

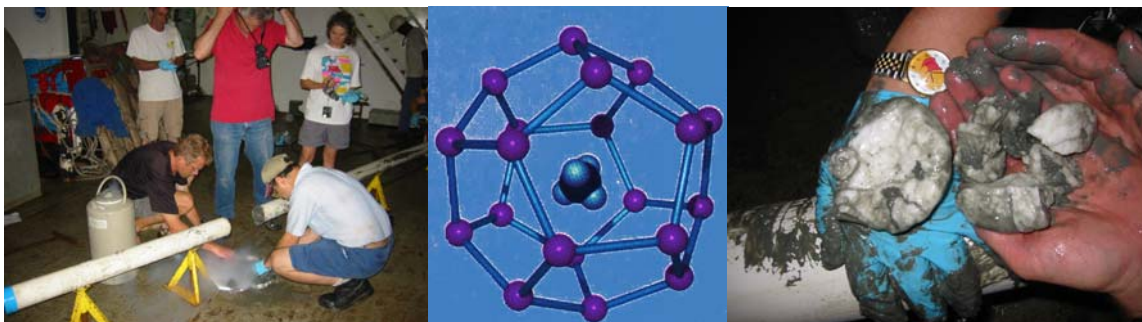


Final Technical Report to the
Department of Energy, National Energy Technology Lab
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September 8, 1997- April 30, 2005

By

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Abstract

This final report to the Department of Energy for Task DE-AT26-97FT34343 covers the period from 1997 to April, 2005 and summarizes the larger research accomplishments, which can be divided in field and laboratory experiments. The geophysical and sampling field programs include 5 experiments conducted between 1998 and 2003 in the Gulf of Mexico (four cruises) and on the Blake Ridge (one cruise). Significant results from the Gulf of Mexico include advancing knowledge of gas hydrate as a potential hazard to drilling at a time when petroleum exploration and production move into deeper water on the continental slope. Anomalous bright reflections called high-reflectivity zones (HRZ's) were identified as possible seismic indicators of gas hydrate. Subsequent sampling through coring identified how methane flux changes from vent regions into mini-basins, and could explain the lack of a known Bottom Simulating Reflection (BSR) in much of the Gulf. In conjunction with the Chevron Gulf of Mexico JIP project, two site surveys were run to characterize gas hydrate prior to drilling in 2005, including detailed analysis of a BSR reflection at one of the sites. The one cruise to the Blake Ridge collected core samples to test the origin and age of the Blake Ridge collapse feature. While the cruise results were equivocal, they results raised new questions about the timing of methane release from hydrate in this well-studied natural laboratory field site. These field programs, particularly in the Gulf of Mexico, helped further DOE goals of understanding gas hydrates in areas where deep-water drilling and production were likely to penetrate the gas hydrate stability zone.

Laboratory experiments were generally integrated with field studies but addressed specific questions about methane hydrate behavior and properties. Studies in the Gas Hydrate and Sediment Testing Laboratory Instrument (GHASTLI) performed some of the first physical property measurements on hydrate-sediment mixtures at simulated in-situ temperatures and pressures. These experiments showed the importance of grain size to hydrate occurrence, and demonstrated how the technique for making hydrate can significantly affect hydrate occurrence in the sample. The thermal properties laboratory made comprehensive thermal characterization of synthetic hydrate demonstrating the linear and non-linear behavior of the material in certain parts of the hydrate stability zone. From the petrophysics laboratory came detailed measurements of physical properties of pure methane hydrate as compared to ice and other hydrocarbon hydrates. This laboratory also developed a cryogenic Scanning Electron Microscope (SEM) capability that has been used to analyze samples returned from the field programs. Most laboratory experiments also included measurements in support of the major DOE-cofunded drilling programs (ODP Leg 204, Mallik, and Hot Ice). These laboratory studies also support DOE objectives of developing well-constrained parameters to use in modeling studies.

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Executive Summary

This final report to the Department of Energy for Task DE-AT26-97FT34343 covers the period from 1997 to April, 2005. Under this task, DOE awarded USGS about \$2.4 million to conduct multidisciplinary research on naturally-occurring marine gas hydrates and on man-made laboratory-formed hydrate-sediment mixtures. Much of the material presented here has already been submitted to DOE in quarterly reports. Therefore, this report covers the larger research accomplishments.

The major gas hydrate research accomplishments under this task can be divided in field experiments and laboratory experiments. Four field experiments were conducted to understand subsurface manifestations of gas hydrate in the Gulf of Mexico, where deep drilling for conventional hydrocarbons now regularly penetrates the gas hydrate stability zone:

- Tommy Munro – 1998; Geophysics
- Gyre – 1999; geophysics
- Marion Dufresne – 2002; Coring
- Gyre – 2003; Geophysics

Each of these cruises contributed to advancing knowledge of gas hydrate as a potential hazard to deep-water drilling on the continental slope. Both the Tommy Munro and first Gyre cruise identified and mapped anomalous bright reflections near the base of the hydrate stability zone called high-reflectivity zones (HRZ's). These were considered possible seismic indicators of gas hydrate. Subsequent sampling through giant piston-coring on the Marion Dufresne sampled in regions of the these HRZ's and results showed how methane flux changes from vent regions into mini-basins. Properties measured in the Marion Dufresne cores, especially high salinities and heat flows, could explain the lack of a known Bottom Simulating Reflection (BSR) in much of the Gulf. In conjunction with the Chevron Gulf of Mexico JIP project, the final Gyre cruise in 2003 collected seismic data as part of two site surveys that were run to characterize gas hydrate prior to drilling in 2005. One of the sites (Keathley Canyon) included detailed analysis of a BSR reflection and its relation to the minibasin seismic stratigraphy

A fifth field experiment consisted of a mixed geophysics and coring cruise on the Blake Ridge (Cape Hatteras – 2000), which was conducted to understand the Blake Ridge collapse structure, hypothesized to be a potential hydrate “blow-out” feature *without* an associated landslide, and therefore a possible smoking gun for how hydrates might cause mass wasting and submarine landslides. Ages of sediments from the piston cores ranged from ~2,000 to ~26,000 years supporting a mix of dates within the collapse structure. An alternative hypothesis was put forward in which the “collapse” structure formed as a field of migrating sand waves. This alternative interpretation of the Blake Ridge feature therefore leaves the question of hydrates causing land slides to be equivocal, until newer data are collected. Results from the Blake Ridge cruise pointed to new questions (of timing of methane release, stratigraphic interpretation of seismic data) needed to refine understanding and knowledge of the role that gas hydrates play in sea floor and oceanic hazard and environmental studies.

Major laboratory support under this interagency agreement comprises three principal parts: (i) the GHASTLI laboratory; (ii) the Thermal Properties System; and (iii) the Petrophysics

laboratory. GHASTLI, the Gas Hydrate and Sediment Test Laboratory Instrument, measures physical properties while simulating natural conditions that are stable for gas hydrate. One aspect of the DOE hydrate research vision is the exploration of hydrate occurrences in all its varied natural settings. The GHASTLI laboratory has supported that vision with natural core measurements, as well as index properties on natural sediment, that have been included in the scientific reports for ODP Leg 164 (Blake Ridge, a sedimentary environment), ODP Leg 204 (Hydrate Ridge, an accretionary complex) and the Mallik 2L-38 and 5L-38 field programs (Mackenzie Delta, a permafrost environment, and a program partially funded by DOE). GHASTLI bridges the gap between field and laboratory investigations because of its flexibility to measure properties of natural core samples and laboratory sediment samples tailored for specific investigations. This versatility led to two key findings: (a) Hydrate formed in nature, a process generally limited by the methane dissolved in pore water, tends not to cement sediment grains. Hydrate formed in the laboratory, most often with a free gas phase to accelerate the formation process, cements sediment grains, producing stiffer samples than generally found in nature. And, (b) sediment grain size plays a significant role in the effect of hydrate formation on sediment properties. hydrate formation causes coarse sands to become more resistant to shear, whereas sediment with silt-sized grains becomes more prone to shear after hydrate formation.

The thermal properties lab was built in 2003 at the USGS Woods Hole Science Center as a generic hydrate research facility. The system supplies high-pressure gas for hydrate formation, oil for sample confinement or compaction, and a temperature-controlled bath for maintaining isothermal conditions or providing a programmable temperature variation. This laboratory produced the first simultaneous estimates of thermal diffusivity and heat capacity from the standard needle-probe thermal conductivity measurement technique. Our first application of this methodology addressed a point made in the 2004 NRC review of DOE gas hydrate research questioning the use of THF hydrate as an analog for methane hydrate. After measuring the thermal properties of THF hydrate, we demonstrated the limited utility of THF hydrate as a thermal property analog for methane hydrate because the thermal properties in THF become highly nonlinear above -5°C, approximately 9°C below the THF hydrate stability temperature, in contrast to the limited information available for methane hydrate.

The Petrophysics Laboratory discovered a methodology for reliably and reproducibly forming pure hydrates. Together with an X-Ray Diffractometer (XRD) and Cryo-Scanning Electron Microscope (CSEM), this lab characterizes hydrate structure and hydrate morphology in laboratory-synthesized pure hydrate or in hydrate-bearing sediment in natural cores. This laboratory demonstrated the phenomenon of self-preservation as a way to optimize preservation of natural hydrate samples and pioneered detailed physical property measurements of pure hydrate and its dissociation and dissolution behaviors. Most laboratory experiments also included measurements in support of the major DOE-cofunded drilling programs (ODP Leg 204, Mallik, and Hot Ice). These laboratory studies also support DOE objectives of developing well-constrained parameters to use in modeling studies.

Finally, this report summarizes other activities that USGS scientists engaged in to support methane hydrate research, such as professional presentations, membership on federal teams coordinating gas hydrate research, participating in Congressional briefings and hearings, and hosting international research delegations.

Part I - Overview

This final report to the Department of Energy for Task DE-AT26-97FT34343 covers the period from 1997 to April, 2005. Under this task, DOE awarded USGS about \$2.4 million to conduct multidisciplinary research on naturally-occurring marine gas hydrates and on man-made laboratory-formed hydrate-sediment mixtures. Much of the material presented here has already been submitted to DOE in quarterly reports. Therefore, this report covers the larger research accomplishments.

The major gas hydrate research accomplishments under this task can be divided in field experiments and laboratory experiments. Within the field experiments, three geophysical (primarily seismic reflection) cruises were conducted to understand subsurface manifestations of gas hydrate in the Gulf of Mexico, where deep drilling for conventional hydrocarbons now regularly penetrates the gas hydrate stability zone; one giant piston-coring cruise was conducted in the northern Gulf of Mexico; and one mixed geophysics and coring cruise on the Blake Ridge took place to understand the Blake Ridge collapse structure, hypothesized to be a potential hydrate “blow-out” feature *without* an associated landslide, and therefore a possible smoking gun for how hydrates might cause mass wasting and submarine landslides. Support from DOE that went towards laboratory studies contributed to (i) moving the USGS Gas Hydrate and Sediment Testing Laboratory Instrument (GHASTLI) from a developmental to an operational phase, with significant upgrades in the performance and reliability of the system; (ii) developing the Woods Hole thermal properties laboratory, used to measure detailed thermal properties of pure hydrate and hydrate-sediment mixtures; and (iii) supporting the Menlo Park petrophysics lab to make gas hydrate measurements (in addition to its ice-measurement capabilities) using the cryogenic SEM. This laboratory also developed a reliable and highly repeatable method for making pure gas hydrate, enabling for the first time inter-lab comparisons and sharing of synthetic hydrate samples. This report summarizes the field program in Part II (authored by D. Hutchinson) and the laboratory efforts in Part III (authored by W. Waite).

Significant other research contributions occurred under this agreement that are lesser in scope and expense although not necessarily in impact. This includes presentations at professional meetings, hosting international visitors, participating in national gas hydrate planning efforts, testifying to Congress etc. Some of these other accomplishments are given in Part IV (authored by D. Hutchinson). Because many of these “other contributions” have been extensively reported in the quarterly reports, only summaries are given here.

Accompanying this report is a DVD that contains pdf files of the publications that are associated with each section of the report. These publications are too extensive to provide paper copies and are therefore only included in electronic form. A pdf file of this report is also on the DVD.

Part II – Field Experiments

By Deborah R. Hutchinson

This section consists of the 5 primary cruises supported under the Interagency Agreement. Each section is organized to give (1) Overview of the experiment; (2) Significant Results from the cruise; (3) Significance of results to DOE Gas Hydrate Goals; and (4) List of publications resulting from the experiment. The publications give the details of all of the results. Copies of all publication are being provided in a separate DVD. The five cruises are:

<u>Year</u>	<u>Ship Name</u>
1998	Tommy Munro
1999	Gyre
2000	Cape Hatteras
2002	Marion Dufresne
2003	Gyre

A. 1998 – Tommy Munro

1. Overview of Work

In collaboration with the University of Mississippi Marine Minerals Technology Center, the USGS conducted a 12-day cruise in the Mississippi Canyon region of the northern Gulf of Mexico in June, 1998, to study the acoustic character and distribution of potential gas hydrates in the shallow subsurface of two regions where gas hydrates were known or suspected from previous studies (Neurauter and Bryant, 1989). Several high-resolution seismic systems were used during the cruise to evaluate the applicability of the various systems for both structural and stratigraphic studies of gas hydrate. Data collected during the cruise included approximately 41 multichannel seismic lines totaling 570 km, 9 ocean-bottom seismometer stations coincident with the multichannel tracklines, and single channel seismic data, all utilizing a variety of GI-gun, water-gun, and boomer sources. See Cooper et al., 1998 for a full description of the data and tracklines (on line at <http://walrus.wr.usgs.gov/infobank/m/m198gm/html/m-1-98-gm.meta.html>). The data were publicly released in Hart et al. (2002), available on line at <http://geopubs.wr.usgs.gov/open-file/of02-368/>).

2. Significant Results

The high-resolution data collected during this cruise reveal a variable and complex upper-sedimentary section in the Mississippi Canyon (Cooper et al., 1998). Despite the lack of conventional geophysical evidence for gas hydrate, such as a Bottom Simulating Reflection (BSR) or blanking, the seismic data show many anomalous acoustic signatures that in all probability are related to the presence of gas and gas hydrate (Cooper and Hart, 2002, 2003). These anomalous zones are labeled High-Reflectivity Zones (HRZs) and occur in proximity to chimney-like features, faults, and sea-floor slides, all features that are also known to be associated in other locations with gas seeps and formation of gas hydrate in surface mounds. The HRZs appear to follow stratigraphic units and are inferred to comprise permeable, sandy units near the base of the gas hydrate stability zone. A large sea-floor slide was imaged on the east side

of the Mississippi Canyon, is a region of extension and salt diapirism. The base of this large slide coincides with on of the HRZs, with the inferred base of the gas hydrate stability zone, and also with a region of known overpressured sands (Cooper and Hart, 2002). This coincidence suggests that the sea-floor sliding may in some way be linked to gas and/or water flow in buried sand-rich units. Because the evidence for gas hydrate occurrence was equivocal from this cruise, the seismic data were used to identify many of the coring targets used on the RV Marion Dufresne giant-piston coring cruise supported by DOE and lead by USGS in summer, 2002. One disappointment of the data from the Tommy Munro cruise was the Ocean Bottom Seismometer data, after considerable effort at processing, filtering, and analyzing, were deemed of insufficient quality to allow for quantitative analysis of gas hydrate (Pecher et al., 1999).

3. Significance of results to DOE Gas Hydrate Goals

One of the significant aspects of this cruise was that it expanded USGS marine studies of gas hydrates into a new continental margin of the United States, the northern Gulf of Mexico, where active petroleum exploration in deep water was occurring. Most USGS marine studies prior to this cruise focused on the Blake Ridge, on the Atlantic margin south of Cape Hatteras, one of the best studied gas hydrate deposits in the world. By conducting experiments in the Gulf of Mexico, this Tommy Munro cruise helped meet DOE objectives of understanding gas hydrates in an area where deep-water drilling and exploration were likely to penetrate the gas-hydrate stability zone. Hence this cruise began the process of studying the data and information needs to understand the consequences of disturbing the gas hydrate stability zone in a region of active drilling, along with the attendant hazards, safety, and resource issues.

4. List of Publications (Abstracts not inclusive)

- 1) Cooper, A.K., and Hart, P.E., 2002, Seismic Studies of the Gas Hydrate Stability Zone, Northern Gulf of Mexico: Proc. 4th International Conference on Gas Hydrates, Yokohama, May 19-23,2002, p. 115-123.
- 2) Cooper, A.K., and Hart, P.E., 2003, High-resolution seismic-reflection investigation of the northern Gulf of Mexico gas-hydrate-stability zone: Marine and Petroleum Geology, v. 19, p. 1275-1293.
- 3) Cooper, A.K., Hart, P.E., and Pecher, I., 1998, Cruise report for a seismic investigation of gas hydrates in the Mississippi Canyon region, northern Gulf of Mexico, Cruise MI-98-GMp. 25 pp.
- 4) Cooper, A.K., Twichell, D.C., and Hart, P., 1999, A seismic-reflection investigation of gas hydrates and sea-floor features of the upper continental slope of the Garden Banks and Green Canyon regions, northern Gulf of Mexico: Report for Cruise G1-99-GM (99002): U.S. Geological Survey Open-File Report OF 99-570, 19 pp.
- 5) Hart, P.E., Cooper, A.K., Twichell, D.C., Lee, M.W., and Agena, W., 2002, High-resolution multichannel seismic-reflection data acquired in the northern Gulf of Mexico, 1998-99 U.S.

Geological Survey Open File Report 02-0368 (<http://geopubs.wr.usgs.gov/open-file/of02-368/>).

- 6) Pecher, I.A., Cooper, A.K., McGee, T., and Hart, P.E., 1999, The distribution of gas hydrates and free gas around a mud diapir in the Gulf of Mexico-- an ocean bottom seismometer experiment during R/V Tommy Munro cruise M1-98-GM: Department of Energy Report, p. 35.
- 7) Pecher, I.A., Cooper, A.K., McGee, T., and Hart, P., 1999, Seismic velocity structure beneath gas hydrate mound in the Gulf of Mexico: results from an OBS experiment (abs.): Third International Conference on Gas Hydrates, Abstracts, Salt Lake City, July, 1999, Abstract Book, unpaginated, 1. p.

II B. 1999 – Gyre

1. Overview of Work

A seismic-reflection field program was conducted for 13 days in April, 1999, aboard R/V Gyre in the Garden Banks and Green Canyon areas of the northern Gulf of Mexico to study shallow seafloor for evidence of gas hydrates and shallow hazards. Gas hydrates were known to be present in sea-floor mounds in this part of the Gulf from earlier coring studies (e.g., Roberts, 1995), but very few publicly available seismic data were available to evaluate the regional distribution and occurrence of features. The tracklines were chosen to coincide with known locations of sea-floor gas hydrate deposits and drill holes with reported shallow-water flow incidents. This cruise collected approximately 1400 km of high-resolution multichannel seismic reflection profiles along 68 lines (15 in3 watertight with a 240-m, 24-channel streamer), about 900 km of Huntec deep-tow Boomer profiles along 44 lines, and approximately 500 km of combined side-scan sonar/Chirp subbottom data on 24 lines. Cruise particulars are published in Cooper et al., (1999, OF99-570, available online at <http://geopubs.wr.usgs.gov/open-file/of99-570/>).

2. Significant Results

Similar to the Tommy Munro cruise in 1998, no Bottom Simulating Reflection (BSR) was identified in the 1999 Gyre cruise. However, High-Reflectivity Zones (HRZs) were observed in the upper sedimentary section and deepened with increasing water depths, similar to the occurrence of BSRs. The HRZs occur near faults, especially at basin edges, and may coincide with the locations of shallow water flows (Cooper and Hart, 2002). Chimney features, indicative of vertical fluid migration, were identified on the basis of disrupted stratigraphy. Detailed analysis of the seismic stratigraphy indicates that the HRZs may in some instances broadly underlie or coincide with interpreted active decollement faults associated with slides. In other areas, the active decollement faults are probably associated with stratigraphic horizons. The HRZs may indicate the presence of gas hydrate or gas, although the seismic data are equivocal. Publications outlining these interpretations are in Cooper and Hart (2002, 2003).

3. Significance of Results to DOE Gas Hydrate Goals

This cruise expanded the geographic coverage and knowledge of shallow hydrate and hazards in the northern Gulf of Mexico that was begun in 1998 with the Tommy Munro cruise. The combined data sets from these two cruises provided hypotheses and targets for testing the nature of near sea-floor and subsurface gas hydrate through giant piston coring (undertaken with the Marion Dufresne, in 2002, see section II D). The large slide on the eastern Mississippi Canyon, the HRZs in the Mississippi Canyon, Garden Banks, and Green Canyon regions, and the localization of hydrate around faults and near-vertical conduits were among the coring targets. This work also helped establish the elusive and complicated nature of gas hydrates in the northern Gulf, especially compared to more classic gas hydrate settings such as the Blake Ridge. This complexity has largely been validated by the 2002 Marion Dufresne coring and the 2005 JIP drilling results.

4. *List of Publications (Abstracts not included)*

- 1) Cooper, A.K., and Hart, P.E., 2002, Seismic Studies of the Gas Hydrate Stability Zone, Northern Gulf of Mexico: Proc. 4th International Conference on Gas Hydrates, Yokohama, May 19-23,2002, p. 115-123.
- 2) Cooper, A.K., and Hart, P.E., 2003, High-resolution seismic-reflection investigation of the northern Gulf of Mexico gas-hydrate-stability zone: Marine and Petroleum Geology, v. 19, p. 1275-1293.
- 3) Cooper, A.K., Twichell, D.C., and Hart, P.E., 1999, A seismic-reflection investigation of gas hydrates and sea-floor features of the upper continental slope of the Garden Banks and Green Canyon Regions, northern Gulf of Mexico: Report for Cruise G1-99-GM (99002): U.S. Geological Survey Open-File Report 99-570, online at <http://geopubs.wr.usgs.gov/open-file/of99-570/>.
- 4) Hart, P.E., Cooper, A.K., Twichell, D.C., Lee, M.W., and Agena, W., 2002, High-resolution multichannel seismic-reflection data acquired in the northern Gulf of Mexico, 1998-99 U.S. Geological Survey Open File Report 02-0368 (<http://geopubs.wr.usgs.gov/open-file/of02-368/>).

II C. 2000 – Cape Hatteras

1. Overview of Work

From 20-29 July, 2000, USGS and MBARI conducted a seismic-profiling and piston-coring cruise on the Blake Ridge to further characterize a feature identified from earlier studies as the Blake Ridge “collapse structure.” This feature was a depression at the top of the Blake Ridge characterized by faults, undulating surface morphology, and a change in the character of the Bottom Simulating Reflection (BSR) beneath it. The goal of the sampling program was to describe the lithologies within the depression, to estimate the age and origin of the feature, and to determine whether fluid venting was occurring along the faults. These faults appeared to terminate near the base of the gas hydrate stability zone and could be conduits for deeper gas-charged fluids to escape. A total of 33 piston cores and 14 gravity cores were collected. The longest core was 14.6 m, and altogether, 240 m of material was collected. Aboard the ship, a total of 240 pore-water samples were analyzed for sulfate, chloride, ammonium, methane, ethane, and total carbon dioxide. Additional samples were taken for microbiology, sulfur isotopes, percent water, hydrocarbon analysis, volatile organic acids, carbon-14, stable carbon isotopes, and sulfur isotopes. Selective sampling was undertaken for nannofossil analysis, detailed stratigraphy, and physical properties. Night time operations of the 3.5 kHz profiler produced 44 survey lines. Navigation, core particulars and other cruise data are available on line at <http://quashnet.er.usgs.gov/data/2000/00016/>. Grain size and other sedimentologic analyses are included in the data base

2. Significant Results

One interpretation of the Blake Ridge collapse structure is that it formed by blowout associated with over-pressured gas trapped beneath the hydrate stability zone. Validating this interpretation therefore provides a potential smoking gun for the ability of hydrates to cause landslides. The challenge of the landslide-hydrate hypothesis is that no studies have precise enough age dates to separate whether gas release (either trapped beneath the hydrate or during hydrate dissociation) can trigger a landslide, or whether the landslide occurs from some other cause and hydrate responds (e.g., disruption of the BSR) as a consequence of the landslide. This is the classic chicken and egg quandary, which came first? The Blake Ridge avoids this uncertainty because no landslides exist on its edges eliminating the question of whether the landslide came first. Hence the Blake Ridge collapse structure, if caused by processes related to hydrate occurrence, would be the smoking gun that hydrate-related processes can significantly disrupt the sea floor. Early publications validated the collapse structure interpretation (Nealon et al., 2000; Dillon et al., 2000; Dillon et al., 2001).

Ages of sediments from the piston cores ranged from ~2,000 to ~26,000 years (Coffin et al., 2004, unpublished report), supporting a mix of dates within the collapse structure. The publication outlining the geometry and character of the collapse structure summarizes the seismic data and presents a model of formation (Dillon et al., 2001). In the same monograph, Holbrook (2001) offered a second possible interpretation, that the collapse structure was not a single catastrophic event, but rather a long-lived feature. In later work (Holbrook et al., 2002; Gorman et al, 2002) using 3D seismic data, an alternative interpretation was proposed in which

the “collapse” structure formed as a field of migrating sand waves. This alternative interpretation of the Blake Ridge feature therefore leaves the question of hydrates causing land slides to be equivocal, until newer data are collected.

3. Significance of Results to DOE Gas Hydrate Goals

The Cape Hatteras cruise provided the first significant data to test the hypothesis that gas hydrates pose a significant sea-floor hazard by causing land slides (or in this case, a blow-out on the sea floor). This issue remains of paramount importance in both industry and government for assessing the potential hazard associated with deep-water drilling, which now occurs in regions where the hydrate is stable in the sea floor and production of deep conventional hydrocarbons has the potential to disturb the hydrate stability field. The Blake Ridge blow-out structure also addresses the potential for methane from gas hydrate to be released catastrophically into the atmosphere and trigger a climate-change response. Understanding the relation between gas hydrates and climate was the focus of the first required report to Congress stipulated in the Methane Hydrate Research and Development Act of 2000. The results from the Cape Hatteras cruise therefore contributed significant data to both of these societally relevant issues (hazards and climate change) and significantly advanced knowledge associated with them. The Cape Hatteras results also pointed to new questions (of timing of methane release, stratigraphic interpretation of seismic data as two) needed to refine understanding and knowledge of the role that gas hydrates play in sea floor and oceanic hazard and environmental studies.

Equally important, the Cape Hatteras cruise contributed to establishing the Blake Ridge as the first natural laboratory for studying natural gas hydrates. This cruise augmented data collected in the region during many years, and preceded drilling on the Blake Ridge by the Ocean Drilling Program Drilling in late 1995, the first ever ODP drilling leg devoted to a gas hydrate experiment.

4. List of Publications (Abstracts not included)

- 1) Coffin, R., Pohlman, J., Knies, D., and Grabowski, K., 2004, Radiocarbon isotope analysis of forams from Blake Ridge: Unpublished report, Delivered to USGS, 9 March, 2004, 3 p.
- 2) Dillon, W.P., and Max, M.D., 2000, The U.S. Atlantic continental margin; the best-known gas hydrate locality, in Max, M.D., ed., *Natural Gas Hydrate In Oceanic and Permafrost Environments*: Dordrecht, Netherlands (NLD), Kluwer Academic Publishers, p. 157-170.
- 3) Dillon, W.P., and Max, M.D., 2001, Gas hydrate in seafloor sediments; impact on future resources and drilling safety; Offshore technology conference; proceedings: Offshore technology conference 2001, Houston, TX, United States, April 30-May 3, 2001, v. 33, Vol. 1, p. 835-845.
- 4) Dillon, W.P., Nealon, J.W., Taylor, M.H., Lee, M.W., Drury, R.M., and Anton, C.H., 2001, Seafloor collapse and methane venting associated with gas hydrate on the Blake Ridge;

causes and implications to seafloor stability and methane release, in Paull, C.K., and Dillon, W.P., eds., *Natural Gas Hydrates: Occurrence, Distribution and Detection*: Washington D.C., American Geophysical Union, p. 211-233.

- 5) 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 environment: *Geology*, v. 30, p. 327-330.
- 6) Holbrook, W.S., 2001, Seismic studies of the Blake Ridge: Implications for Hydrate Distribution, methane expulsion, and free gas dynamics, in Paull, C.K., and Dillon, W.P., eds., *Natural Gas Hydrates: Occurrence, Distribution, and Detection*: AGU Monograph 124, p. 235-256.
- 7) Holbrook, W.S., Lizarralde, D., Pecher, I.A., Gorman, A.R., Hackwith, K.L., Hornbach, M., and Saffer, D., 2002, Escape of methane gas through sediment waves in a large methane hydrate province: *Geology*, v. 30, p. 467-470.
- 8) Max, M.D., and Dillon, W.P., 1999, Oceanic methane hydrate: The character of the Blake Ridge hydrate stability zone and the potential for methane extraction: Author's correction.: *Journal of Petroleum Geology*, v. 22, p. 227-228.
- 9) Taylor, M.H., Dillon, W.P., and Pecher, I.A., 2000, Trapping and migration of methane associated with the gas hydrate stability zone at the Blake Ridge Diapir: new insights from seismic data: *Marine Geology*, v. 164, no. 1-2, p. 79-89.

II D. 2002 – Marion Dufresne

1. Overview of Work

The next phase of hydrate research after the acquisition of remote-sensing seismic reflection data from the cruises summarized in the 1998 Tommy Munro (section II A) and 1999 Gyre (section II B) sections was to collect sediment and hydrate samples in the northern Gulf of Mexico to validate the interpretation of the remote data. The French research vessel the Marion Dufresne was chosen because of its unique capability to collect unusually long cores with the Calypso giant piston corer (capable of collecting 50 – 60 m cores). The core locations were chosen to lie along transects that extended from known gas hydrate mounds or vent sites towards the centers of salt-withdrawal minibasins. Four general locations were targeted: Tunica Mound (in the Garden Banks protraction area defined by MMS), Bush Hill (in the Green Canyon protraction area), Mississippi Canyon (in the Mississippi protraction area), and the Pygmy and Orca Basins which were the subject of DSDP drilling in Leg XX). Coring objectives were to sample subsurface gas hydrates away from the faulted mound/vent/seep sites and to identify possible reservoir sediments. In all, the July, 2002 cruise collected 17 giant piston cores (the longest was 38 m), 4 giant box cores, 4 gravity cores, and 17 measurements utilizing the heat-flow probe. Gas hydrate was collected from 4 of the cores in the vicinity of known vent sites. The lack of hydrate recovered in cores away from known fault/vent sites suggests that (a) hydrate is not common in the adjacent sedimentary basins in the northern Gulf of Mexico, (b) the hydrate is more deeply buried than the core penetrations, or (c) the hydrate occurs in other locations than the ones sampled.

A description of the data collected and locations of the coring sites are available on the USGS internet site <http://walrus.wr.usgs.gov/infobank/d/d102gm/html>. A cruise report with photographs of operations is available at (DOE FITI WEB SITE).

2. Significant Results

The Marion Dufresne coring cruise provided the first regional information about gas hydrates deeper than samples obtained by conventional (4-6 m-long) piston cores (excepting the hydrate samples from approximately 20-m subbottom from the Orca Basin acquired on DSDP Leg 96, site 618 (Pflaum et al, XXX). Although hydrate was not consistently recovered, pore water geochemistry, gas composition, geothermal gradients, and other sedimentary characteristics were analyzed to indicate properties of the hydrate stability zone and to estimate proxies for upward methane fluid flux (Paull et al., 2005-GeoMarLetts, Winters et al., 2006-DVD). One of the unexpected results was the unusually high salinity and geothermal measurements obtained, suggesting that both thermal and chemical processes may be inhibiting gas hydrate occurrence in the minibasins (Paull et al., 2005). In some of the first SEM images of natural gas hydrate, Stern et al. (2005-ICGH) showed textures that favorably compared the grain-boundary and grain-morphology images of synthetic and natural hydrate, demonstrating the utility and success of creating laboratory-formed gas hydrate. A complete scientific and data report is currently in press at USGS (Winters, Lorenson, and Paull, in press – DVD).

3. Significance of results to DOE Gas Hydrate Goals

Understanding the occurrence of gas hydrates as both a hazard and a resource in areas of active hydrocarbon exploration has been a priority of the DOE Methane Hydrates program. With billions of dollars invested in drilling for deeper conventional hydrocarbons, both industry and government have considerable stake in anticipating and managing the risk to infrastructure from drilling through potential hydrate deposits. Likewise, the bonus from knowing whether gas hydrates are a potential resource has enormous economic pay-off, especially in regions where conventional drilling has existing infrastructure that might reduce the cost of development. Both these conditions apply to the northern Gulf of Mexico, where deep-water drilling on continental margins is being pioneered.

4. List of Publications

- 1) Bout-Roumazelles, V., and Trentesaux, A., in press, Sedimentologic analysis of cores recovered from the RV Marion Dufresne cruise in the Gulf of Mexico, 2-18 July, 2002, in Winters, W.J., Lorenson, T.D., and Paull, C.K., eds., *Initial Report of the IMAGES VIII/PAGE 127 Gas Hydrate and Paleoclimate Cruise on the RV Marion Dufresne in the Gulf of Mexico, 2-18 July 2002*: U.S. Geological Survey Open-File Report 2004-1358, 29 pp.
- 2) Brunner, C.A., in press, Qualitative planktonic foraminiferal biostratigraphy of a latest Quaternary core, MD02-2570, from the northern Gulf of Mexico, in Winters, W.J., Lorenson, T.D., and Paull, C.K., eds., *Initial Report of the IMAGES VIII/PAGE 127 Gas Hydrate and Paleoclimate Cruise on the RV Marion Dufresne in the Gulf of Mexico, 2-18 July 2002*: U.S. Geological Survey Open-File Report 2004-1358, 23 pp.
- 3) Chen, Y., Matsumoto, R., and Ussler, W., III, in press, Methane-driven authigenic carbonates from the IMAGES VIII/PAGE 127 Gas Hydrate and Paleoclimate Cruise on the RV Marion Dufresne in the Gulf of Mexico, 2-18 July 2002, in Winters, W.J., Lorenson, T.D., and Paull, C.K., eds., *Initial Report of the IMAGES VIII/PAGE 127 Gas Hydrate and Paleoclimate Cruise on the RV Marion Dufresne in the Gulf of Mexico, 2-18 July 2002*: U.S. Geological Survey Open-File Report 2004-1358, 44 pp.
- 4) Dugan, B., Germaine, J., Winters, W.J., Flemings, P.B., 2003, Near-seafloor overpressure in the deepwater Gulf of Mexico interpreted from laboratory experiments: Eos, Transactions, American Geophysical Union, v. 84, no. 46, Fall Meet. Suppl., Abstract H12K-02, AGU 2003 fall meeting, San Francisco, CA.
- 5) Dugan, Brandon, Germaine, Jack, Winters, William, and Flemings, Peter, 2004, Laboratory constraints and models of pressure, hydrate, and stability in shallow Mississippi Canyon sediments (MC 855), deepwater Gulf of Mexico: Abstracts, American Association of Petroleum Geologists 2004 Annual Convention, Dallas, TX, April 18-21, 2004, p. A378.
- 6) Flocks, J., and Swarzenski, P., in press, Cruise report: sediment collection from Orca and Pigmy basins, Gulf of Mexico, and analyses for texture and trace-metal concentrations, July 2002, 127 PAGE Campaign, in Winters, W.J., Lorenson, T.D., and Paull, C.K., eds., *Initial Report of the IMAGES VIII/PAGE 127 Gas Hydrate and Paleoclimate Cruise on the RV Marion Dufresne in the Gulf of Mexico, 2-18 July 2002*: U.S. Geological Survey Open-File Report 2004-1358, 42 pp.

- 7) Gilbert, L.Y., Waite, W.F., Winters, W.J., and Mason, D.H., 2004, Characterization of Gulf of Mexico sediment in hydrate and non-hydrate bearing cores using specific surface area: Eos, Transactions, American Geophysical Union, Fall Meeting Supplement, San Francisco, CA, 13-17 December 2004, v. 85, n. 47, abstract #OS41C-0491.
- 8) Hallam, S.J., DeLong, E.F., Ussler, W., III, and Paull, C.K., in press, Methanogenic and methanotrophic archaeal diversity in northern Gulf of Mexico sediments, in Winters, W.J., Lorenson, T.D., and Paull, C.K., eds., *Initial Report of the IMAGES VIII/PAGE 127 Gas Hydrate and Paleoclimate Cruise on the RV Marion Dufresne in the Gulf of Mexico, 2-18 July 2002*: U.S. Geological Survey Open-File Report 2004-1358, 16 pp.
- 9) Labails, C., Géli, L., Sultan, N., Novosel, I., and Winters, W., in press, Thermal measurements from the Gulf of Mexico continental slope: results from the PAGE cruise, in Winters, W.J., Lorenson, T.D., and Paull, C.K., eds., *Initial Report of the IMAGES VIII/PAGE 127 Gas Hydrate and Paleoclimate Cruise on the RV Marion Dufresne in the Gulf of Mexico, 2-18 July 2002*: U.S. Geological Survey Open-File Report 2004-1358, 17 pp.
- 10) Lorenson, T.D., Cooper, A.K., Hart, P.E., and Winters, W.J., in press, Geologic Setting and context of cores taken during the IMAGES VIII/PAGE 127 Cruise of the RV *Marion Dufresne* in the Northern Gulf of Mexico, in Winters, W.J., Lorenson, T.D., and Paull, C.K., eds., *Initial Report of the IMAGES VIII/PAGE 127 Gas Hydrate and Paleoclimate Cruise on the RV Marion Dufresne in the Gulf of Mexico, 2-18 July 2002*: U.S. Geological Survey Open-File Report 2004-1358, 37 pp.
- 11) Lorenson, T.D., Dougherty, J.A., and Flocks, J.G., in press, Hydrocarbon gases from giant piston cores in the northern Gulf of Mexico: Results from the IMAGES VIII/PAGE 127 cruise on the RV *Marion Dufresne* in the Gulf of Mexico, 2-18 July 2002, in Winters, W.J., Lorenson, T.D., and Paull, C.K., eds., *Initial Report of the IMAGES VIII/PAGE 127 Gas Hydrate and Paleoclimate Cruise on the RV Marion Dufresne in the Gulf of Mexico, 2-18 July 2002*: U.S. Geological Survey Open-File Report 2004-1358, 57 pp.
- 12) Lorenson, T.D., Winters, W., Hart, P.E., and Paull, C.K., 2002, Gas Hydrate Occurrence in the Northern Gulf of Mexico Studied with Giant Piston Cores: EOS, Transactions, American Geophysical Union, v. 83, n. 51, Dec., p. 601, 607-608.
- 13) Lorenson, Thomas D., Winters, William J., Paull, Charles K., Ussler, William III, and Dougherty, Jennifer A., 2003, Modeling gas hydrate occurrences in the northern Gulf of Mexico from giant piston cores: Abstracts with Programs, v. 35, n. 6, Geological Society of America Annual Meeting, Seattle, Nov. 2-5, 2003, p. 533.
- 14) Lorenson, T.D., Winters, W.J., Paull, C.K. and Ussler, W., III, 2003, Gas hydrate occurrence in the northern Gulf of Mexico studies with giant piston cores; from seafloor vents to minibasins: Abstracts, EGS-AGU-EUG Joint Assembly, Nice, France, 6-11 April 2003, Geophysical Research Abstracts, v. 5, #07457.
- 15) Lorenson, T.D., Winters, W., Paull, C., and Ussler, W. III., and the PAGE 127 Shipboard Scientific Party, 2003, Gas Hydrate in the Northern Gulf of Mexico: New Insights Learned from Giant Piston Coring: AAPG Annual Meeting Salt Lake City, Utah.
- 16) Novosel, I., Winters, W.J., Boldina, O.M., Labails, C., and Géli, L., in press, Thermal conductivity of sediment recovered from the IMAGES VIII/PAGE 127 Gas Hydrate and Paleoclimate Cruise on the RV *Marion Dufresne* in the Gulf of Mexico, 2-18 July 2002, in

- Winters, W.J., Lorenson, T.D., and Paull, C.K., eds., *Initial Report of the IMAGES VIII/PAGE 127 Gas Hydrate and Paleoclimate Cruise on the RV Marion Dufresne in the Gulf of Mexico, 2-18 July 2002*: U.S. Geological Survey Open-File Report 2004-1358, 14 pp.
- 17) Paull, C.K., Ussler, W., III, Lorenson, T.D., Winters, W., and Dougherty, J.A., 2005, Geochemical constraints on the distribution of gas hydrates in the Gulf of Mexico: *Geo-Marine Letters*, v. 25, p. 273-280.
 - 18) Paull, C.K., Ussler, W., III, Winters, W.J. and Lorenson, T.D., 2003, Constraints on the distribution of gas hydrates in the Gulf of Mexico: Abstracts, EGS-AGU-EUG Joint Assembly, Nice, France, 6-11 April 2003, *Geophysical Research Abstracts*, v. 5, #12019.
 - 19) Stern, L.A., and Kirby, S.H., in press, Grain and pore-structure imaging of gas hydrate from Core MD02-2569 (Mississippi Canyon, Gulf of Mexico): a first look by SEM, in Winters, W.J., Lorenson, T.D., and Paull, C.K., eds., *Initial Report of the IMAGES VIII/PAGE 127 Gas Hydrate and Paleoclimate Cruise on the RV Marion Dufresne in the Gulf of Mexico, 2-18 July 2002*: U.S. Geological Survey Open-File Report 2004-1358, 10 pp.
 - 20) Ussler, W., III, and Paull, C.K., in press, Pore water gradients in giant piston cores from the northern Gulf of Mexico, in Winters, W.J., Lorenson, T.D., and Paull, C.K., eds., *Initial Report of the IMAGES VIII/PAGE 127 Gas Hydrate and Paleoclimate Cruise on the RV Marion Dufresne in the Gulf of Mexico, 2-18 July 2002*: U.S. Geological Survey Open-File Report 2004-1358, 49 pp.
 - 21) Ussler, W. III, Paull, Charles K., Hallam, Steven, Delong, Ed, Chen, Yifeng, Matsumoto, Ryo, Lorenson, Thomas, and Winters, William J., 2003, The anatomy of the sulfate-methane interface in a methane-rich core from the Gulf of Mexico: Abstracts with Programs, v. 35, n. 6, Geological Society of America Annual Meeting, Seattle, Nov. 2-5, 2003, p. 287.
 - 22) Ussler, W., III, Paull, C.K., Chen, Y., Matsumoto, R., Lorenson, T.D., and Winters, W.J., 2005, The consequences of methane oxidation at the sulfate-methane interface in a methane-rich core from the northern Gulf of Mexico: Fifth International Conference on Gas Hydrates, Trondheim, Norway, 12-16 June, 2005, 7 pp.
 - 23) Winters, W.J., Lorenson, T.D., and Paull, C.K., in press, IMAGES VIII/PAGE 127 Gas Hydrate and Paleoclimate Cruise on the *RV Marion Dufresne* in the Gulf of Mexico, 2-18 July 2002: Introduction, in Winters, W.J., Lorenson, T.D., and Paull, C.K., eds., *Initial Report of the IMAGES VIII/PAGE 127 Gas Hydrate and Paleoclimate Cruise on the RV Marion Dufresne in the Gulf of Mexico, 2-18 July 2002*: U.S. Geological Survey Open-File Report 2004-1358, 12 pp.
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 - 25) Winters, W.J., Lorenson, T.D., Paull, C.K., and Balut, Y., in press, Coring and gas hydrate-related operations during the IMAGES VIII/PAGE 127 Gas Hydrate and Paleoclimate Cruise on the *RV Marion Dufresne* in the Gulf of Mexico, 2-18 July 2002, in Winters, W.J., Lorenson, T.D., and Paull, C.K., eds., *Initial Report of the IMAGES VIII/PAGE 127 Gas*

Hydrate and Paleoclimate Cruise on the RV Marion Dufresne in the Gulf of Mexico, 2-18 July 2002: U.S. Geological Survey Open-File Report 2004-1358, 82 pp.

- 26) Winters, W.J., Novosel, I., Boldina, O. M., Waite, W. F., Kelsey, S.A., and Hallett, B.W., in press, Physical properties of sediment obtained during the IMAGES VIII/PAGE 127 Gas Hydrate and Paleoclimate Cruise on the RV Marion Dufresne in the Gulf of Mexico, 2-18 July 2002, in Winters, W.J., Lorenson, T.D., and Paull, C.K., eds., *Initial Report of the IMAGES VIII/PAGE 127 Gas Hydrate and Paleoclimate Cruise on the RV Marion Dufresne in the Gulf of Mexico, 2-18 July 2002*: U.S. Geological Survey Open-File Report 2004-1358, 98 pp.
- 27) Winters, W.J., Novosel, I., Boldina, O. M., Waite, W. F., Lorenson, T. D., Paull, C.K., and Bryant, W., 2002, Physical Properties of Sediment Related to Gas Hydrate in the Northern Gulf of Mexico: EOS. Trans. American Geophysical Union, 83 (47), Fall Meeting Supplement, San Francisco, Dec. 6-10, Abstract T22B-1144, p. F1388.
- 28) Winters, W.J., Waite, W.F., Mason, D.H., Lorenson, T.L., Paull, C.K., Novosel, I., Boldina, O.M., Dallimore, S.R., Collett, T.S., and the PAGE 127 Shipboard Scientific Party (abs); EGS-AGU-EUG Joint Assembly, Nice, France, April 7-11
- 29) Winters, W.J., Waite, W., Mason, D.H., Lorenson, T.D., Paull, C.K., Novosel, I., Boldina, O.M., Dallimore, S.R. and Collett, T.S., 2003, Physical properties of northern Gulf of Mexico sediment and laboratory samples containing natural and synthetic methane gas hydrate: Abstracts, EGS-AGU-EUG Joint Assembly, Nice, France, 6-11 April 2003, Geophysical Research Abstracts, v. 5, #07110.

II E. 2003 – Gyre

1. Overview of Work

For two weeks in May, 2003, USGS conducted a seismic reflection experiment aboard the R/V Gyre (Texas A&M University) to understand the geologic setting around two sites chosen for additional study and potential drilling by the ChevronTexaco Gulf of Mexico Gas Hydrates Joint Industry Project (JIP). The primary purpose of the JIP program is to assess the hazard that hydrates might pose to deep water drilling on the continental slope of the northern Gulf of Mexico. Developing a geologic framework using seismic reflection data is a fundamental part of understanding hazards. The two study areas identified are in the Keathley Canyon and Atwater Valley Protraction areas in lease blocks KC 195 and AT 14. In these two areas, 101 lines comprising 1033 km were collected, mostly with 24-channel high-resolution multichannel sensor and a 13/13 in3 Generator-Injector (GI) air gun. For the Keathley Canyon site, 59 lines were acquired with line spacings of 1 km, 500 m, or 100 m; for the Atwater Valley site, 35 short lines in various configurations were collected. Four additional lines provided seismic ties with the USGS data collected previously on the Tommy Munro (1998, see Section II A) and the Gyre (1999, see Section II B). One of the unique aspects of the 2003 Gyre cruise was the participation by two on-board marine-mammal observers to ensure that marine mammals were not incidentally harassed under the guidelines set forth in the Marine Mammals Protection Act. Although three species of dolphins and one basking shark were observed during the cruise, seismic operations were neither delayed nor terminated as a result of marine mammal activities. A complete overview of the cruise and full statistics are contained in the on-line cruise report (Hutchinson and Hart, 2004).

2. Significant Results

The good quality and extensive coverage of the seismic data provide excellent imaging of the surface and subsurface geologic setting of the two sites. This cruise represented the first time that USGS multichannel seismic reflection data were processed through stack with full geometry and final navigation. All data were also archived in the field. The data show that the Keathley Canyon site typifies minibasin geometry and morphology in the northern Gulf of Mexico with the added unusual occurrence of a Bottom Simulating Reflection (BSR). BSRs are not well known in the northern Gulf despite extensive mapping and exploration of many of the minibasins. The seismic stratigraphy has major and secondary unconformities, pinch-outs, layered units, and evidence of mass wasting. The BSR covers a region of about 15-18 km² on the southeast corner of the minibasin, adjacent to a region of faulting and disruption. Abundant evidence exists for gas near the vicinity of the BSR, with bright spots and blanking, mostly east of the BSR on the structural high. A small mound on the structural high may be a site of venting and seepage with a well defined gas chimney in the subsurface (Snyder et al., 2004, Hutchinson et al, in press). Thermal and chemical data further illustrate the complicated stratigraphic and chemical relations (Ruppel et al., 2004, Pohlman et al., 2004).

The Atwater Valley Site lies at water depths similar to the Keathley Canyon site, although in an entirely different physiographic regime. It is within the gently sloping floor of the Mississippi Canyon in a region of numerous sea-floor mounds of dimensions of tens to hundreds

of meters across by several to perhaps 25 m high. The seismic stratigraphy is complicated and disrupted, with few continuous horizons, consistent with the inferred turbidite and mass wasting origin of the Canyon. A bright spot at about 100 m beneath one of the mounds, mound F, has been interpreted as the possible top of free gas/base of the hydrate stability zone, lying much closer to the surface than in the surrounding intra-mound regions because of the rise of warm (gas-charged??) fluids (Hutchinson et al., 2003, Wood et al., 2004).

3. Significance of results to DOE Gas Hydrate Goals

One of the primary research efforts in the first five years of the Methane Hydrates Research and Development Act of 2000 was to understand the safety issues and potential hazards associated with drilling through gas hydrates during conventional deep-water oil and gas production. The Chevron Texas Gulf of Mexico JIP project directly addressed this subject. Prior to 2003, USGS acted as a science advisor for the JIP in its initial site evaluations. Through the data collected on the Gyre cruise in 2003, USGS participated in the final site selection and the geological characterization. The Gyre cruise also served as the basis for identifying heat flow and coring stations conducted as part of the site survey operations.

4. List of Publications

- 1) Geresi, E., Hutchinson, D.R., Hart, P.E., and McGee, T.M., 2003, Using multiple attenuation to image geologic structures beneath the gas hydrate stability zone in the northern Gulf of Mexico (abs.): Geological Society of America Abstracts with Programs, v. 35, no. 7, 2-5 November, p. 533.
- 2) Hart, P.E., Hutchinson, D.R., and Dugan, B., 2003, USGS conducts deep-water gas hydrate research cruise in the northern Gulf of Mexico, in press, Fire in the Ice, National Energy Technology Laboratory Methane Hydrate Newsletter, Fall, 2003.
- 3) Hart, P.E., Hutchinson, D.R., and Lee, M.W., 2005, High-resolution multichannel seismic-reflection data acquired in the northern Gulf of Mexico, 2003: U.S. Geological Survey Open-File Report 2005-1411, 28 pp., available on line at <http://pubs.usgs.gov/of/2005/1411/index.html>.
- 4) Hart, P.E., Hutchinson, D.R., Dugan, G., Fowler, M., Wood, W., Snyder, F., Dutta, N., Coffin, R., Gardner, J., Hagen, R., Evans, R., and Fornari, D., 2005, A multidisciplinary investigation of a deep-water gas hydrate mound, Atwater Valley, northern Gulf of Mexico: Fourth International Workshop on Methane Hydrate Research and Development, 9-11 May, 2005, Victoria, British Columbia (unpaginated).
- 5) Hutchinson, D.R., Hart, P.E., Ruppel, C.D., Snyder, F., and Dugan, B., in press, Seismic and Thermal Characterization of a Bottom Simulating Reflection in the Northern Gulf of Mexico: AAPG Hedberg Volume, 38 pp.

- 6) Hutchinson, D.R., Hart, P.E. Dugan, B., Geresi, E., Sliter, R., and Newman, K., 2003, Subsurface gas hydrates in the Northern Gulf of Mexico (abs.): Geological Society of America Abstracts with Programs, v. 34, no. 7, 2-5 November, p. 533.
- 7) Hutchinson, D.R., Hart, P.E., Snyder, F., Lee, M.W., Dutta, N., Muller, L., Dugan, B., Ruppel, C., Wood, W., Coffin, R., Evans, R., and Jones, E., in press, Evidence of subsurface gas hydrate in the northern Gulf of Mexico (abs.): American Geophysical Union, Fall meeting, December, 2003.
- 8) Hutchinson, D.R., and Hart, P.E., 2003, Cruise Report for G1-03-GM USGS Gas Hydrates Cruise, R/V Gyre, 1-14 May, 2003, Northern Gulf of Mexico: USGS Open-File Report OF 03-474, 100 pp.
- 9) Hutchinson, D.R., Ruppel, C.D., Roberts, H.S., Carney, R.S., and Smith, M.A., in press, Gas Hydrates in the Gulf of Mexico, in Holmes, C.W., ed., Gulf of Mexico – it's Origin (History, Archeology, and Geology), v. 1., 53 pp.
- 10) Hutchinson, D.R., Ruppel, C.D., Pohlman, J., Hart, P., Dugan, B., Snyder, F., and Coffin, R.B. 2004, An integrated geological, geophysical, and geochemical analysis of subsurface gas hydrates in the northern Gulf of Mexico (abs.): Abstracts, American Association of Petroleum Geologists Hedberg conference, Vancouver, BC, Canada. Sept. 12-16, 2004, http://www.searchanddiscovery.com/documents/abstracts/2004hedberg_vancouver/extended/hutchinson/hutchinson.htm.
- 11) Hutchinson, D.R., Ruppel, C.D., Pohlman, J., Hart, P.E., Snyder, F., Dugan, B., and Coffin, R., 2005, Geophysical and geochemical characterization of the hydrate stability zone in a region of active salt tectonics, Keathley Canyon, northern Gulf of Mexico (abs.): Fourth International Workshop on Methane Hydrate Research and Development, 9-11 May, 2005, Victoria, British Columbia (unpaginated).
- 12) Newman, K.R., 2003, Acoustic characteristics of hydrate mounds in the Mississippi Canyon, northern Gulf of Mexico: WHOI summer fellow report, 18 pp.
- 13) Pohlman, J., Wood, W., Ruppel, C., Hart, P.E., Dugan, B., and Hutchinson, D.R., in press, Interstitial sulfate gradients as indicators of gas hydrates: How reliable are they? (abs): 32nd International Geological Congress Meeting, Florence, Italy, 21-28 August, 2004.
- 14) Ruppel, C., Hutchinson, D.R., Dugan, B., and Hart, P.E., 2004, Predicting the Subsurface Distribution of Gas Hydrate in the Northern Gulf of Mexico (abs.): American Association of Petroleum Geologists 2004 Annual Convention, Dallas, TX, April 18-21, 2004, <http://www.searchanddiscovery.com/documents/abstracts/annual2004/Dallas/Ruppel.htm>.
- 15) Snyder, F.F., Muller, L., Dutta, N., Hutchinson, D.R., Hart, P.E., Lee, M.W., Dugan, B., Ruppel, C., Wood, W., Coffin, R., Evans, R., and Jones, E., 2004, Seismic Analysis and Characterization of Gas Hydrates in the Northern Deepwater Gulf of Mexico (abs.): AAPG

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- 17) Wood, W.T., Gardner, J., Hagen, R.A., Coffin, R.B., Pohlman, J.W., Hart, P.E., and Hutchinson, D.R., 2004, Modelling heat and fluid flux of seafloor mounds in the Gulf of Mexico (abs.): EOS, Tran. AGU, v. 85, no. 47, Fall Meeting Supplement, Abstract OS34B-08.

Part III Laboratory Experiments

By William F. Waite

Part III summarizes major laboratory support under this interagency agreement and comprises three principal pieces, (i) the GHASTLI laboratory; (ii) the Thermal Properties System; and (iii) the Petrophysics laboratory. Like the previous section on the field experiments, each section here has four parts: System Overview, Significant Results, Significance of Results to DOE Gas Hydrate Goals, and a List of Publications. Copies of the publications are included in a separate DVD accompanying this report.

III A. GHASTLI Laboratory

1. System Overview:

GHASTLI, the Gas Hydrate and Sediment Test Laboratory Instrument, measures physical properties while simulating natural conditions that are stable for gas hydrate. GHASTLI has the flexibility to test cores containing rare and valuable natural gas hydrate that have been transported to the Woods Hole Science Center. In addition, sample behavior can be continually monitored as methane hydrate is grown in the pore space of different natural and reconstituted sediments. The paramount focus of GHASTLI is to precisely control the test environment while measuring as many physical properties as possible. Confining pressure, pore pressure, axial load, and temperature, as well as gas and fluid flow through the sample, are monitored and adjusted as required by testing protocol. Some measured properties, such as acoustic wave speed and electrical resistivity are used to assess the relative degree of hydrate formation and they can also be compared to seismic or borehole field results. Other properties measured with GHASTLI, such as permeability and shear strength, are not easily determined in the field. However, they provide critical insight to the interrelationships between gas hydrate and host sediment. Simultaneous measurement of multiple properties provides a comprehensive dataset with which to observe correlations between properties and to further our understanding of hydrate in nature.

2. Significant Results

GHASTLI bridges the gap between field and laboratory investigations because of its flexibility to measure properties of natural core samples and laboratory sediment samples tailored for specific investigations. This versatility led to several key findings, chiefly:

- 1) Hydrate formed in nature, a process generally limited by the supply of methane dissolved in pore water, tends not to cement sediment grains together. Hydrate formed in the laboratory, most often with a free gas phase to accelerate the formation process, cements sediment grains, producing stiffer samples than generally found in nature.
- 2) Sediment grain size plays a significant role in the effect of hydrate formation on sediment properties. For instance, hydrate formation causes coarse sands to become more resistant to shear, whereas sediment with silt-sized grains becomes more prone to shear after hydrate formation.

3. Significance of Results to DOE Gas Hydrate Goals

One aspect of the DOE hydrate research vision is the exploration of hydrate occurrences in all its varied natural settings. The GHASTLI laboratory has supported that vision with natural core measurements, as well as index properties on natural sediment, that have been included in the scientific reports for ODP Leg 164 (Blake Ridge, a sedimentary environment), ODP Leg 204 (Hydrate Ridge, an accretionary complex) and the Mallik 2L-38 and 5L-38 field programs (Mackenzie Delta, a permafrost environment, and a program partially funded by DOE). The comparison of natural and laboratory-formed hydrate led to the realization that the hydrate formation technique itself was a controlling factor in determining the physical properties of hydrate-bearing sediment (Winters et al., 2004). This critical point continues to be an issue, and was raised during discussions of future hydrate research at the 2006 DOE merit review of the National Laboratory gas hydrate research projects.

The sediment grain size study in GHASTLI was undertaken in support of modeling efforts underway at the time by the DOE-supported Gulf of Mexico Joint Industry Project (JIP). Updates were supplied directly to the JIP throughout the investigation. The journal paper by Winters et al. (2006) serves as the final report for the study.

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III B. Thermal Properties Laboratory

1. System Overview:

The thermal properties lab was built in 2003 at the USGS Woods Hole Science Center as a generic hydrate research facility. The system supplies high-pressure gas for hydrate formation, oil for sample confinement or compaction, and a temperature-controlled bath for maintaining isothermal conditions or providing a programmable temperature variation. The strategy for use is taken from the Petrophysical laboratory philosophy of making physical property measurements on pure hydrate, or hydrate/sediment mixtures, synthesized directly in pressure vessels designed specifically for a particular property measurement (see section III C. of this report). The system has been used only with the thermal properties pressure vessel, but also accepts the wave-speed measurement vessel used in the Petrophysical lab. Unlike the Petrophysical lab however, the Woods Hole system operates within a fume hood, and can therefore be used to study hazardous compounds such as Tetrahydrofuran (THF) hydrate.

2. Significant Results

By incorporating a high-speed data acquisition system and developing additional computational processing strategies, we obtained the first simultaneous estimates of thermal diffusivity and heat capacity from the standard needle-probe thermal conductivity measurement technique. Our first application of this methodology addressed a point made in the 2004 NRC review of DOE gas hydrate research questioning the use of THF hydrate as an analog for methane hydrate. Very few comparative studies between the two materials had been performed prior to the NRC report, so after measuring the thermal properties of THF hydrate (Waite et al., 2003), we demonstrated the limited utility of THF hydrate as a thermal property analog for methane hydrate (Waite et al., 2004). The thermal properties in THF become highly nonlinear above -5°C , approximately 9°C below the THF hydrate stability temperature, in stark contrast to the limited information available for methane hydrate. We showed that to estimate methane hydrate thermal properties at temperatures relevant to natural systems, linear results for THF hydrate obtained below -5°C had to be extrapolated to the temperatures of interest.

3. Significance of Results to DOE Gas Hydrate Goals

By simultaneously measuring thermal conductivity, diffusivity, and heat capacity, we were able to provide the comprehensive thermal description for hydrate required to model heat propagation through hydrate-bearing sediment. These thermal properties were requested for models being developed by the DOE-supported Gulf of Mexico Joint Industry Project (JIP). In consultation with the JIP, we undertook a thermal property study of THF hydrate in sediment. Based on our experience with the limitations of THF hydrate mentioned above, we were able to show sediment porosity, not sediment grain size, controlled the system's thermal properties. These results were shared with the JIP as we obtained them, with the paper published at the 5th International Conference on Gas Hydrates (Waite et al., 2005) serving as the study's final report.

4. List of Publications

- 1) Waite, W.F., Winters, W.J., Mason, D.H., 2003, Thermal conductivity of THF hydrate between -25 °C and +4 °C (abstract): *Eos, Transactions, American Geophysical Union*, v. 84, no. 46, Fall Meet. Suppl., Abstract OS51B-0840.
- 2) Waite, W.F., Gilbert, L.Y., Winters, W.J., Mason, D.H., 2004, Thermal property measurements in Tetrahydrofuran (THF) hydrate between -25 and +4 °C, and their application to methane hydrate (abstract): *Eos, Transactions, American Geophysical Union*, vol. 85, no. 47, Fall Meet. Suppl., Abstract OS51A-0323.
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III C. Petrophysics Laboratory

1. System Overview:

The Petrophysics Laboratory discovered a methodology for reliably and reproducibly forming pure hydrates. This method, developed in 1996, involves slowly warming granular ice in a high-pressure environment of hydrate-forming gas. Based on the philosophy that hydrate purity can only be ensured if hydrate is formed directly in the physical property measurement vessel, the laboratory was designed to supply hydrate-forming gas at high pressure to an arbitrary measurement vessel suspended in a temperature-controlled bath. Physical property measurement vessels have been developed and utilized for reaction kinetics, as well as acoustic and thermal property experiments. To better characterize hydrate formed from ice, and to investigate hydrate dissociation kinetics, a custom designed flowmeter was developed to measure hydrate dissociation rates and dissociated gas volume. An X-Ray Diffractometer (XRD) and Cryo-Scanning Electron Microscope (CSEM) were also acquired to characterize the hydrate structure and hydrate morphology in hydrate-bearing sediment in natural cores or in laboratory-synthesized hydrate.

2. Significant Results

The capacity to reliably and reproducibly synthesize pure hydrate, a breakthrough that earned the Petrophysical Laboratory the R.A. Glenn Award from the American Chemical Society (Stern et al., 1998), has led to several advances in hydrate characterization and property measurement:

- a) Self preservation: Near -5°C, methane hydrate dissociates over a matter of weeks rather than minutes (Circone et al., 2004). This property is being exploited for developing new strategies for temporary low-pressure transport and storage of natural gas, and is also being used to optimize the retrieval of naturally-occurring gas hydrate from remote settings as well as from laboratory experiments.
- b) Acoustic wave speeds: Our simultaneous measurements of compressional and shear wave speeds in sI and sII hydrates (Helgerud et al., 2003), the first ever measurements of shear wave speeds, are now standards that are widely used for making quantitative inferences of gas hydrate content in sediment columns as determined from conventional sonic well logs or seismic surveys.
- c) Thermal properties: Our thermal conductivity measurements in methane hydrate and hydrate-bearing sands (Waite et al., 2002) have been used in analyses of field data by researchers around the world, including application to the DOE-funded Mallik program.
- d) Material strength: In collaboration with Lawrence Livermore National Laboratory, we found hydrate to be 20 to 100 times stronger than ice (Durham et al., 2003). Its high strength as hydrate, coupled with the overpressures it can generate during dissociation, have important geotechnical implications for drilling and other seafloor operations.

- e) Dissolution: In collaboration with the Monterey Bay Aquarium Research Institute, laboratory-formed hydrate was exposed to seawater at the seafloor in Monterey Bay. This first measurement of hydrate dissolution showed that even in the hydrate stability zone, hydrate outcropped at the seafloor must be actively recharged with methane from the underlying sediment, or it will rapidly dissolve (Rehder et al., 2004).

3. Significance of Results to DOE Gas Hydrate Goals

DOE-sponsored national laboratory research programs have benefited from hydrate formed in the Petrophysics Lab that was shipped to the national labs for further study: Oak Ridge National Laboratory - neutron diffraction studies of sI and sII hydrate (Chakoumakos et al., 2003; Rawn et al., 2003); Lawrence Berkeley Laboratory - proof of concept for the CT scanning technology, which led to the creation of a portable CT scanner now in use in ODP and other field programs (Freifeld et al., 2002; Tomutsa et al., 2002).

The Petrophysics lab also supported the DOE-funded "Hot Ice" drilling program. At the request of the Maurer/Anadarko Joint Industry Project, hydrate self-preservation tests were run to optimize the drilling mud temperature in the field for maximizing hydrate preservation in recovered core (Kirby et al., 2003). A hydrate/sediment sample fabricated in the Petrophysical Lab was sent to the JIP for field-testing their equipment. The Cryo-SEM facility operated by the Petrophysics Lab has contributed to sample characterization, with publications in the scientific reports for those programs, for DOE-sponsored fieldwork such as the Marion Dufresne Piston coring cruise (Stern and Kirby, 2005) and the Mallik 5L-38 permafrost drilling program (Stern et al., 2005).

4. List of Publications

- 1) Chakoumakos, B.C., Rawn, C.J., Jones, C.Y., Marshall, S.L., Stern, L.A., Ishii, Y., Toby, B.H., Dender, D.C., 2001, Physical and thermodynamic properties of gas clathrate hydrates determined by in situ neutron scattering. 11th Annual Goldschmidt Conference, 2001, Hot Springs, VA.
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Part IV – Other Accomplishments

Many of the activities performed in conjunction with this interagency agreement are summarized in this section, to give a flavor of the breadth and depth of gas hydrate research performed.

1) Presentations

- B. Dillon co-chaired DOE National Gas Hydrate Workshop, Washington, DC (1998)
- Several presentations at International Symposium on Methane Hydrates, Chiba City, Japan (1998)
- Several presentations at Third International Conference on Gas Hydrates, Salt Lake City (1999)
- B. Dillon organized a session at the AAPG National Meeting on gas hydrates in the Gulf of Mexico (2000)
- Several USGS scientists participated in DOE workshop on Gulf of Mexico gas hydrates in Houston, TX (2000)
- Invited participation at the American Crystallographic Association National Meeting, Los Angeles, CA (2001).
- USGS scientists interviewed on Lehrer News hour on segment about Carbon Sequestration.
- Presentation at Offshore Technology Conference (2001)
- Two scientists participated in Deep Water Geohazards Workshop, Houston, TX (2001)
- Presentation at Centre for Gas Hydrate Research, Heriot-Watt University, Edinburgh, Scotland (2001)
- Several presentations in Russian meetings (2001),
- Presentation at GeoForschungsZentrum, Potsdam, Germany (2001)
- Coordination meetings with MMS in 2002 in preparation for Marion Dufresne coring cruise.
- Several presentations at AAPG National Meeting (2002)
- Several USGS scientists participated in the ChevronTexaco JIP Data Collection Workshop in Houston, TX (2002)
- Several USGS scientists participated in the DOE/NETL Methane Hydrate R&D Conference in Washington, DC, including 2 keynote presentations (B. Dillon and Tim Collett), co-organizing East Coast Session (D. Hutchinson), and providing oral and poster presentations (2002)
- Several USGS scientists participated in the ChevronTexaco JIP workshop on “Naturally occurring gas hydrates JIP workshop: drilling, coring, and wellbore stability; modeling, measurements, and sensors,” (2002).
- Several presentations at the 4th International conference on Gas Hydrates in Yokohama, Japan (2002)
- Presentation at “International Symposium on the Physics and Chemistry of Ice,” (2002).
- Presentation to DOE (NETL) on results from DOE-funded Marion Dufresne cruise in the Gulf of Mexico (2003).

- Participation in ODP/DOE pressure core meeting in College Station, TX (2003).
- Participation in Gas Hydrates JIP Site Selection Progress Meeting in Houston, TX (2003)
- Several presentations at EGS-AGU-EUG joint meeting, Nice, France (2003)
- Several presentations at AAGP National Meeting (2002)
- Several USGS participated in MMS brainstorming session on conducting a hydrates resource assessment, Herndon, VA (2003)
- Presentation at Gas Hydrates JIP Seafloor Stability Team Meeting, Houston, TX (2003)
- Several presentations at the DOE Methane Hydrate R&D Conference, Westminster, CO (2003)
- Presentation at “Symposium on Gas Hydrates – a Potential New Energy Source for the New Millennium” Qingdao, China (2004)
- Several Presentations at the Geological Society of America annual meeting (2004)
- Several scientists participated in the JIP Site Selection meeting, New Orleans, LA (2004)
- Participation in JIP drilling coordination meeting, Houston, TX (2004)
- Participation in NOAA Workshop on “The Role of Methane and Gas Hydrates in Global Climate Change,” Boulder, CO, (2004)
- Several presentations at AAPG Hedberg Research Conference, Vancouver, BC (2004)
- Participation in JIP Pre-drilling Planning Cruise, Houston, TX, (2005)
- Presentation at American Chemical Society National Meeting (2005)

2) *Federal Agency Coordination*

- Participation in various Technical Coordinating Team meetings and conference calls organized by DOE and including the major federal agencies working in gas hydrate research.
- USGS and NRL participated in several joint sessions on how to further enhance interagency collaboration (2004-2005).
- Presentation at Department of State Workshop on “Foreign Policy Implications of Gas Hydrates,” Arlington, VA (2005).

3) *Gas Hydrate Planning and Legislation*

- B. Dillon addressed the AAAS in preparation for briefings on gas hydrate to be provided to the House of Representatives, Oceans Caucus (2000).
- D. Hutchinson participated in National Petroleum Council, Supply Team – Technology Subgroup, Gas Hydrates Workshop, Houston, TX (2003)

4) *Other (Reviews, Outreach, Visitors)*

- Hosted delegation from China interested in Collaborative work on gas hydrates (primarily from Qingdao Institute of Marine Geology), (2002)
- Hosted S. Bunz (Univ. Trondheim) to discuss gas hydrates in the Storegga Slide region (2002)

- Hosted Project Leader (S. Tanaka) of the Japan Research Consortium for Methane Hydrate Resources in Japan (2003)
- Hosted P. Schulteiss to discuss mutual interest in pressure vessels and transfer of core samples into pressure vessels (2004)
- Hosted Indonesian visitor with mutual interest in pursuing gas hydrate research (2005)
- Reviewed Westport Technology Report on Gas Hydrate Coring and Preservation Manual (2003).
- Presentation at first meeting of the NRC Committee to Review Activities authorized under the Methane Hydrate Research and Development Act of 2000 (D. Hutchinson), (2003)
- Reviewed NRL Gas Hydrates 5-year project plan (2003)
- Conducted various interviews with members of the media (Discover Magazine, Lehrer news, various radio and television segments), (2002-2005)
- Pursued various collaborations with the National Labs, with Universities (e.g., Georgia Tech) and with other federal agencies (e.g., NRL), (1998-2005).