

# Oil & Natural Gas Technology

DOE Award No.: FWP FEAB111

## Topical Report

Experimental formation of massive hydrate deposits from accumulation of CH<sub>4</sub> gas bubbles within synthetic and natural sediments

# Hydrate Formation and Dissociation via Depressurization in Simulated and Field Samples

Submitted by:  
Oak Ridge National Laboratory  
Oak Ridge, Tennessee

Prepared for:  
United States Department of Energy  
National Energy Technology Laboratory

June 28, 2007



Office of Fossil Energy

## **Experimental formation of massive hydrate deposits from accumulation of CH<sub>4</sub> gas bubbles within synthetic and natural sediments**

Megan Elwood Madden<sup>1</sup>, Shannon Ulrich<sup>2</sup>, Phillip Szymcek<sup>2</sup>, Scott McCallum<sup>2</sup>, and Tommy Phelps<sup>2</sup>

<sup>1</sup>School of Geology and Geophysics, University of Oklahoma, Norman, OK 73019

<sup>2</sup>Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831

**Acknowledgements:** Funding for this project was provided by DOE's Fossil Energy Methane Hydrate Program. MEEM was supported by ORNL's Wigner Fellowship Program. ORNL is managed by UT-Battelle, LCC, for the U.S. Department of Energy under contract DE-AC05-00OR22725. The authors wish to thank Dave Riestenberg, Patricia Taboada-Serrano, and Lisa Fagan who provided experimental and technical support for the project as well as helpful discussions.

**Abstract:** In order for methane to be economically produced from the seafloor, prediction and detection of massive hydrate deposits will be necessary. In many cases, hydrate samples recovered from seafloor sediments appear as veins or nodules, suggesting that there are strong geologic controls on where hydrate is likely to accumulate. Experiments have been conducted examining massive hydrate accumulation from methane gas bubbles within natural and synthetic sediments in a large volume pressure vessels through temperature and pressure data, as well as visual observations. Observations of hydrate growth suggest that accumulation of gas bubbles within void spaces and at sediment interfaces likely results in the formation of massive hydrate deposits. Methane hydrate was first observed as a thin film forming at the gas/water interface of methane bubbles trapped within sediment void spaces. As bubbles accumulated, massive hydrate growth occurred. These experiments suggest that in systems containing free methane gas, bubble pathways and accumulation points likely control the location and habit of massive hydrate deposits.

### **Introduction:**

As global reservoirs for methane and higher hydrocarbon gases, gas hydrates are of significant interest both as an energy resource and as reservoirs within the global carbon cycle. Over the past twenty years there has been considerable effort to characterize gas hydrates in nature and determine the thermodynamics and kinetics of hydrate stability and dissociation. However, formation mechanisms and geologic controls on hydrate formation, distribution, and habit remain unresolved.

In nature, gas hydrates are observed as either disseminated small particles of hydrate within sediments (often fine grained clays), or as massive nodules or vein-like sheets within fractures or faults. From an economic viewpoint, locating and utilizing massive hydrate deposits is key to producing methane hydrates as an energy resource. However, the bulk of gas hydrate within seafloor sediments are likely to be found as disseminated particles that would be difficult to utilize economically. Therefore, if seafloor gas hydrates are to be used as a hydrocarbon resource, it is necessary to understand how massive hydrates form in the seafloor and the geologic controls on their distribution.

In this study, methane hydrate accumulation processes and controls were examined in the laboratory through hydrate accumulation experiments using free methane gas bubbles percolated through simulated and natural sediment systems. These experiments aim to simulate hydrate accumulation processes which may be occurring within seafloor sediments, allowing observation of hydrate accumulation and growth in the laboratory.

## **Background:**

Gas hydrates occur naturally in seafloor sediments and permafrost deposits where significant concentrations of natural gas are present and the pressure/temperature conditions lie within the hydrate stability field. Gas hydrates have been observed and/or recovered at numerous locations across the globe and are found within diverse sediment contexts from permafrost conglomerates to seafloor clays. Within these deposits, hydrate accumulation may take different forms from fine grained disseminated particles of hydrate within the sediment matrix to massive accumulations of nearly pure hydrate veins or nodules. The mechanism for gas hydrate formation in nature remains under debate and may vary under different conditions. However, three common theories suggest hydrate may be formed by: 1) in-situ biogenic methane production, 2) dissolved methane in water, and/or 3) the presence of free gas bubbles in water.

### *In-situ biogenic methane production*

Brooks et al. (1987) suggest that biogenic methane production within the sediment raises local methane concentrations, resulting hydrate formation. However, uncommonly high methane concentrations would be required to form hydrate in the majority of field settings (Hyndman and Davis, 1992) and, under ideal conditions, only account for 3- 4% of hydrate in sediment (Paull et al. 1994; Minshull et al. 1994). This indicates that while in-situ methane generation could produce disseminated hydrate particles, this mechanism is likely not responsible for massive hydrate formation (nodules, veins, etc.).

### *Dissolved methane in water*

Rapid changes in methane solubility in water as pressure and temperature decrease with upward fluid migration may also result in hydrate formation from dissolved methane. Hyndman and Davis (1992) suggest that as methane-laden water migrates from depth to the base of the BSR (bottom simulating reflector), the temperature and overlying pressure decrease, methane solubility in water also decreases. This allows methane to exsolve, combine with water, and form hydrate. This model suggests that the vast majority of hydrate formation occurs at the BSR. However, slow fluid migration may not give the rapid solubility changes necessary to force methane to exsolve (Handa, 1990).

### *Free gas bubbles in water*

In this model, positively buoyant free gas bubbles rise through conduits such as fractures or through pore space in coarse- to medium-grained sediments until they encounter a barrier where they collect and convert to hydrate. The barrier could be an existing hydrate cap, the termination of a fracture, or an overlying impermeable sediment layer. A hydrate film forms at the gas-water interface along the surface of the bubble as gas diffuses into the surrounding water. Through this mechanism, the coalescence of many bubbles forms large deposits of hydrate such as veins, nodules and massive hydrates.

Recent studies have indicated the presence of free gas within the gas hydrate stability zone (GHSZ) (Dickens, 1997; Egeberg and Dickens, 1999; Flemings et al., 2003; Gorman et al., 2002; Milkov et al. 2004a; Milkov et al., 2005; Netzeband et al., 2005; Schmidt et al., 2005; Zillmer et al., 2005). Multiple mechanisms have been suggested to explain the presence of free gas bubbles within the GHSZ, the most commonly cited being the formation of a hydrate “shield” at the gas-water interface of the bubble, which protects the gas inside from conversion to hydrate (Leifer and McDonald, 2003; Suess et al. 2001). Over time, diffusion of methane through the hydrate “shield” allows for further hydrate formation until all free gas has been incorporated into hydrate. The coalescence of the hydrate films results in either hydrate aggregates (as reported from field samples by Milkov et al., 2004b; Charlou et al., 2004; and Ginsburg et al., 1999), or recrystallization of the hydrate spheres, yielding larger coherent, homogenous hydrate crystals.

### *Field Observations*

Field observations of hydrate formation within natural sediments suggest that sediment type and geologic setting may be the primary dictators of hydrate habit. Coarse-grained sediments such as gravels or breccias generally contain sheets or massive hydrates, while sand, silt and ash generally contain hydrate in the form of cement (Clennell et al., 1999; Harrison and Curiale, 1982; Milkov et al., 2004b; Shipboard Scientific Party (leg 67), 1982[a]; Shipboard Scientific Party (leg 66), 1982[a]; Shipboard Scientific Party (leg 66), 1982[b]; Shipboard Scientific Party (leg 66), 1982[c]; von Huene et al., 1982). Fractured bedrock and impermeable sediments such as mud and clay often contain hydrate nodules, layers, and fracture- and vein-infillings (Brooks et al., 1991; Brooks et al., 1994; Clennell et al., 1999; Ginsburg et al., 1993; Ginsburg et al., 1999; Kvenvolden and McDonald, 1985; Matthews and von Huene, 1985; Matveeva et al., 2003; Milkov et al., 2004b; Sassen et al., 2004; Shipboard Scientific Party, 1982, 1985, 1994). The formation of these specific habits is due to hydrate formation either in large pore spaces, existing fractures in bedrock, or through the creation of new fractures in impermeable sediments when pore fluid (liquid and gas) pressure below exceeds the strength of the sediment above, effectively venting the gas and liquid pressure from below (Flemings et al., 2003).

This work examines methane hydrate formation from a free gas phase in controlled sediment-water-gas systems in the laboratory. The results of these experiments are compared with methane hydrate deposits in the field to determine if methane bubble accumulation points are likely precursors to massive hydrate accumulation within sedimentary systems.

### **Materials and Methods**

Experiments were conducted within a transparent cylinder (60 cm length, 4.8 cm diameter), using commercially available Ottawa sand and black aquarium sand (<500 micron grain size) as well as natural sediments collected by ODP Leg 204 at Hydrate Ridge (Trehu et al., 2004) and the Hot Ice I drilling project in Alaska’s North Slope permafrost gas zone (Millheim et al., 2005). Table 1 provides a summary of the conditions and materials used in the experiments.

The column was mounted inside the Seafloor Processes Simulator (SPS), a cylindrical Hastelloy C-22 vessel of 31.75-cm diameter, 91.44-cm length, and 72-l volume (Phelps et al., 2001), see Figure 1. The vessel is equipped with several sapphire windows and sampling ports. The SPS allows for operational pressures equivalent to those encountered at various ocean depths to be maintained during experiments. The column was submerged in distilled water.

The glass column was filled with approximately equal volumes of small glass beads (3mm diameter) below the sediment, natural or synthetic sediments in the middle third of the column, and larger glass beads (4mm diameter) in the upper third of the column. The glass beads were separated from the sediment by rubber o-rings and fine wire mesh placed below and above the sediment layer. One or more thermocouples were placed at different intervals within the column and a pressure transducer was used to monitor pressure changes within the SPS. In the black sand experiments (5 and 6) a conductivity meter was also inserted into the sediment, however, no meaningful data was recovered. The general design of the column is shown in figure 1B.

Experiment 1 used commercially available Ottawa sand as the sediment medium, while experiments 2-4 used clay-rich sediments recovered from hydrate-bearing drill cores collected by ODP Leg 204 at Hydrate Ridge. The sediments had been thawed prior to delivery, so therefore had lost all of their sediment structures. Due to the low permeability clayey nature of the cores, the sediment had to be broken into grape-sized chunks to allow for gas migration through the column. Experiments 5-6 used sieved (<500 micron grain size) black aquarium sand chosen for its optical contrast with light colored hydrate. This sand appears to be made of mostly crushed black glass. Experiment 7 used intact permafrost sediments from the Hot Ice 1 drilling project collected on the North Slope of Alaska. These sand-silt sediments were introduced directly into the column after being stored in a freezer and then the cold room at 2 degrees centigrade for several days.

The SPS was pressurized to 95% of the 3-point stability field as calculated using the CSMHYD hydrate stability model (Sloan, 1998). These pressure and temperature conditions were maintained for at least 12 hours prior to experiments to allow the water of the SPS to become saturated in methane. Temperatures of 2-5 degrees C were maintained by placing the entire vessel within an explosion-proof cold room similar to an industrial refrigerator.

In experiments 1-4, methane gas was introduced through a diffuser at the base of the sediment column, gradually increasing the total pressure of the vessel. Hydrate formation was monitored visually via macroscopic observations through three sapphire windows, placed at 90 degree intervals around the vessel. The temperature within the sediment column was monitored to determine if and when hydrate formation occurred. Since hydrate formation is an exothermic process, an increase in temperature is observed during hydrate crystallization. This temperature increase was observed in all four experiments, and was coincident with visual observations of hydrate formation through the sapphire observation ports. The cold room was then turned off and the sediment column was allowed to warm slowly, while still at pressure to observe the dissociation of hydrate via a temperature plateau in the thermocouple data due to the endothermic nature of hydrate dissociation.

A HPLC pump was used in experiments 5 and 7 to circulate water from the SPS through the column at variable flow rates. Again, the vessel was then pressurized to 95% of the 3-point stability field for >12 hours prior to the experiment to ensure that the water was methane-saturated. The HPLC pump was then turned on, pumping water from the vessel through the base of the sediment column at  $\sim 6 \text{ ml min}^{-1}$ . The water which passed through the column was collected in a sealed secondary container within the vessel to prevent the bulk water in the vessel from becoming cloudy and impeding observations. Flow was verified visually via a drip into the collection tank within the vessel. The vessel was then pressurized to 1500 psi, and free methane

gas was introduced into the sediment through a flexible capillary tube placed at the edge of the column (within the lower glass beads in experiment 5 and within the sediment in experiments 6 and 7). Formation of methane hydrate was monitored visually and via changes in temperature which were recorded by 2 thermocouples within the sediment column. The natural ice nucleating protein SnowMax was dispersed within the sediment column in experiments 5 and 6 (black sand) to promote hydrate nucleation. In experiments 5 and 7, water and gas flow were terminated before the end of the experiment to determine if further hydrate growth was observed without additional flux of methane through the system. Experiments 5-7 ended when the vessel was depressurized at low temperature, resulting in hydrate dissociation.

## **Results**

Massive hydrate formation was observed visually in each of the experiments as a result of gas bubble accumulation in void spaces. In experiments 1-4, gas hydrate was observed to form first in the large pore spaces between beads either below or above the sediment, then grow into the void spaces between clay clasts within the sediment (Figure 2). Hydrate formation and dissociation were also observed as temperature increases and plateaus, respectively, in the thermocouple data (Figure 3).

In experiments 5 and 6, methane hydrate formed initially in void spaces created by escaping gas bubbles in the vicinity of the capillary injector as well as in the large pore spaces between the glass beads and along the edge of the column near the rubber o-ring (Figure 2). In these experiments bubbles were observed accumulating within the void spaces. Hydrate formation began as a film at the gas-water interface along the surface of the bubbles. As hydrate formation continued, these films amassed to form a massive hydrate accumulation which eventually grew out into the surrounding sediment pore spaces. Gas hydrate formation was also inferred based on the temperature increase in the thermocouple data within an hour of initiating the experiment (Figure 4).

Within the permafrost sediments in experiment 7, hydrate formation was observed initially in void spaces near the capillary gas injector and also at the sediment-bead interface above the capillary as gas bubbles accumulated beneath the o-ring and within pores between glass beads (Figure 2). Repeated hydrate formation within the capillary tube required depressurization of the vessel to dissociate the hydrate and re-pressurization to restart the experiment (temperature and pressure data shown in Figure 5).

## **Discussion**

The results of these experiments demonstrate that in systems containing free methane gas, hydrate is likely to nucleate on the surface of methane gas bubbles, forming a film of methane hydrate. This is likely due to the supersaturation of methane at the bubble/water interface as a result of sluggish methane diffusion into surrounding water (Ginsburg and Soloviev, 1997; Sauter et al., 2006). If bubbles accumulate within the sediments within void spaces or at interfaces between sediment types, massive hydrate growth is likely to occur. Therefore, bubble accumulation points are likely to control where massive hydrate nodules and deposits will form in systems with a free gas phase.

In this conceptual model, massive gas hydrates are expected to form along gas bubble migration routes within faults and fractures, as well as within void spaces at sediment interfaces where upward migrating bubbles become trapped by overlying finer grained sediments (Figure 6). Both of these scenarios are observed frequently in natural settings. Veins of methane hydrate are often recovered from drill cores suggesting fracture or fault-filling behavior (Sassen et al., 2001; Ginsburg and Soloviev, 1997), and nodules or massive hydrate deposits have been reported within coarse grain sand layers or lenses within fine grained silts and clays which were free of massive hydrate (Kraemer et al., 2000; Jin et al., 2002; Ginsburg et al., 2000). As gas bubbles move through sediment, they may accumulate in areas of high porosity, particularly at sediment interfaces or within faults and fractures.

In some cases, gas movement may trigger fracturing of overlying sediments, creating pathways for gas escape through fine grained sediments as suggested by Flemings et al. (2003). Gas bubble accumulation within these fractures may result in hydrate growth and subsequent re-sealing of the fractures, leading to a cycle of further fracturing followed by hydrate growth.

## **Conclusions**

Large volume laboratory experiments examining hydrate formation in natural and synthetic sediments containing free methane gas suggest that massive hydrate deposits may form initially in areas of gas bubble accumulation. Hydrate films were observed to form along the surface of methane gas bubbles which accumulated in void spaces within the sediments. These films amassed, and may have recrystallized to form a massive hydrate nodule within the sediment. Gas bubbles, and subsequent hydrate, were also observed accumulating at the interface of the sediment with an overlying rubber o-ring, as well as within void spaces between glass beads above and below the sediment. These observations suggest that in systems containing free methane gas, stratigraphy as well as tectonic and sedimentary structures are likely to control the location of massive gas hydrate deposits.

## **References:**

- Brooks, J.M., Kennicutt, M.C., Bidigare, R.R., Wade, T.L., Powell, E.N., Denoux, G.J., Fay, R.R., Childress, J.J., Fisher, C.R., Rossman, I., Boland, G., 1987. Hydrates, oil seepage, and chemosynthetic ecosystems on the Gulf of Mexico slope: an update EOS 68, 498.
- Brooks, J.M., Field, M.E., Kennicutt, M.C., II, 1991. Observations of gas hydrates in marine sediments, offshore northern California. *Marine Geology* 96, 103-109.
- Brooks, J.M., Anderson, A.L., Sassen, R., MacDonald, I.R., Kennicutt, M.C., II, and Guinasso, N.L., Jr., 1994. Hydrate occurrence in shallow subsurface cores from continental slope sediments, in Sloan, E.D., Jr., Hoppel, J., and Hnatow, M.A. (Eds), *International Conference on Natural Gas Hydrates*, Annals of the New York Academy of Sciences, 715, 381-391.
- Buffet, B.A., 2000. Clathrate hydrates. *An. Rev. Earth & Planet. Sci.* 28, 477-507.
- Charlou, J.L., Donval, J.P., Fouquet, Y., Ondreas, H., Knoery, J., Cochonat, P., Levache, D., Poirier, Y., Jean-Baptiste, P., Fourre, E., Chazallon, B., 2004. Physical and chemical characterization of gas hydrates and associated methane plumes in the Congo-Angola Basin. *Chem. Geol.* 205, 405-425.

- Clennell, M.B., Hovland, M., Booth, J.S., Henry, P. and Winters, W.J., 1999, Formation of natural gas hydrates in marine sediments 1. Conceptual model of gas hydrate growth conditioned by host sediment properties. *J Geophys. Res.* 104, 22,985-23,003.
- Davie, M.K. and B.A. Buffett, 2003, Sources of methane for marine gas hydrate: inferences from a comparison of observations and numerical models. *Earth and Planet. Sci. Lett.* 206, 51-63.
- Dickens, G.R., Paull, C.K., Wallace, P., and the ODP Leg 164 Scientific Party, 1997. Direct measurement of *in-situ* methane quantities in a large gas-hydrate reservoir. *Nature*, 385, 426-428.
- Egeberg, P.K. and Dickens, G.R., 1999. Thermodynamic and pore water halogen constraints on gas hydrate distribution at ODP Site 997 (Blake Ridge). *Chem. Geol.* 153, 53-79.
- Flemings, P.B., Liu, X., and Winters, W.J., 2003. Critical pressure and multiphase flow in Blake Ridge gas hydrates. *Geology* 31, 1057-1060.
- Ginsburg, G.D., Soloviev, V.A., Cranston, R.E., Lorenson, T.D., and Kvenvolden, K.A., 1993. Gas hydrates from the continental slope, offshore Sakhalin Island, Okhotsk Sea. *Geo-Marine Letters*, 13, 41-48.
- Ginsburg, G.D., Milkov, A.V., Soloviev, V.A., Egorov, A.V., Cherkashev, G.A., Vogt, P.R., Crane, K, Lorenson, T.D., Khutorskoy, M.D., 1999. Gas hydrate accumulation at the Hakon Mosby Mud Volcano. *Geo-Marine Letters*, 19, 57-67.
- Ginsburg, G., V. Soloviev, T. Matveeva, and I. Andreeva, 2000, Sediment grain-size control on gas hydrates presence, sites 994,995, and 997, in C.K. Paull, P.J. Wallace, and Dillon, eds., *Proceedings of the Ocean Drilling Program, Scientific Results*, 164, 237-245.
- Ginsburg, G.D. and V.A. Soloviev, 1997. Methane migration within the submarine gas-hydrate stability zone under deep-water conditions. *Methane Geology*, 137, 49-57.
- Gorman, A.R., Holbrook, W.S., Hornbach, M.J., Hackwith, K.L., Lizarralde, D., and Pecher, I., 2002. Migration of methane gas through the hydrate stability zone in a low-flux hydrate province. *Geology*, 30, 327-330.
- Handa, Y.P., 1990. Effect of Hydrostatic Pressure and Salinity on the Stability of Gas Hydrates. *Journal of Physical Chemistry*, 94, 2652-2657.
- Haeckel, M., E. Suess, K. Wallmann, and D. Rickert, 2004. Rising methane gas bubbles form massive hydrate layers at the seafloor. *Geochimica et Cosmochimica Acta*, 68, 4335-4345.
- Harrison, W.E., and Curiale, J.A., 1982. Gas hydrates in sediments of holes 497 and 498A, in Aubouin, J., von Huene, R., and others, *Initial Reports of the Deep Sea Drilling Project*. U.S. Government Printing Office, Washington, D.C., 67, 591-594.
- Hyndman, R.D., and Davis, E.E., 1992. A mechanism for the formation of methane hydrate and seafloor bottom-simulating reflectors by vertical fluid expulsion. *Journal of Geophysical Research*, 97, 7025-7041.



- Jin, Y.K., M.W. Lee, and T.S. Collett, 2002. Relationship of gas hydrate concentration to porosity and reflection amplitude in a research well, Mackenzie Delta, Canada. *Marine and Petroleum Geology*, 19, 407-415.
- Kraemer, L.M., R.M. Owen, and G.R. Dickens, 2000. Lithology of the upper gas hydrate zone, Blake Outer Ridge: A link between diatoms, porosity, and gas hydrate, in C.K. Paull, P.J. Wallace, and W.P. Dillon, eds., *Proceedings of the Ocean Drilling Program, Scientific Results*, 164, 237-245.
- Kvenvolden, K.A., and MacDonald, T.J., 1985. Gas hydrates of the Middle America Trench-Deep Sea Drilling Project Leg 84, in von Huene, R., Aubouin, J., and others, *Initial Reports of the Deep Sea Drilling Project*. U.S. Government Printing Office, Washington, D.C., 84, 667-682.
- Leifer, I. and MacDonald, I., 2003. Dynamics of the gas flux from shallow gas hydrate deposits: interaction between oily hydrate bubbles and the oceanic environment. *Earth and Planetary Science Letters*, 210, 411-424.
- Liu, X., and P.B. Fleming, 2005. Passing gas through the hydrate stability zone at southern Hydrate Ridge, offshore Oregon. *Earth and Planetary Science Letters*, 241, 211-226.
- Lu, H., I. Moudrakovski, M. Riedel, G. Spence, R. Dutrisac, J. Ripmeester, F. Wright and S. Dallimore, 2005. Occurrence and structural characterization of gas hydrates associated with a cold vent field, offshore Vancouver Island. *Journal of Geophysical Research*, 110, B10204, doi: 10.1029/2005JB003900.
- Mathews, M.A., and von Huene, R., 1984. Site 570 methane hydrate zone, in von Huene, R., Aubouin, J., and others, *Initial Reports of the Deep Sea Drilling Project*. U.S. Government Printing Office, Washington, D.C., 84, 773-790.
- Matveeva, T.V., Mazurenko, L.L., Soloviev, V.A., Klerkx, J., Kaulio, V.V., and Prasolov, E.M., 2003. Gas hydrate accumulation in the subsurface sediments of Lake Baikal (Eastern Siberia). *Geo-Mar Letters*, 23, 289-299.
- Milkov, A.V., Claypool, G.E., Lee, Y.-J., and Sassen, R., 2005. Gas hydrate systems at Hydrate Ridge offshore Oregon inferred from molecular and isotopic properties of hydrate-bound and void gases. *Geochimica et Cosmochimica Acta*, 69, 1007-1026.
- Milkov, A.V., Dickens, G.R., Claypool, G.E., Lee, Y.-J., Borowski, W.S., Torres, M.E., Xu, W., Tomaru, H., Trehu, A.M., and Schultheiss, P., 2004a. Co-existence of gas hydrate, free gas, and brine within the regional gas hydrate stability zone at Hydrate Ridge (Oregon margin): evidence from prolonged degassing of a pressurized core. *Earth and Planetary Science Letters*, 222, 829-843.
- Milkov, A.V., and R. Sassen, 2002. Economic Geology of offshore gas hydrate accumulations and provinces. *Marine and Petroleum Geology*, 19, 1-11.
- Milkov, A.V., Vogt, P.R., Crane, K., Lein, A.Y., Sassen, R., and Cherkashev, G.A., 2004b. Geological, geochemical, and microbial processes at the hydrate-bearing Hakon Mosby mud volcano. a review. *Chemical Geology*, 205, 347-366.

Millheim, K., J. Kwan, T. Williams, W. Maurer, W. MacDonald, A. Kadaster, T. Thompson, R. Sigal, D. Copeland, D. McGuire, S. Runyon, and B. Liddell, 2005. A project update of methane hydrate production from Alaskan permafrost, *in* Taylor, C. and J. Kwan, eds., *Advances in the Studies of Gas Hydrates*, New York, Kluwer Academic/Plenum Publishers, 75-85.

Minshull, T.A., Singh, S.C. and Westbrook, G.K., 1994. Seismic velocity structure at a gas hydrate reflector, offshore western Colombia, from full waveform inversion. *Journal of Geophysical Research*, 99, 4715-4734.

Netzeband, G.L., Hubscher, C.P., Gajewski, D., Grobys, J.W.G., and Bailas, J., 2005. Seismic velocities from the Yaquina forearc basin off Peru: evidence for free gas within the gas hydrate stability zone. *International Journal of Earth Science*, 94, 420-432.

Paull, C.K., Ussler, W. III, and Borowski, W.S., 1994. Source of methane to form marine gas hydrates, In: (First) International Conference on Natural Gas Hydrates, *Annals of New York Academy of Sciences*, eds. Sloan, E.D., Happel Jr., J., and Hnatow, M.A., 715, 161–176.

Sassen, R., S.L. Losh, L. Cathles III, H.H. Roberts, J.K. Whelan, A.V. Milkov, S.T. Sweet, and D.A. DeFreitas, 2001. Massive vein-filling gas hydrate: relation to ongoing gas migration from the deep subsurface in the Gulf of Mexico. *Marine and Petroleum Geology*, 18, 551-560.

Sassen, R., Roberts, H.H., Carney, R., Milkov, A.V., DeFreitas, D.A., Lanoil, B., and Zhang, C., 2004. Free hydrocarbon gas, gas hydrate, and authigenic minerals in chemosynthetic communities of the northern Gulf of Mexico continental slope: relation to microbial processes. *Chemical Geology*, 205, 195-217.

Sauter, E., S. Muyakshin, J. Charlou, M. Schlueter, A. Boetius, K. Jerosch, E. Damm, J. Foucher, and M. Klages, 2006. Methane discharge from a deep-sea submarine mud volcano into the upper water column by gas hydrate-coated methane bubbles. *Earth and Planetary Science Letters*, 243, 354-365.

Schmidt, M., Hensen, C., Morz, T., Muller, C., Grevemeyer, I., Wallman, K., Mau, S., and Kaul, N., 2005. Methane hydrate accumulation in “Mound 11” mud volcano, Costa Rica forearc. *Marine Geology*, 216, 83-100.

Shipboard Scientific Party (Leg 66), 1982a. Site 490, *in* Watkins, J.S., Moore, J.C., and others, *Initial Reports of the Deep Sea Drilling Project*. U.S. Government Printing Office, Washington, D.C., 66, 151-217.

Shipboard Scientific Party (Leg 66), 1982b. Site 491, *in* Watkins, J.S., Moore, J.C., and others, *Initial Reports of the Deep Sea Drilling Project*. U.S. Government, Washington, D.C., 66, 219-287.

Shipboard Scientific Party (Leg 66), 1982c. Site 492, *in* Watkins, J.S., Moore, J.C., and others, *Initial Reports of the Deep Sea Drilling Project*. U.S. Government, Washington, D.C., 66, 289-340.

Shipboard Scientific Party (Leg 67), 1982. Site 497: Middle America Trench upper slope, *in* Aubouin, J., von Huene, R., and others, Initial Reports of the Deep Sea Drilling Project. U.S. Government Printing Office, Washington, D.C., 67, 193-243.

Sloan, E.D., 1998. Gas Hydrates: Review of physical/chemical properties. *Energy and Fuels*, 12, 191-196.

Soloviev, V., and Ginsburg, G.D., 1994. Formation of submarine gas hydrates. *Bulletin of the Geological Society of Denmark*, 41, 86-94.

Suess, E., Torres, M.E., Bohrmann, G., Collier, R.W., Rickert, D., Goldfinger, C., Linke, P., Heuser, A., Sahling, H., Heeschen, K., Jung, C., Nakamura, K., Greinert, J., Pfannkuche, O., Trehu, A., Klinkhammer, G., Whiticar, M.J., Eisenhauer, A., Teichert, B., and Elvert, M., 2001. Sea floor methane hydrates at Hydrate Ridge, Cascadia Margin, In: *Natural Gas Hydrates: Occurrence, Distribution, and Detection*, eds. Paull, C.K. and Dillon, W.P., American Geophysical Union, Washington D.C., 87-981.

Torres, M.E., J. McManus, D.E. Hammond, M.A. deAngelis, K.U Heeschen, S.L. Colbert, M.D. Tyron, K.M. Brown, and E. Suess, 2002. Fluid and chemical fluxes in and out of sediments hosting methane hydrate deposits on Hydrate Ridge, OR, I. hydrogeological provinces. *Earth and Planetary Sciences Letters*, 201, 525-504.

von Huene, R., Langseth, M., Nasu, N., and Okada, H., 1982. Summary of Cenozoic tectonic history along the IPOD Japan Trench transect. *Geological Society of America Bulletin*, 93, 829-846.

Zatsepina, O.Ye. and B.A. Buffett, 1998. Thermodynamic conditions for the stability of gas hydrate in the seafloor. *Journal of Geophysical Research*, 103, 24127-24139.

Zillmer, M., Reston, T., Leythaeuser, T., and Flueh, E.R., 2005. Imaging and quantification of gas hydrate and free gas at the Storegga slide offshore Norway. *Geophysical Research Letters*, 32, L04308, doi:10.1029/2004GL021535.

## Figure Captions

Figure 1. (A) 72-liter Seafloor Process Simulator (SPS) pressure vessel used in the experiments. The SPS has >30 access ports and windows for instrumentation and observation of experiments. The sediment column (B) was suspended within the vessel and submerged in distilled water throughout the experiments. Methane gas was introduced into the column either through the bottom endcap or a capillary placed within the sediment. In some experiments (see Table 1) methane saturated water was also circulated through the column using an external HPLC pump and collected in a secondary reservoir within the vessel (C).

Figure 2. Digital photographs of methane accumulation experiments in seafloor sediments from Hydrate Ridge (A and B- experiment 2), black aquarium sand (C, D and E-experiment 5) and permafrost sediments from Alaska's North Slope (F and G-experiment 7). Images A, C, and F show sediment column before methane injection. The other images show hydrate filling void spaces within the sediments. Methane gas was introduced through the lower endcap in experiment 2, resulting in initial hydrate formation within void spaces between the small beads in the lower portion of the column, then moving upwards and filling void spaces between chunks of clay and between larger glass beads in the upper portion of the column (B). Experiment 5 injected methane gas through a capillary (red arrow in C) placed in the beads below the black sand. Initial hydrate formation occurred in the pore spaces between the beads and along the edge of the rubber o-ring separating the beads from the sediment (D). Continued hydrate growth then moved into the pore space of the black aquarium sand (E). A capillary was also used to inject methane gas into the permafrost sediments in experiment 7 (red arrow in F). The end of the capillary was placed within the sediment and hydrate was observed filling void space created by sediment settling and bubble extrusion within the sediment, and within void spaces along the edge of the upper o-ring (G).

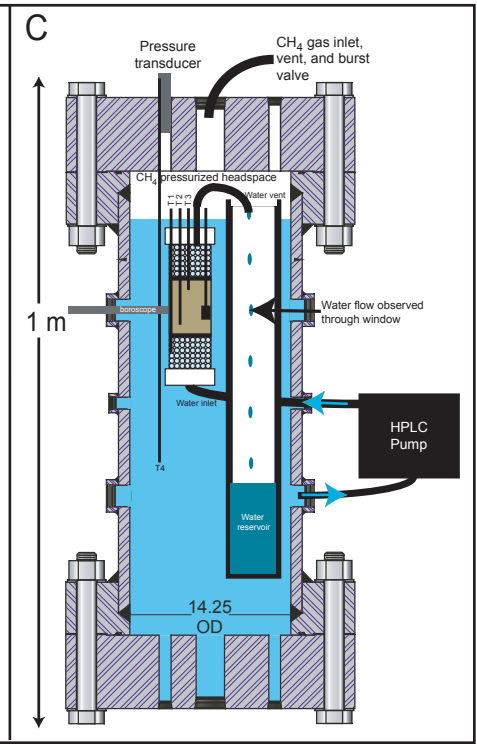
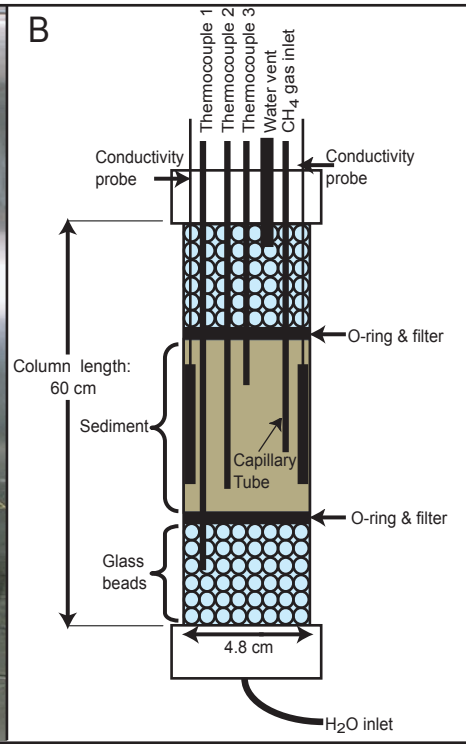
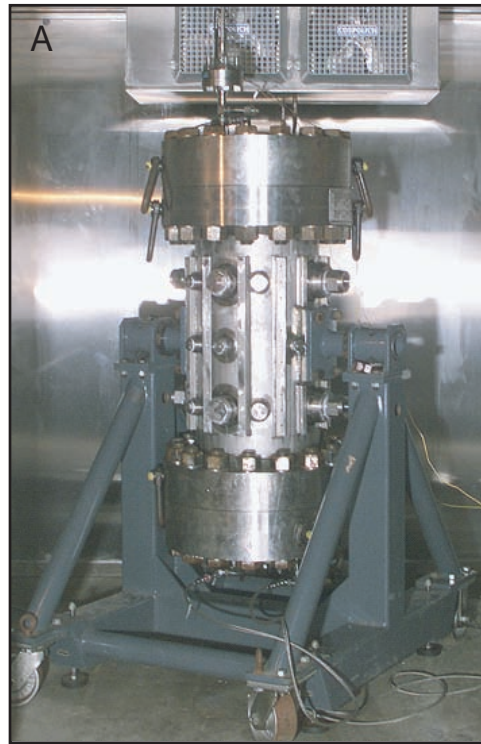
Figure 3. Temperature and pressure data collected during experiment 2 using natural sediments from Hydrate Ridge. Time zero represents the point of initial pressurization with methane gas through the sediment column. The lower thermocouple trace was placed in the glass beads below the sediment, while the upper thermocouple trace is from the thermocouple within the sediment. The temperature increase during pressurization is due to hydrate formation, an exothermic process. The plateau in temperature data and change in slope in the pressure data at approximately 12 hours after pressurization are due to hydrate dissociation, an endothermic reaction.

Figure 4. Temperature (upper graph) and pressure (lower graph) data collected during experiment 5 where methane gas and methane saturated water flowed through a sediment column containing black aquarium sand. Time zero is the point of initial pressurization. Data from the thermocouple in the lower portion of the sediment is shown in black, while data from the upper sediment is light gray and water in the vessel outside the sediment column is medium gray. Water and methane gas were passed through the sediment column for approximately 1.25 hours during and following pressurization. Moderate temperature increases were observed via the thermocouples in the sediment during this period, while a significant increase in the outside water temperature was observed, likely due to hydrate formation at the gas/water interface within the SPS (verified visually). Hydrate formation was also visually observed during this time within void spaces in the sand and along the rubber o-ring and in larger glass beads below the sand (see

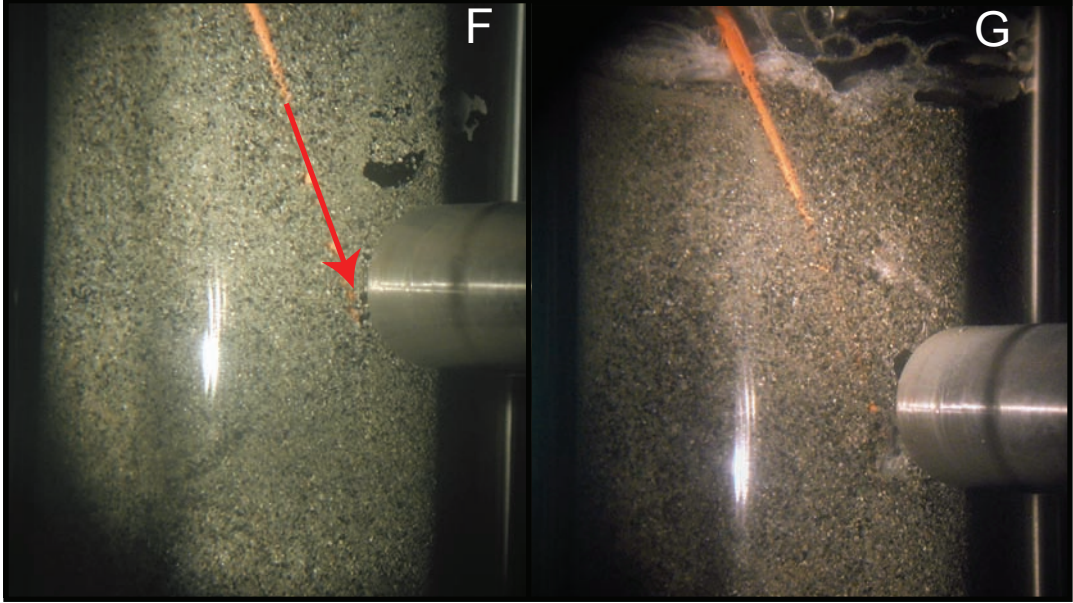
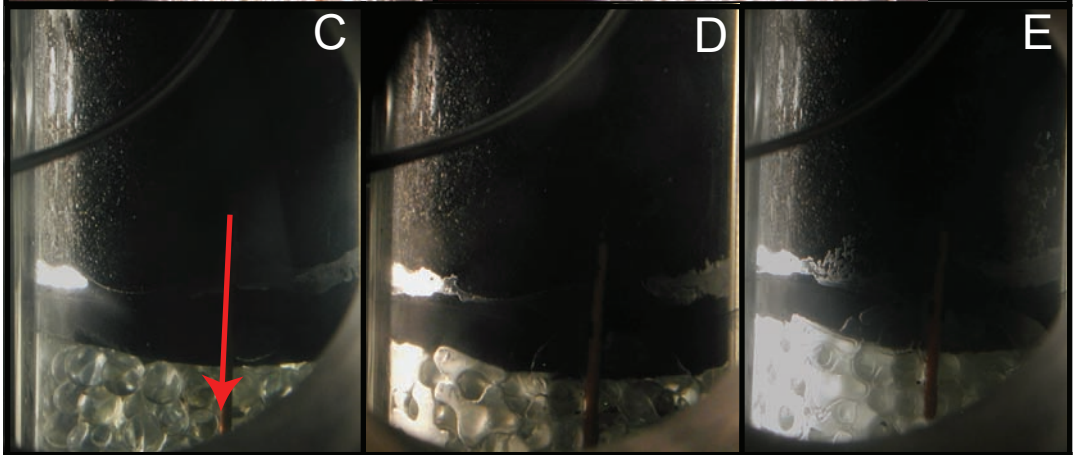
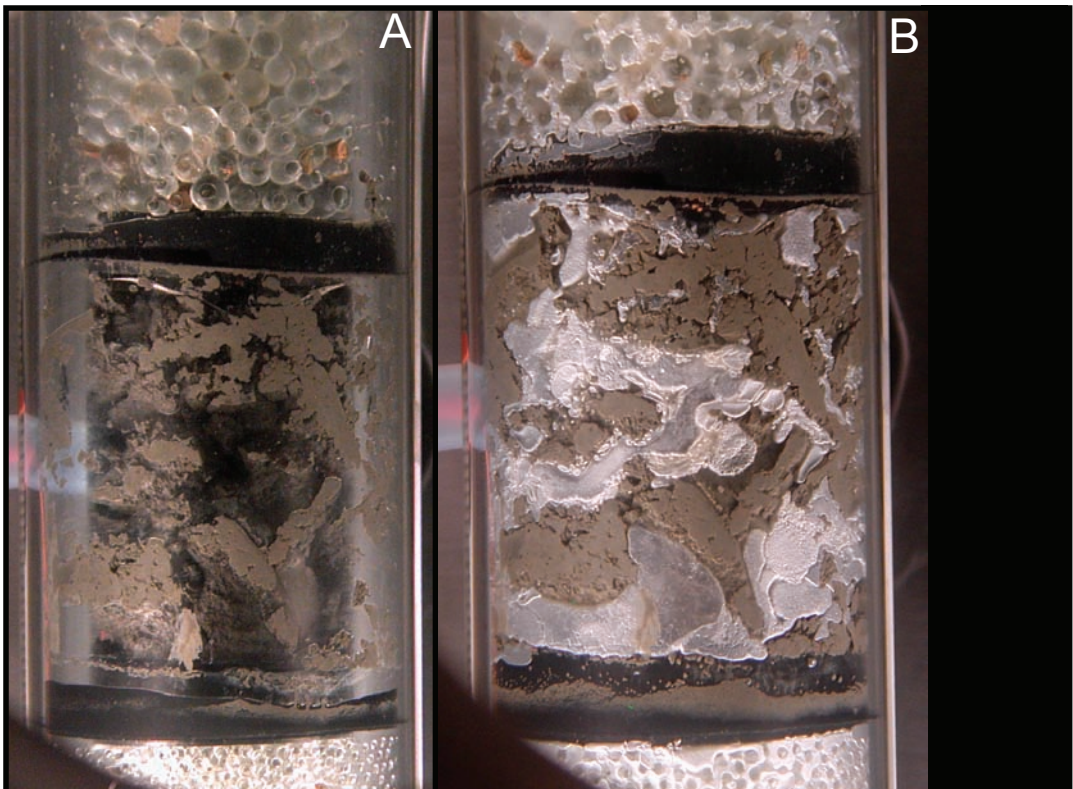
figure 2). Further hydrate growth is indicated by the increase in the sediment temperature after the water and gas flow ended, however, this growth was not visually observed.

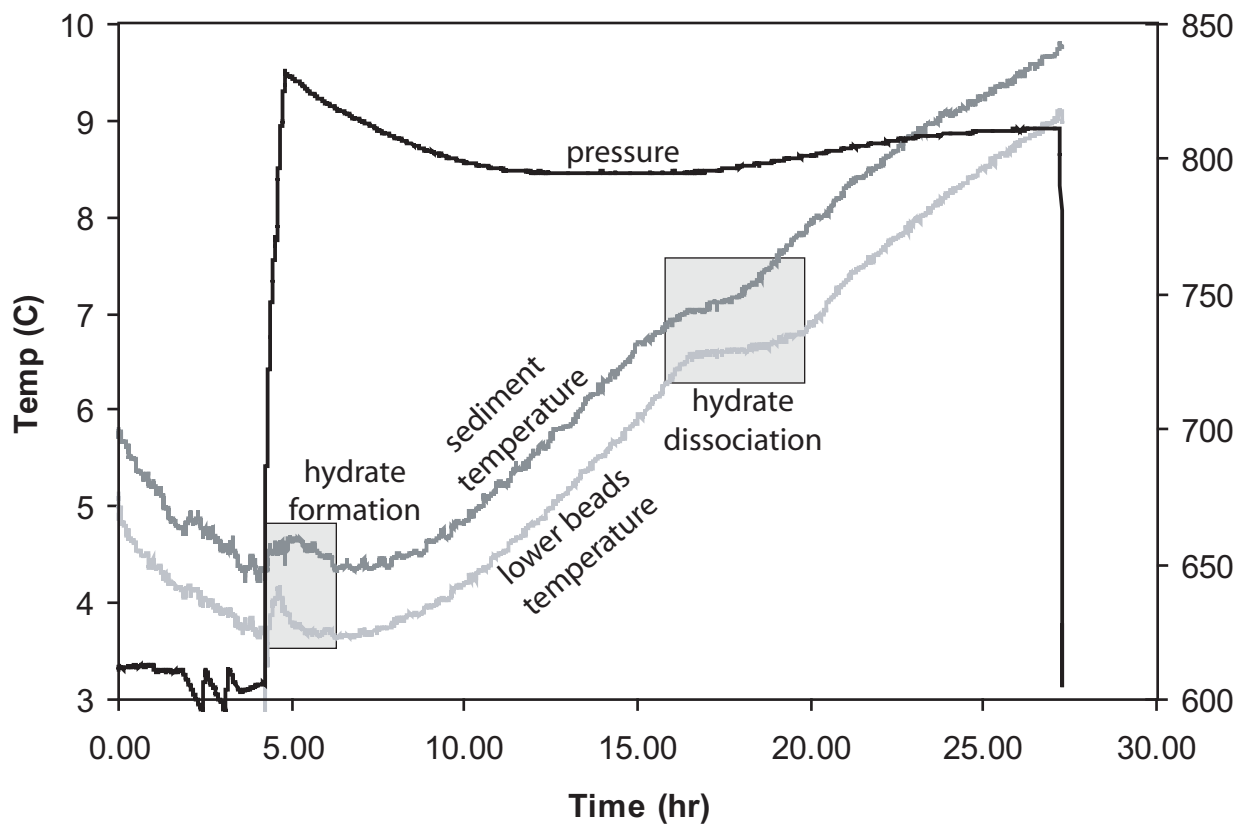
Figure 5. Temperature (upper graph) and pressure (lower graph) data collected during experiment 7 examining gas hydrate formation from flowing methane gas and methane saturated water through natural permafrost sediments from the Hot Ice 1 drilling project in Alaska. Time zero is the point of initial pressurization. Data from the thermocouple in the lower portion of the sediment is shown in black, while data from the upper sediment is light gray and water in the vessel outside the sediment column is medium gray. Following initial pressurization, hydrate formed in void spaces within the sediment formed by migration of gas bubbles through the sediment (see Figure 2), causing an increase in temperature at both sediment thermocouples. The capillary delivering methane gas then clogged several times, making it necessary to de-pressurize the SPS to dissociate the hydrate clog and then repressurize to experimental conditions. Further hydrate formation was observed via increases in the thermocouple data following each repressurization procedure.

Figure 6. Conceptual model for formation of massive hydrate deposits through accumulation of methane gas bubbles. As methane gas bubbles rise through seafloor sediments, they follow preferential pathways along faults and fractures (left) and accumulate within void spaces and beneath less permeable sediments (right). Hydrate nucleation is likely to occur along the surface of these bubbles as methane diffuses out into surrounding water. Therefore, accumulation of bubbles, and hence hydrate films on bubble surfaces, may be a formation mechanism for massive hydrate deposits in systems containing free methane gas.

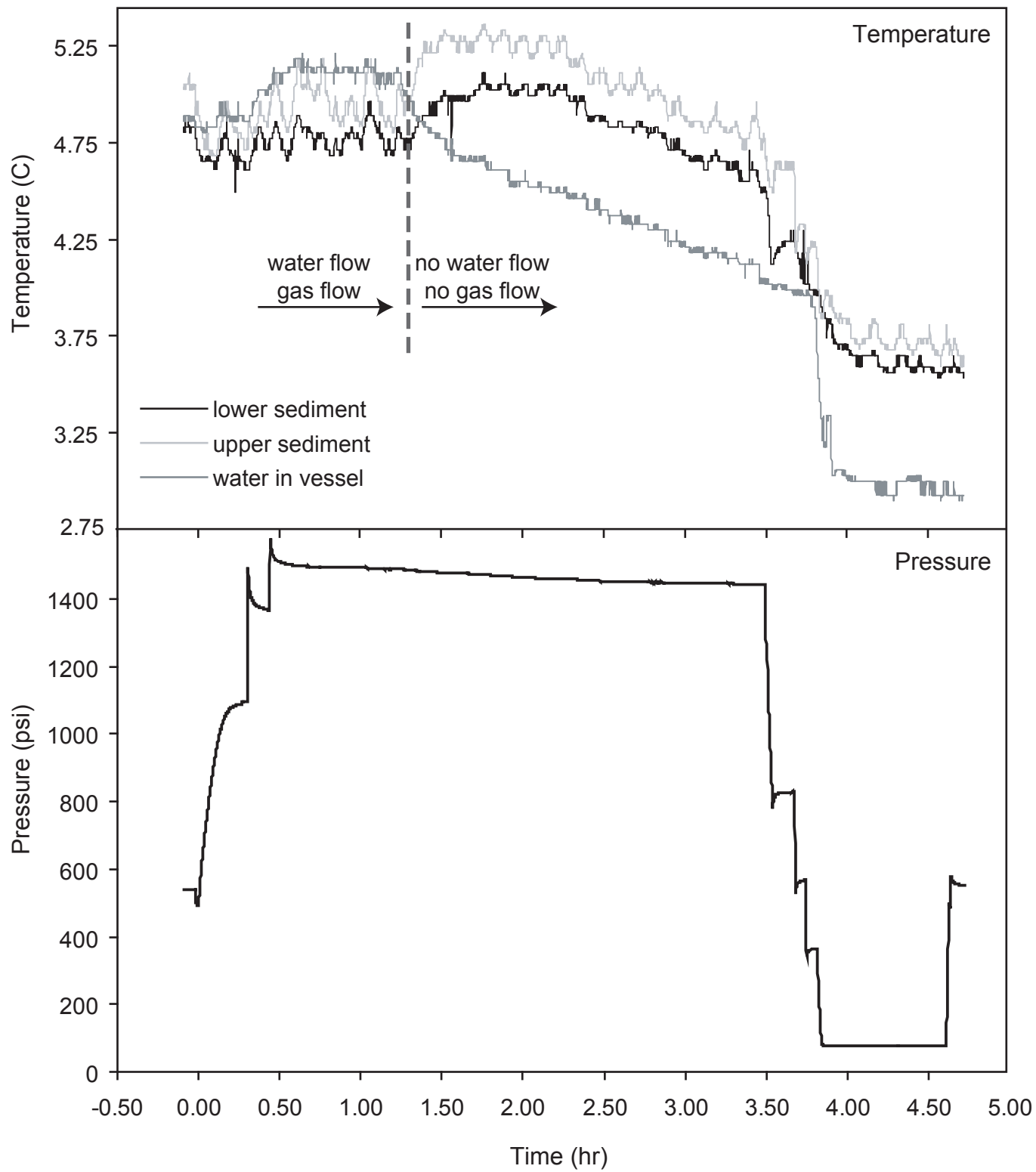




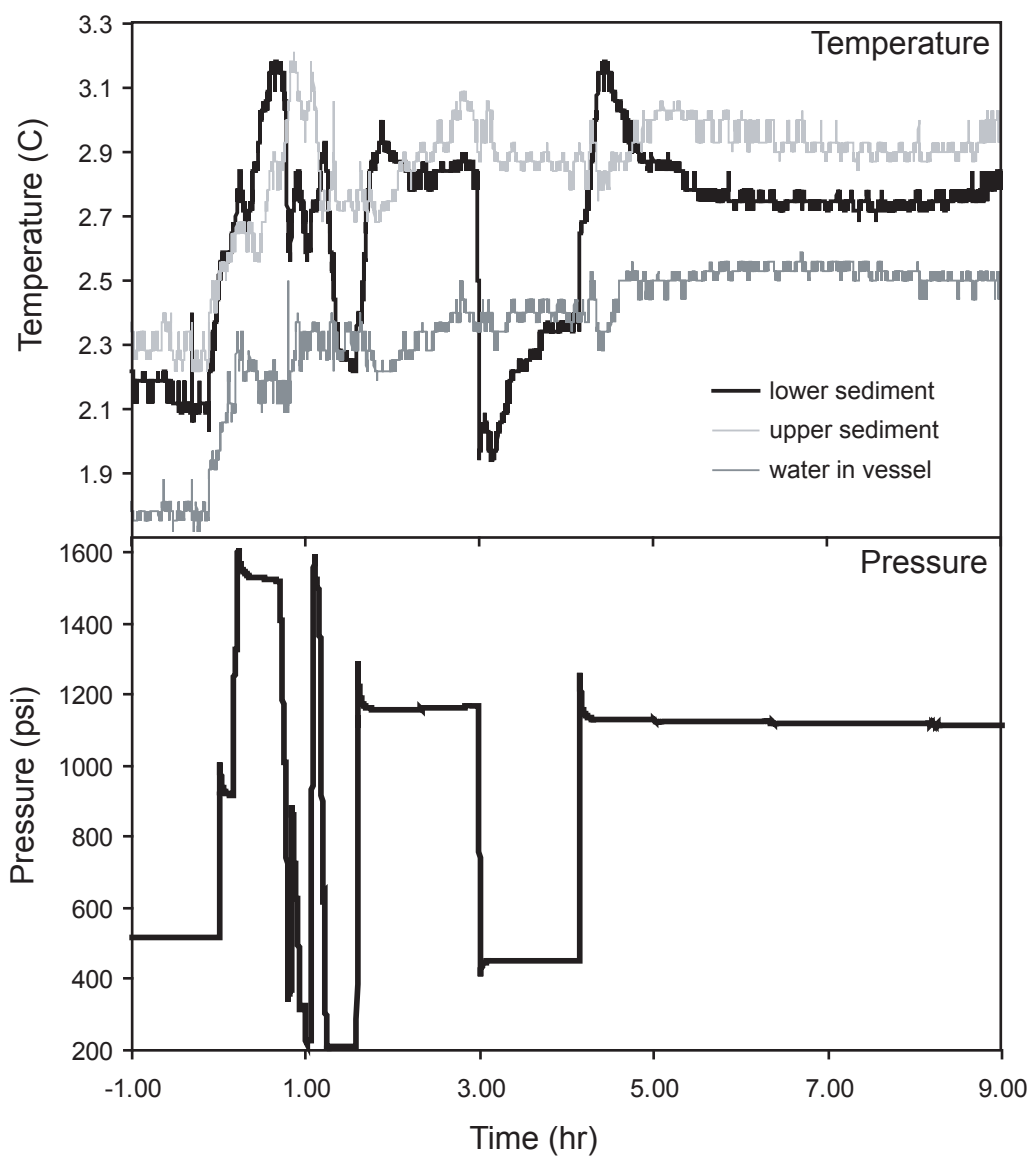








12-1-05



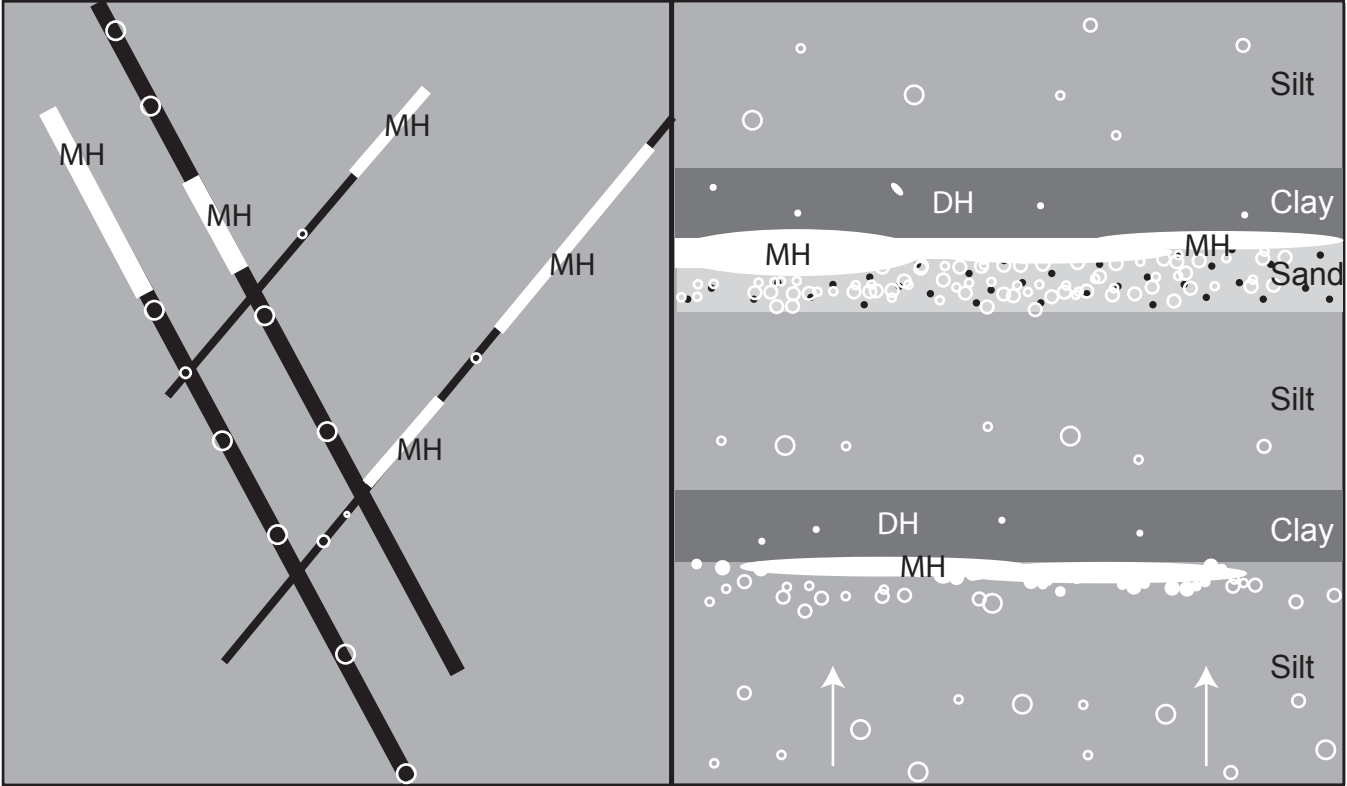


Table 2. Summary of Experiments

Experiment Number	Sediment Type	Gas Flow	Water flow	Temperature (C)	Pressure (MPa)	Hydrate formation observations
1	Ottawa sand	Diffuser in lower glass beads	none	2.2	3.5	Hydrate formation within 3.5 hours of initiation; first in lower glass beads, then moved up into void spaces between clay nodules
2	Leg 204	Diffuser in lower glass beads	none	5	4.1	Hydrate formation within 4.5 hours of initiation; first in glass beads, then moved up into void spaces between clay nodules
3	Leg 204	Diffuser in lower glass beads	none	2	3.1	Same sediment column as 2-25 experiment. Hydrate formation within 0.5 hours of initiation; began in large beads above sediment, then grew through sediment to small beads below sediment.
4	Leg 204	Diffuser in lower glass beads	none	2.5	3.1	Hydrate formation initiated in lower glass beads.
5	Black sand	Capillary in sediment	Circulating methane-saturated water	4.5	10.3	Hydrate formation observed in void space of sediment near capillary; first hydrate formation observed on bubble surface.
6	Black sand	Capillary in sediment	none	2	10.3	Hydrate formation observed within 0.5 hours of initiation along upper o-ring and in upper glass beads. Clog in gas line forced end of experiment.
7	Hot Ice 1	Capillary in sediment	Circulating methane-saturated water	2.5	10.3	Clog in gas injector caused numerous depressurization/re-pressurization cycles to unclog. Hydrate formed in void spaces in sediments near capillary and at upper sediment/beads interface.

## **National Energy Technology Laboratory**

626 Cochrans Mill Road  
P.O. Box 10940  
Pittsburgh, PA 15236-0940

3610 Collins Ferry Road  
P.O. Box 880  
Morgantown, WV 26507-0880

One West Third Street, Suite 1400  
Tulsa, OK 74103-3519

1450 Queen Avenue SW  
Albany, OR 97321-2198

2175 University Ave. South  
Suite 201  
Fairbanks, AK 99709

Visit the NETL website at:  
[www.netl.doe.gov](http://www.netl.doe.gov)

Customer Service:  
1-800-553-7681

