"In-Situ Sampling and Characterization of Naturally Occurring Marine Methane Hydrate Using the D/V JOIDES Resolution."

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ABSTRACT

The primary accomplishments of the JOI Cooperative Agreement with DOE/NETL in this quarter were that: (1) Frank Rack presented preliminary results and operational outcomes of ODP Leg 204 at the DOE/NETL project review and two made two presentations at the ChevronTexaco Gulf of Mexico Hydrate JIP meeting, which were both held in Westminster, CO; and, (2) postcruise evaluation of the data, tools and measurement systems that were used during ODP Leg 204 continued in the preparation of deliverables under this agreement. Work continued on analyzing data collected during ODP Leg 204 and preparing reports on the outcomes of Phase 1 projects as well as developing plans for Phase 2.

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INTRODUCTION

The primary accomplishments of the JOI Cooperative Agreement with DOE/NETL in this quarter were the completion of all outstanding quarterly reports and the completion of a comprehensive final report describing the outcomes of all tasks. These documents have been submitted to DOE/NETL to complete all remaining Phase 1 requirements and to present the primary accomplishments of this cooperative agreement.

The primary accomplishments of the JOI Cooperative Agreement with DOE/NETL were the deployment of specialized tools and measurement systems for use on ODP Leg 204, which studied hydrate deposits on Hydrate Ridge, offshore Oregon. Earlier deployments of these tools on ODP Leg 201 (Peru Margin) were made to prepare the tools and measurement systems for extensive use on ODP Leg 204. Prior to undertaking these field deployments, a baseline survey of the state-of-the-art in pressure coring systems was conducted (**Task 1.1**) and delivered to DOE/NETL shortly after this contract was awarded. The operational results from the frequent use of the PCS Gas Manifold with the Pressure Core Sampler (PCS) tool on ODP Legs 201 and 204 (**Task 2.0**) are evaluated. The ODP Pressure Core System (PCS) was deployed 17 times during ODP Leg 201 and 39 times during ODP Leg 204. It successfully retrieved cores from a broad range of lithologies and sediment depths along both the Peru margin and on Hydrate Ridge. The PCS gas manifold was used in conjunction with the PCS throughout ODP Legs 201 and 204 to measure the total volume and composition of gases recovered in sediment cores. The DVTP, DVTP-P, APC-methane, and APC-Temperature tools (ODP memory tools) were used extensively during ODP Legs 201 and 204 aboard the D/V JOIDES *Resolution* (**Task 3.0**). The data obtained from the successful deployments of these tools has been evaluated by the scientists and engineers involved in this testing. Infrared-thermal imaging systems (IR-TIS) were deployed on ODP Legs 201 and 204. These systems were used to identify methane hydrate intervals in the recovered cores (**Task 4.0**) through systematic measurements followed by discrete sampling and preservation of these samples. Leg 204 scientists and LDEO logging engineers conducted LWD and VSP experiments during ODP Leg 204 and evaluated the results (**Task 5.0**). Tool modifications were made to create a LWD Resistivity-at-the-Bit with Coring (RAB-C) tool, which resulted from the integration of the ODP motor-driven core barrel (MDCB) inner core tube with the Schlumberger/Anadrill RAB landing sub. ODP and FUGRO engineers deployed the modified FUGRO Piezoprobe tool for use with the ODP APC/XCB bottom hole assembly (BHA) on ODP Leg 204 (**Task 6.0**). This required changes to the lay out, space out, and completion of crossover subs for the piezoprobe deployment and the establishment of operational protocols for tool use. Finally, a series of additional holes were cored at the crest of Hydrate Ridge (Site 1249) to accomplish the rapid recovery and preservation of hydrate samples as part of a hydrate geriatric study. This report will present an overview of the results obtained from tool and instrument deployments on ODP Legs 201 and 204 as part of this project.

EXECUTIVE SUMMARY

The primary accomplishments of the JOI Cooperative Agreement with DOE/NETL were the deployment of specialized tools and measurement systems for use on ODP Leg 204, which studied hydrate deposits on Hydrate Ridge, offshore Oregon. Earlier deployments of these tools on ODP Leg 201 (Peru Margin) were made to prepare the tools and measurement systems for extensive use on ODP Leg 204.

Prior to undertaking these field deployments, a baseline survey of the state-of-the-art in pressure coring systems was conducted (**Task 1.1**) and delivered to DOE/NETL shortly after this contract was awarded.

The PCS is a downhole tool designed to recover a cylindrical sediment core -- including gas and interstitial water -- at in situ pressure (Pettigrew, 1992). When properly sealed at depth, controlled release of pressure from the PCS through a manifold permits collection of gases that would otherwise escape on the wireline trip. The operational results from the frequent use of the PCS Gas Manifold with the Pressure Core Sampler (PCS) tool on ODP Legs 201 and 204 (**Task 2.0**) are evaluated herein.

The ODP Pressure Core System (PCS) was deployed 17 times during ODP Leg 201 and 39 times during ODP Leg 204. It successfully retrieved cores from a broad range of lithologies and sediment depths along both the Peru margin and on Hydrate Ridge. The PCS gas manifold was used in conjunction with the PCS throughout ODP Legs 201 and 204 to measure the total volume and composition of gases recovered in sediment cores.

The HYACINTH project, a European Union (EU) funded effort to develop tools to characterize methane hydrate and measure physical properties under in-situ conditions, provided additional pressure-coring tools for collaborative testing during ODP Legs 201 and 204. The FUGRO pressure corer (FPC) was deployed 7 times during ODP Legs 201 at sites located offshore Peru in preparation for deployments offshore Oregon on ODP Leg 204. The initial FPC deployments met with limited success in recovering pressurized cores, but much was learned about the operation of the tool with shipboard systems on the D/V JOIDES *Resolution*. Both the FPC and the HYACE Rotary Corer (HRC) were then deployed on the D/V JOIDES *Resolution* during ODP Leg 204 to field-test these coring systems at several sites located offshore Oregon. The field-testing of these tools by JOI/ODP provided a corollary benefit to DOE/NETL at no cost to this project. The testing was negotiated as part of a cooperative agreement between JOI/ODP and the HYACINTH partners.

Two core-logging chambers (ODP-LC) were fabricated for use on ODP Leg 204. These chambers were able to accept standard ODP APC/XCB core sections in their existing core liners and allowed them to be re-pressurized and logged to collect gamma ray attenuation (bulk density) and compressional-wave acoustic velocity measurements. These measurements were made using a vertical multi-sensor (pressure) core logging

(MSCL-V) system that was deployed on Leg 204. These chambers allowed physical properties data to be collected on hydrate cores recovered using conventional coring techniques and re-pressurized.

The DVTP, DVTP-P, APC-methane, and APC-Temperature tools (ODP memory tools) were used extensively during ODP Legs 201 and 204 (**Task 3.0**). The data from tool deployments have been evaluated.

An infrared-thermal imaging system (IR-TIS) was deployed for the first time on ODP Leg 201 to identify methane hydrate intervals in the recovered cores. A second system was purchased for ODP Leg 204 and both systems were used throughout the cruise to identify cold anomalies in cores (**Task 4.0**). A track-mounted infrared-thermal imaging system (IR-TIS) was deployed for the first time on ODP Leg 204 to automate the process to routinely identify methane hydrate intervals in the recovered cores through systematic measurements followed by discrete sampling and preservation of these samples.

Leg 204 scientists and LDEO logging engineers conducted LWD and VSP experiments during ODP Leg 204 and evaluated the results (**Task 5.0**). Tool modifications were made to create a LWD Resistivity-at-the-Bit with Coring (RAB-C) tool, which resulted from the integration of the ODP motor-driven core barrel (MDCB) inner core tube with the Schlumberger/Anadrill RAB landing sub.

ODP and FUGRO engineers deployed the modified FUGRO Piezoprobe tool for use with the ODP APC/XCB bottom hole assembly (BHA) on ODP Leg 204 (**Task 6.0**). This required changes to the lay out, space out, and completion of crossover subs for the piezoprobe deployment and the establishment of operational protocols for the deployment and use of this tool on Leg 204.

Finally, a series of additional holes were cored at the crest of Hydrate Ridge (Site 1249) specifically geared toward the rapid recovery and preservation of hydrate samples as part of a hydrate geriatric study partially funded by the Department of Energy (DOE).

These results and accomplishments are presented in detail in the final report of this cooperative agreement. The overall conclusion is that all objectives of this project were successfully achieved, the tools and experimental systems worked well, and much was learned about conducting hydrate coring operations, preserving naturally-occurring hydrates in the field, and making in situ measurements. All of these results have been communicated broadly through talks at professional and technical meetings as well as to DOE/NETL program managers.

Additional information and data are available online at the ODP Publications website for Leg 201: <http://www-odp.tamu.edu/publications/201_IR/201TOC.HTM> and for Leg 204: <http://www-odp.tamu.edu/publications/204_IR/204TOC.HTM>.

EXPERIMENTAL

ODP has a critical role to play in addressing the study of naturally-occurring methane hydrates because it provides the only means available to the international academic community of directly sampling gas hydrates and underlying sediments beneath the oceans. Hydrates have been sampled during several ODP cruises.

Leg 164 to the Blake Ridge was the first (and, prior to Leg 204, the only) Leg focused primarily on understanding the dynamics of hydrate formation. Hydrates were secondary objectives of ODP cruises to the Chile (Leg 141) and Oregon (Leg 146) accretionary complexes, which were focused on understanding the mechanics and hydrology of accretionary wedges. Results from these expeditions have highlighted the need to 1) dedicate a Leg to exploring gas hydrate formation in active accretionary wedges, and 2) develop new tools and techniques to better estimate in situ hydrate and gas concentrations. ODP Leg 204 was dedicated to addressing these needs.

Additional results and data that relate to ODP Legs 201 and 204, as well as specific outcomes from this DOE/NETL project, are available online at the ODP Publications website for Leg 201: <http://www-odp.tamu.edu/publications/201_IR/201TOC.HTM> and for Leg 204: <http://www-odp.tamu.edu/publications/204_IR/204TOC.HTM>.

Accurate quantification of hydrate and gas concentrations has been elusive so far due to hydrate dissociation and gas loss during core retrieval unless core is retrieved at in situ pressure (Paull and Ussler, 2001). Furthermore, commonly used geochemical proxies for estimating the in situ hydrate concentration of sediments are not adequate because the initial composition of pore waters is not known and can be very variable. Consequently, a major focus of Leg 204, following on the testing conducted during Leg 201, was to acquire samples under pressure using the ODP PCS system and the recently developed HYACE system (http://www.tu-berlin.de/fb10/MAT/hyace.html), which includes a laboratory transfer chamber for maintaining pressure while making physical properties measurements (http://www.geotek.co.uk/hyace.html).

Infrared Thermal Imaging

IR thermal imaging of the surface of the core liner was fully implemented during Leg 204. The initial development of the technique was accomplished during Leg 201, where IR imaging was shown to successfully identify thermal anomalies associated with gas hydrate and voids.

Thermal anomalies in marine sediment cores on short length scales (less than a few meters) could result from (1) adiabatic gas expansion, (2) gas exsolution from pore water, or (3) gas hydrate dissociation. All of these processes cool cores (Ussler et al., unpubl. data). However, discrete, strong cold anomalies in Leg 204 cores were shown to be directly associated, spatially, with gas hydrate. These negative temperature anomalies, in general, were caused by gas hydrate dissociation in the core line after the core arrived on deck. Variations in heat capacity also impact core temperatures, but generally differences in thermal conductivity or density are relatively small and do not result in large enough heat capacity differences to cause discrete, negative thermal anomalies.

IR imaging on Leg 204 also confirms earlier thermistor measurements that show variations in thermal structure along entire cores, which are typically warmer at the bottom and cooler at the top (Ussler et al., unpubl. data). Gas expansion and gas exsolution may account for the observed gradient along cores. If so, the thermal structure developed principally during ascent of the core through the upper part of the water column. Alternatively, the thermal structure along entire cores may reflect differences in frictional heating during coring, creating warmer temperatures near the core barrel shoe (APC) or bit (XCB) and cooler temperatures near the core top. Analysis of data from the advanced piston corer methane (APCM) tool from Leg 204 is expected to help determine the origin of temperature gradients typically observed along each core. Regardless of the origin of the overall thermal structure of cores, the discrete, negative thermal anomalies associated with gas hydrate are superimposed on the broader gradient, providing a robust proxy for the location and abundance of gas hydrate in cores. Gas shows up as warm anomalies because of the low heat capacity of gas voids compared to sediment and in spite of the cooling effect of gas expansion.

The primary benefits of using IR cameras (rather than running a hand down the length of the core) include the following: (1) more precise identification of thermal anomalies, (2) the estimation of hydrate volume in processed images, and (3) determinations of shapes of gas hydrate. The IR camera is also quicker and simpler to use and has a much higher spatial resolution than an array of thermistors. Hydrate veins or lenses, hydrate nodules, and disseminated gas hydrate were all identified. The resolution of thermal anomalies observed indicates that the camera can detect small volumes of gas hydrate if they are adjacent to the core liner. Determining precise, quantitative volumetric estimates of gas hydrate in cores was an objective during Leg 204, but realizing this objective will require further analysis of collected data.

IR images were used to do the following:

1. Rapid identification of gas hydrate in cores from temperature anomalies on the surface of the core liner for immediate sampling of gas hydrate;
2. Preliminary assessment of the abundance of gas hydrate in cores based on the volume of core that shows thermal anomalies of varying ΔTs;
3. Quantification of the relative proportions of different gas hydrate textures;
4. Estimation of the cross-sectional temperature gradient in cores prior to sampling for microbiology;
5. Assessment of the thermal structure of entire cores and the differences in thermal structure between APC and XCB cores.

Downhole Tools on Leg 204

During Leg 204, a suite of downhole tools was employed to measure in situ temperature and pore pressure, to retrieve cores under pressure, and to estimate the in situ concentration of methane and other natural gases. Temperature, pressure, and gas composition and concentration are the critical factors for determining the extent of the GHSZ and whether gas hydrate can form in that zone. In addition, temperature affects rates of sediment diagenesis and microbial activity. Pore pressure is important because fluid flow occurs if the pressure gradient differs from hydrostatic, thus transporting natural gas into the GHSZ, providing nutrients for microbes, and modifying the temperature and pressure field.

In situ sediment thermal measurements were made during Leg 204 using the APC temperature (APCT) tool and the Davis-Villinger Temperature Probe (DVTP) (Davis et al., 1997). Temperatures and pressures were measured using a DVTP modified to include a pressure port and sensor (Davis-Villinger Temperature-Pressure Probe [DVTPP]) that was previously used during Legs 190 and 201. Pressure was also measured during a trial run of the Fugro-McClelland piezoprobe, which operates on similar principles as the DVTPP. Finally, pressure, temperature and conductivity were measured using the APC-Methane and PCS-Methane tools to collect samples from Hydrate Ridge.

Advanced Piston Corer Temperature (APCT) Tool

The APCT tool fits directly into the cutting shoe on the APC and can, therefore, be used to measure sediment temperatures during regular piston coring. The tool consists of electronic components, including battery packs, a data logger, and a platinum resistance–temperature device calibrated over a temperature range of 0°–30°C. Descriptions of the tool and of the principles behind analysis of the data it acquires can be found in Pribnow et al. (2000) and Graber et al. (2002) and the references therein. The thermal time constant of the cutting shoe assembly where the APCT tool is inserted is ~2–3 min. The only modification to normal APC procedures required to obtain temperature measurements is to hold the corer in place for ~10 min after cutting the core. During this time, the APCT tool logs temperature data on a microprocessor contained within the instrument as it approaches equilibrium with the in situ temperature of the sediments. Following deployment, the data are downloaded for processing. The tool can be preprogrammed to record temperatures at a range of sampling rates. Sampling rates of 10 s were used during Leg 204. A typical APCT measurement consists of a mudline temperature record lasting 10 min for the first deployment at each borehole and 2 min on subsequent runs. This is followed by a pulse of frictional heating when the piston is fired, a period of thermal decay that is monitored for 10 min or more, and a frictional pulse upon removal of the corer.

A second source of uncertainty in these data is possible temporal change of the bottom-water temperature resulting from tides, seasons, and longer-term climate change.

Evidence for short-term changes in this region is seen in data from a near-bottom current meter that was deployed for 6 months at a water depth of 800 m in the saddle between the northern and southern summits of Hydrate Ridge (R. Collier, pers. comm., 2000). These data show peak-to-peak tidal variations of up to 0.3°C, a superimposed variation with a timescale of 2 months and peak-to-peak amplitude of 0.04°C, and an apparent seasonal variation of 0.3°C. These multiple sources of bottom-water temperature variation, which occur on a timescale that will not be felt at subseafloor depths greater than a few meters lead to significant temporal variability in the mudline temperature. Because of these observations, it may, in general, be inappropriate to include the mudline temperature when determining the subsurface temperature gradient from downhole temperature data. Mudline temperatures, however, are reported in the data tables because they can provide a useful data point for postcruise studies.

Davis-Villinger Temperature Probe

The temperature measurement aspects of the DVTP are described in detail by Davis et al. (1997) and summarized by Pribnow et al. (2000) and Graber et al. (2002). The probe is conical and has two thermistors; the first is located 1 cm from the tip of the probe and the other 12 cm above the tip. A third thermistor, referred to as the internal thermistor, is in the electronics package. Thermistor sensitivity is 1 mK in an operating range of –5° to 20°C, and the total operating range is –5° to 100°C.

The thermistors were calibrated at the factory and on the laboratory bench before installation in the probe. In addition to the thermistors, the probe contains an accelerometer sensitive to 0.98 m/s2. Both peak, and mean acceleration are recorded by the data logger. The accelerometer data are used to track disturbances to the instrument package during the equilibration interval. In a DVTP deployment, mudline temperatures (within the drill pipe) are measured for 10 min during the first run within each hole and for 2 min during subsequent runs, before descent into the hole for a 10-min equilibration time series at the measurement depth in the subseafloor. The time constants for the sensors are ~1 min for the probe-tip thermistor and ~2 min for the thermistor 12 cm from the tip. Only data from the probe tip thermistor were used for estimation of in situ temperatures.

Davis-Villinger Temperature-Pressure Probe

Simultaneous measurement of formation temperature and pressure was achieved using a modified DVTP. The probe has a tip that incorporates both a single thermistor in an oil-filled needle and ports to allow hydraulic transmission of formation fluid pressures to a precision Paroscientific pressure gauge inside. A standard data logger was modified to accept the pressure signal instead of the second thermistor signal in the normal DVTP described above. Thermistor sensitivity of the modified tool is reduced to 0.02 K in an operating range of –5° to 20°C. A typical deployment of the tool consists of lowering the tool by wireline to the mudline where there is a 10-min pause to collect data.

Subsequently, the tool is lowered to the base of the hole and latched in at the bottom of the drill string, with the end of the tool extending 1.1 m below the drill bit. The extended probe is pushed into the sediment below the bottom of the hole and pressure is recorded for ~40 min. If smooth pressure decay curves are recorded after penetration, then theoretical extrapolations to in situ pore pressures are possible.

Temperature data from the DVTPP were treated as discussed for the DVTP. For both the DVTPP and the piezoprobe (discussed below), the pressure response is qualitatively similar to, but slower, than the thermal response. The decay time is a function of the sediment permeability and the magnitude of the initial pulse, which is a function of the taper angle and diameter of the tool (Whittle et al., 2001; Heeseman, 2002).

Fugro-McClelland Piezoprobe

In April 2001, a proposal was submitted to the U.S. Department of Energy to modify and implement the use of the Fugro-McClelland piezoprobe tool on the *JOIDES Resolution* during ODP Leg 204. The piezoprobe has been tested and proven (e.g., Ostermeier et al., 2000; Whittle et al., 2001) on numerous geotechnical cruises that measured pressure and temperature, but it had not been adapted for ODP until Leg 204. To adapt it on the *JOIDES Resolution* for testing and use with the APC/XCB bottom-hole assembly (BHA) required modifications prior to the leg. The modifications made by Fugro-McClelland and ODP were designed to (1) adapt the piezoprobe for a Schlumberger wireline, (2) increase the landing ring size, (3) implement a stabilizer sleeve to prevent bending, (4) shorten the bit to minimize risk of bending, and (5) extend pawls for the four-cone APC bit used on the *JOIDES Resolution*.

The piezoprobe works within the borehole and measures pressure through a transducer at its tip, which is similar to the pop-up pore pressure instrument (PUPPI) (see Schultheiss and McPhail, 1986). The probe is lowered through the drill pipe, measures hydrostatic pressure, and is pushed into the sediment ~1 m beyond the base of the borehole, where pressure is again measured. The resultant pressure vs. time curves for multiple experiments provide estimates of in situ pressure as a function of depth. The pressure decay can be used to evaluate the permeability and coefficient of consolidation (e.g., Elsworth et al., 1998; Schnaid et al., 1997), two parameters that are necessary to describe fluid flow and deformation within the shallow subsurface. The narrow taper of the piezoprobe allows a pressure decay to be measured in low-permeability sediments within an hour, a time frame that is reasonable for use on the *JOIDES Resolution*. The piezoprobe also records temperature data during each measurement. Similar to the APCT tool and the DVTP tool, the temperature decay can be used to estimate in situ temperature. During Leg 204, the piezoprobe was deployed twice, with the second run being successful.

Comparison between the Piezoprobe and the Davis-Villinger Temperature-Pressure Probe

The DVTPP and the piezoprobe both provide the ability to make estimates of in situ temperature and pressure in low-permeability strata at a relatively quick rate (i.e., multiple measurements per hole and dozens of measurements per cruise). The basic operational procedure for each is similar to that for the temperature tools: (1) insert probe at the base of the borehole, (2) monitor pressure disturbance from probe insertion, and (3) record pressure decay and extrapolate out to infinite time for estimate of in situ pressure. The decay time is a function of the sediment permeability and the size of the initial pulse. The magnitude of the pressure pulse is a function of the taper angle and diameter of the tool (Whittle et al., 2001). The piezoprobe has a narrower diameter (6.4 mm) and smaller taper angle (<2°) than the DVTPP (diameter = 8 mm and taper = 2.5°) and therefore produces a smaller pressure disturbance.

Whittle et al. (2001) have demonstrated that it is beneficial to monitor the pressure decay long enough so that a significant proportion of the pulse has dissipated before recovery of the tool; with the piezoprobe, this takes ~2 hr in low-permeability strata (Whittle et al., 2001), longer than is generally allowed for the DVTPP during ODP legs.

Methane Tools

The Advanced Piston Corer Methane (APCM) tool and the Pressure Coring System Methane (PCSM) tool continuously record the temperature, pressure, and electrical conductivity changes in the core headspace from the time the core is cut through its ascent to the rig floor. The APCM sensors are mounted in a special piston head on the standard ODP APC piston, and the data acquisition electronics are embedded within the piston. The PCSM is a slimmed-down version of the APCM, which is mounted on the top of the PCS manifold mandrel.

Both tools operate passively and require little shipboard attention. Variations in the relative amounts of gas stored in different types of sediment can be determined by establishing families of ascent curves composed of data from successive cores. Models indicate that these data will also provide information on whether gas hydrate was present in the sediment before core retrieval. The two methane tools are being developed through a collaborative activity involving the ODP engineering staff and Monterrey Bay Aquarium Research Institute (MBARI). They are derivatives of MBARI's Temperature-Pressure-Conductivity (TPC) tool.

Both tools are very similar in construction, the only difference being that the APCM replaces the piston-rod snubber in the APC coring system and therefore has a seal package on its exterior. The tools consist of an instrumented sensor head with the electronics and battery pack housed in a sealed case. The three sensors (temperature, pressure, and conductivity) and a data port are packaged in the face of the 23/8-indiameter sensor head. The temperature sensor is a ±0.05°C accuracy thermistor installed in a 3/16-in-diameter °— 1/-in-long probe. The pressure sensor is a 0- to 10,000-psi "Downhole Series" transducer with a ±0.15% full-scale accuracy that is especially designed for temperature stability. The electrical conductivity sensor is a three-pin bulkhead connector with an inconel body and gold-plated 0.040-in-diameter Kovar pins. The data port is a three-pin keyed bulkhead connector for RS-232 communication. The electronics consists of two boards, an analog to digital (A/D) board and a commercial microcontroller board. The microcontroller board plugs directly into the A/D board, and the A/D board is mounted on an aluminum backbone. The microcontroller includes a Motorola 68338 processor, a DOS-like operating system, and 48 MB of flash memory. The A/D board is an ODP/MBARI-designed board with one A/D device for the pressure transducer and one for the thermistor and conductivity sensors. The battery pack consists of an assembly of two double-C lithium/thionyl chloride batteries in series and an integral hard-mounted nine-pin connector. The 1-in-diameter 9-in-long battery pack provides 7.3 V, with a 100-mA rating. The APCM is installed on the APC piston after the APC piston-rod snubber and piston-head body is removed from the lower piston rod. The connection at the lower piston rod consists of a threaded connection with a transverse spring pin running through the thread relief. The spring pin prevents the connection from unscrewing as a result of vibration. After the spring pin is punched out, the piston-rod snubber is removed and replaced with the APCM. This swap-out operation takes <3 min. The PCSM replaces the accumulator on the PCS and threads onto the top of the PCS manifold mandrel.

The APCM and PCSM tools were successfully deployed 107 times during Leg 204, but all data analysis was deferred until postcruise.

Pressure Coring

Retrieval of cores at in situ pressure was a high priority during Leg 204. Natural gas in deep sediment may be present in three phases. If the concentration (molality) of gas in pore water is less than the solubility, the gas is dissolved. If the concentration of gas is greater than its solubility, gas is present as a free phase (bubbles) below the GHSZ and as solid hydrate within the GHSZ. Knowledge of the gas concentration in deep sediment is critical for understanding the dynamics of hydrate formation and the effect hydrates have on the physical properties of the sediment. However, reliable data on gas concentration are difficult to obtain. Because gas solubility decreases as pressure decreases and temperature increases, cores recovered from great depth often release a large volume of gas during recovery (Wallace et al., 2000; Paull and Ussler, 2001). The only way to determine true in situ concentrations of natural gas in the subseafloor is to retrieve cores in an autoclave that maintains in situ conditions. The original ODP pressure core sampler (PCS) has proven to be an essential tool that is very effective for estimating in situ gas concentrations (Dickens et al., 1997, 2000b) and was used extensively during Leg 204.

However, it is less effective for studies of physical properties of gas hydrate–bearing sediments at in situ conditions.

The HYACINTH (deployment of Hydrate Autoclave Coring Equipment [HYACE] tools in new tests on hydrates) program, funded by the European Union (EU), is developing the next generation of pressure corers. Both HYACE coring systems were used during Leg 204. The Fugro Pressure Corer (FPC) is designed for sediments that are normally cored with the APC and XCB, and the HYACE Rotary Corer (HRC) is designed to drill more lithified sediments and rocks normally cored with the XCB and RCB. These pressure cores are contained in an inner plastic liner that can be transferred (under full pressure) from the autoclave into other pressure chambers. When transferred into a logging chamber, the pressurized cores can be logged using the V-MSCL. This was used to make measurements on cores collected by the HYACE coring tools and on standard ODP cores re-pressurized to in situ pressures. By measuring VP, P-wave attenuation, and GRA density at in situ pressures and by pressure cycling, we anticipated being able to distinguish between hydrate and free gas while also measuring some in situ properties that would help to constrain models of hydrate and free gas distribution.

ODP Pressure Core Sampler (PCS)

The PCS is a downhole tool designed to recover a 1-m-long sediment core with a diameter of 4.32 cm at in situ pressure up to a maximum of 10,000 psi (Pettigrew, 1992; Graber et al., 2002). It consists of an inner core barrel and a detachable sample chamber. When its valves seal properly, controlled release of pressure from the PCS through a manifold permits collection of gases that would otherwise escape on the wireline trip. The PCS currently provides the only proven means to determine in situ gas abundance in deep-sea sediments where gas concentrations at depth exceed saturation at atmospheric pressure and room temperature (Dickens et al., 1997). The analysis of recorded data (e.g., time series of pressure and the volume of released gas) may also help to determine if gas hydrate is present in the cored interval (Dickens et al., 2000b).

After retrieval, the PCS is placed into an ice bath to keep the inside temperature at ~0°C. A manifold is connected to the PCS to decrease pressure by releasing gas under manual control. Only a small volume of gas (~100–150 mL) should be collected during the first gas release. This is because it has been empirically determined that the first gas sample thus obtained is contaminated by air. Additional gas releases should lead to immediate pressure drops. Ideally, the pressure in the PCS should then increase with time as gas exsolves from pore water or from decomposing gas hydrate. Gas should be released when pressure does not increase significantly over a 10- to 15-min time interval, and the process should be repeated. Sometimes gas may be released before the pressure has built up because of constraints with operational logistics.

At the end of the experiment, ice should be removed from around the PCS and the PCS should be warmed up to release all gas remaining in the core. Splits of gases are collected into a 1-L bubbling chamber that consists of an inverted graduated cylinder placed in a plexiglass tube filled with a saturated NaCl solution. After measuring the volume of collected gas, gas aliquots are sampled from a valve at the top of the cylinder using a syringe.

Prior to Leg 204, the PCS was successfully used to study in situ gases during ODP Leg 164 on the gas hydrate–bearing Blake Ridge (Paull, Matsumoto, Wallace, et al., 1996; Dickens et al., 1997) and during Leg 201 at sites along the gas-rich Peru margin (Dickens et al., 2003). One of the objectives of PCS use during Leg 201 was to test the coring capabilities in a variety of lithologic conditions. Several modifications to the PCS were made prior to Leg 201 (Dickens et al., 2003), including the addition of an optional cutting shoe for rotary coring and the construction of a new gas manifold. The PCS was deployed 17 times during Leg 201. Dickens et al. (2003) concluded that (1) the tool performed better during Leg 201 than on Leg 164, (2) the PCS can operate successfully in a variety of submarine environments, and (3) cores collected at shallow sediment depth can be degassed to generate gas concentration profiles.

Two significant modifications were made between Legs 201 and 204 in order to better address the scientific objectives of Leg 204. First, a methane tool was installed inside the PCS to measure temperature, pressure, and conductivity during the PCS recovery (see below). Second, pressure transducers that permit continuous monitoring of pressure, both on the manifold and inside the PCS were installed. Pressure is recorded on a personal computer every 5 s and is presented as a graph during the experiment. An ASCII file of the data is preserved at the end of the experiment. These modifications should permit better monitoring of pressure and temperature inside the PCS after the core is retrieved from the subsurface.

HYACINTH Coring Equipment

Although the PCS was successful during Leg 164, there were a number of aspects worthy of improvement as described by Dickens et al. (2000a). A proposal submitted to the EU resulted in HYACE, which was a 3-yr project aimed at developing new wireline pressure coring tools that would address a wide range of scientific problems. The HYACE project resulted in the development of two new pressure-coring tools.

These tools underwent only limited testing on land and at sea during ODP Legs 194 and 201 (Leg 201 was after the end of the HYACE project and at the beginning of the HYACINTH project). The current HYACINTH project is a continuation of the HYACE project and is also funded by the EU. It is designed to bring these new coring tools into operational use and to develop new techniques of subsampling and analyzing cores under pressure. Leg 204 provided the opportunity for further testing and use of these new coring tools. Other important objectives of Leg 204 were to test and use the HYACINTH family of pressure chambers and the core-transfer mechanisms and to measure the physical properties of cores at in situ pressures.

The design and operation of the HYACE tools differs in two significant respects from that of the existing PCS. First, the HYACE tools penetrate the seabed using downhole driving-mechanisms powered by fluid circulation rather than by top-driven rotation with the drill string. This allows the drill string to hang stationary in the hole while core is being cut, which should improve core quality and recovery. Second, the HYACE tools recover lined cores, which enables them to be transferred under pressure into a family of chambers, allowing cores to be preserved and studied under pressure.

Two different coring tools have been developed in order to accommodate a wide range of lithologies, a “percussion” corer and a “rotary” corer. Both tools have been designed for use with the same ODP BHA as the PCS (i.e., the APC/XCB BHA). The FPC is designed for recovering unlithified sediment ranging from clay to sand and gravel. When used in a gas hydrate–bearing environment, it is considered to be most applicable where any hydrate present has not significantly cemented the sedimentary particles. The core barrel is driven into the sediment by a hammer mechanism that is driven by fluid circulation. In soft sediments, the core barrel strokes out quickly so that in these lithologies the FPC essentially behaves like a push core.

The HRC is designed to cut a rotary core in more lithified sediment formations and incorporates a downhole mud motor. A dry auger-type of bit, extending beyond the reach of the circulating seawater, is used to cut the core, providing as contamination-free a core as is possible with rotary coring. It is designed, primarily, to recover cores in well-lithified sediments and rocks that can be obtained with the XCB and RCB. The phase II PCS development proposed by Pettigrew (1992) is similar to the approach used in the HRC. However, this was not pursued by ODP because of insufficient funds.

Both the FPC and the HRC use specially designed but different flapper valves to seal the tool’s pressure chamber (autoclave), where the core is contained on recovery. This enables larger cores to be cut than with the PCS, which uses a ball valve as the sealing mechanism. The FPC cuts a 58-mm-diameter core, and the HRC cuts a 50-mm-diameter core. Like the PCS, both cores are ~1 m in length. Pressures up to 250 kbar (3625 psi) can be maintained in the present design.

After initial testing on land, the FPC and HRC underwent their first sea trials on the *JOIDES Resolution* at the start of ODP Leg 194. The FPC had limited success in recovering a core under pressure, whereas the HRC encountered significant problems because of its failure to latch properly in the BHA (Rack, 2001). A core was finally cut but was not retrieved under pressure. The FPC had further trials during Leg 201, but hole conditions are thought to have been unfavorable, which prevented the recovery of a pressure core. Valuable lessons were learned during both of these engineering trials of the FPC and the HRC (Rack, 2001), and a number of significant modifications were made to the tools and to the handling procedures prior to the start of Leg 204.

RESULTS AND DISCUSSION

The primary objectives of the JOI proposal to DOE/NETL, which resulted in Cooperative Agreement #DE-FC26-01NT41329, were to sample and characterize methane hydrates using the systems and capabilities of the D/V *JOIDES Resolution* during ODP Leg 204, to enable scientists the opportunity to establish the mass and distribution of naturally occurring gas and gas hydrate at all relevant spatial and temporal scales, and to contribute to the DOE methane hydrate research and development effort. The goal of the work was to provide expanded measurement capabilities on the *JOIDES Resolution* for a dedicated hydrate cruise to Hydrate Ridge off Oregon (ODP Leg 204) so that hydrate deposits in this region are well characterized. This goal was accomplished along with many other aspects of this project, which have contributed to ongoing hydrate studies and joint industry project preparation to characterize hydrate deposits in the Gulf of Mexico.

The projects identified in the JOI proposal were all focused on providing enhanced capabilities for existing tools and developing new approaches to the study of naturally-occurring marine methane hydrate. This was accomplished by the development and testing of tools and measurement systems on ODP Leg 201 (Peru Margin) in preparation for their extensive use on ODP Leg 204 (Hydrate Ridge, offshore Oregon).

This project involved very complex operational planning and the enhancement or development of complicated downhole sampling and measurement tools, as well as well-thought out approaches to laboratory procedures and measurements, some requiring the deployment of specialized equipment never before used in scientific ocean drilling. More detailed information about the testing and deployment of a range of tools and systems during ODP Legs 201 and 204 with discussions about some of the important results is presented in the Phase 1 Final Report of this cooperative agreement.

Further detailed information, including methods and procedures used throughout each of these two expeditions, can be obtained online, for Leg 201 at: <http://www-odp.tamu.edu/publications/201_IR/201TOC.HTM> and for Leg 204 at: <http://www-odp.tamu.edu/publications/204_IR/204TOC.HTM>.

Leg 204 was originally scheduled to begin in San Francisco, California and end in San Diego. Due to an impending West Coast dock strike both port calls were ultimately moved to Victoria, B. C. Leg 204 officially began with the first line ashore Westcan Terminal B at 0655 hrs 7 July 2002.

In many ways the leg turned out to be extraordinary. All science objectives were successfully achieved during the course of drilling/coring the 7 primary sites. In addition, 2 alternate sites were also successfully cored. Finally, a series of additional holes were cored at the crest of Hydrate Ridge (Site 1249) specifically geared toward the rapid recovery and preservation of hydrate samples as part of a hydrate geriatric study funded by the Department of Energy (DOE). Bulleted highlights of the leg are shown below followed by a more descriptive discussion.

Summary of Leg 204 Gas Hydrate Coring

- The leg was planned as a 59.4 day leg – ended up as 57.1 day leg
- 50.4 days (88.3%) of time was spent on-site operating; 6.7 days (11.7%) in port/transit
- 23 rig moves were made using dynamic positioning totaling 29 NMI (43.8 hours)
- 3 positioning beacons were used – successfully deployed and recovered 21 times
- Plan included 23 holes at 7 sites – ultimately 45 holes were drilled/cored at 9 sites
- Water depths ranged from 788.5 mbrf to 1228.0 mbrf
- Penetration depths varied from 9.5 to 540.3 mbsf
- 8 of 9 sites drilled using LWD (resistivity at bit, NMR, density/neutron) technology
- 11 holes were drilled using a tricone bit for LWD/RAB-8 or wire line logging
- 33 holes were cored with the APC and/or XCB coring systems; 1 hole was RCB cored
- Over all 3674.5 meters were cored and 3068.3 meters or 83.5% were recovered
- 9 rendezvous took place during the leg using 7 helicopters and 2 supply boats
- 42 personnel were exchanged on/off the ship - these included an engineer from DOE National Technology Laboratory and a drilling engineer from ChevronTexaco
- Series of holes at end of leg were dedicated to the rapid recovery and preservation of hydrate samples as part of a hydrate geriatric study co-funded by the NSF and DOE
- 50 meters of hydrate core recovered/stored under pressure in a methane environment
- 35 meters of additional samples recovered/stored in 6 liquid nitrogen dewars
- Cores scanned for hydrate "cold spots" with track mounted infrared camera
- Most cores were processed through a linear x-ray logging system that was provided to Leg 204 by Dr. Barry Freifeld from Lawrence-Berkley National Laboratory

Summary of Leg 204 Special Tools Deployments

- 30 out of 39 successful runs with the TAMU Pressure Core Sampler (PCS)
- 16 out of 16 successful runs with Davis-Villinger Temperature Tool w/Pressure
- 8 out of 8 successful runs with Davis-Villinger Temperature Tool (DVTP)
- 61 out of 61 successful runs with the TAMU Advanced Piston Corer Temperature Tool
- 107 of 110 successful runs with Temp/Pressure/Conductivity (TPC) "Methane" Tool
- 1 out of 2 successful deployments of the Fugro-McClelland Piezoprobe
- 2 of 10 cores recovered w/pressure using Hyacinth Fugro Pressure Corer (FPC)
- 4 of 8 cores recovered under pressure using the Hyace Rotary Corer (HRC)
- 28 runs with LDEO Drill String Accelerometer (DSA) tool; 17+ all/partially successful
- 8 of 8 cores successfully recovered using the RAB-8 logging-while-coring technology
- Whirlpak glass micro-beads and Perfluorocarbon tracers (PFT's) used on 85 cores

Leg 204 operations were not only complicated with all of the special tool deployments and rendezvous scheduled. Operations on the Southern Hydrate Ridge also required continual coordination with several other oceanographic research vessels. The R/V Sonne, a German research vessel, operated in the same area deploying and recovering instrumented sea floor landers. The R/V Ewing, from LDEO, worked in conjunction with the *Resolution* conducting 2-ship seismic operations and also conducted independent research including the setting of OBS packages on the sea floor. The R/V Atlantis, from Woods Hole Oceanographic Institution (WHOI), was on-site for 4-days of Alvin diving at the ridge crest. And finally, the New Horizon, a Scripps Institution of Oceanography (SIO) vessel, was on-location briefly doing independent oceanographic research work.

The first part of Leg 204 was dedicated to logging-while-drilling (LWD) to identify regions of rapid change in physical properties prior to coring. This permitted the optimization of special tools to measure in situ temperature and pressure and to retrieve cores at in situ pressure.

The leg also included a two-ship seismic program conducted in conjunction with the R/V Ewing to acquire vertical, constant offset, and walkaway vertical seismic profiles (VSP). A new Schlumberger tool called the Vertical Seismic Imager (VSI) was used for most of the VSP work whereas the older Well Seismic Tool (WST) was used for the remaining holes. Deployment of the VSI tool was problematic because of it’s more fragile construction and because the tool is not designed to have the electric line slacked off during the data acquisition period. None-the-less the tool worked well enough to fully achieve the seismic objectives.

Eight of the sites were drilled using LWD technology. A developmental logging-while-coring (LWC) system jointly developed by Lamont-Dougherty Earth Observatory (LDEO), Anadrill, and Texas A & M University (TAMU) was also successfully tested using a Resistance-At-Bit (RAB-8) LWD tool. This marked the first time ever that core samples have been recovered simultaneously with LWD data.

Several other specialized tools developed all or in part by TAMU were successfully deployed during the leg. These include the Pressure Core Sampler (PCS), Methane Tool (MT), Advanced Piston Corer Temperature (APCT) shoe, Davis-Villinger Temperature Probe (DVTP), and the Davis-Villinger Temperature Probe with pressure (DVTPP).

Two other developmental pressure-coring systems developed by the European consortium referred to as Hyacinth were deployed. These tools were designed to allow transfer of a pressurized core sample from the down hole tools autoclave chamber to a pressurized logging chamber. The Fugro Pressure Corer (FPC) and Hyace Rotary Corer (HRC) were deployed 10 times and 8 times respectively. Two runs with the FPC and 4 runs with the HRC successfully recovered core at or near in situ pressure. Functionally the pressurized core transfer and logging chambers worked well although some tolerance variations with the FPC made the transferring the FPC cores more problematic.

Prior to the leg TAMU worked with Fugro-McClelland on the adaptation of their Piezoprobe tool to the ODP/TAMU bottom hole assembly (BHA). This tool was deployed twice on the first site with the second attempt fully successful. Data from this electric line deployed tool will be compared to DVTPP data. The DVTPP tool is deployed in a much faster and simpler fashion by being free fall deployed and then recovered using the standard ODP coring line.

LDEO deployed their Drill String Accelerometer (DSA) tool to gather down hole data in support of the Hyacinth tool deployments and also as part of an experimental study using the Advanced Piston Corer (APC) as an energy source. The APC impact energy was recorded using Ocean Bottom Seismic (OBS) stations placed on the sea floor earlier by the R/V Ewing. Initial results indicated that this experiment was successful and that useful data was obtained.

While the scientific and operational achievements were impressive the leg was extremely demanding because of the confined operating area. All 9 drillsites were located within 3.6 nmi of each other. Due to the close proximity of the sites all moves between sites were done using the ship's dynamic positioning system. Because of the commonality of the coring BHA's to be used, most of these moves were made with the pipe suspended below the ship. When a BHA change or bit replacement was required the move was made simultaneously with the pipe trip to/from the surface. With no transit time other then traveling to and from port, and limited pipe trips between sites, the operating time available for drilling and coring was considerable. For the 57.1 day leg 50.4 days or 88.3 % of the available time was spent on-site. The remaining 6.7 days were spent in port (4.14 days) and underway (2.54 days).

Leg 204 operations were confined to an area located ~50 nmi off the coast of Oregon. The close proximity of land meant that this leg was a candidate for numerous changes of personnel and equipment. An initial supply boat rendezvous was planned to allow removal of specialized, and expensive, VSP equipment along with an Anadrill VSP engineer. This soon grew to include numerous other personnel changes via helicopter and another supply boat bringing out special pressure vessels, dewars, and liquid nitrogen to support the add-on effort to recover and preserve the additional hydrate samples. Ultimately there were a total of 9 rendezvous completed with the *JOIDES Resolution* including 7 helicopters and 2 supply vessels. Leg 204 officially ended at 0900 hours 2 September 2002 with the first line ashore Westcan Terminal B in Victoria, B. C.

The primary objectives of the JOI proposal to DOE/NETL, which resulted in Cooperative Agreement #DE-FC26-01NT41329, were to sample and characterize methane hydrates using the systems and capabilities of the D/V *JOIDES Resolution* during ODP Leg 204, to enable scientists the opportunity to establish the mass and distribution of naturally occurring gas and gas hydrate at all relevant spatial and temporal scales, and to contribute to the DOE methane hydrate research and development effort. The goal of the work was to provide expanded measurement capabilities on the *JOIDES Resolution* for a dedicated hydrate cruise to Hydrate Ridge off Oregon (ODP Leg 204) so that hydrate deposits in this region are well characterized. This goal was accomplished along with many other aspects of this project, which have contributed to ongoing hydrate studies and joint industry project preparation to characterize hydrate deposits in the Gulf of Mexico.

The projects identified in the JOI proposal were all focused on providing enhanced capabilities for existing tools and developing new approaches to the study of naturally-occurring marine methane hydrate. This was accomplished by the development and testing of tools and measurement systems on ODP Leg 201 (Peru Margin) and their extensive use on ODP Leg 204 (Hydrate Ridge, offshore Oregon) to characterize, sample, and preserve large quantities of naturally-occurring methane hydrate for onshore studies.

This project involved very complex operational planning and the enhancement or development of complicated downhole sampling and measurement tools, as well as well-thought out approaches to laboratory procedures and measurements, some requiring the deployment of specialized equipment never before used in scientific ocean drilling.

CONCLUSION

The primary objectives of the JOI proposal to DOE/NETL, which resulted in Cooperative Agreement #DE-FC26-01NT41329, were to sample and characterize methane hydrates using the systems and capabilities of the D/V *JOIDES Resolution* during ODP Leg 204, to enable scientists the opportunity to establish the mass and distribution of naturally occurring gas and gas hydrate at all relevant spatial and temporal scales, and to contribute to the DOE methane hydrate research and development effort. The goal of the work was to provide expanded measurement capabilities on the *JOIDES Resolution* for a dedicated hydrate cruise to Hydrate Ridge off Oregon (ODP Leg 204) so that hydrate deposits in this region are well characterized. This goal was accomplished along with many other aspects of this project, which have contributed to ongoing hydrate studies and joint industry project preparation to characterize hydrate deposits in the Gulf of Mexico.

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More detailed information about the testing and deployment of a range of tools and systems during ODP Legs 201 and 204 with discussions about some of the important results is presented in the Phase 1 Final Report of this cooperative agreement.

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LIST OF ACRONYMS AND ABBREVIATIONS

APC	Advanced Piston Corer
APC-M	Advanced Piston Corer-methane tool
APC-T	Advanced Piston Corer-temperature tool
BHA	Bottom Hole Assembly
BSR	Bottom Simulating Reflector
DOE	Department of Energy
DVTP	Davis Villinger Temperature Probe
DVTP-P	Davis Villinger Temperature Probe with Pressure
FMMG	Fugro-McCleland Marine Geosciences
FPC	Fugro Pressure Corer
GHSZ	Gas Hydrate Stability Zone
HR	Hydrate Ridge
HRC	HYACE Rotary Corer
HYACE	Hydrate Autoclave Coring Equipment
HYACINTH	Deployment of HYACE tools In New Tests on Hydrates
IR-TIS	Infrared Thermal Imaging System
JOI	Joint Oceanographic Institutions
JOIDES	Joint Oceanographic Institutions for Deep Earth Sampling
LDEO	Lamont Doherty Earth Observatory (Columbia University)
L/L	Liters per Liter
LTC	Laboratory Transfer Chamber
LWD	Logging While Drilling
MBRF	Meters Below Rig Floor
MBSF	Meters Below Sea Floor
MH	Methane Hydrate
MPa	Mega-Pascals
MSCL-V	Multi-Sensor Core Logger - Vertical
NETL	National Energy Technology Laboratory
NSF	National Science Foundation
ODP	Ocean Drilling Program
ODP-LC	Ocean Drilling Program – Logging Chamber
PCS	Pressure Core Sampler
PSI	Pounds per Square Inch
RAB	Resistivity at the Bit
RAB-c	Resistivity at the Bit with Coring
RCB	Rotary Core Barrel
R/V	Research Vessel
TAMU	Texas A&M University
XCB	Extended Core Barrel

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