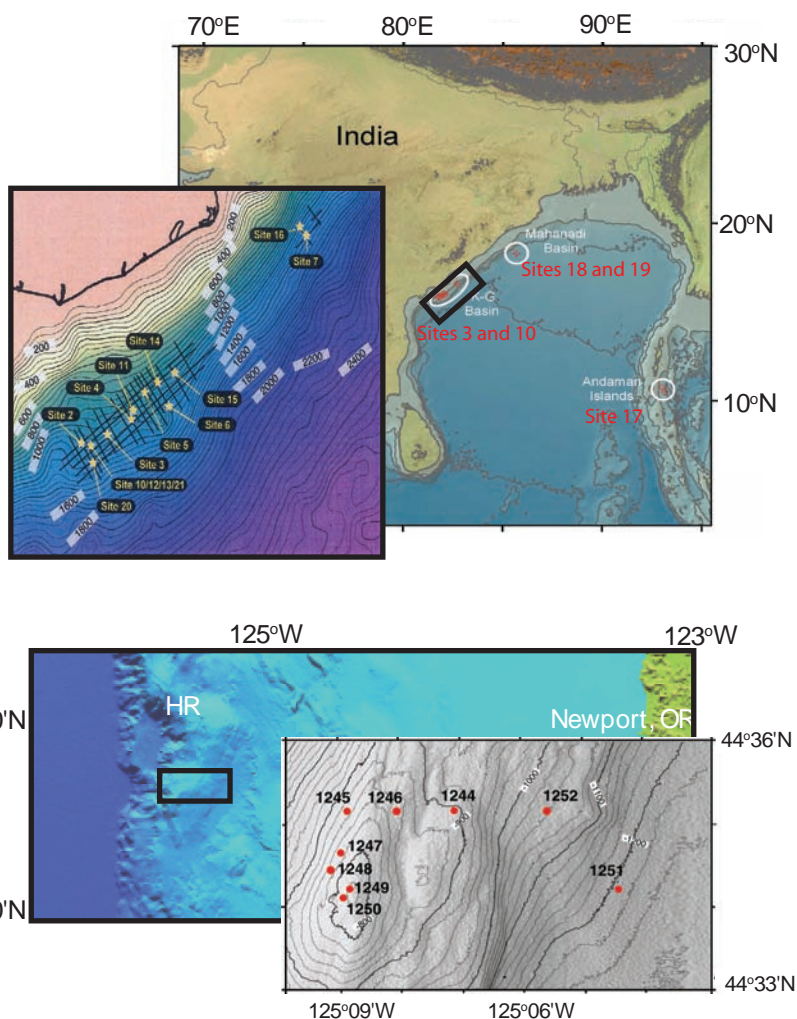
Figure 1: Schematic location maps of the sites discussed in the KG and Mahanadi Basins in the Bengal Sea, in the Andaman Sea, and at Hydrate Ridge (HR). The insert maps show all the sites drilled during NGHP Expedition 01 in the KG Basin, and the sites drilled at HR on ODP Leg 204.

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Figure 2: Pore fluid $\delta^{13}C$ (‰ PDB) and SO_4 concentrations (mM) – depth profiles in (A) the Krishna-Godavari Basin, (B) Mahanadi Basin, (C) Andaman Sea, and (D) Hydrate Ridge (HR). The dotted horizontal lines indicate the depth of the SMT at each of the sites. (E) A cross plot of excess alkalinity corrected for carbonate precipitation versus SO_4 (mM) at two of the HR sites shown in D.

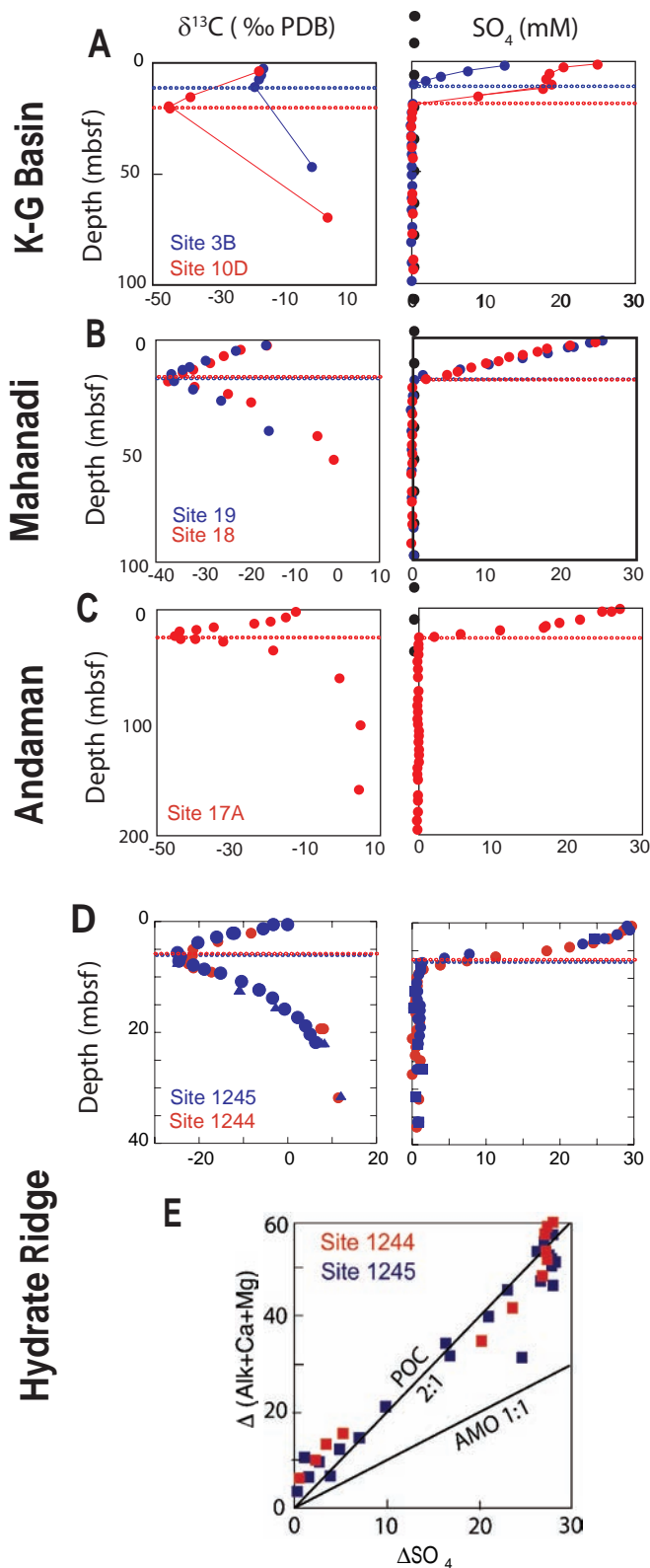All gas hydrates in marine sediments occur below the sulfate-methane transition (SMT) zone, a biogeochemical redox boundary that separates sulfate-bearing and methane-depleted sediments from sulfate-depleted and methane-rich sediments. When the SMT is at the sediment/water interface gas hydrate may breach the seafloor.

In this redox transition zone the coupled reaction of anaerobic oxidation of methane (AOM) with sulfate reduction is mediated by a marine microbial consortium (e.g. Hinrichs *et al.*, 1999; Boetius *et al.*, 2000). This reaction produces one mole of bicarbonate per one mole of sulfate reduced. The observation by Borowski *et al.*, (1996)—that the steepness of the sulfate concentration profiles is directly related to the depth of the SMT and to the magnitude of the methane flux (Borowski *et al.*, 1996), and hence, can be applied for methane flux calculations— is applicable only if AOM is the dominant reaction responsible for the dissolved sulfate reduction profiles.

Sulfate reduction that is linked to anaerobic organic matter oxidation is, however, a reaction that produces approximately 2 moles of bicarbonate per mole sulfate reduced. In this case, as in most cases, if the two sulfate reducing pathways are active, the sulfate concentration profiles cannot be used to unambiguously calculate methane fluxes. The two pathways can be distinguished by either: (1) the different stoichiometries of sulfate reduced and bicarbonate produced, or by (2) the $\delta^{13}C$–DIC values that provide a clear distinction between these metabolic pathways, because the $\delta^{13}C$ of methane is 20 to 75‰ more negative than that of organic matter (e.g. Claypool *et al.*, 1985; Whiticar, 1999).

In the Bengal and Andaman Seas, gas hydrate is most abundant in the KG Basin. The sulfate concentration gradients at the eight sites drilled in this basin show significant variations, with the shallowest and deepest SMT zone at ~9 and 30 mbsf. At six sites, the $\delta^{13}C$ of the DIC is dominated by organic matter oxidation linked to sulfate reduction, with $\delta^{13}C$-DIC values that range from -12‰ to - 26‰. Only, at two of the sites (10 and 14) AOM dominates, with $\delta^{13}C$-DIC values of -36‰ and -47‰, respectively. Gas hydrate is very abundant at Site 10 and not at Site 14, but the SMT occurs at both sites at ~20 mbsf (Figure 2).

A predominance of the AOM reaction is also documented in the Mahanadi Basin and the Andaman Sea sites, with δ^{13}C-DIC values at these sites of -38‰ and -46‰, respectively. Although the SMT at these locations as well occurs at ~20 mbsf, at the Mahanadi Basin there are only minor occurrences of disseminated gas hydrate, and in the Andaman Sea, significant accumulation of gas hydrate was observed associated with coarser grained, mostly volcanic ash-rich intervals, below ~250 mbsf (Figure 2).

At the Hydrate Ridge summit, Sites 1244 and 1255, the SMT is very shallow, at ~7 mbsf, and the δ^{13}C-DIC at this SMT depth is -28‰ at both sites (Figure 2). After correcting the bicarbonate data for carbonate precipitation, the different stoichiometric approach was used by Claypool, *et al*. (2006), as shown in Figure 2E, to document the preponderance of sulfate consumption by organic matter diagenesis in these gas hydrate bearing sediments.

These results indicate that the steepness of the sulfate concentration profiles does not necessarily indicate that AOM is the main reaction consuming sulfate, rather a more comprehensive analysis of pore fluid metabolites and/or δ^{13}C-DIC data is required to distinguish between the dominant reactions responsible for the sulfate concentration profiles.

Furthermore, data recovered from the Indian Ocean and Hydrate Ridge expeditions show that there is no relationship between the depth of the SMT or the steepness of the sulfate profile with gas hydrate abundance or its subsurface distribution. There is also no correspondence between depth of the SMT and the amplitude of the bottom simulating reflector (BSR), suggesting that these two interfaces reflect different aspects of the subsurface methane hydrology.

ADDITIONAL READING

Boetius, A., Rovenschlag, N.K., Schubert, C.K., Rickert, D., Widdel, F., Fieseke, A., Amann, R., Jorgensen, B.B., Witte, U., and Pfannkuche, O., 2000, A marine consortium apparently mediating anaerobic oxidation of methane. *Nature*, V. 407, 623-626.

Borowski, W.S., Paull, C.K., and Ussler III, W., 1996, Marine pore-water sulfate profiles indicate in situ methane flux from underlying methane hydrate. *Geology,* V. 24, 655-658.

Claypool, G.E., Milkov, A.V., Lee, Y.–J., Torres, M.E., Borowski, W.S., and Tomaru, H. 2006, Microbial methane generation and gas transport in shallow sediments of an accretionary complex, southern Hydrate Ridge (ODP Leg 204), offshore Oregon, USA, in *Proc. ODP, Sci. Results*, 204, Trehu, A.M., Bohrmann, G., Torres, M.E., and Colwell, F.S., editors, Ocean Drilling Program, College Station, TX.

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, Deep Sea Drilling Project Leg 84, in: *Initial Reports of the Deep Sea Drilling Project*, 84, von Huene, R., Aubouin, J., et al., Washington, DC, US Government Printing Office, 693-691.

Hinrichs, K.-U., Hayes, J.M., Sylva, S.P., Brewer, P.G., and DeLong, E.F., 1999, Methane-consuming archaebacteria in marine sediments. *Nature*, V. 398, 802-805.

Whiticar, M.J., 1999, Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane. *Chem. Geol.*, V. 161, 291-314.

METHANE RELEASE FROM GAS HYDRATES DURING THE PALEOCENE-EOCENE THERMAL MAXIMUM: CURRENT PERSPECTIVE ON THE ISSUE

By Gerald R. Dickens (Rice University)

The Paleocene-Eocene thermal maximum (PETM) was a brief (~200 kyr) interval of profound global environmental change about 55 million years ago (Zachos *et al.*, 2008). Since 1995, numerous articles have suggested that widespread dissociation of submarine gas hydrates played a prominent role during this event (Dickens *et al.*, 1995). Thirteen years later, and with abundant new information, including some discussed here, massive methane release from the ancient seafloor, during the PETM or other similar events, remains a viable but challenging hypothesis.
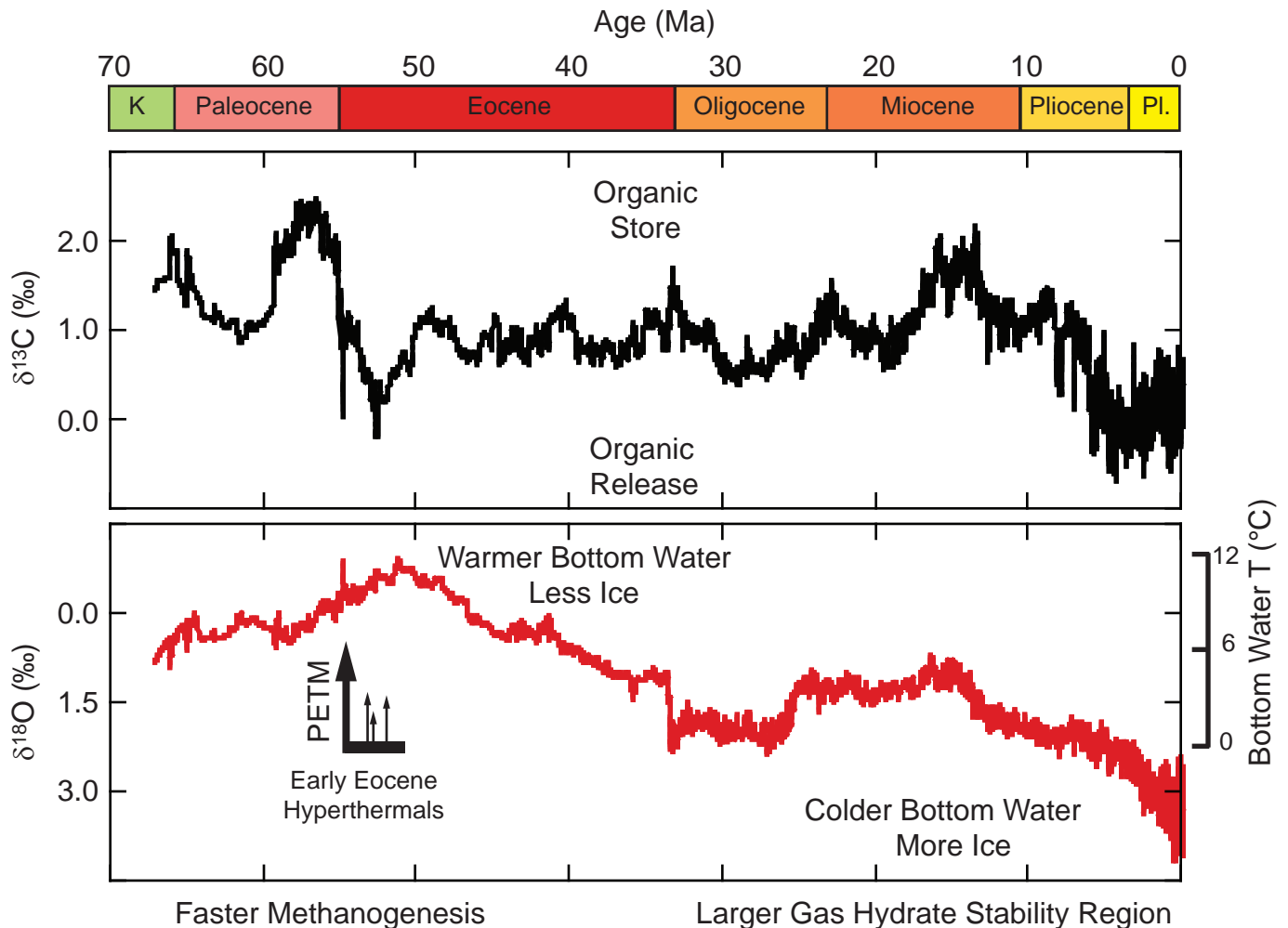

Figure 1: Secular changes in carbon and oxygen isotopes of benthic foraminifera over the last 70 million years (see Zachos et al., 2008). Changes in $\delta^{13}C$ record past variations in inputs and outputs of carbon to the ocean and atmosphere, most likely through changes in organic carbon fluxes. Changes in $\delta^{18}O$ record past variations in ice volume and bottom water temperature. Significant inputs of methane and rapid bottom warming would manifest as brief negative excursions in both curves, such as occurred across the PETM. Recent literature has suggested a series of hyperthemal events in the early Eocene similar to but of lesser magnitude than the PETM, although these do not appear in the records because of data averaging. In general, the volume of the gas hydrate stability zone must have increased since the Early Eocene because of cooling bottom water; however, the rate of methanogenesis must have also diminished for the same reason.

Unquestionably, the first 10 to 30 kyr of the PETM were characterized by intense global warming and by a massive input of ^{13}C-depleted carbon dioxide (Zachos *et al.*, 2008) (Figure 1). The PETM has been identified in about 80 sediment sequences deposited in a wide range of environments around the world. A rapid 5 to 8° C temperature rise across Earth's surface is inferred from pronounced changes in sedimentary components spanning the base of the event. Such changes include latitudinal migrations of terrestrial and marine flora and fauna, and major shifts in the chemistry of calcium carbonate (e.g., $^{18}O/^{16}O$ and Mg/Ca ratios) and organic carbon (e.g., lipid ratios) made by marine organisms. Crucially, the warming extended to high latitude and deep ocean environments. At nearly the same time, a tremendous amount of ^{13}C-depleted carbon entered the ocean and atmosphere. This is evidenced by a significant decrease in the $^{13}C/^{12}C$ ratio (or $\delta^{13}C$) of carbon bearing phases (e.g., organic carbon and carbonate) across the start of the PETM. Moreover, carbon addition must have involved CO_2, either directly or as a product of organic oxidation, because the carbonate content of deep-sea cores drops across the PETM, which attests to ocean acidification (Zeebe and Zachos, 2007).

The magnitude and abruptness of both ocean warming and carbon injection during the PETM were extremes within the last 65 million years (Zachos *et al.*, 2008). At issue is how the two phenomena relate. One general idea concerns thermal perturbation of a large global gas hydrate capacitor (Dickens, 2003). Similar to present-day, the upper few hundreds of meters of pore space on continental margins hosted ^{13}C-depleted CH_4 as gas hydrate, dissolved gas and free gas bubbles. This CH_4 was dynamic, with inputs and outputs of carbon to and from the ocean. Microbial and thermal breakdown of buried organic compounds slowly transferred carbon from the ocean to CH_4. At steady-state conditions, most of the CH_4 occurred as gas hydrate, and venting of gas bubbles from the seafloor and anaerobic oxidation of dissolved CH_4 in shallow sediment slowly returned carbon to the ocean. When deep ocean temperatures rose by 5° C or more at the start of the PETM, however, large quantities of gas hydrate converted to free gas, and the output of ^{13}C-depleted CH_4 from the seafloor increased dramatically. This would have occurred especially at locations under 1000-2000 m of water as the base of the gas hydrate stability zone would effectively rise through the seafloor. Once released, the CH_4 was oxidized to CO_2 in the ocean, the atmosphere, or both.

Two recent studies support this overall scenario. Sluijs *et al.* (2007) have examined proxies for ocean warming and environmental perturbations in carbon bearing compounds where $\delta^{13}C$ can also be measured. They show that oceanographic change began several thousands of years before the rapid injection of ^{13}C-depleted carbon, a result consistent with previous work on foraminiferal carbonate. Importantly, this is about the time necessary to propagate heat from bottom water into marine sediment and to convert gas hydrate to free gas bubbles. Nicolo *et al.* (2007) show that other, lesser negative $\delta^{13}C$ excursions after the PETM are also marked by environmental perturbations, including global warming and carbonate dissolution. This would be predicted for a large carbon capacitor, such as submarine gas hydrates, that can release mass quickly and repeatedly upon successive ocean warming events but can only recharge slowly (Dickens, 2003).

Some basic problems preclude acceptance of widespread CH_4 release from submarine gas hydrate systems during the PETM (Dickens, 2003; Pagani *et al.*, 2007). First, no study has uniquely demonstrated that oxidized CH_4 (or another compound) was the source of the carbon addition. There are also issues regarding the mass of carbon injected during the PETM, and whether gas hydrates at this time could furnish such a quantity.

The amount of carbon added during the PETM can be estimated from the magnitude of the global $\delta^{13}C$ anomaly and the $\delta^{13}C$ of the carbon source (Dickens *et al*., 1995). If the excursion was -2‰ to -3‰, as indicated by some records, and seafloor CH_4 with a $\delta^{13}C$ of -60‰ was indeed the source, then nominally 2000 Gt of carbon were released. To place this in perspective, this is about half of the total amount expected from anthropogenic fossil fuel emissions through the year 2500. Recent papers (e.g., Pagani *et al*., 2007) have suggested that the $\delta^{13}C$ of the ocean and atmosphere shifted by -5‰ to -6‰ across the PETM. This would imply a much greater input of carbon, especially if the source was less depleted in ^{13}C. However, this magnitude seems too large because of processes that impact certain carbon isotope records. For example, about half of the 6‰ $\delta^{13}C$ excursion observed in plant n-alkane records from Arctic Ocean sediment cores results from a major switch in the relative abundance of these compounds produced by angiosperms or gymnosperms (Schouten *et al*., 2007).

Theoretically, the size of the carbon injection across the PETM could also be determined from the amount of carbonate dissolution in seafloor sediment. Drilling on Walvis Ridge clearly demonstrated that the calcite compensation depth (CCD) rose by at least 2 km during the PETM in the southeast Atlantic Ocean. Various works (e.g., Pagani *et al*., 2007) have taken this as representative of the entire ocean, which would necessitate a carbon input much greater than 2000 Gt. This interpretation is incorrect, however, because sediment records from the much larger Pacific Basin indicate a minimal rise in the CCD (Zeebe and Zachos, 2007). The extreme dissolution in the southeast Atlantic appears to signify mostly a change in the flow direction of deep waters during and immediately after massive carbon injection (Zeebe and Zachos, 2007).

Thermal dissociation of marine gas hydrates and release of nominally 2000 Gt of biogenic methane carbon from the seafloor remains a satisfactory, if not the best, explanation for anomalies observed in the sedimentary record spanning the PETM. Indeed, no other hypothesis offered to date conforms to carbon mass balance constraints and the fact that ocean warming preceded the carbon input. It is worth noting that magnetite grains suggestive of a comet impact are actually the remains of bacteria (Kopp *et al*., 2007; Lippert and Zachos, 2007), and the notion that marine sediments could have released carbon during subaerial exposure is demonstrably wrong because sea level rose during the PETM (Sluijs *et al*., in press). However, if release of methane from marine gas hydrates is the correct explanation for the PETM carbon injection, it seriously challenges current thinking on the overall mass of carbon in gas hydrate systems, both at present-day and in the past.

A 2000 Gt release of carbon from marine gas hydrates upon a 5° C rise in deep ocean temperature necessarily implies a global mass of carbon stored in these systems of 5,000 to 10,000 Gt (Dickens *et al*., 1995; Dickens, 2003). This is consistent with some estimates for the present-day but not others (e.g., Milkov, 2004; Buffett and Archer, 2004). There are two general possibilities: recent estimates for the total amount of carbon in modern gas hydrate systems are too low, or continental margins in the early Paleogene (i.e., before the PETM) held much more methane than today. Clearly, extrapolations from specific sites to larger regions (Milkov, 2004) carry considerable uncertainty given established heterogeneities in modern gas hydrate systems. The usefulness of modeling the current global abundance and distribution using present-day organic carbon inputs (Buffett and Archer, 2004) is also questionable given known changes in such supply and the long residence time of methane (>1 million years) in most gas hydrate systems (e.g., Dickens, 2003). The other possibility is more intriguing. Simple

intuition would dictate that continental margins held much less methane in the early Paleogene compared to present day because significantly warmer ocean bottom water at the time (~10° C before the PETM) would mean thinner gas hydrate stability zones (Dickens *et al.*, 1995; Buffett and Archer, 2004; Milkov, 2004). However, nobody seems to have considered the facts that microbial methanogenesis proceeds much faster at higher temperatures, and that methane production within gas hydrate stability zones would be at an optima in the early Paleogene. It is entirely conceivable that the volume of sediment hosting gas hydrates was smaller in the past, but that the mass of carbon stored within this volume was greater.

In summary, the PETM is a special time when conditions impacting marine gas hydrate stability (rapid but sustained bottom water warming) were maximized, and when the most obvious consequence of widespread seafloor methane release (massive input of ^{13}C-depleted carbon) is clearly observed. As yet, there is no conclusive evidence that gas hydrates furnished the carbon, but there is no better explanation, either. In any case, a full appreciation of the topic forces those interested in gas hydrates to think laterally.

ADDITIIONAL READING

Buffett, B. and Archer, D., 2004. Global inventory of methane clathrate: sensitivity to changes in the deep ocean. *Earth and Planetary Science Letters*, 227: 185-199.

Dickens, G. R., O'Neil, J. R., Rea, D. K. and Owen, R. M., 1995. Dissociation of oceanic methane hydrate as a cause of the carbon isotope excursion at the end of the Paleocene. *Paleoceanography*, 10: 965-971.

Dickens, G. R., 2003. Rethinking the global carbon cycle with a large, dynamic and microbially mediated gas hydrate capacitor. *Earth and Planetary Science Letters*, 213: 169-182.

Kopp, R.E., Raub, T.D., Schumann, D., Vali, H., Smirnov, A.V. and Kirschvink, J.L., 2007. Magnetofossil spike during the Paleocene-Eocene thermal maximum: Ferromagnetic resonance, rock magnetic, and electron microscopy evidence from Ancora, New Jersey, United States. *Paleoceanography*, 22: PA4103, doi: 10.1029/2007PA001473.

Lippert, P.C. and Zachos, J.C., 2007. A biogenic origin for anomalous fine-grained magnetic material at the Paleocene-Eocene boundary at Wilson Lake, New Jersey. *Paleoceanography*, 22: PA4104, doi: 10.1029/2007PA001471.

Milkov, A.V., 2004. Global estimates of hydrate-bound gas in marine sediments: how much is really out there? *Earth-Science Reviews*, 66: 183-197.

Nicolo, M.J., Dickens, G.R., Hollis, C.J. and Zachos, J.C., 2007. Multiple early Eocene hyperthermals: Their sedimentary expression on the New Zealand continental margin and in the deep sea. *Geology*, 35: 699-702.

Pagani, M., Caldeira, K., Archer, D. and Zachos, J.C, 2007. An ancient carbon mystery. *Science*, 314: 1556.

Schouten S., Woltering, M., Rijpstra, W.I.C., Sluijs, A., Brinkhuis, H. and Sinninghe Damsté, J.S., 2007. The Paleocene-Eocene carbon isotope excursion in higher plant organic matter: Differential stable carbon isotopic fractionation of angiosperms and conifers on the Arctic continent. *Earth and Planetary Science Letters*, 258: 581-592.

Sluijs, A., Brinkhuis, H., Schouten, S., Bohaty, S.M., John, C.M., Zachos, J.C., Reichert, G.-J., Sinninghe-Damste, J.S., Crouch, E.M. and Dickens, G.R., 2007. Environmental precursors to rapid light carbon injection at the Palaeocene/Eocene boundary. *Nature*, 450: 1218-1221.

Sluijs A., Brinkhuis, H., Crouch, E.M., John, C.M., Handley, L., Munsterman, D., Bohaty, S., Zachos, J.C., Reichart, G.-J., Schouten, S., Pancost, R.D., Sinninghe Damsté, Welters, N.L.D., Lotter, A.F. and Dickens, G.R., in press. Sea level rise during the Paleocene-Eocene thermal maximum: evidence from dinoflagellate cysts, organic biomarkers, and sediment properties. *Paleoceanography*, in press.

Zachos, J.C., Dickens, G.R. and Zeebe, R.E., 2008. An early Cenozoic perspective on greenhouse warming and carbon-cycle dynamics. *Nature*, 451: 279-283.

Zeebe, R.E. and Zachos, J.C., 2007. Reversed deep-sea carbonate ion gradient during Paleocene-Eocene thermal maximum. *Paleoceanography*, 22: PA3201, doi: 10.1029/2006PA0011395.

SEISMIC-SCALE ROCK PHYSICS OF METHANE HYDRATES

By Jack Dvorkin (Stanford University)

The main question posed in this DOE-sponsored project was: What bulk properties of a methane hydrate reservoir, such as hydrate saturation and the porosity of the host sediment, may stand behind a seismic record? The approach used to answer this question or, in other words, to quantify a natural methane hydrate reservoir, was by generating synthetic seismic traces and comparing them to real data. If they match, the reservoir properties and conditions used in synthetic modeling might be the same as those *in-situ*. Such methodology has to be based upon a link between (a) the porosity and mineralogy of the host sediment, pressure, and hydrate saturation, and (b) the resulting elastic-wave velocity and density. Several rock physics models can provide this link. One of them that appears essentially universal across various methane hydrate provinces is the model for unconsolidated sediment, where the hydrate acts as part of the mineral frame (Figure 1). The utility of this model was established using well log data from Mallik (Figure 2), Outer Blake Ridge (Figure 3), and Nankai Trough (Figure 4).
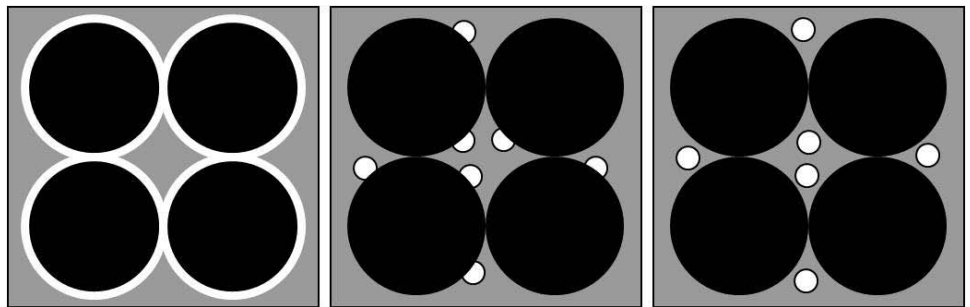

Figure 1: Three hypothetical types of methane hydrate arrangement in the pore space. From left to right – (a) hydrate as contact cement; (b) non-cementing hydrate as part of the mineral frame; and (c) hydrate as part of the pore fluid. The mineral grains are black; brine is gray; and hydrate is white. Model (b) appears to match data from many methane hydrate provinces.

Seismic reflections depend on the contrast of the *P*- and *S*-wave velocity and density in the subsurface while the velocity and density, in turn, depend on lithology, porosity, pore fluid, and pressure. These two links, one between rock's structure and its elasticity and the other between the elasticity and signal propagation, form the physical basis of seismic interpretation for rock properties and conditions. One approach to interpreting seismic data for the physical state of rock is forward modeling. Lithology, porosity, and fluid in the rock, as well as the reservoir geometry, are varied, the corresponding elastic properties are calculated, and then synthetic seismic traces are generated. The underlying supposition is that if the seismic response is similar, the properties and conditions in the subsurface that give rise to this response are similar as well.
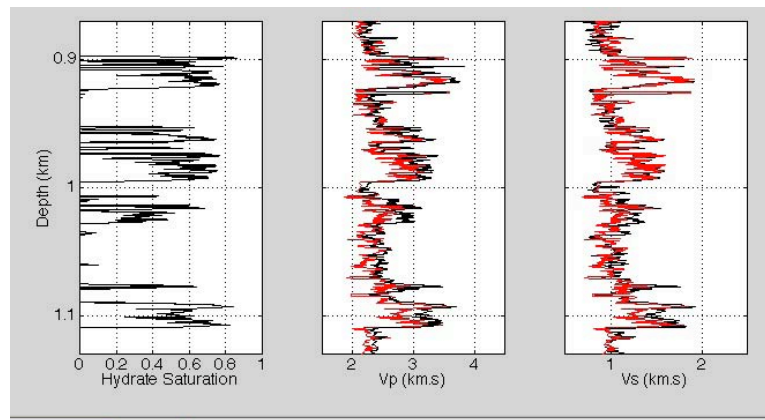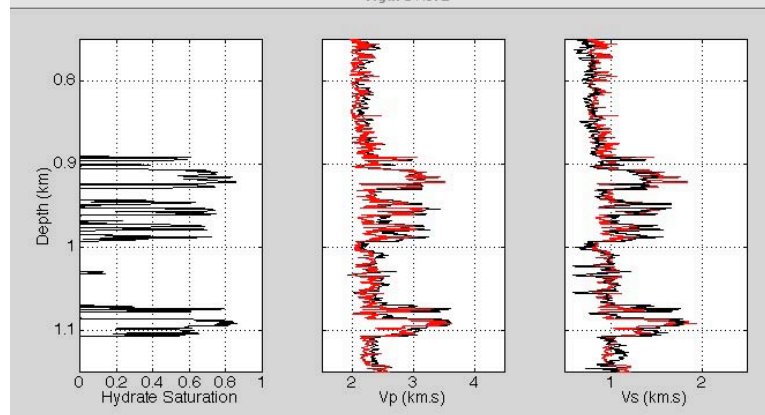
Figure No. 2

Figure 2: Mallik well 2L-38 (left) and 5L-38 (right) depth curves. From left to right in both displays – hydrate saturation as calculated from resistivity (Cordon et al., 2006); the P-wave velocity measured (black) and calculated (gray) using model (b); and the S-wave velocity measured (black) and calculated (gray) using model (b).
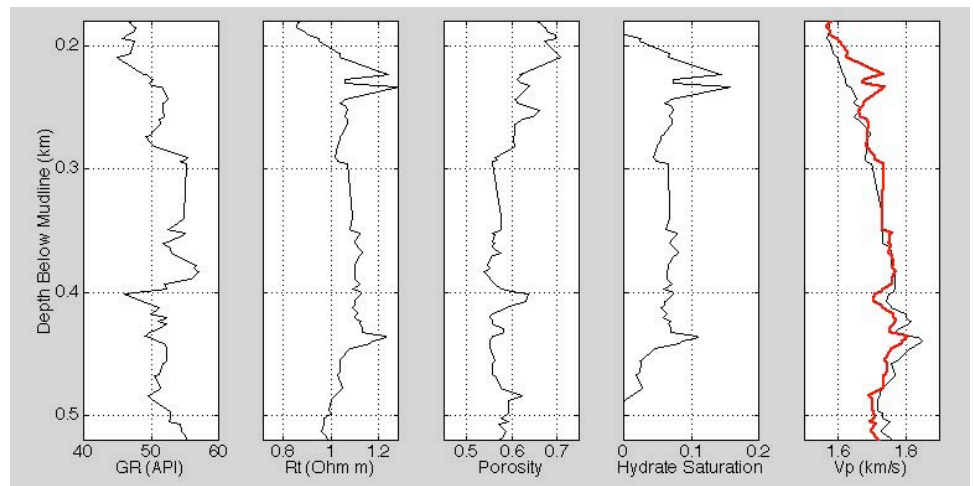

Figure 3: Well 995 at the Outer Blake Ridge depth curves. From left to right – GR; resistivity; porosity of the mineral frame without gas hydrate; hydrate saturation; and P-wave velocity measured (fine gray) and reproduced by model (bold gray).
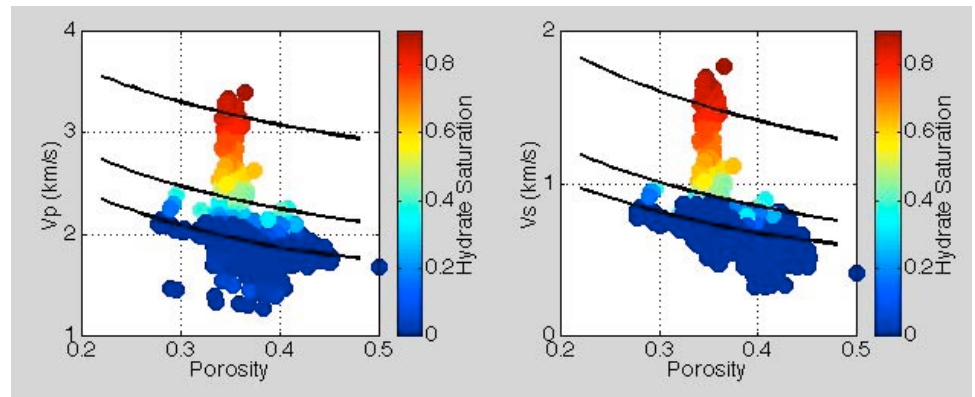
Figure 4: Velocity data from two Nankai Trough wells. P- (left) and S-wave velocity (right) versus porosity of the mineral frame (without hydrate) color-coded by hydrate saturation. The model (b) curves are (from top to bottom) for 0.8, 0.4, and zero hydrate saturation in clean sand with 10% clay. The data points falling below the zero hydrate saturation curves are from intervals with clay.

Systematically conducted *perturbational forward modeling* helps create a catalogue of seismic signatures of lithology, porosity, and fluid away from well control and, by so doing, sets realistic expectations for hydrocarbon detection and optimizes the selection of seismic attributes in an anticipated depositional setting. The key to such perturbational forward modeling are rock physics based relations between the lithology, mineralogy, texture, porosity, fluid, and stress in a reservoir and surrounding rock and their elastic-wave velocity and density. To this end, the goal here was to develop methodologies of transforming geologically-plausible rock properties and conditions as well as reservoir and non-reservoir geometries into synthetic seismic traces and build-up *catalogues* of the synthetic *seismic reflections of methane hydrate*. Such catalogues of synthetic traces may serve as a field guide to hydrate quantification (Figure 5). They also allow the interpreter to interactively assess the ambiguity of such quantification.

An example of directly applying the forward-modeling principle to real seismic data is illustrated in Figure 6. Here we selected a real seismic stack at the Hydrate Ridge and attempted to match it by calculating synthetic traces for a simple earth model. We see that the upper seismic event might have been triggered by small amounts of free gas while the lower event may be due to small amounts of hydrate with free gas underneath.

The question remains regarding the uniqueness of this interpretation. Figure 7 zooms on the main seismic event and synthetically reproduces it by assuming that there is only free gas present in the sand, without methane hydrate above it. It appears that we can still reach a synthetic-to-real match even if the hydrate is absent in the sand. This example emphasizes the non-uniqueness of seismic interpretation even if an appropriate rock physics model is used. The physical foundation of the observed ambiguity is that small amounts of hydrate do not affect the impedance in the sand to the point that the presence of a methane hydrate reservoir can be established without doubt.
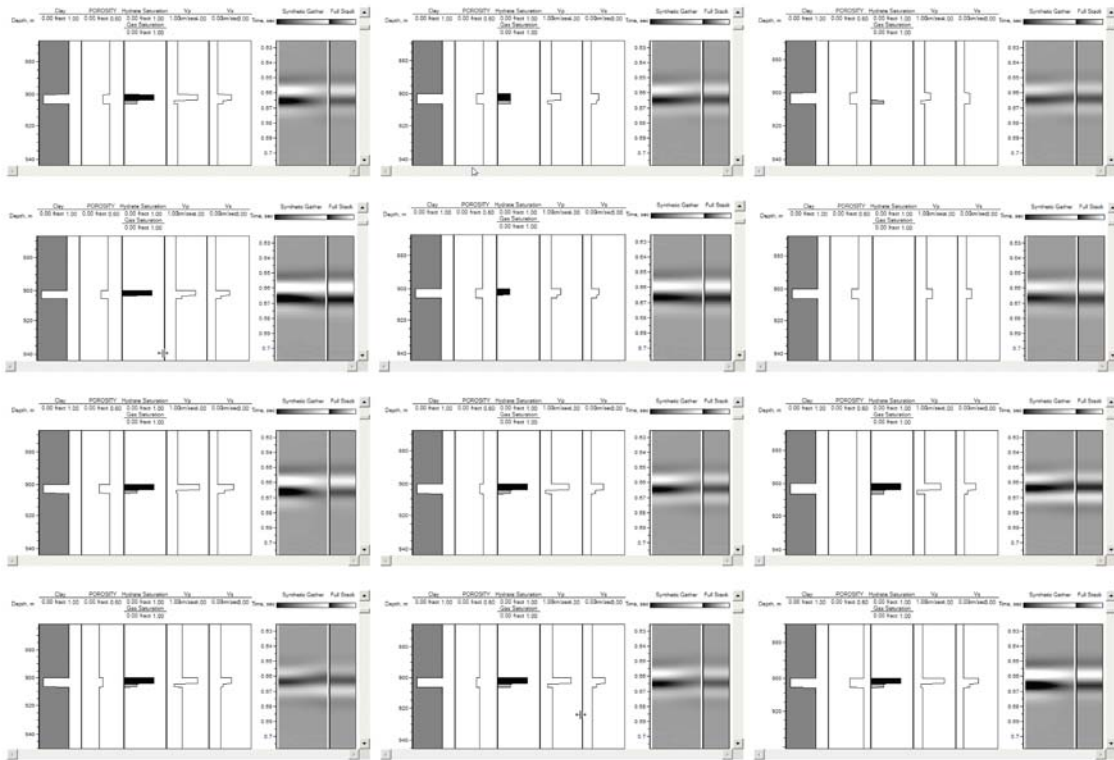
Figure 5: A rock-physics-based catalogue of the seismic reflections (full stacks and gathers) of disjoined gas hydrate and free gas layers. In each display, the first track is the assumed clay content; the second track is the total porosity; the third track is hydrate saturation (black) and free-gas saturation (gray); the fourth and fifth tracks are the P- and S-wave velocity, respectively, calculated from the inputs in the first three tracks and using Model (b). The sixth and seventh tracks are the synthetic seismic gather and full stack, respectively, where light color is for peak while dark color is for trough. Top row: hydrate with free gas directly underneath. The amount of hydrate is reduced from left to right. Second row: hydrate without free gas. The amount of hydrate is reduced from left to right. Third row: hydrate with free gas underneath. The porosity of the sand layer increases from left to right. Bottom row: hydrate with free gas underneath. The porosity of shale increases from left to right.
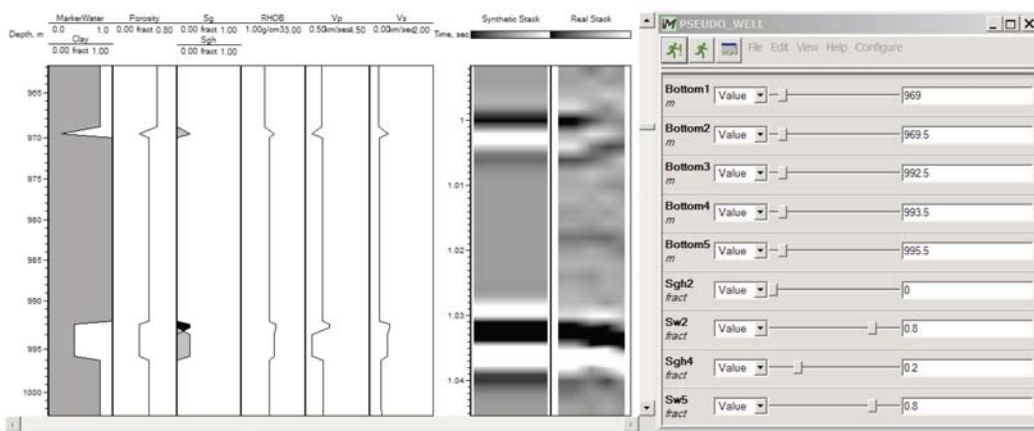

Figure 6: The Hydrate Ridge full-stack section with a synthetic stack to the left. The display is similar to that in Figure 5. The interactive panel on the right specifies the geometry of the layers as well as water saturation in the free-gas layers ("Sw2" and "Sw5") and hydrate saturation in sand layers ("Sgh2" and "Sgh4").
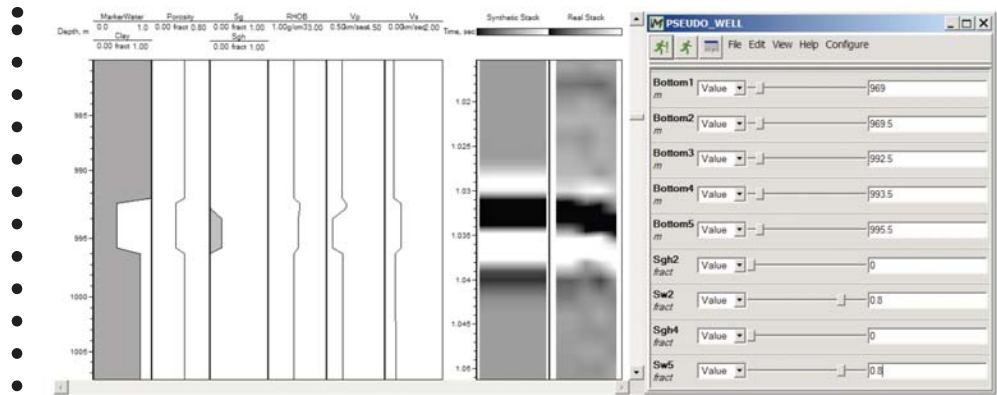
Figure 7: Same as Figure 6 but without hydrate and with free gas. Zooming on the main seismic event.

This example also points to the importance of geological reasoning in such interpretation. If the observed BSR can be explained solely by the presence of free gas, one has to ask what is the seal that sequesters this gas and why it has a classical BSR shape. An answer could be that the only possibility is sealing by methane hydrate that occupies the pores and essentially eliminates the relative gas permeability. This argument in favor of the presence of hydrate needs to be further supported by geochemical proof that the observed feature falls within the hydrate stability window with hydrostatic pressure and temperature gradient as inputs.

Rock physics that links the properties and conditions of a natural methane hydrate reservoir to its elastic properties can help create synthetic variants of the reservoir's seismic response. This technique, combined with complementary geologic and geochemical considerations, can help quantify hydrate resource from seismic data. Catalogues of synthetic traces may serve as a field guide to hydrate quantification. The use of a first-principle-based model is crucial for hydrate characterization because only within a physics-based framework can one consistently perturb reservoir properties and conditions to estimate the elastic response with the ultimate goal of characterizing the reservoir from field elastic data. Of course, this approach relies on the assumption that the same model is appropriate at all instances—which should not be taken for granted.

ADDITIONAL READING:

Cordon, I., Dvorkin, J., and Mavko, G., 2006, Seismic reflections of gas hydrate from perturbational forward modeling, *Geophysics*, 71: F165-F171.

Dvorkin, J., Nur, A., Uden, R., and Taner, T., 2003, Rock physics of gas hydrate reservoir, *The Leading Edge*, 22: 842-847.

Dvorkin, J., and Uden, R., 2004, Seismic wave attenuation in a methane hydrate reservoir, *The Leading Edge*, 23: 730-734.

Ecker, C., Dvorkin, J., and Nur, A., 2000, Estimating the amount of gas hydrate and free gas from marine seismic data, *Geophysics*, 65: 565-573.

Helgerud, M., Dvorkin, J., Nur, A., Sakai, A., and Collett, T., 1999, Elastic-wave velocity in marine sediments with gas hydrates: Effective medium modeling, *GRL*, 26: 2021-2024.

Hydrates surf the "Waves of Change" at the 2008 Offshore Technology Conference

The theme of this year's Offshore Technology Conference was "Waves of Change," with methane hydrates making a big splash with oil and natural gas industry attendees. The conference held every year in Houston, Texas, USA is the premier event for those involved in the offshore oil and natural gas industry. The conference serves as an annual forum where economic, political, environmental, and technological aspects of the oil and gas industry are discussed, with an emphasis on technology.

During two of the conference's four days, over 20 papers relating to methane hydrate research and development were presented in a series of four technical sessions, all of which were well-attended. The first session highlighted the large potential resource found in gas hydrate and the research efforts underway to develop it. The other sessions covered topics related to laboratory research projects currently under way and production strategies under consideration, with a large number of papers presented by researchers involved in Japan's gas hydrate research program. The contributions of George Moridis of LBNL (for developing the sessions) and Dr. Hideo Narita of AIST (for enabling the participation of scientists from Japan) should be recognized.

At a luncheon held during the final day of the conference, Brad Tomer, former Director of the Strategic Center for Natural Gas and Oil, US Department of Energy, spoke on the topic of "Methane Hydrate Challenges and Future" to a sold-out lunch crowd. The presentation covered the progress made by the U.S. methane hydrate research program over the past five years, with the success being largely attributed to the unprecedented level of cooperation among federal agencies, academia, industry, and research labs.

# SPE Selects Hydrate Scientist for International Lecture Tour

The Society of Petroleum Engineers (SPE) has for the first time selected a methane hydrates researcher to participate in its highly acclaimed Distinguished Lecturer Program. Dr. George Moridis, a scientist in the Earth Sciences Division at Lawrence Berkeley National Laboratory and a past contributor to *Fire in the Ice*, has begun the process of formal approval of his lecture on the subject of gas production from hydrates. Moridis will be asked to deliver his 30-minute lecture to SPE chapters around the world from September 2009 through May 2010. The average number of presentations per lecturer is typically 15 but particularly popular topics have been requested as many as 40 times. SPE relies on its Distinguished Lecturer Program to help keep its members informed of recent developments in engineering practices and techniques. Between 25 and 30 individuals are chosen each year to participate.

Dr. Moridis has broad experience in the area of gas hydrates. He is personally responsible for many of the U.S. Dept. of Energy computer models pertaining to the modeling of gas hydrates. His recent efforts have focused on the assessment of gas hydrates relative to the potential for commercial production as well as existing and needed technologies for the development of gas hydrate resources.

His lecture provides a quantitative assessment of gas hydrates, the classification of gas hydrates by potential production type, and a modeling study designed to demonstrate the feasibility of producing different classes of gas hydrates.

DR. GEORGE MORIDIS
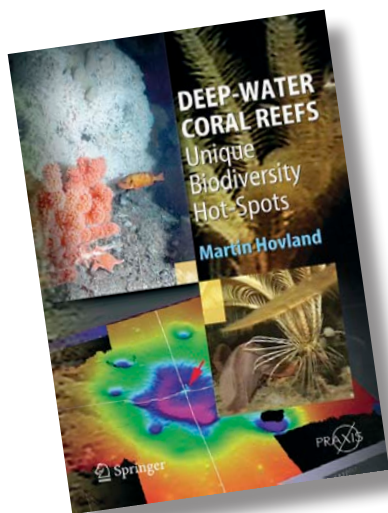
**Deep-Water Coral Reefs
Unique Biodiversity
Hot-Spots**

A new book from Springer Praxis Books Subseries by Martin Hovland (300 p. 60 illus.) is now available.

Deep-water coral reefs are found along large sections of the outer continental shelves and slopes of Europe, from North Cape to the Gulf of Cadiz, and because they also occur along the Atlantic seaboard of USA, the Gulf of Mexico, off Brazil, in the Mediterranean, and off New Zealand, they are currently being targeted by international groups of marine scientists.

The Integrated Ocean Drilling Program (IODP) has arranged a deep-sea scientific drilling campaign on giant carbonate banks off Ireland. Because the reefs currently defy traditional marine-ecological theories, they represent future research opportunities and will enjoy scientific scrutiny for many years to come.

Fire in the Ice readers benefit from a special discount of 20% - Valid until 31 December 2008 To order at the reduced rate, please follow the link http://www.springer.com/978-1-4020-8461-4 and enter the SpringerToken xEk2R6Mq94wC86c when requested during the ordering process. For more instructions, link to http://www.springer.com/cda/content/document/cda_downloaddocument?SGWID=0-0-45-304789-0)

Announcements

INTERNATIONAL COOPERATION IN METHANE HYDRATE RESEARCH AND DEVELOPMENT

India – DOE Under Secretary of Energy C. H. "Bud" Albright and India's Secretary of Petroleum and Natural Gas, M.S. Srinivasan signed a Memorandum of Understanding for Cooperation in Methane Hydrate Research and Development in New Delhi on April 4, 2008. The agreement aims to enhance and accelerate the understanding of the geologic occurrence, distribution, and production of natural gas hydrates along the continental margin of India and in the United States of America. The agreement provides for exchange of information and personnel in the areas of exploration and quantification of natural gas hydrates, resource assessments, laboratory characterization, and production testing. The planned cooperation will provide US scientists greater access to data and samples of the unique methane hydrate deposits offshore India.

Korea – On April 18, 2008, Energy Secretary Samuel Bodman and South Korea Minister for Knowledge Economy Lee Youn-ho signed a Statement of Intent to exchange information on gas hydrate exploration and resource assessment, methods of production of gas hydrates, field testing of gas hydrate production, and gas hydrate dissociation and the potential to mitigate its effects on climate change. Korea is looking to gas hydrates as a future energy source that has the potential to provide up to a 30 year supply of gas.

Japan – Energy Secretary Samuel Bodman and Japanese Minister of Economy, Trade and Industry, Akira Amari signed a Statement of Intent for cooperation in methane hydrate research and development on June 6, 2008 in Aomori, Japan. Japan has an energetic and successful methane hydrate research and development (R&D) program that has resulted in the discovery of large offshore methane hydrate resources and successful short-term production testing in the Canadian arctic (see article on page 1). They also have a comprehensive program of supporting R&D including resource assessment, production modeling, and assessing the environmental impacts of hydrate degassing. Cooperation will allow each country to accelerate commercial production of methane from hydrates by sharing research results. Under the proposed MOU, the U.S. and Japan will cooperate on long-term production testing and offshore exploration, areas where combined resources will be essential to timely accomplishment of goals.

The Department of Energy will be meeting with representatives of the three countries in the next few months to define specific projects for cooperation. Specific details of the cooperation have not been resolved.

GULF OF MEXICO GAS HYDRATE JIP DRILLING PROGRAM UPDATE

The planned July 2008 Hydrate Logging-While-Drilling leg to Alaminos Canyon , Green Canyon, and Walker Ridge will be delayed until at least February of 2009. The reason for the delay is that the current operations for the drill ship have caused the schedule to slip beyond the July 15 last acceptance date in the contract with the drill ship operator. Over the next six months, the JIP and its partners will plan a more comprehensive data collection program at these (and potentially other) sites to occur at a time of substantially-reduced risk of weather-related delays.

ENGINEER HELPS TO GUIDE JAPANESE HYDRATE RESEARCH EFFORT

For Koji Yamamoto, the challenges in understanding the geomechanical and geophysical characteristics of gas hydrate are the most interesting. "The dynamic formation responses of hydrate-bearing sediments are exotic and quite different from those exhibited by conventional rocks. This makes their study all the more interesting!"

Koji believes that the most important challenges currently facing hydrate researchers are related to the issues surrounding climate change, with "environmental concerns related to both naturally occurring and gas production related events," as being the most important. "I suppose that most of the fears people feel are groundless or manageable, but there is too much unknown in regard to deep water sediments. We need to learn more from natural phenomena."

It was after the 2002 Mallik and the Ministry of Economy, Trade and Industry (METI) Tokai-oki to Kumano-nada drilling campaigns, that "we realized the mechanical issues, such as fractures and faults, are an important element of both exploration and production." Due in part to his experiences with the 2002 Mallik and METI Tokai-oki research efforts, Dr. Yamamoto's responsibilities were increased, leading to his serving as the field leader of the Japanese R&D team for the 2008 Mallik operation.

It was during the MITI Nankai Trough drilling expedition that Koji had his first opportunity to experience the collection of marine gas hydrate data. "During the Tokai-oki to Kumano-nada expedition, my colleagues introduced me to the colorful world of marine gas hydrates and that really served to attract my interest. It also gave me a chance to learn more about other scientific fields such as geology, which has deepened my understanding of my own field."

Koji received his PhD in civil engineering from Tohoku University in Sendai, Japan. While there, he performed an inversion study of wave scattering in fluid-filled porous media using integral boundary equation techniques. Upon completion of his studies, Koji worked as an engineer performing numerical modeling of petroleum rock mechanics for a private consulting firm and at Japan Oil, Gas and Metals National Corporation (JOGMEC).

The rewards of studying gas hydrate for Koji include getting to travel to places like northern Canada. "When I left the Mallik well location for home, the entire landscape was frozen. Upon arriving home in Tokyo, I was able to travel north and experience the cherry blossoms in bloom … I really felt the diversity of the planet."

But rewards often come with a few frustrations. Understanding the "big picture" with a subject like gas hydrates is a task that is almost "too broad to manage by myself. If I get too involved with managing the work of such big science, I'm a little afraid that I may lose the mind of an engineer."

When he is not studying gas hydrates, Koji loves to learn about the history of the places he visits during his travels. He also enjoys riding his bicycle through the streets of Tokyo. He and his wife also enjoy skiing in the mountains during the winter months.