

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

DOE COOPERATIVE AGREEMENT: DE-FC26-01NT41329

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ABSTRACT

Cooperative Agreement #DE-FC26-01NT41329 between Joint Oceanographic Institutions and DOE-NETL was divided into two phases based on successive proposals and negotiated statements of work pertaining to activities to sample and characterize methane hydrates on ODP Leg 204 (Phase 1) and on IODP Expedition 311 (Phase 2). The Phase 1 Final Report was submitted to DOE-NETL in April 2004. This report is the Phase 2 Final Report to DOE-NETL.

The primary objectives of Phase 2 were to sample and characterize methane hydrates using the systems and capabilities of the D/V *JOIDES Resolution* during IODP Expedition 311, 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 the Cascadia continental margin off Vancouver Island, British Columbia, Canada (IODP Expedition 311) so that hydrate deposits in this region would be well characterized and technology development continued for hydrate research.

IODP Expedition 311 shipboard activities on the *JOIDES Resolution* began on August 28 and were concluded on October 28, 2005. The statement of work for this project included three primary tasks: (1) research management oversight, provided by JOI; (2) mobilization, deployment and demobilization of pressure coring and core logging systems, through a subcontract with Geotek Ltd.; and, (3) mobilization, deployment and demobilization of a refrigerated container van that will be used for degassing of the Pressure Core Sampler and density logging of these pressure cores, through a subcontract with the Texas A&M Research Foundation (TAMRF). Additional small tasks that arose during the course of the research were included under these three primary tasks in consultation with the DOE-NETL Program Manager.

All tasks outlined in the original statement of work were accomplished except for the deployment and use of the X-ray CT system under Subtask 2-2. This reduction in scope provided resources that were applied to other activities to support the overall project. Post-expedition analysis of results and report writing will continue beyond this reporting period, however, all field deployments associated with this project have been successfully concluded as of this writing.

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INTRODUCTION

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EXECUTIVE SUMMARY

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The main objectives of pressure coring during IODP Expedition 311 were to quantify natural gas composition and concentration in sediments and to determine the nature and distribution of gas hydrate and free gas within the sediment matrix. To achieve these objectives, the IODP Expedition 311 scientists: (a) measured the quantity and composition of gases released during controlled degassing experiments, (b) conducted nondestructive measurements (X-ray imaging, P-wave velocity, gamma density) at in situ pressures and during depressurization, and (c) archived hydrate-bearing sediments at in situ pressures for more comprehensive investigations on shore. The nondestructive measurements not only provide a direct indication of the existence of gas hydrate, but the resulting data (acoustic impedance) can be used to help interpret regional seismic data.

IODP Expedition 311 had the most ambitious pressure coring and onboard pressure core analysis program ever attempted in the history of ocean drilling. Pressure cores retrieved at in situ pressures were used to determine methane hydrate quantity, using degassing techniques and mass balance calculations, and methane hydrate distribution using non-

destructive measurement of the physical properties of the cores at in situ pressures. Large improvements in temperature control over previous expeditions (e.g., ODP Leg 204) made the recovery and analysis of pressure cores more practical.

Pressure cores were collected using the IODP Pressure Core Sampler (PCS) and HYACINTH Fugro Percussion Corer (FPC) and HYACE Rotary Corer (HRC) pressure corers. After a pressure core was retrieved, initial non-destructive measurements were made to characterize the core, determine the core length and identify massive gas hydrate. PCS cores were then degassed on board ship to determine total methane composition and concentration in sediments. The HYACINTH cores were degassed on shore, immediately following Expedition 311, after X-ray imaging and subsampling under pressure. All cores had non-destructive measurements made on them while undergoing degassing to document gas evolution, gas hydrate dissociation, or other changes in the core: PCS cores were routinely scanned for gamma density, whereas HYACINTH cores were scanned for gamma density and X-ray imaged. Following degassing, all pressure cores were X-rayed a final time and the released gas volume, the Xrays, and the density scans were used to guide sub-sampling for interstitial water, physical properties, and other related analyses.

All tasks outlined in the original statement of work were accomplished except for the deployment and use of the X-ray CT system under Subtask 2-2. This reduction in scope provided resources that were applied to other activities to support the overall project. Post-expedition analysis of results and report writing will continue beyond this reporting period, however, all field deployments associated with this project have been successfully concluded as of this writing.

Dr. Frank R. Rack presented the results of both phases of the cooperative agreement between JOI and DOE-NETL in Morgantown, WV on October 20, 2006. The slides used for this presentation are included in this report as Appendix A.

Research continues on both ODP Leg 204 and IODP Expedition 311 samples and data. Publications submitted by shipboard and shore-based participants of these two expeditions are published online as they are accepted, and links to publications in journals and books are provided whenever possible on either the ODP or IODP Publications websites, as described below.

The *Proceedings of the ODP, Scientific Results, 204*, are available at URL: [http://www-odp.tamu.edu/publications/204_SR/204TOC.HTM].

The *Proceedings of the IODP, Expedition 311*, are available at URL: [<http://iodp.tamu.edu/publications/proceedings.html>].

Additional scientific contributions from both of these expeditions will continue to be produced. A summary of the current citation listings for ODP Leg 204 and IODP Expedition 311 is provided in this report as Appendix B.

EXPERIMENTAL

Phase 2 of the JOI Cooperative Agreement with DOE/NETL focused on enhancements related to the scheduling of a scientific ocean drilling expedition to study marine methane hydrates along the Cascadia margin, in the NE Pacific as part of the Integrated Ocean Drilling Program (IODP) Expedition 311 using the R/V JOIDES Resolution. The statement of work for Phase 2 of this cooperative agreement is outlined below:

TASK 1-0: Research Management Oversight - JOI

Under this task, the Recipient shall provide management oversight of all subcontracts for various tasks as defined in the Statement of Project Objectives and as justified below. The Recipient shall provide the required statements of work for all subcontracted work, conduct oversight of all tasks, and prepare progress reports, annual reports, talks and other presentations for DOE/NETL, as appropriate. The Recipient shall also conduct subcontractor site visits to ensure that work is being carried out according to plans.

The Recipient will issue two sole-source subcontracts to provide the appropriate equipment and technical or engineering staff on IODP Expedition 311 as described in Task 2-0 and 3-0 below.

TASK 2-0: Deployment and Use of Pressure Coring and Core Logging Systems and Subsystems aboard the JOIDES Resolution and Onshore – GEOTEK

Under this task, the Recipient will establish a primary subcontracts with Geotek Ltd., who will work with Fugro (Subtask 2-1) to mobilize and deploy the HYACINTH pressure coring systems and associated core logging subsystems aboard the JOIDES Resolution for IODP Expedition 311 (Cascadia Margin Hydrates) and provide adequate engineering and technical support to operate these coring tool and measurement systems; and will work with Lawrence Berkeley National Laboratory (Dr. Barry Freifeld; Subtask 2-2) to provide the capability for X-ray linear scanning of pressure cores and post-expedition X-ray computed tomography of samples, as appropriate.

Subtask 2-1: HYACINTH Pressure Core Logging Systems

Subtask 2-1-1: Deployment and Use of HYACINTH Pressure Coring Tools

Geotek, Ltd. (working with Fugro) will mobilize and use both the HYACINTH wireline pressure coring tools, the FPC and HRC aboard the JOIDES Resolution during IODP Expedition 311. Both these tools enable core to be recovered and retained up to a maximum pressure of 250 bar (3,625 psi) using specially designed flap valves and, coupled with the use of the IODP PCS system, will ensure maximum flexibility for obtaining pressure cores depending on the technical, logistical and geological constraints that prevail.

Fugro Pressure Corer (FPC). The FPC was designed and built by Fugro Engineers BV in The Netherlands. It is a percussion corer, which uses a

water hammer driven by the fluid circulation to drive the core barrel into the sediment up to 1 m ahead of the roller cone bit, and is suitable for sampling unlithified sediments ranging from soft or stiff clays to sandy and gravelly material. It acquires a core 57 mm in diameter and up to 1 m in length in a plastic liner whose OD is 63 mm.

HYACE Rotary Corer (HRC). The HRC was designed and built by the Technical University of Clausthal and the Technical University of Berlin in Germany. It uses a downhole motor driven by the fluid circulation to cut a core up to 1 m ahead of the roller cone bit in consolidated sediment, lithified sediment or rock. It acquires a core 51 mm in diameter and up to 1 m in length in a plastic liner whose OD is 56 mm.

Subtask 2-1-2: HYACINTH Core Handling and Logging and Analysis

For pressure core analysis, Geotek (working with Fugro) will supply a complete range of equipment that will enable the pressure cores to be transferred from the autoclaves into storage chambers for subsequent analysis. On board they will be able to measure P wave velocity and gamma density using the MSCL-P as well as X-Ray linear scans (in collaboration with Barry Friefeld at LBNL; Subtask 2-2).

All the pressure core handling/transfer and core logging will be performed in a 20 ft chilled van that we will supply for the purpose. Aluminium storage chambers will be provided for work with X-Rays, either onboard or subsequently on shore.

Immediately following the Expedition, the equipment (the core handling transfer van and the chambers containing pressure core) will be made available for subsequent work at the Pacific Geoscience Center (PGC) north of Victoria, British Columbia, Canada. This work might include further logging of pressure cores using X-Ray CT scanning (LBNL) or other devices (see Subtask 2-2). Geotek (working with Fugro) will make this equipment available for a period of at least 10 days. In addition, they will supply staff to operate this equipment or train others for a similar period immediately following the Expedition.

Subtask 2-1-3: Deployment of MSCL-V System

Geotek will deploy the MSCL-V (multi-sensor core logger – vertical) system and manufacture the necessary clamps to hold the Pressure Core Sampler (PCS) tool during core logging. The MSCL-V system will be installed in a second 20 ft refrigerated van, to be supplied and retained by IODP-TAMU (see Subtask 2-3), along with the PCS degassing equipment.

Subtask 2-1-4: IR Imaging Track Enhancements

Geotek will also deploy an enhanced IR thermal imaging track system, with a number of modifications for use on the JOIDES Resolution, which will integrate with the use of the FLIR IR thermal imaging cameras provided by JOI. Track system enhancements will provide improved thermal shielding for the sensors,

improved calibration procedures, enhancements to the user interface allowing increased speed of operation, and software modification controlling data output and post processing functions.

Subtask 2-2: X-ray (linear and CT) scanning of hydrates and pressure cores.

The Berkeley Lab x-ray Computed Tomography system offers the capability to rapidly and non-invasively provide sediment textural information in addition to assessing the quantity and spatial distribution of hydrates contained within a whole-round core on location and immediately after coring. Using the Fugro pressure coring system with a modified storage chamber, cores will be recovered and x-ray imaged while hydrates are kept within their stability region. The information collected from the x-ray CT is complementary to the information obtained using the multi-sensor core logger and will be fully integrated into the planned core analysis program. Post-cruise analysis will look at petrophysical properties of recovered core and kinetic rates of dissociation for selected hydrate-bearing core samples.

Subtask 2-2-1: Preparation for Field Operations.

Prepare the x-ray system for scanning pressure cores on the JOIDES Resolution. This task will involve modifications so that x-ray images can be acquired as part of the MSCL-P logging of Hyacinth Pressure Cores. This work will be conducted in close cooperation with Geotek, Ltd, which is responsible for the design and preparation of the MSCL-P system. Berkeley Lab will be responsible for the engineering and development of the x-ray portion of the MSCL-P system.

Subtask 2-2-2: Port-Call Activities.

A Berkeley lab scientist will attend the Astoria port call and assist in set-up and installation of the MSCL-P/x-ray system on the JOIDES Resolution. This includes tuning and calibration of the system as well as performing final radiation safety surveys.

Subtask 2-2-3: Demobilization and Data Interpretation and Reporting.

Demobilize equipment back to Berkeley Laboratory. Perform analysis of collected data, including reporting results of baseline core imaging and interpretation of dissociation experiments. Comparisons between the x-ray data and other available logs and core measurements will be performed. A peer-reviewed publication will be prepared based on the data collected and the observations.

Subtask 2-2-4: Fabrication of PCS x-ray transparent core barrels.

Working with engineers at IODP-TAMU, fabricate three pressure core barrels that will permit x-raying PCS pressure cores. This will include testing and certification of the vessels at Berkeley Lab. This work includes modifications of the MSCL-P system to accommodate both the Hyacinth pressure cores as well as x-ray imaging the PCS cores.

TASK 3-0: Deployment of Refrigerated Van for PCS Core Logging aboard the JOIDES Resolution – TAMRF/TAMU

Under this task, which is related to equipment and activities described in Task 2-0, the Recipient will establish a second subcontract with Texas A&M Research Foundation (TAMRF) to procure, outfit and deploy a refrigerated van that will house pressure core logging equipment (provided by Geotek, Ltd. under the previously described subcontract) and degassing equipment used in the analysis and characterization of pressure cores. These costs include purchase of the refrigerated van, outfitting and installation of electrical, safety and laboratory infrastructure, and shipping costs related to deployment aboard the JOIDES Resolution for IODP Expedition 311.

The following sections of this report will describe the activities that were accomplished as part of the previously described statement of work and the rationale for the work performed in concert with the objectives of IODP Expedition 311.

Preparation for, and Implementation of IODP Expedition 311

Prior to the start of IODP Expedition 311 shipboard activities, modified IODP Pressure Coring System (PCS) aluminum autoclave chambers were fabricated and delivered to the IODP facilities at Texas A&M University.

Geotek, Ltd was awarded a contract by JOI to provide equipment and personnel to perform pressure coring and related work on IODP Expedition 311. Geotek, Ltd. provided an automated track for use with JOI's infrared camera systems whereby images were collected from 185 cores during the expedition and processed to provide continuous core temperature data. Both HYACINTH pressure coring tools, the HRC (HYACE Rotary Corer) and the FPC (Fugro Pressure Corer) were mobilized and used during the expedition. Two HYACINTH engineers supervised the use of the tools and five good pressure cores were obtained. Dr. Barry Freifeld from Lawrence Berkeley National Laboratory (LBNL) provided an X-ray source and detector for X-ray imaging of pressure cores and helped Geotek with the design and mobilization of the MSCL-P (multi-sensor core logger-pressure) system. Pressure core handling, transfer, and logging was performed in a refrigerated 20-foot container supplied by Geotek, Ltd. After scanning, the pressure cores were stored for on-shore analysis in aluminum barrels.

The Geotek MSCL-V (multi-sensor core logger-vertical) was set up in a 20-foot-long refrigerated container provided by Texas A&M University (TAMU) through the JOI contract with the Texas A&M Research Foundation (TAMRF). Geotek, Ltd. assisted TAMRF and TAMU staff in outfitting this container with equipment used for pressure core logging and degassing prior to deployment on the JOIDES Resolution.

IODP Expedition 311 activities officially began when the *JOIDES Resolution* arrived in Balboa, Panama and dropped anchor at 0029 hr 28 August 2005. The initial Expedition

311 transit from Panama to Oregon was completed by the afternoon of September 15, 2005. Following completion of all dockside preparatory work, the loading of supplies and the boarding of the scientific party, the JOIDES Resolution departed Astoria at 10:00 hr on 19 September. During the transit to the first site, preparation continued for deployment of the Pressure Core Sampler (PCS) and assistance was provided with readying the APCT/APCT3 and DVTP temperature tools. In addition, the PCS gas manifold system was installed and plumbed in the PCS van and a dry run of PCS core handling was conducted with key participants. The transit was also used to continue to prepare the vans and laboratories for coring. The installation of the IR camera track on the catwalk was completed. The marine specialists were trained in the use of the Parr pressure vessels for gas hydrate sampling and in the use of the IR camera track.

Once underway, technicians began the placement of plywood to enclose the catwalk for assembly of the infrared (IR) track and fabricated inserts for shipping pressure vessels. The IR track was initially installed on the catwalk during the transit, while final completion of the installation was accomplished during the Astoria port call once the GEOTEK crew came aboard to fine-tune the installation. IODP-USIO staff undertook the construction of tables and furniture designed for use in the new refrigerated van and all laboratories were prepared for the Cascadia gas hydrate expedition.

A vertical ice bath for temporary storage of pressurized core barrels and a jib crane to lift pressurized core barrels from the rig floor to the Lab Stack roof for processing in a refrigerated van were assembled and installed. The rails for the ice bath were welded in place on the moon pool doors. The ice bath, constructed of 10-3/4" casing with 4" of foam insulating material, was suspended on the rails into the moon pool and aligned with the middle core barrel shuck on the rig floor. The ice machine, dedicated to keeping the ice bath filled, was located in the Subsea Shop. A chute structure was designed to be mounted in the Subsea Shop floor hatch opening and extend down approximately 15 feet to the vertical ice bath. The chute was fabricated from 10" diameter PVC pipe that came onboard in Astoria. The jib crane pedestal was welded to the Lab Stack roof and the crane assembled and made operational. The crane was positioned on the inboard aft corner of the Lab Stack roof. The reach of the crane was designed to allow pressurized core barrels to be hoisted from the rig floor to the Lab Stack roof and quickly moved into a refrigerated van for degassing and logging.

An I-beam support structure was installed on the lab stack roof to provide a base for storage of the two 250 gallon and one 400 gallon liquid nitrogen supply tanks. In addition, two 20 ft. reefer vans, which will be used for pressure core processing and analyses, were installed on the lab stack roof and core tech shop roof. Schlumberger LWD/MWD tools and equipment were loaded aboard as well as the Fugro Pressure Corer and the HYACE Rotary Corer.

Why Pressure Core?

Pressure coring is crucial for understanding the concentration of gas hydrate and free methane gas in marine sediments, their nature and distribution, and their effect on the intrinsic properties of the sediment. Methane and other components of natural gas in deep sediment may be present in three phases: (1) if the concentration of methane in pore water is less than its solubility, the methane is dissolved; (2) if the concentration of methane is greater than its solubility, excess methane over saturation is present as a free phase (methane gas bubbles) below the gas hydrate stability zone (GHSZ) and; (3) as solid methane hydrate within the GHSZ.

However, reliable data on methane concentrations are impossible to obtain from conventional coring techniques because conventional cores recovered from ocean depth often release large volumes of gas during recovery (Wallace et al., 2000; Paull and Ussler, 2000). Natural gas solubility decreases significantly as pressure decreases during the recovery of cores to the surface, and any gas volume measurements made on conventional cores are gross underestimates of the in situ natural gas concentrations.

The only way to directly determine the in situ concentrations of natural gas in the sub-seafloor is to retrieve cores that are sealed immediately after the coring process and recovered to the surface without any losses of the constituents. To achieve this objective, the core must be sealed in an autoclave that is able to withstand the hydrostatic pressure at the coring depth when brought to the surface. This was the concept behind the original ODP pressure core sampler (PCS) and it has proven to be an essential tool for estimating in situ gas concentrations (Dickens et al., 1997, 2000a & b; Milkov et al., 2004).

Although the PCS is very effective at obtaining samples that are suitable for overall gas concentration analysis, this tool was not specifically designed for other types of analyses that might reveal the physical structure of gas or gas hydrate in the core. It is also not possible to transfer or sample the PCS core without releasing the pressure. To enable a more comprehensive investigation of gas-hydrate-bearing sediments, a more recent engineering program, HYACINTH, has developed, not only the next generation of pressure coring tools, but has initiated the development of techniques to non-destructively analyze the cores and to take sub-samples for microbiological, chemical and physical analysis at in situ pressures.

Description & Operation of Pressure Coring Systems

Pressure Core Sampler (PCS) Operations and Core Flow

The Pressure Core Sampler (PCS) is a downhole tool designed to recover a one-meter-long sediment core with a diameter of 4.32 cm at in situ pressure up to a maximum of 69 MPa (Pettigrew, 1992; Graber et. al, 2002). The pressure autoclave consists of an inner core barrel, which ideally collects a 1465 cm³ sediment core, and an outer chamber, which holds 2964 cm³ of seawater/drilling fluids. The last time the PCS was used in

earnest was during ODP Leg 204, where it collected 30 pressure cores, including cores of massive gas hydrate (Tréhu, Bohrmann, Rack, Torres, et al., 2003). For IODP Expedition 311, the steel outer and inner barrels of the PCS autoclave were replaced with aluminum barrels with a maximum working pressure of 25 MPa so that it could be used with the Geotek MSCL-P X-ray system.

Each PCS autoclave had a long journey between its initial assembly and the final removal of the core. The PCS tool is assembled in and on top of the core tech shop, and deployed as on ODP Leg 204 (Tréhu, Bohrmann, Rack, Torres, et al., 2003). When the core was retrieved on Expedition 311, it was immediately inserted into the ice shuck for 20 to 30 minutes to counteract any warming during the wireline trip. The cooled PCS autoclave was removed from the rest of the tool on the rig floor and delivered to the refrigerated HYACINTH logging van on top of the core tech shop. After X-ray imaging, the PCS autoclave was moved to the refrigerated PCS degassing van on top of the lab stack, either using a winch rigged on the porch outside the downhole tools laboratory or simply hand-carried up the stairs.

When degassing experiments were completed, the core was moved back to the core tech shop for core removal. Some pressure cores were X-ray imaged again in the HYACINTH van before the inner barrel was removed from the autoclave. Before removing the core, the water in the autoclave was carefully collected by opening the top valves all the way and the ball valve very slightly to allow water in the inner and outer barrel to flow out of the ball valve. This volume of water was collected and measured to enable the mass balance calculations from the depressurization experiments to be completed. The inner barrel was removed from the rest of the PCS autoclave and taken back to the HYACINTH logging van for X-ray analysis of the entire core. Final extrusion of the core into a half-liner took place in the core tech shop using a metal plug and broom handle or hydraulic pump (as dictated by the sediment stiffness). The core was given to the IODP curator and, with the aid of the X-ray images and differential density profiles, samples were taken for analysis of interstitial water, physical properties, and dissolved gases.

HYACINTH Coring Systems

Two types of wireline pressure coring tools were developed in the European-Union-funded HYACE/HYACINTH programs: a percussion corer and a rotary corer, which were designed to cut and recover core in a wide range of lithologies where gas-hydrate-bearing formations might exist. Both tools have been designed for use with the same IODP bottom-hole assembly (BHA) as the PCS (i.e., the APC/XCB BHA). The HYACINTH pressure coring systems were used successfully on Leg 204 to recover gas hydrate and surrounding sediments (Tréhu, Bohrmann, Rack, Torres, et al., 2003).

The design and operation of the HYACINTH tools differs in four significant respects from that of the PCS, namely:

- (1) The HYACINTH tools penetrate the sediment using downhole driving mechanisms powered by fluid circulation rather than by top-driven rotation with

- the drill string. This allows the drill string to remain stationary in the hole while core is being cut, which will improve core quality;
- (2) The coring portion of the HYACINTH tools moves relative to the main bit during the coring process, which also improves core quality. However, the extension of the core barrel up to one meter past the drill bit makes them far more susceptible to ship heave than other coring tools, and it is essential that the bit remain stationary on the bottom of the hole during coring;
 - (3) Both HYACINTH tools use "flapper valve" sealing mechanisms at the bottom end above the cutting shoe, rather than a ball valve, to maximize the diameter of the recovered core;
 - (4) The recovered HYACINTH cores are in plastic liner and the pressure autoclaves mate to a common transfer system so the cores can be manipulated and transferred into other chambers for analysis, storage and transportation under full pressure.

Fugro Pressure Corer

The HYACINTH percussion corer was developed by Fugro Engineers BV and is known as the Fugro Pressure Corer (FPC). The FPC uses a water hammer, driven by the circulating fluid pumped down the drill pipe, to drive the core barrel into the sediment up to one meter ahead of the drill bit. The core diameter is 57 mm (liner outer diameter is 63 mm). On completion of coring, the drill string is lifted to extract the core barrel from the sediment. Once the core barrel is free from the sediment the wireline pulls the core barrel liner containing the core into the autoclave. A specially designed flapper valve is used to seal the bottom end of the autoclave after the core has been retrieved. The FPC is designed to retain a pressure of up to 25 MPa. It is suitable for use with unlithified sediments ranging from soft through stiff clays to sandy or gravelly material. In soft sediments it acts like a push corer prior to the hammer mechanism becoming active. It has operated effectively in sediments with shear strengths up to 500 kPa or even higher.

HYACE Rotary Corer

The HYACINTH rotary corer was developed by the Technical University of Berlin and the Technical University of Clausthal and is known as the HYACE Rotary Corer (HRC). HYACE was name of the original engineering development program. The HRC uses an Inverse Moineau Motor driven by the circulating fluid pumped down the drill pipe to rotate the cutting shoe up to 1 m ahead of the roller cone bit. A narrow kerf, dry auger design cutting shoe, with polycrystalline diamond cutting elements is used on the HRC. This design allows the core to enter into the inner barrel before any flushing fluid can contaminate the material being cored. The core diameter is 51 mm (liner outer diameter is 56 mm). On completion of coring, the tool is lifted off bottom with the drill string and then the core is retracted into the autoclave by pulling in on the wireline in a similar manner to the FPC, and the pressure is sealed inside the barrel by a specially designed flapper valve. The HRC is designed to retain a pressure of up to 25 Mpa and was primarily designed for use in sampling lithified sediment or rock. However, in practice

scientists have found that the HRC can also sample much softer formations very effectively, presumably acting as a push corer with minimal rotation.

HYACINTH Coring Operations

As on Leg 204, the HRC and the FPC were prepared and assembled on tool trestles located on the port side of the piperacker. The normal tool assembly area above the core tech shop was in use for PCS tool assembly and impacted by the 20-foot HYACINTH container. Stands of drill pipe normally used from the port side were moved to the starboard side to reduce disruption to the tool preparations.

Both tools followed similar operational procedures on the rig floor. They were initially transferred from the pipe-racker working area into the vertical position. To achieve this, a tugger line from the derrick was attached to the upper end of the tool while the base of the tool was lowered onto the pipe-racker skate using the port side racker crane. The tool was then hauled into a vertical position using the tugger line and lowered into the rig floor shuck as the strongbacks were removed by hand. Finally the tool was deployed in the open drill string that was then closed and the tools were lowered on the wireline while pumping and rotating.

When the tools were recovered to the rig floor, they were placed into the ice-water-filled shuck in the moon pool for 30 minutes, similar to the recovery of the PCS. Once removed from the ice shuck, both the FPC and the HRC followed a reverse procedure back to the trestles on the pipe-racker, including replacing the strongbacks. Autoclaves were removed from the tools in a timely manner (less than 15 minutes) and placed in the HYACINTH cold van. It was at one time thought that additional ice baths might be necessary to re-chill the autoclaves at this point; however, temperature data from the autoclave data loggers proved this to be unnecessary.

HYACINTH Core Transfer

Between Leg 204 and Expedition 311, the HYACINTH transfer and analysis systems were redesigned and integrated to fit inside a 20-foot refrigerated container and procedures differ significantly from those described in Tréhu, Bohrmann, Rack, Torres, et al. (2003). To remove the core from the pressure corer autoclave, the autoclave was connected to the manipulator/shear transfer chamber (STC) with quick-clamps and then pressure balanced with the autoclave before opening the ball valves. The "technical" end of the pressure core, containing the piston and other components, was captured by a catcher on the end of the manipulator, and the full core was withdrawn from the autoclave into the shear transfer chamber, the ball valves closed, and the autoclave removed from the system.

The manipulator/STC, now containing the core at full in situ pressure, was attached to the MSCL-P (see "MSCL-P measurements on HYACINTH cores"), pressures were balanced, and ball valves opened. The core was pushed and pulled through the sensors

using the manipulator under computer control. Once the analyses were completed, the core was withdrawn to the cutting position and the "geological" portion of the core was cut free from the "technical" portion of the core with the shear blades. A storage chamber was then attached to the manipulator/STC and pressures balanced. The "geological" portion of the core was pushed into this storage chamber for storage at in situ pressure and temperature-controlled conditions (5°-7°C) for shorebased analyses.

At the first two sites (Sites U1329 and U1328) scientists used seawater as the pressurizing medium, as had been done previously, but at the remaining three sites they used fresh water, which is much less corrosive for long-term storage. The fresh water pressurizing fluid was spiked with fluorescein (1-10 mg/ liter) and samples of pressurizing fluid were taken when each pressure core was stored so that shorebased investigators might monitor any infiltration of the pressurizing fluid into the core.

Pressure and Temperature Control

To study the properties of gas-hydrate-bearing sediments from sediment cores, an ideal core would retain the in situ effective pressures, the hydrostatic pressure, and the temperature. It is currently only practical to retain the hydrostatic pressure in a coring tool; however, some degree of temperature control is also necessary if gas hydrate is to be kept within the GHSZ during the recovery, handling, and analysis of a pressure core. On previous pressure coring expeditions, and especially the most recent (Leg 204), temperature control was poor. On Expedition 311 scientists aimed to improve the temperature control of the complete process from the seafloor through to the final analysis of the cores, both on board ship or on shore. These new procedures significantly improved the ease in which scientists handled the pressure cores and resulted in more consistent, interpretable data.

Pressure Control in Pressure Corers

Pressure cores rarely (if ever) arrive in the laboratory with the in situ pressure (Dickens et al, 2003; Tréhu, Bohrmann, Rack, Torres, et al., 2003). The recovery pressure is generally below the in situ pressure, but occasionally the recovery pressure has been higher when there are gas hydrates present. The main causes of pressure loss are (1) seals that do not close immediately (or at all, which results in zero pressure), (2) differential volume changes of the tool and its contents caused by changes in temperature, and (3) volume changes in the tool caused by changes in the differential pressure that occurs during recovery. Volume changes from differential pressure occur mainly from the initial compression of compliant components ("O" rings, etc.) as the tool seals, though a small component is caused by the volume expansion of the tool itself as the pressure on the outside falls with respect to the inside pressure.

Even cores recovered at substantially below in situ pressure and those that have been outside the GHSZ for a significant period of time are still of value if the corer sealed soon after coring, capturing all the core constituents—especially the methane, in whatever phase

it exists. If pressure losses can be attributed mainly to tool volume changes due to pressure and temperature, although the methane may have changed phase during the retrieval process, the total quantity of methane will remain unchanged and the in situ phases can be calculated. However, cores that have been outside gas hydrate stability cannot be used to investigate the nature and distribution of gas hydrate in the core with confidence using the nondestructive techniques (P-wave velocities, gamma density, X-ray imaging) available. The difficulty arises in recognizing the difference between pressure losses due to late sealing of a pressure-coring tool versus losses due to pressure and temperature. Thus, the operation of the tools, somewhat surprisingly, has become an area of ongoing investigation.

To minimize the reduction in pressure caused by differential expansion from temperature and pressure effects, the HRC and FPC systems contain a gas accumulator that is normally set at around 80-90% of the anticipated in situ pressure. This allows the tool to expand slightly without any significant change in pressure, keeping the pressure high and minimizing the chances of the core moving out of the gas hydrate stability zone.

Improvement of Temperature Control

None of the pressure coring tools have any active temperature control and hence the best that can be achieved is to minimize or reverse any adverse rises in temperature during the complete coring and handling processes. To achieve this, scientists recovered the core to the rig floor on the wireline “as fast as practically possible” – normally at a speed of 100 m/min, but up to 250 m/min. After breaking the corer out of the pipe, it was quickly inserted through a rat hole in the rig floor into a newly designed, vertical, insulated ice-water-filled shuck that was suspended in the moonpool. This ice shuck is deep enough to quickly cool the autoclave containing the core at the bottom of the tools and was filled via a chute from the ice machine located below the drill floor in the sub-sea shack. After examining the temperature records for the first few pressure corer deployments, a 30-minute ice soak before tool removal and breakdown was deemed optimal. During this chilling period, the next rig floor operation/tool deployment was performed and hence the cooling time had little or no impact on drilling activities. The autoclave temperature was 0 to 3°C after chilling, and the thermal mass of the tool allowed it to stand at ambient temperature during the 10-20 minute autoclave removal without a large change in temperature. The autoclave was then immediately delivered to the refrigerated HYACINTH logging container van. With this procedure scientists maximized the chances of keeping the core within the GHSZ during its journey from the seafloor to the laboratory.

A major change from previous expeditions was the inclusion of dedicated cold vans for analysis of pressurized cores. During Leg 204, the degassing of the PCS cores took place in iced cylinders in the “Hard Rock Lab,” next to the thin section laboratory, while the transfer of HYACINTH cores took place on the walkway above the catwalk with ice bags being used (rather unsatisfactorily) for cooling. The degassing and logging of the HYACINTH cores took place in very warm conditions in the scientific hold, with

frequent interruptions—despite insulating foam around the pressure chamber—to take the core back into the adjacent reefers in an effort to prevent rapid dissociation of the gas hydrate. During Expedition 311, all of these operations took place in temperature-controlled (5-7°C) 20-foot containers. A refrigerated van (the PCS degassing van), placed on top of the lab stack, was used for the depressurization experiments on the PCS cores (including the MSCL-V density logs). Another refrigerated van (the HYACINTH logging van) was located over the core tech shop and used for transferring and logging the HYACINTH cores in the MSCL-P, as well as for X-raying the PCS cores before and after depressurization.

Non-destructive Measurements on Pressure Cores

Although pressure cores are particularly valuable for providing accurate methane volumes for gas hydrate concentration calculations, nondestructive measurements made before or during the depressurization process can provide additional information on the nature and distribution of gas hydrate within the sediment and rare data on near-in-situ physical properties of gas-hydrate-bearing sediments.

X-ray images of the pressure cores show the overall structure of the core and gas hydrate within them (as well as contributing to the core length estimate), gamma ray attenuation provides accurate densities of sediment/gas hydrate structures, and measurement of P-wave velocity on undisturbed gas-hydrate-bearing core at in situ pressure provides acoustic parameters valuable for analysis of seismic data. Two measurement systems were used during IODP Expedition 311 to collect data on pressure cores: the Geotek Pressure Multi-sensor Core Logger (MSCL-P), mainly used for the HYACINTH cores; and the Geotek Vertical Multi-sensor Core Logger (MSCL-V), used with the PCS cores.

Measurements on PCS cores

Expedition 311 was the first time that non-destructive measurements were attempted on the PCS cores while still in the autoclave under pressure. The aluminum core barrels (specially fabricated for this expedition) allowed X-ray analysis of the PCS cores. Being able to “see” the core prior to degassing enabled the original length (and hence volume) of the core to be measured, which is critical in the calculation of gas hydrate content. The density measurements taken during degassing using the MSCL-V provided information similar to that collected on HYACINTH cores during Leg 204, where low-density, potential-hydrate-bearing layers could be monitored as the core was depressurized to observe hydrate dissociation and gas evolution.

The PCS autoclave was brought to the HYACINTH logging van for X-ray scanning after it was removed from the tool body. The top of the autoclave was mated to the end of an unpressurized HYACINTH manipulator, allowing the MSCL-P software and manipulator to push the PCS autoclave through the X-ray imaging system. As the PCS was moved past the image intensifier, the character of the S-distortion changed, possibly due to the moving steel interacting with the magnetic fields in the image intensifier. An X-ray

montage from 0 to 51 cm relative to the top of the PCS inner barrel was created (normally in 0.5 cm increments) for each PCS core. The lower half of the barrel was completely obscured by a steel sleeve.

Once the PCS autoclaves were moved to the PCS degassing van atop the lab stack, they were placed in the MSCL-V (Tréhu, Bohrmann, Rack, Torres, et al., 2003). The MSCL-V accommodates cores vertically and the sensor cluster moves up and down along the stationary core. The gamma ray source and detectors are the same as used on the MSCL-P and IODP MST, and calibration was performed in a similar fashion. The gamma attenuation of an aluminum calibration sample of varying, known thickness was measured within a water-filled PCS autoclave to provide the density calibration. The PCS autoclaves were always oriented the same way in the MSCL-V, with the transducer port facing forward, and gamma attenuation for the PCS autoclaves, filled with water, was measured so that the data could be corrected as a function of vertical position.

The densities measured on core in the upper half of the PCS autoclave had an estimated error of $\pm 0.05 \text{ g/cm}^3$, but because the lower half of the autoclave outer barrel contains a spring and other steel sleeves, the density could not be determined as accurately. There was also an unexplained interaction between the PCS and the gamma attenuation sensor between 30-50 centimeters core depth, causing a lowering of count rate in this area that varied over time. However, the primary use of the tool was to look at density differences that occurred during degassing and hence most of the data was simply plotted as differential density (the initial density profile subtracted from each of the subsequent profiles) to observe the evolution and migration of gas within the core barrel during depressurization.

MSCL-P measurements on HYACINTH cores

The MSCL-P is an automated measurement system for the collection of acoustic P-wave velocity, gamma ray attenuation, and X-ray image data on HYACINTH pressure cores under pressures up to 25 MPa. The MSCL-P pressure chamber is constructed of aluminum and contains an internal set of ultrasonic transducers. X-ray and gamma ray sources and detectors are situated outside of the pressure chamber. The system moves pressurized HYACINTH cores incrementally past these sensors under computer control with a positional precision of better than one millimeter, allowing detailed gamma density and acoustic velocity profiles to be obtained rapidly and automatically along the core as well as creating automated full-core X-ray montages. The manipulator mechanism ensures that the core does not rotate during the linear translation.

Core logging under pressure using the MSCL-P is in principle very similar to core logging with the IODP MST or a standard Geotek Multi-sensor Core Logger (MSCL). One exception is the increased distance and varied material between the sensors and the core. Sensors are separated from the core by the plastic liner, the pressurizing fluid (seawater), and, in the case of the gamma and X-ray sensors, the aluminum pressure chamber. To calibrate for measurements of acoustic velocity and gamma density, similar

techniques are used to those developed for the MST and MSCL, which use distilled water and aluminum as standards. During logging of pressure cores, the inner liner is assumed to have a constant diameter because it cannot be directly measured under pressure.

Gamma density was measured using a ^{137}Cs source and NaI detector very similar to those used on the MST. Errors are proportional to the square root of the total counts (generally around 5000 cps), giving a density precision of 2%. Calibration of the gamma density measurement was performed by measuring the intensity of the gamma beam through a stepped aluminum bar of varying thickness sitting centrally in a core liner filled and surrounded with salt water of known salinity. This calibration procedure, using aluminum and water, provides a good approximation for a water-saturated sediment (minerals and water) and has proven to be an excellent calibration protocol for determining density from the attenuation of gamma rays. Separate calibrations were performed for FPC and HRC liners and no effect was seen with increasing pressure.

Ultrasonic P-wave velocity (VP) was measured using two 500 kHz acoustic transducers mounted inside the pressure chamber, perpendicular to the core and the gamma ray beam. Travel times were measured with a precision of 50 ns, and the error associated with the velocity was +/- 3 m/sec assuming a core thickness of around 6 cm. To calibrate VP, the total P-wave travel time was measured when both the core liner and the pressure chamber were filled with water of known velocity (from temperature, pressure and salinity). Changes in travel time as a function of pressure were also measured (up to 25 MPa). The measured variation in VP with pressure was close to the theoretical variation for water, and therefore the travel times in the liner material were essentially constant with changing pressure (as was found on ODP Leg 204; Tréhu, Bohrmann, Rack, Torres, et al., 2003).

X-ray images were obtained using a linear X-ray device consisting of a lead-shielded microfocal X-ray source and phosphor image intensifier. An aluminum compensator was used to minimize the intensity variations, which are caused when illuminating round objects. With the geometrical arrangement used and with a typical X-ray spot size used of around 8-12 μm [micrometers], the intrinsic spatial resolution of the images is about 150 μm . All final core images were obtained by creating montages from a series of area images taken along the core. The normal spatial interval used for the final image was 0.5 cm, which creates a relatively flat image along the core without any apparent significant spherical distortion. However, an unexpected electromagnetic distortion in the image intensifier limited our ability to create perfectly smoothed montages. The X-ray images were not density calibrated because the gamma attenuation measurements give higher accuracy than the polychromatic X-rays. Instead, we varied the X-ray energy and power levels to maximize the qualitative resolution of the image in an effort to examine subtle structures within the core. X-ray energies up to 110 kV were used depending on the density of the cores being measured.

Degassing Experiments

During IODP Expedition 311, we used the PCS to retrieve pressurized sediments for onboard degassing experiments. Controlled release of pressure from the PCS through a manifold permits (a) collecting all gas discharged from the sediment's free gas and gas hydrate phase for quantitative and qualitative analysis, (b) estimating the in situ abundance of gas hydrate and free gas based on mass balance, methane solubility and gas hydrate stability considerations (Dickens et al. 1997), (c) identifying the presence of gas hydrate from volume-pressure-time relations (Hunt 1997, Dickens et al. 2000, Milkov et al. 2004), and (d) monitoring the controlled decomposition of gas hydrate with non-destructive methods in the course of the degassing experiment.

Prior to Expedition 311, the PCS was successfully used to study in situ gases in gas-rich and gas hydrate-bearing sediments during ODP Legs 164 on the Blake Ridge (Paull, Matsumoto, Wallace, et al., 1996; Dickens et al., 1997), 201 on the Peru margin (Dickens et al., 2003), and 204 on Hydrate Ridge (Tréhu, Bohrmann, Rack, Torres, et al., 2003; Milkov et al., 2004). In the course of these ODP legs degassing technology had been improved continuously and further modifications were made for Expedition 311 to optimize the control and monitoring of the PCS degassing experiments. Most importantly, the steel outer and inner barrels of the PCS were replaced with aluminum barrels with a maximum working pressure of 250 bar so that recovered sediment could be investigated by the MSCL-P X-ray system before and after depressurization (see below).

During the degassing experiment scientists used a one-dimensional vertical gamma ray density scanner to evaluate the distribution of sediment, gas hydrate, and gas voids in the recovered PCS core and to monitor changes in the course of the degassing experiment. In addition, the manifold was equipped with a water trap (i.e., an additional valve for the collection and analysis of fluids that might be extruded from the PCS in the course of the degassing experiment). Furthermore, a backpressure valve was added and allowed to degas the PCS continuously at a manually controlled pressure. Finally, all physical investigations and degassing experiments were carried out in temperature-controlled laboratories at 7°C. Ideally, the ambient temperature would equal the in situ temperature of the recovered sediment. However, because scientists simultaneously investigated several PCS cores from different sediment depths and because they needed to counteract the incomplete recovery of pressure during core recovery, they kept the laboratories constantly at the expected minimal in situ temperature of 7°C.

After the PCS was retrieved on the wireline, chilled in the ice shuck, and X-rayed to determine the core length, the corer autoclave was moved into the PCS lab. In the PCS Lab, some time was allowed for the PCS to equilibrate to ambient temperature (7°C) and a vertical gamma ray scan was run to determine the initial density distribution within the PCS core. The PCS was connected to a pressure transducer, to a helium-flushed degassing manifold for controlled release of pressure, and via the manifold to a bubbling chamber that allows collection of released gas. Scientists used a liquid leak detector to

check the connection between the PCS and the manifold for leakages. Thereafter, they carefully released and collected a small volume of gas that was usually extruded together with some water from the outer core barrel (~200 mL) to flush the lines connecting the PCS to the manifold. All water that escaped from the PCS was collected in a water trap attached to the manifold, quantified and subsampled for geochemical analysis. In the following steps, gas was released, collected, and subsampled from the bubbling chamber for quantitative and qualitative analysis as outlined in the degassing protocols below. During the degassing procedure, scientists ran additional gamma ray scans of the PCS to monitor the evolution of gas voids and pathways. Degassing experiments were terminated when (a) the pressure within the PCS had equilibrated to atmospheric pressure and (b) less than 5 mL of gas had exsolved from the core within three hours.

When the pressure inside the PCS equaled ambient air pressure, scientists collected a final gas sample and ran a final gamma ray scan. The degassed core was removed from the outer core barrel, X-rayed, extruded, and sampled for interstitial water chemistry, dissolved gases and physical properties, including parameters critical for calculating methane concentration.

During Expedition 311 degassing was carried out either in incremental steps or continuously. When degassing in incremental steps, the manifold is first closed with respect to the bubbling chamber and then opened with respect to the PCS. In this manner, a constant volume of gas is allowed to move into the manifold. The pressure inside the manifold is not constant throughout the experiment but equilibrates with the residual pressure of the PCS core. Next, the valve between manifold and PCS is closed and the gas inside the manifold is released into the bubbling chamber where its volume expands due to the pressure release. When degassing continuously, the backpressure valve is set to a pre-defined backpressure and subsequently the valves between manifold and bubbling chamber and manifold and PCS are both opened, thus allowing a constant flux of gas into the bubbling chamber. In the continuous degassing mode, valves are only closed for either specific scientific reasons (e.g. to examine the increase of pressure due to gas hydrate composition), or for operational reasons (e.g. when the bubbling chamber is subsampled or when a gamma density scan is carried out). In general, scientists degassed in incremental steps when the pressure inside the PCS was high and continuously when the pressure was lower than 0.4 MPa.

PCS cores that had strong indications for the presence of gas hydrates were degassed in the following way. During an initial phase, gas and any water that was expelled from the outer core barrel were released in small incremental steps. At this stage degassing caused immediate pressure drops inside the PCS. Once pressure had reached equilibrium conditions for gas hydrate stability, further release of gas caused only relatively small decreases in pressure. The reason for this behavior is twofold: (1) gas hydrate dissociation releases free gas, which, in a closed container, increases pressure until dissociation ceases, and (2) gas hydrate dissociation releases fresh water, which increases the stability of gas hydrate at given pressure and temperature conditions (Dickens et al., 2000). During the gas hydrate dissociation phase, depressurization was repeatedly

stopped to sample the gas phase, to monitor the pressure response, and to carry out gamma ray density scans. Once pressure had dropped below equilibrium conditions for gas hydrate stability, scientists monitored carefully whether further incremental release of gas was followed by pressure increases due to gas hydrate dissociation. When pressure decreases indicated the absence of gas hydrate, depressurization was carried on continuously.

During each degassing experiment, the internal PCS pressure was monitored by analog pressure gauges and recorded by digital pressured transducers recorded on a personal computer. However, due to technical problems, digital pressure records are not available for all degassing experiments conducted during Expedition 311. The released gas was collected in a 1-L bubbling chamber consisting of an inverted graduated cylinder and a plexiglass tube filled with a saturated NaCl solution.

The released gas volume was recorded as a function of PCS opening number and pressure. After measuring the volume of collected gas, gas aliquots were sampled from a valve at the top of the cylinder using a syringe. One aliquot (6 mL) was taken for immediate analysis of the gas composition (C1, C2, CO₂, N₂, O₂) using an Agilent 3000A MicroGC gas chromatograph equipped with Plot U and molecular sieve columns and a thermal conductivity detector that was located in the PCS lab. Another aliquot (10 mL) was taken for further shipboard analysis (e.g., low concentrations of C₂ and higher hydrocarbon gases) and for shorebased isotopic analysis. These samples were stored in saturated NaCl solution containing headspace vial that were closely sealed with stoppers and crimp capped.

Aside from released gas volume and pressure response inside the PCS, further parameters were documented that are crucial for accurate mass balance calculations and interpretation of the degassing experiments, namely:

- (1) To calculate the quantity of released methane via ideal gas law, ambient air pressure and air temperature in the PCS Lab were continuously recorded throughout the experiment;
- (2) When pressure is released from the PCS, free gas can evolve in such a way that it forces water out of the core. The total volume of expelled water corresponds to a volume of gas left inside the PCS at the end of depressurization. Expedition 311 scientists accounted for the gas remaining in the PCS by recording the volume of expelled water and assigning the composition of the final gas sample;
- (3) After degassing was finished, scientists collected the water remaining in the outer core barrel to account for an additional headspace that might have been present in the PCS; and,
- (4) To account for the total pore water volume, the accurate length of the recovered sediment interval was obtained by an initial density scan and the porosity of the sediment was analyzed from solid phase samples taken at the end of the experiment.

Degassing experiments at Site U1329 were the first ones performed during IODP Expedition 311. They revealed that an initial gas volume of 500 mL needed to be released before all helium is removed from the hoses that connect the PCS port to the bubbling chamber. The hoses and manifold hold a dead volume of 261 mL. Methane that was released within the initial gas volume was included when calculating the total amount of methane released from the core. However, the methane concentration of the helium diluted initial gas volume was excluded when the average composition of the released gas phase was determined.

RESULTS AND DISCUSSION

IODP EXPEDITION 311

The main objectives of pressure coring during IODP Expedition 311 were to quantify natural gas composition and concentration in sediments and to determine the nature and distribution of gas hydrate and free gas within the sediment matrix. To achieve these objectives, the IODP Expedition 311 scientists: (a) measured the quantity and composition of gases released during controlled degassing experiments, (b) conducted nondestructive measurements (X-ray imaging, P-wave velocity, gamma density) at in situ pressures and during depressurization, and (c) archived hydrate-bearing sediments at in situ pressures for more comprehensive investigations on shore. The nondestructive measurements not only provide a direct indication of the existence of gas hydrate, but the resulting data (acoustic impedance) can be used to help interpret regional seismic data.

IODP Expedition 311 had the most ambitious pressure coring and onboard pressure core analysis program ever attempted in the history of ocean drilling. Pressure cores retrieved at in situ pressures were used to determine methane hydrate quantity, using degassing techniques and mass balance calculations, and methane hydrate distribution using non-destructive measurement of the physical properties of the cores at in situ pressures. Large improvements in temperature control over previous expeditions (e.g., ODP Leg 204) made the recovery and analysis of pressure cores more practical.

Pressure cores were collected using the IODP Pressure Core Sampler (PCS) and HYACINTH Fugro Percussion Corer (FPC) and HYACE Rotary Corer (HRC) pressure corers. After a pressure core was retrieved, initial non-destructive measurements were made to characterize the core, determine the core length and identify massive gas hydrate. PCS cores were then degassed on board ship to determine total methane composition and concentration in sediments. The HYACINTH cores were degassed on shore, immediately following Expedition 311, after X-ray imaging and subsampling under pressure. All cores had non-destructive measurements made on them while undergoing degassing to document gas evolution, gas hydrate dissociation, or other changes in the core: PCS cores were routinely scanned for gamma density, whereas HYACINTH cores were scanned for gamma density and X-ray imaged. Following degassing, all pressure cores were X-rayed a final time and the released gas volume, the X-rays, and the density scans were used to guide sub-sampling for interstitial water, physical properties, and other related analyses.

IODP Site U1325

The BSR at Site U1325, drilled in the first slope basin, is a relatively weak reflector with an estimated depth of 230 (+/- 5) mbsf. LWD data from Hole U1325A showed alternating high and low resistivities from 122-260 mbsf that are especially well defined from 190-220 mbsf. Specific objectives at Site U1325 were to confirm and quantify the

presence of gas hydrate above the BSR, with special attention to the layers of alternating resistivities, and free gas below the BSR.

Operation of Pressure Coring Systems

Pressure coring tools were deployed seven times at Site U1325 (Table U1325-I-1). Two PCS cores, two HRC cores and one FPC core were taken in Hole U1325B, including two cores within the layer of alternating high and low resistivities from 190-220 mbsf. In Hole U1325C, an FPC core was deployed within the alternating resistivity layer and a PCS core well below the estimated depth of the BSR. The expedition scientists recorded the pressure history of the cores during deployment, coring, recovery, and chilling (in the ice shuck) of the pressure coring tools. Only the pressure cores from Hole U1325C were retrieved under pressure, and only the last one (Core 311-U1325C-10P) contained a core under pressure.

Pressure coring was extremely difficult at Site U1325. The PCS became stuck in the BHA during the deployment that recovered Core 311-U1325B-28P because the PCS outer barrel had deformed, possibly due to loss of circulation, and a pipe trip was required to free the tool. The HRC deployments both failed due to incomplete penetration that resulted in collapsed/deformed liners that prevented the lower flapper valve from operating correctly. The FPC deployment that returned an autoclave under near in-situ pressure had an inverted core catcher, which indicted that the stiffness of the sediments was very high and probably exceeded the capabilities of this tool. These problems resulted from attempting pressure cores in sandy lithologies in which even the XCB system had trouble recovering any core.

Degassing Experiments

At Site U1325, only the deepest PCS (Core 311-U1325C-10P) was recovered successfully under pressure and investigated by a controlled shipboard degassing experiment. This core was taken at a depth of 256.6 mbsf, which is ~25 m deeper than the estimated depth of the BSR.

The degassing experiment included the following steps. First, the volume and density of sediment inside the inner core barrel of the PCS was monitored by X-ray analysis. Subsequently, the PCS was slowly degassed in a temperature-controlled laboratory (7°C) and the volume and composition of released gas and water, the pressure inside the core, the ambient air pressure and temperature were monitored. During the degassing procedure, the vertical density distribution of the PCS cores was repeatedly determined by gamma attenuation scans to examine the evolution of gas voids within the sediment. After degassing was completed, scientists X-rayed the PCS core again, collected the water remaining in the outer core barrel for mass balance considerations, and subsampled the sediment that was extruded from the cores for interstitial water chemistry, dissolved gases and physical properties.

The degassing of Core 311-U1325C-10P yielded 2.9 liters of gas. The composition of the released gas did not change significantly in the course of degassing. Methane was the major component accounting on average for $89 \pm 3\%$ of the emitted gas. Nitrogen was the second most abundant gas contributing $8.6 \pm 3\%$ to the gas released. Carbon dioxide, ethane and higher hydrocarbon concentrations were below the detection limit of the Agilent gas chromatograph used for continuous gas analysis during the degassing experiment. The pressure inside the PCS core dropped below the predicted gas hydrate stability conditions when the port valve of the PCS was first opened and water expanded from the outer core barrel into the manifold system. Therefore no pressure plateaus or rebounds from dissociation of gas hydrate could be expected and a steady decrease of core pressure versus removed gas volume was observed for Core 311-U1325C-10P.

X-ray images and density profiles showed limited gas evolution during depressurization. A low-density zone from 5-15 cm core depth seen in the pre-depressurization X-ray remained in the post-depressurization X-ray and was probably an area of disturbed core.

IODP Site U1325 Summary

Site U1325 (Prospectus Site CAS-02C) is located near the southwestern end of the margin perpendicular transect established during Expedition 311 and is within a major slope basin that developed eastward of the deformation front behind a steep ridge of accreted sediments. Bathymetry data show that the seafloor in the western part of this slope basin is relatively flat with water depths around 2200 m. Around Site U1325 the seafloor becomes gradually shallower before it rises rapidly to the east to form the plateau of the second main accreted ridge at water depths around 1200 m, on which Sites U1327 and 889 are located. A bottom-simulating reflector (BSR) is clearly visible in the eastern part of the slope basin, but it fades to the west (CDP 1180 – 1280 along MCS line 89-08). The BSR also shows the typical frequency dependent reflection strength pattern as observed at all other sites. At Site U1325 the BSR is less strong than at the core of a buried ridge of accreted sediments, which is located about 700 m west of this Site. The primary research objectives for this site are linked to the transect-concept of this expedition. The objectives include (a) studying the distribution of gas hydrates, (b) defining the nature of the BSR, (c) developing baseline geochemical and microbiological profiles, and (d) obtaining data needed to ground-truth remotely acquired imaging techniques such as seismic or controlled-source EM. The slope basin is expected to show a different geochemical regime and related geophysical properties than the uplifted ridges of accreted sediments.

Four holes were occupied at Site U1325. Hole U1325A was dedicated for the LWD/MWD program to a total depth of 300 mbsf. Hole U1325B was spudded with the APC system but problems arose due to thick sand accumulation causing a switch to XCB core barrel for one core section and a switch back to APC. The hole was then advanced by combination of APC, XCB, and pressure coring to a depth of 206.5 mbsf. Interspersed with the XCB cores was a DVTP run at 140.5 mbsf, which yielded high quality temperature data. Five pressure cores were deployed in Hole U1325B but all attempts

failed to retrieve sediments under pressure. The last run with a PCS resulted in a stuck tool, which led to the abandonment of the hole. Hole U1325C was drilled to a depth of 188 mbsf where core recovery in Hole U1325B began to deteriorate. Coring operations resumed with the XCB system, interspersed with two pressure coring runs (one failed FPC run, one successful run with the PCS) and two DVTP deployments, deepening the hole to a TD of 304.3 mbsf.

Pressure coring tools were deployed seven times at Site U1325, including two PCS cores, two HRC cores and one FPC core in Hole U1325B. Hole U1325C included one FPC core from above the projected depth of the BSR and a PCS core from well below the estimated depth of the BSR. Pressure coring proved to be extremely difficult at Site U1325, with only the deepest PCS (Core 311-U1325C-10P, 256.5 mbsf) recovered successfully under pressure, which was investigated by a controlled shipboard degassing experiment. All other attempts to deploy pressure cores failed for various reasons, partially due to difficult lithologic conditions (the presence of unconsolidated fine sand) and the potential effect of adverse ship heave conditions. The degassing of Core 311-U1325C-10P yielded 2.07 liters of methane gas and may have contained small amounts of gas hydrates (0.4%) or free gas (0.3%) depending where the base of gas hydrate stability (BGHS) is situated (see uncertainty in temperature-derived BGHS above).

Infrared (IR) imaging of the recovered APC/XCB cores was routinely carried out on the catwalk to detect and characterize the nature of gas hydrates in the cores. A large number of IR imaged cold spots were detected in the cores from Holes U1325B and U1325C and were partially subsampled for focused interstitial water analyses and microbiology studies. In many cases the IR imaged cold temperature anomalies correlated with layers of high resistivity and low interstitial water salinities and chloride concentrations, which have been shown to be associated with the occurrence of gas hydrate.

IODP Site U1326

Site U1326, situated on the first uplifted ridge, had a strong BSR. The LWD/MWD data from Hole U1326A displayed the highest resistivity values seen on IODP Expedition 311, with gas hydrate saturations calculated from Archie's relationship as high as 60%. There were also high resistivities below the estimated depth of the BSR, potentially indicating free gas. Specific objectives at Site U1326 were to confirm and quantify the presence of gas hydrate above the BSR, targeting the very high resistivity layer near 90 mbsf, and free gas below the BSR.

Operation of Pressure Coring Systems

Pressure coring tools were deployed only three times at Site U1326 (Table U1326-I-1): one FPC (311-U1326C-11Y), one PCS (311-U1326C-12P), and one HRC (311-U1326C-13E). The pressure coring tools were all deployed in succession in a narrow interval between 82.7 mbsf and 86.7 mbsf where the LWD data had shown very high resistivity

values. Shipboard scientists recorded the pressure history of the cores during deployment, coring, recovery, and chilling (in the ice shuck).

The FPC deployment that recovered Core 311-U1326C-11Y was unexceptional until the sandline tension when lifting the bit from the BHA exceeded the expected load by 2 tons. It was later concluded that a significant amount of sand had entered the BHA and had hindered the recovery. Scouring of the outer barrel of the FPC also indicated clean sand had been penetrated. The autoclave was retrieved under nearly full pressure (17.5 MPa, compared with an in situ pressure of 19.2 MPa). X-ray images showed that this core was very short (15 cm) and situated in the center of the core barrel, implying that the core below it had washed out of the core liner. The liner and recovered portion of Core 311-U1326C-11Y was transferred from the autoclave, analyzed in the MSCL-P, and transferred to a storage chamber for further shorebased studies.

The PCS deployment (Core 311-U1326C-12P) recovered a partial core at 3.0 MPa. While the core was in the X-ray system, scientists observed a gas bubble trapped in the inner core barrel. After degassing was completed, the short core was extruded and some very coarse sand and rocky material was found in the outer barrel.

The final pressure core deployment with the HRC (Core 311-U1326C-13E) ended Hole U1326C by losing the lower part of the autoclave and bit assembly. Two pipe joints had become unscrewed during coring. Fine sand found near the top of the tool, 11 m above the bottom, lead scientists to conclude that sand and fluid must have flowed back up the BHA and into the tool during the deployment, jamming the corer in a way that allowed the left hand threads to come unscrewed.

Degassing Experiments

At Site U1326, only one PCS (Core 311-U1326C-12P) was recovered successfully under pressure and investigated by controlled shipboard degassing experiments. This core was taken at a depth of 84.2 mbsf.

The degassing experiment included the following steps. First, the volume and density of sediment inside the inner core barrel of the PCS was monitored by X-ray analysis. Subsequently, the PCS was slowly degassed in a temperature-controlled laboratory (7°C) and the volume and composition of released gas and water, the pressure inside the core, the ambient air pressure and temperature were monitored. During the degassing procedure, the vertical density distribution of the PCS cores was repeatedly determined by gamma attenuation scans to examine the evolution of gas voids within the sediment. After degassing was completed, scientists X-rayed the PCS core again, collected the water remaining in the outer core barrel for mass balance considerations, and subsampled the sediment that was extruded from the cores for interstitial water chemistry, dissolved gases and physical properties.

The degassing of Core 311-U1326C-12P yielded 21.0 liters of gas. The composition of the released gas did not change significantly in the course of degassing. Methane was the major component accounting on average for $89 \pm 2\%$ of the emitted gas. Nitrogen was the second most abundant gas contributing $6.1 \pm 3\%$ to the gas released. Carbon dioxide, ethane and higher hydrocarbon concentrations were below the detection limit of the Agilent gas chromatograph used for continuous gas analysis during the degassing experiment.

For Core 311-U1326C-12P recovery was particularly low; recovery is estimated at 40 cm from the gamma density profiles, though only 26 cm of sediment was extruded from the 1 m long PCS core. The pressure inside the PCS core dropped below the predicted gas hydrate stability conditions when the port valve of the PCS was first opened and water expanded from the outer core barrel into the manifold system. Therefore no pressure plateaus or rebounds from dissociation of gas hydrate could be expected and a steady decrease of core pressure versus removed gas volume was observed for Core 311-U1326C-12P. The X-ray image taken before the core was degassed showed 28 cm of sediment at the top of the barrel, along with a gas bubble in the inner core barrel below this sediment. The water below this sediment core also appeared to contain some suspended sediment.

Measurements on HYACINTH cores

Simultaneous and automated gamma density, P-wave velocity and X-ray measurements were made in the MSCL-P system on Core 311-U1326C-11Y. All measurements took place at 18 MPa (near recovery pressure; 95% of in situ pressure). The velocity and density profiles and the X-ray image for Core 311-U1326C-11Y indicate that there may be some gas hydrate in this short sample, especially when compared to other pressure cores retrieved during Expedition 311.

Gas Hydrate Concentration, Nature, and Distribution from Pressure Coring

Core 311-U1326C-12P was recovered from a depth of 83.7 mbsf. The gas hydrate content of Core 311-U1326C-12P is estimated at 40%, placing it in the gas hydrate stability zone, independent of the choice of thermal gradient. This pressure core was targeted at a zone of extremely high resistivity found in the LWD data from Hole U1326A, and we can confirm that this high-resistivity zone contains gas hydrate.

Infrared images and visual observations in the porewater chemistry laboratory showed that at Site U1326, most of the gas hydrate was associated with sandy layers. Core 311-U1326C-12Y contained some extremely coarse sands and possible concretions, but because this core was recovered outside of the gas hydrate stability zone, there was no evidence of layered gas hydrate structure.

IODP Site U1326 Summary

Site U1326 (Prospectus Site CAS-03C) is located on an uplifted ridge of accreted sediments at the southwest end of the multi-site transect established during Expedition 311. Recently acquired bathymetry data reveals a collapse structure near the originally proposed primary site CAS-03B. We decided to switch the former alternate location CAS-03C to the primary site to avoid coring directly into the slump feature, which may have complicated the recent geologic history of this site.

The objectives of coring and logging this site are tied to completing the transect of scientific research holes across the Northern Cascadia Margin near Vancouver Island. Site U1326 is the closest location to the deformation front and it probably represents the tectonically youngest occurrence of gas hydrate on the Northern Cascadia Margin, as such our primary research objectives include (a) studying the distribution of gas hydrates, (b) defining the nature of the BSR, (c) developing baseline geochemical and microbiological profiles, and (d) obtaining data needed to ground-truth remotely acquired imaging techniques such as seismic.

Hole U1326B was spudded 15 m NE of Hole U1326A at 12:05 hr on 23 October, but the first core failed to establish the depth of the mud line and it was decided to start a new hole. Without offsetting from the location of Hole U1326B, Hole U1326C was spudded at 12:45 hr on 23 October. The first core established a seafloor depth of 1828.0 mbsl (1839.6 mbrf). On the fourth APC core (~30 mbsf), we unexpectedly hit APC refusal and switched to XCB coring. Hole U1326C was advanced by XCB coring to a depth of 82.7 mbsf, which was followed by three consecutive pressure core deployments within a high electrical resistivity zone identified on LWD/MWD downhole logs. In this case, the FPC and HRC pressure core runs were added to the traditional continuous core hole to increase the total number of pressure core runs at this site.

The FPC was the first pressure core system deployed at this site, it recovered a partial core (15 cm) at less than full pressure. The second system to be deployed was the PCS, which recovered a partial core under pressure. The third pressure core system deployed was the HRC, which was “packed off” with a sand and the cutting shoe and the lower part of the autoclave was unscrewed and left behind in the hole, resulting in the termination of Hole U1326C at a total depth of 86.7 mbsf. After tripping the BHA back to the seafloor, the ship was moved 30 m to the southwest (15 m from Hole U1326A). Hole U1326D was spudded at 11:30 hr on October 24 and drilled to a depth of 78.8 mbsf in preparation for continued coring to a target depth of 300 mbsf. Because of problems associated with the heave state and schedule limitations, all pressure coring operations were suspended for the remainder of the hole. XCB coring deepened the hole to 271.4 mbsf, with the forecast of deteriorating weather conditions on the morning of 26 October, it was decided to stop coring and complete the hole by drilling to 300 mbsf. After completing coring and drilling operations, we then decided to conduct a single downhole log run with a non-standard IODP tool string, which included the Scintillation Gamma Ray (SGT) Tool, Phasor Dual Induction (DIT) tool, and the Dipole Sonic Imager (DSI).

At 23:15 hr on 26 October the logging tool was lowered to a logging depth of 298.4 mbsf; two successful logging passes were made with tool string back on deck at 03:45 hr. The drill string was pulled clear of the seafloor at 05:30 hr on 27 October, ending operations in Hole U1326D.

Cold temperature anomalies were observed at a wide range of depths from 70-250 mbsf, and catwalk sampling was conducted based on these scans. Many IW samples were taken based on IR data to extend the chlorinity anomaly database available for calibrating IR data as a proxy for gas hydrate saturation. We note that the maximum depth of observed IR anomalies is deeper than the anticipated BSR depth of 230 mbsf.

At Site U1326, only one PCS core (Core 311-U1326C-12P) was recovered successfully under pressure and investigated by controlled shipboard degassing experiments. This core was taken at a depth of 84.2 mbsf. The degassing of this single PCS core yielded 21.0 liters of gas, which was determined to be equivalent to a pore space gas hydrate saturation of 40%, which is in close agreement with the gas hydrate saturations estimated from the Archie resistivity calculations in the same interval.

IODP Site U1327

Site U1327 was a near-reoccupation (375-600 m) of ODP Site 889, drilled on Leg 146. The gas hydrate occurrence at Site 889 was estimated at 20-30% of pore space in the 100-m-thick interval above the BSR (Westbrook, Carson, Musgrave, et al., 1994). The BSR at Site 889 is a strong reflection event and occurs at 225 mbsf, with evidence of free gas beneath the BSR (Westbrook, Carson, Musgrave, et al., 1994). LWD data from Hole U1327A show a thick, high-resistivity layer at about 125-140 mbsf that was calculated using Archie's relation to be equivalent to gas hydrate occupying 40-70% of the pore space. Specific objectives at Site U1327 were to confirm and quantify the presence of gas hydrate above the BSR, with special attention to the high-resistivity layer, and free gas below the BSR.

Operation of Pressure Coring Systems

Pressure coring tools were deployed fourteen times at Site U1327 (Table U1327-I-1): eight PCS cores (three in Hole U1327C, three in Hole U1327D and two in Hole U1327E), three HRC cores (two in Hole U1327D and one in Hole U1327E) and two FPC cores (both in Hole U1327D). Scientists recorded the pressure history of the cores during deployment, coring, recovery, and chilling (in the ice shuck) of the pressure coring tools. Based on the temperature/pressure records from the data loggers, all successful pressure cores were stabilized in the gas hydrate stability field, though some of the PCS cores made brief (5-10 minute) excursions out of the gas hydrate stability field during the latter portion of core recovery.

The PCS recovered five cores under pressure, one above all target zones (Core 311-U1327E-3P; 80 mbsf), two near the depth of the high-resistivity layer in Hole U1327A

(Cores 311-U1237C-15P and 311-U1237D-10P; 121.8 and 155.1 mbsf, respectively), one between the high-resistivity layer and the BSR (Core 311-U1237C-24P; 197.3 mbsf), and one below the BSR (Core 311-U1237D-17P; 246 mbsf). The recovered pressures as measured by the internal data loggers were approximately half of in situ pressures.

The HRC recovered three cores under pressure, one at the depth of the high-resistivity layer seen in Hole U1327A (Core 311-U1327D-4E; 121.8 mbsf) and two between this layer and the BSR (Cores 311-U1327D-12E and -14E; 170.5 and 217.7 mbsf, respectively). These cores recovered about 80% of full in situ pressure. A broken catcher ring in the “technical” portion of the HRC core prevented the transfer of Core 311-U1237D-4E and it had to be depressurized in the transfer chamber.

The FPC recovered one pressurized core (Core 311-U1327D-13Y). This core became jammed in the transfer system, likely due to the expansion caused by partial depressurization, and was completely depressurized in the transfer chamber. The other FPC deployment at this site, which recovered Core 311-U1327D-6Y, suffered from a core liner implosion and corer over-retraction.

After all the varied analyses were complete the PCS cores were extruded using a hydraulic pump and samples for interstitial water analysis were taken. HRC Cores 311-U1237D-12E and 311-U1237D-14E were transferred to storage chambers for further analysis.

Degassing Experiments

At Site U1327, five PCS cores were successfully recovered under pressure and investigated by controlled shipboard degassing experiments. The deepest PCS core was taken at a depth of 246.5 mbsf, which is ~25 m deeper than the seismically inferred BSR depth (Core 311-U1237D-17P). The other four PCS cores were taken from within the predicted depth interval of the methane hydrate stability zone (Cores 311-U1237C-15P, 122.3 mbsf; Core 311-U1237D-10P, 155.6 mbsf; Core 311-U1237C-24P; 197.8 mbsf). Core 311-U-1327E-3P is the shallowest PCS core taken at this site, which was from a depth of 80.5 mbsf.

All degassing experiments included the following steps: First, the volume and density of sediment inside the inner core barrel of the PCS was monitored by X-ray analysis. Subsequently, the PCS was slowly degassed in a temperature-controlled laboratory (7°C) and the volume and composition of released gas and water, the pressure inside the core, the ambient air pressure and temperature were monitored. However, initial pressure readings are not available for Core 311-1327C-15P since the analog pressure gauge used was not suitable for the recovered low pressures. During the degassing procedure, the vertical density distribution of the PCS cores was repeatedly determined by gamma attenuation scans to examine the evolution of gas voids within the sediment. After degassing was completed, shipboard scientists X-rayed the PCS cores again, collected the water remaining in the outer core barrel for mass balance considerations, and subsampled

the sediment that was extruded from the cores for interstitial water chemistry, dissolved gases and physical properties.

The degassing of the five PCS cores from this site yielded 1.2 to 10.3 liters of gas and showed variable methane concentrations with depth. For all PCS cores, the composition of the released gas did not change significantly in the course of degassing. Methane was the major component accounting on average for $85 \pm 8\%$ of gas emitted from Core 311-U1327C-15 P and for $95 \pm 3\%$ to $98 \pm 2\%$ in all other cores. Nitrogen was the second most abundant gas contributing $12 \pm 5\%$ to the gas released from Core 311-U1327C-15P and less than 2% to the gas obtained from all other PCS cores. Carbon dioxide, ethane and higher hydrocarbon concentrations were below the detection limit of the Agilent gas chromatograph used for continuous gas analysis during the degassing experiment.

In all degassing experiments, the pressure inside the PCS cores dropped below the predicted gas hydrate stability conditions when the port valve of the PCS was first opened and water expanded from the outer core barrel into the manifold system. Therefore no pressure plateaus or rebounds from dissociation of gas hydrate could be expected and a steady decrease of core pressure versus removed gas volume was observed for all cores.

X-ray scans of PCS cores before depressurization showed no evidence of massive gas hydrate (e.g., veins or nodules), though clasts or rocks were evident in Cores 311-U1327C-24P and 311-U1327D-10P. Repeated density scans during depressurization experiments showed overall lowering of densities due to gas exsolution and core expansion, with some isolated sediment cracking. Gas voids preferentially developed near the bottom of the PCS cores because core expansion can only occur out of the bottom of the inner core barrel. Large cracks near the bottom of Core 311-U1327D-10P could indicate the presence of massive gas hydrate, though the rapid evolution of these cracks during depressurization does not support this interpretation, nor does the measured interstitial water chloride concentration. None of the measured interstitial water chloride concentrations in the PCS cores differed significantly from the background chloride trend.

Measurements on HYACINTH cores

Simultaneous and automated gamma density, P-wave velocity and X-ray measurements were made in the MSCL-P system on Cores 311-U1327D-12E and -14E; the velocity and density profiles and the X-ray images for Cores 311-U1327D-12E and -14E were evaluated by shipboard scientists. All measurements took place at 12 MPa (near recovery pressure; 80% of in situ pressure). Unlike the velocity profiles obtained for Core U1329E-9E, there are no distinctive velocity highs in the profiles, yet in both cores the velocities are relatively high compared with what would be expected for unconsolidated sediments. The X-ray images, while showing subtle changes in density, do not show any anomalies that might be related to massive gas hydrate structures (e.g., veins or nodules). The provisional interpretation of these cores is that they may contain small amounts of disseminated gas hydrate that has created a stiffer sediment matrix throughout the core

with a commensurate increase in the compressional wave velocity. Alternately, the sediments may be indurated with carbonate or other minerals. Shorebased depressurization and gas collection experiments as well as sediment sampling will support or disprove these hypotheses.

Gas Hydrate Concentration, Nature, and Distribution from Pressure Coring

Core 311-U1327D-10P contained much more methane than the other PCS cores, corresponding to a gas hydrate saturation of 8.2% of pore space. The presence of free gas beneath the BSR, seen in the VSP velocities was confirmed by Core 311-U1327D-17P.

A high-resistivity layer found in Hole U1327A proved to be a moving target. Lateral heterogeneity was responsible for the mismatch of infrared data, wireline resistivity logs, and LWD resistivity logs at this site. The depth of the pressure cores at this site cannot be used as a simple measure of their location relative to this layer; the lateral correlation of the core position between holes must be taken into account. Core 311-U1327C-15P was taken deliberately well above the layer of increased gas hydrate concentration, Cores 311-U1327C-24P, 311-U1327D-12E, and -14E were taken below this layer, and Core 311-U1327D-10P was within the layer. Thermal anomalies were found in the XCB cores both above and below Core 311-U1327D-10P.

The P-wave velocity and gamma density profiles of Cores 311-U1327D-12E and -14E show convincing evidence that gas hydrate at this site may be distributed uniformly through the sediment. The X-ray images of the PCS cores and the gamma density profiles taken during depressurization of the PCS cores, as well as the X-ray on the two HRC cores, are all consistent with this interpretation. The gas hydrate may be distributed uniformly, but it may not necessarily be filling pore space alone. The X-ray image of Core 311-U1327D-14E shows fine, wispy low-density structures, that could be distributed cracks in the clay sediment, filled with gas hydrate.

No direct evidence of massive gas hydrate could be found in any of the pressure cores. However, the repeated density profiles taken on Core 311-U1327D-10P, which released over nine liters of methane, do not show the pervasive cracking that would be expected if this amount of methane were evenly distributed throughout the core. The gas hydrate may have been concentrated near the bottom of the core, although other interpretations are possible.

IODP Site U1327 Summary

Site U1327 (Scientific Prospectus Site CAS-01B) is located near ODP Site 889/890 approximately at the mid-slope of the accretionary prism over a clearly defined BSR, estimated to be at a depth of 223 mbsf. The primary research objectives for this site are linked to the transect-concept of this expedition.

Five holes were occupied at Site U1327. Hole U1327A was dedicated to LWD/MWD measurements to a total depth of 300 mbsf. Initially we had planned to drill to a depth of 350 mbsf, but tight time constraints during the LWD/MWD operations made it necessary to reduce the depth of the planned deepest penetrations at this site. The first APC in Hole U1327B missed mudline with a full core, the core was curated and a new hole was spudded without offsetting the ship. Hole U1327C was then cored (10 APC, 22 XCB, 3 PCS cores; 88.3% recovery) to 300.0 mbsf. The PCS was deployed three times in Hole U1327C and four APCT temperature measurements were made (Cores 311-U1327C-3H, 5H, 7H, 9H). In Hole U1327D, which was drilled and cored as a special tools hole, two APC cores were also taken from the surface to a depth of 16.4 mbsf for a high resolution microbiological and geochemical study of the sulfate/methane interface (SMI). In this hole, the PCS was deployed three times, together with four deployments of the HRC and two deployments of the FPC pressure coring system. The last pressure core was taken at a depth of 246.5 mbsf and the hole was advanced to a TD of 300 mbsf for the logging program.

Hole U1327E was advanced to 3 mbsf and a single 9.5 m long APC core was taken for high resolution microbiological and geochemical sampling of the SMI, which was partially missed during an earlier attempt. Two additional PCS pressure cores and one HRC core were taken, out of which only the second PCS at ~80 mbsf recovered sediment under pressure. Excessive heave over 3.5 m forced the termination of pressure coring operations and the hole was advanced by drilling to a completion depth of 300 mbsf to prepare the second wireline logging run.

Infrared (IR) imaging of the recovered cores was routinely carried out on the catwalk to detect and characterize the nature of gas hydrates in the cores. A large number of IR identified cold spots were detected in the cores from Holes U1327C and U1327D; however, an apparent depth mismatch in the occurrence of major cold core sections between the holes indicated significant intra-site geologic variability. Apparent mismatches between the IR inferred gas hydrate occurrences in Hole U1327C with the LWD/MWD resistivity inferred gas hydrate occurrences in Hole U1327A further documents the lack of lateral continuity at this site.

The PCS was deployed eight times at Site U1327 (three in Hole U1327C, three in Hole U1327D, two in Hole U1327E), five of which recovered sediment under pressure. In addition to the PCS deployment, the HRC was used four times (with three core recoveries under pressure) and the FPC was used twice, but only one of the FPC cores was recovered under pressure. The degassing of the five PCS cores from this site that were recovered under pressure showed variable gas concentrations with depth. The deepest PCS core was taken at a depth of 246.5 mbsf, which is ~25 m deeper than the seismically inferred BSR depth. The other four PCS cores were taken from within the predicted depth interval of the methane hydrate stability zone. Core 311-U1327E-3P is the shallowest PCS core taken at this site, which was from a depth of ~80 mbsf.

Three PCS Cores 311-U1327C-15P, 311-U1327D-10P, and 311-U1327C-24P were taken at 122.3, 155.6, and 197.8 mbsf, respectively. Out of these three cores, only Core 311-U1327D-10P yielded enough gas to infer the occurrence of a significant amount of gas hydrate; with an estimated gas hydrate pore-space concentration of ~8%. The other two PCS cores yielded gas hydrate pore-space concentrations of less than 1%.

Three HRC cores (311-U1327D-4E from 125.3 mbsf, 311-U1327D-12E from 170.5 mbsf, 311-U1327D-14E from 217.7 mbsf) and one FPC core (311-U1327D-13Y from 203.6 mbsf) were successfully recovered and transferred under pressure to storage chambers for shorebased analyses. All of these cores were X-ray imaged, P-wave velocity and density logged within their storage vessels. Some of the recovered pressure cores exhibited evidence of gas hydrate, including high P-wave velocities and anomalous low density readings.

IODP Site U1328

Site U1328 was situated at the “Bullseye” cold vent, where seismic records show a blank zone beneath the seep and a weak BSR. Massive gas hydrate had previously been found at the surface of this site (Riedel et al., 2004; 2006) and very high resistivity layers associated with low densities, indicating massive gas hydrate, were seen in the LWD data from 0-46 mbsf and near 95 mbsf. LWD resistivities did not show evidence of free gas below the BSR, but there were some indications of gas below the BSR in the sonic waveform coherence. Specific objectives at this site were to determine the concentration of gas hydrate in the sediment column, free gas below the BSR (and potential free gas above the BSR), and to retrieve samples of massive gas hydrate.

Operation of Pressure Coring Systems

Pressure coring tools were deployed eleven times at Site U1328 (Table U1328-I-1): two PCS cores in Hole U1328B, the top core targeting massive gas hydrate; one PCS core in Hole U1328C, targeted at the high resistivity layer near 95 mbsf; one FPC core in Hole U1328D, targeting massive gas hydrate; and two deployments each of the HRC and the FPC along with three deployments of the PCS in Hole U1328E, the top HRC and FPC targeting massive gas hydrate, the middle PCS targeting the ~95 mbsf high-resistivity layer, and the bottom PCS targeting free gas below the BSR. Scientists evaluated the pressure history of the cores during deployment, coring, recovery, and chilling (in the ice shuck) of the pressure coring tools.

Five of the six PCS runs recovered full cores at some pressure (Table U1328-I-1). The first two deployments (Cores 311-U1328B-4P and -7P) had particularly unusual pressure profiles. Despite immersion of the autoclave in the ice shuck, the pressures rose rapidly and peaked sharply at pressures well above in situ pressures (20 and 24 MPa respectively), before rapidly falling again prior to the tool being removed from the ice. Pressures were still falling rapidly when the data loggers were removed. As with previous PCS runs on Expedition 311, the other PCS deployments generally recovered cores with

only about 50-60% of the in situ pressure. The PCS could benefit from a gas-filled pressure accumulator connected to the autoclave to help prevent the pressure drop from volume changes after tool sealing or other pressure and temperature effects on core or autoclave volumes. After the PCS cores were degassed and X-rayed, they were extruded using a hydraulic pump and samples for interstitial water analysis, porosity, and headspace gas analysis were taken.

Both the first deployment of the FPC (Core 311-U1328D-3Y) and the HRC (Core 311-U1328E-3E) at this site were targeted at massive hydrate. Core 311-U1328E-3E penetrated massive gas hydrate that was not retained as an intact core due to a pressure leak. In contrast, Core 311-U1328D-3Y showed no evidence of penetrating the formation. The depth of Core 311-U1328E-3E had been determined by the previous partial XCB core, which had been drilled until a hard formation was reached. The recovered pressure in Core 311-U1328E-3E (4 MPa) was below in situ pressure (12.8 MPa) due to the failure of the side valve on the HRC; the core was returned to full in situ pressure and quickly X-rayed, but the core liner was nearly empty. When the autoclave was depressurized and inspected, much gas was released and small pieces of gas hydrate were found in the autoclave, though there was very little associated sediment.

The remaining deployments of the HYACINTH tools (Cores 311-U1328E-7Y, -11Y and -12E) all failed due to adverse heave and weather conditions. The two FPC deployments that recovered Cores 311-U1328E-7Y and -11Y suffered from large tensions on the sand line during coring (as confirmed subsequently from the rig data), when during normal operation the sand line should be slack. The HRC deployment was unlucky enough to be terminated by a 4 m heave that lifted the drill string and tool off the bottom during the crucial coring stroke, returning the corer with an empty and shattered liner.

Degassing Experiments

At Site U1328, five PCS cores were successfully recovered under pressure and investigated by controlled shipboard degassing experiments. Two PCS cores were taken within the near-surface gas-hydrate bearing section from 0 to 46 mbsf (Core U1328B-4P at 14.5 mbsf and Core U1328B-7P at 26 mbsf). PCS Cores U1328C-5P and U1328E-10P were recovered from 92 mbsf where very high resistivity layers associated with low densities were seen in the LWD data. The deepest PCS core was taken at a depth of 233.5 mbsf, very close to the seismically inferred BSR depth (Core 311-U1328E-13P).

All degassing experiments included the following steps: First, the volume and density of sediment inside the inner core barrel of the PCS was monitored by X-ray analysis. Subsequently, the PCS was slowly degassed in a temperature-controlled laboratory (7°C) and the volume and composition of released gas and water, the pressure inside the core, the ambient air pressure and temperature were monitored. During the degassing procedure, the vertical density distribution of the PCS cores was repeatedly determined by gamma attenuation scans to examine the evolution of gas voids within the sediment. After degassing was completed, scientists X-rayed the PCS cores again, collected the

water remaining in the outer core barrel for mass balance considerations, and subsampled the sediment that was extruded from the cores for interstitial water chemistry, dissolved gases and physical properties.

The degassing of the five PCS cores from this site yielded 2.7 to 60 liters of gas and showed variable methane concentrations with depth. For all PCS cores, methane was the major component of the released gas. In Cores 311-U1328C-5P and 311-U1328B-7P with low gas hydrate contents, methane accounted on average for $70 \pm 8\%$ and $76 \pm 4\%$ of the emitted gas, respectively. In all other cores, methane concentrations ranged from $91 \pm 5\%$ to $98 \pm 1\%$. Nitrogen was the second most abundant gas contributing $0.7 \pm 0.3\%$ to $23 \pm 9\%$ to the gas released. Carbon dioxide, ethane and higher hydrocarbon concentrations were below the detection limit of the Agilent gas chromatograph used for continuous gas analysis during the degassing experiment.

In four degassing experiments, the pressure inside the PCS cores dropped below the predicted gas hydrate stability conditions when the port valve of the PCS was first opened and water expanded from the outer core barrel into the manifold system. Therefore no pressure plateaus or rebounds from gas hydrate dissociation could be expected and a steady decrease of core pressure versus removed gas volume was observed for these cores. In contrast, during the degassing of Core 311-U1328E-13P from below the depth of the BSR, the pressure inside the PCS remained at a constant high level of 5 Mpa while the initial 25 liters of gas were released. This pressure indicates gas hydrate stability and the observed pressure plateau and rebound of pressure are typical for the gas hydrate dissociation. However, X-ray images and repeated gamma density profiles of Core 311-U1328E-13P showed no evidence for gas evolution within the sediment and interstitial water analysis did not indicate pore water freshening due to the decomposition of gas hydrate. Therefore it was concluded that the observed gas hydrate was artificially formed from free gas when the PCS was brought into the gas hydrate stability field upon entering the temperature-controlled laboratories.

X-ray scans before and after depressurization, as well as differential density scans during degassing experiments, confirmed the presence of gas hydrate within some of the cores. The initial X-rays of Core 311-U1328B-4P showed low-density layers that had turned into gas cracks by the final X-ray, and a large void in the bottom of the core barrel. The repeat density profiles showed the formation of this “void” in the core barrel, as gas and sediment are forced down out of the bottom of the inner core barrel.

Differential density profiles of Core 311-U1328B-7P showed expansion throughout the core, with movement of pieces of sediment out of the bottom of the barrel, and the final X-ray showed a low-density, highly expanded core. Based on the gamma density measurements and the X-ray image, this core was initially 95 cm long, ± 3 cm.

Core 311-U1328C-5P, in contrast to most of the other pressure cores from Site U1328, showed only a small amount of expansion, all of which occurred between the first and second scans. Core 311-U1328E-10P, collected in a steel barrel, originally contained

about 42 cm of core, based on the differential density scans, but this core was completely homogenized during the degassing process as sediment and gas forced their way down and out of the inner core barrel.

Compared to the rest of the pressure cores from Site U1328, the X-ray images and repeat gamma density profiles of Core 311-U1328E-13P showed the least evidence for gas evolution. Although some expansion took place in the bottom 10 cm of the core, the overall density decrease in the core was less than that seen in Core 311-U1328C-5P, which only released 2.74 liters of gas. None of the three interstitial water samples taken showed evidence of porewater freshening.

Gas Hydrate Concentration, Nature, and Distribution from Pressure Coring

Site U1328, the cold vent site, was expected to contain large amounts of gas hydrate but also to be laterally heterogeneous; both of these expectations were met in the pressure coring. The single core from below the BSR, Core 311-U1328B-13P, which may or may not have been below the base of the gas hydrate stability zone given the uncertainty of the temperature data at this stage, contained evidence for free gas.

The highest concentrations of gas hydrate were found, not near the seafloor as expected, but in a core from 92 mbsf (Core 311-U1328E-10P), which corresponded to a zone of very high resistivity in the LWD data from Hole U1328A. A pressure core taken at the same depth in Hole U1328C (Core 311-U1328C-5P) contained almost no gas hydrate, and the infrared images and salinity and chlorinity profiles for this hole show no anomalies near 90-100 mbsf. The targeted resistivity feature may have actually been a steeply dipping fracture in Hole U1328A, in which case any attempt to correlate this feature with other holes would be futile. There is also evidence for general lateral heterogeneity from LWD and wireline logs from different holes at Site U1328.

On two occasions during Expedition 311, the PCS returned a significant amount natural gas that could not be attributed to the recovered core (Cores 311-U1328E-13P and 311-U1329C-23P). Under certain circumstances, it may be possible for the PCS to collect free gas directly from the formation in the outer core barrel. During the coring operation, the outer barrel of the PCS is unlikely to collect gas because drilling fluids are flowing down the outer core barrel. However, when coring is completed, this flow is stopped and the actuator raises the inner barrel, enlarging the opening from the formation to the outer core barrel. At this stage in the recovery of the PCS core, gas in the formation could freely bubble into the outer core barrel prior to the ball valve being closed. If cuttings were to block the main hole, the actuator would “swab” any gases trapped in the bottom of the hole into the outer core barrel. In this way the outer barrel may end up as a “gas sampler” for free gas that has either been released from the formation during drilling or released by the dissociation of gas hydrate during the heating caused by drilling.

The abrupt pressure rise that Cores 311-U1328B-4P and -7P experienced in the ice shuck might be associated with gas hydrate dissociation, assuming a thermal lag between the

core and the recording thermistor above the autoclave. The equally abrupt pressure decrease would then correspond to the reformation of gas hydrate; however, such a pressure increase (or decrease) was not shown by other cores containing large amounts of gas hydrate (e.g., 311-U1327D-10P, 311-U1328E-10P) that also were near the gas hydrate phase boundary. Pressure increases of this type were seen in gas-hydrate-bearing pressure cores on Leg 204 (Tréhu, Bohrmann, Rack, Torres, et al., 2003), and could contain kinetic information about the distribution and surface area of the gas hydrate.

IODP Site U1328 Summary

Site U1328 (Scientific Prospectus Site CAS-06A) is located within a seafloor cold-vent field, with dimensions 2 km by 4 km, consisting of at least four vents associated with near-surface faults. The cold vents surrounding this site are characterized by near-vertical seismic blank (or wipe-out) zones that are between 80 and several 100 m wide, and show a clear E-W trend as identified from 3D seismic imaging. The most prominent vent in the field, referred to as Bullseye vent, is the target of this site and has been the subject of intensive geophysical and geochemical studies since 1999. Site U1328 is different than all of the other sites visited during this expedition in that it represents an area of active, focused fluid flow.

Five holes were occupied at Site U1328. Hole U1328A was dedicated to LWD/MWD measurements to a total depth of 300 mbsf. Hole U1328B was continuously cored (6 APC, 2 XCB, 2 PCS cores; 72.8 % recovery) to a depth of only 56.6 mbsf, and was terminated after strong winds and severe ship heave conditions required us to pull out of the hole. After waiting on weather for 16 hours, conditions had improved to the point to allow drilling and coring operations to continue. Hole U1328C was drilled from the seafloor to the maximum depth of Hole U1328B (56.5 mbsf). Hole U1328C was then continuously cored (4 APC, 22 XCB, 1 PCS cores; 80.7 % recovery) to a total depth of 300 mbsf. Hole U1328D was cored as a special high-resolution combined microbiology and geochemistry research hole with two XCB cores and a single FPC taken at the bottom of the hole. Hole U1328E was a special tool hole, which also included the deployment of six XCB cores within the upper 46.0 mbsf to recover additional samples of gas hydrate. Seven pressure cores were taken (3 PCS, 2 HRC, and 2 FPC) separated by XCB cores and drilled intervals.

All cores from this site were systematically scanned upon arrival on the catwalk to detect infrared (IR) anomalies indicative of gas hydrate dissociation during core recovery. Strong cold anomalies were detected in the shallowest cores from this site.

At Site U1328 we attempted 11 deployments of the three different pressure coring tools. The PCS was deployed six times at Site U1328 (twice in Hole U1328B, once in Hole U1328C, and three times in Hole U1328E), five of which recovered sediment under pressure. In addition to the PCS deployment, the HRC was used two times and the FPC was used three times, but none of these cores were recovered under pressure. The degassing of the five successful PCS cores from this site showed variable gas

concentrations with depth. Two PCS cores were taken within the near-surface gas-hydrate-bearing section from 0 to 46 mbsf (Core U1328B-4P at 14.5 and Core U1328B-7P at 26 mbsf). The X-ray images of Core U1328B-4P under pressure show 2-6-mm-thick low-density structures that disappeared after degassing and are interpreted as gas hydrate veins. This core showed large amounts of gas expansion and sediment extrusion during depressurization, as did Cores U1328B-7P and U1328E-10P to a lesser extent. The two PCS cores taken in Holes U1328C and U1328E at 92.0 mbsf (Cores U1328C-5P, U1328E-10P) yielded each quite different amounts of methane gas. One PCS core was taken from a depth of 233 mbsf, very close to the seismically inferred BSR depth.

IODP Site U1329

Site U1329 was expected to be at the eastern limit of gas hydrate occurrence on the Northern Cascadia Margin, based on seismic evidence. A specific objective at this site was to confirm or disprove the presence of gas hydrate and free gas beneath the BSR. Site U1329 had a relatively weak BSR estimated at 126 mbsf, but high resistivity values in the LWD logs for Hole U1329A indicated the possible presence of free gas between 145-165 mbsf.

Operation of Pressure Coring Systems

At Site U1329 six Pressure Core Samplers (PCS) were deployed for shipboard degassing experiments as well as one HYACE Rotary Corer (HRC) and one Fugro Pressure Corer (FPC) for both analysis on board and archiving of cores at in situ pressure (Table U1329-I-1). Scientists evaluated the pressure history of the cores during deployment, coring, recovery, and chilling (in the ice shuck) of the pressure coring tools. Pressure cores rarely retain full in situ pressure for various reasons and can stray across the gas hydrate stability boundary when warming during tool recovery and handling. The ice-water-filled shuck keeps this warming to a minimum by reversing the trend on recovery; but cores recovered far below in situ pressure (e.g., Core 311-U1329C-7P and other PCS cores at this site) may spend 10-20 minutes outside the gas hydrate stability field before re-entering gas hydrate stability conditions.

The PCS deployment that recovered Core U1329C-23P was particularly unusual. This was the only pressure core deployment well below the depth of the BSR and extremely important for the site goals. The coring lasted over an hour. During the protracted coring operation, a low-pressure event was recorded that lasted more than 10 minutes, which was also recorded in the PCS pressure logger. When the corer was retrieved, we discovered that the bit had sheared off in the formation, damaging the aluminum outer barrel beyond repair and ending the hole. In spite of this, a core was recovered, though it was at very low pressure (350 kPa).

The deployment of HRC Core 311-U1329E-9E shows the value of immediately cooling the tool in the cold shuck after recovery at the rig floor. The autoclave was not recovered under full in situ pressure. Water had filled the pressure accumulator, which is designed

to buffer the pressure inside the core from changes in tool volume. As the core warmed on recovery, it approached the gas hydrate stability boundary but quickly moved away from this boundary as it chilled in the cold shuck. After shipboard analyses were completed, the HRC core was stored in seawater at 10 MPa in a pressurized storage chamber for further shorebased studies. The FPC deployment at this site recovered a good core Core 311-U1329E-8Y but the inner rod over retracted and the core was not recovered at pressure.

Degassing Experiments

At Site U1329 six PCS cores were taken for controlled shipboard degassing experiments. The main objectives were (1) to determine the concentration and composition of natural gases, (2) to identify the presence/absence and concentration of gas hydrate within the GHSZ, and (3) to constrain the presence of free gas below the BSR. Out of the six PCS deployments, four runs retrieved sediments under pressure. They represent sediments both above (Cores 311-U1329C 7P, 311-U1329E 7P, 311-U1329E 10P) and below the BSR (311-U1329C 23P). The low pressure readings for the recovered PCS cores were all below predicted gas hydrate stability conditions at the temperature of the laboratory (7°C), and therefore no pressure plateaus or rebounds from dissociation of gas hydrate could be expected.

All degassing experiments included the following steps: First, the volume and density of sediment inside the inner core barrel of the PCS was monitored by X-ray analysis. Subsequently, the PCS was slowly degassed in a temperature-controlled laboratory (7°C) and the volume and composition of released gas and water, the pressure inside the core, the ambient air pressure and temperature were monitored. During the degassing procedure, the vertical density distribution of the PCS cores was repeatedly determined by gamma attenuation scans to examine the evolution of gas voids within the sediment. However, due to a failure of the digital pressure recorder, no pressure readings are available for the degassing of Core 311-U1329C 7P, and an unresolved problem occasionally interfered with the collection of gamma density data from Core 311-U1329C-7P from 35-50 cm depths. After degassing was completed, PCS cores were X-rayed again. From Core 311-1329C 23P onward, scientists collected the water remaining in the outer core barrel for mass balance considerations and sub-sampled the sediment that was extruded from the cores for interstitial water chemistry, dissolved gases and physical properties.

The degassing of the four PCS cores from Site U1329 showed variable gas concentrations and compositions with depth. PCS Cores U1329C-7P (55.6-56.6 mbsf) and U1329E-7P (73.5-74.5 mbsf) taken within the predicted depth of the methane hydrate stability zone, each yielded 1.80 liters of gas. The composition of the released gas did not change significantly in the course of degassing. Methane was the major component accounting on average for $68 \pm 4\%$ of the gas emitted from Core U1329C-7P and for $78 \pm 3\%$ of the gas released from Core U1329E-7P. In both cores, nitrogen was the second most abundant gas, contributing $19 \pm 2\%$ and $17 \pm 3\%$, respectively. Carbon dioxide,

ethane and higher hydrocarbon gases were below the detection limit of the Agilent gas chromatograph used for continuous gas analysis during the degassing experiments.

For Core 311-U1329E-7P, the steady decrease of core pressure versus removed gas volume indicates that the majority of the gas comes from solution rather than from decomposing gas hydrate. This observation is supported by repeated density scans, which show a few gas cracks developing during the depressurization, and an overall decrease in sediment density from gas exsolution. The X-ray scans showed no evidence of any heterogeneities in the sediment except for a zone of what appeared to be disturbed core from 27-47 cm in Core 311-U1329E-7P. A large gas crack did develop in this zone of presumed disturbance.

PCS Core 311-U1329E-10P (125.0-126.0 mbsf), from near the base of the predicted methane hydrate stability zone for this site, yielded 2.26 liters of gas. Throughout the degassing procedure, methane accounted for $91 \pm 7\%$ of the released gas, and nitrogen amounted to $8 \pm 5\%$. Carbon dioxide, ethane and higher hydrocarbon gases were below the detection limit of the Agilent gas chromatograph used for continuous gas analysis during the degassing experiments. The X-ray scan before depressurization showed some inhomogeneities in the core, but none of the lower-density regions between 5-25 cm developed gas cracks during depressurization, and hence these regions were not considered to be gas-hydrate-related.

The deepest PCS core, Core 311-U1329C-23P (188.5-189.5 mbsf) was taken at a considerable depth below the base of the gas hydrate stability zone. The 5.86 liters of gas obtained from this core represent by far the highest gas yield at this site. At the same time, the composition of gas differs distinctly from that obtained from the three cores taken above the BSR. High methane concentrations ($88 \pm 5\%$) were accompanied by carbon dioxide ($6 \pm 0.3\%$) and ethane ($0.2 \pm 0.01\%$). The measured C1/C2 ratio may indicate a thermogenic origin for the gas. Unlike the other cores from this site, the core pressure did not decrease steadily in the course of the degassing experiment but stayed on a constant level of 0.22 MPa while the first 1.75 liters of gas were released. Densities did not decrease much during depressurization, but some minor shifting of the steel PCS internals—or the rocks and clasts seen in the X-ray—is evident in the lower half of the core. It is noteworthy that the large yield of gas coincided with a very large headspace volume in the outer core barrel (1.67 liters).

Measurements on HYACINTH cores

Core 311-U1329E-9E was recovered with 8 MPa pressure and was returned to 10 MPa (near in situ pressure) during the transfer into the MSCL-P. Simultaneous and automated gamma density, P-wave velocity and X-ray measurements were made in the MSCL-P system. Examination of the velocity and density profiles and the X-ray image indicates two high-velocity zones at 18-28 cm (velocities up to 1630 m/sec) and 73-84 cm (velocities up to 1730 m/sec). These zones were associated with small density lows, deviating from the norm by less than 0.05 g/cm^3 . These low-density layers were also

clearly visible on the X-ray images but could not be distinguished via the X-rays alone from other low-density zones in the same core.

The distinctive nature of the two high-velocity zones is illustrated in a cross-plot of gamma density and P-wave velocity. Gamma density and P-wave velocity in these two high velocity zones are inversely correlated, whereas the other subtle variations in velocity and density throughout the core show a positive correlation of increasing velocity with increasing density. The slope of this trend is similar to that found in the measurements made on APC and XCB cores from this site.

The high-velocity zones fall well outside the normal trend for ocean sediments and we interpret this anomaly as being indicative of the presence of gas hydrate. X-ray images and gamma density profiles show that these zones do not contain any veins, nodules or other massive gas hydrate, so any gas hydrate in these zones is likely to be disseminated in nature. The small decrease in density associated with these zones, if solely attributed to replacement of porewater by gas hydrate, would require 40% of the pore space to be filled with gas hydrate. However, simple replacement of pore fluid by gas hydrate with little to no effect on the sediment structure seems unlikely. The disseminated gas hydrate might inhabit layers that are intrinsically low in density, and the gas hydrate itself may contribute little to the density anomaly. Another possibility is that the formation of gas hydrate in silty clays could cause the sediment matrix to expand and hence lower the overall matrix density. This “hydrate micro-heave” could be a precursor to the formation of massive hydrate veins, which have been observed elsewhere in silty clays (ODP Leg 204) and which must have forced the sediments apart. The lithology of these zones should be carefully examined following shorebased depressurization experiments in an effort to understand the nature of these likely gas hydrate zones in fine-grained sediments.

Gas Hydrate Concentration, Nature, and Distribution from Pressure Coring

The low estimates of gas hydrate concentration for Site U1329 from degassing experiments were consistent with the distributed nature of gas release from the PCS, with the resistivity-derived water saturations near 100%, and with the lack of infrared anomalies or chlorinity anomalies measured at this site. Gas hydrate concentrations equivalent to less than 0.5% of pore volume would likely be undetectable via infrared imaging or chlorinity.

Although integrated measures of gas hydrate may show concentrations on the edge of detectability, Core 311-U1329E-9E contains evidence for higher concentrations of disseminated gas hydrate within 10-cm-thick low-density, high-velocity layers at 114 mbsf. No similar layers of gas hydrate were observed in any of the X-ray images obtained from PCS cores or infrared images of APC and XCB cores, though the exact gas hydrate concentration in the observed layers is not constrained and might still be low enough to completely dissociate during recovery of an unpressurized, conventional core.

The single PCS core from below the gas hydrate stability zone, Core 311-U1329C-23P, had a distinctly complex history, given the significance of the results from this core. The calculation of free gas percentage in Table U1329-I-5 assumes that all the methane released from the PCS during depressurization comes from the captured sediment material. The methane contained within the outer barrel of PCS Core 311-U1329C-23P, recovered at extremely low pressure, must have come from the formation, but did not necessarily all derive from the recovered sediment core. An alternate explanation for this gas comes from the low-pressure event recorded during the coring operation, which, to drilling crews, indicates a gas release from the formation. If a mere 15 ml of free gas had been captured in the PCS outer barrel at core depth, this could account for the 1.67 liters of gas found the outer core barrel after depressurization. Although a gas release event does not change the conclusion that free gas exists below the BSR at Site U1329, such an event would render the Core 311-U1329C-23P results qualitative rather than quantitative.

IODP Site U1329 Summary

Site U1329 (Scientific Prospectus Site CAS-05D) is at the eastern end of the southwest-northeast trending, margin-perpendicular, transect of sites occupied during this expedition and is located closest to shore (65 km) at a water depth of 946 mbsl. The location of this site is interpreted to be at the eastern limit of gas hydrate occurrence on the Northern Cascadia Margin. The objectives of coring and downhole logging at this site are tied to completing the transect of scientific drill sites across the Northern Cascadia Margin to further constrain models for the formation of marine gas hydrate in a subduction zone accretionary prism.

Five holes were occupied at Site U1329 (CAS-05D). Hole U1329A was dedicated to LWD/MWD measurements to a total depth of 220 mbsf. Hole U1329B consisted of only one missed mudline APC core to 9.5 mbsf. Hole U1329C was continuously cored (17 APC, 5 XCB, 3 PCS cores; 99.3 % recovery) to 189.5 mbsf, and was terminated before the target depth of 220 mbsf when the PCS cutting shoe broke off and was left in the bottom of the hole. With a forecast for improving weather the following day, we decided to abandon Hole U1329C to drill a dedicated logging hole. Hole U1329D was drilled from the seafloor to 201.0 mbsf, which included another 1.5 hr of suspended operations due to excessive ship heave, and a single XCB core was taken to 210.5 mbsf. Hole U1329D was wireline logged with the triple-combo and FMS-sonic tool strings. Hole U1329E was a special tool hole to 127.1 mbsf where five APC cores were taken for high-resolution microbiological and geochemical studies. Five pressure cores were taken (3 PCS, 1 HRC, and 1 FPC) separated by drilled intervals.

Infrared (IR) imaging of the recovered core was used to assist in immediate gas hydrate detection on the catwalk. At this site, core IR temperatures did not show any significant cold-spot anomalies from gas hydrate dissociation that could be related to the presence of gas hydrate in the recovered core.

In total six PCS deployments were made, three in Hole U1329C and three in Hole U1329E. Out of the six deployments, two runs did not recover sediment under pressure and all other runs retrieved sediments under pressure, although at measured surface pressures approximately half the expected in-situ hydrostatic pressure. It was concluded that the tool is sealing only when a certain differential pressure is reached, not at the in-situ pressure of the cored interval. All PCS cores that were successfully retrieved under pressure were degassed and subsamples of the recovered gas were analyzed on the ship and additional subsamples were taken for shore-based isotope studies. In addition to the PCS, one HRC and one FPC were deployed in Hole U1329E. A full core at near in situ pressure was recovered by the HRC that revealed 10 cm high velocity zones indicative of gas hydrate. The FPC deployment recovered a core without pressure. The degassing of the four PCS cores from this site that were recovered under pressure showed variable gas concentrations with depth.

SUMMARY AND CONCLUSIONS

Cooperative Agreement #DE-FC26-01NT41329 between Joint Oceanographic Institutions and DOE-NETL was divided into two phases based on successive proposals and negotiated statements of work pertaining to activities to sample and characterize methane hydrates on ODP Leg 204 (Phase 1) and on IODP Expedition 311 (Phase 2). The Phase 1 Final Report was submitted to DOE-NETL in April 2004. This report is the Phase 2 Final Report to DOE-NETL.

The primary objectives of Phase 2 were to sample and characterize methane hydrates using the systems and capabilities of the D/V *JOIDES Resolution* during IODP Expedition 311, 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 the Cascadia continental margin off Vancouver Island, British Columbia, Canada (IODP Expedition 311) so that hydrate deposits in this region would be well characterized and technology development continued for hydrate research.

IODP Expedition 311 shipboard activities on the *JOIDES Resolution* began on August 28 and were concluded on October 28, 2005. The statement of work for this project included three primary tasks: (1) research management oversight, provided by JOI; (2) mobilization, deployment and demobilization of pressure coring and core logging systems, through a subcontract with Geotek Ltd.; and, (3) mobilization, deployment and demobilization of a refrigerated container van that will be used for degassing of the Pressure Core Sampler and density logging of these pressure cores, through a subcontract with the Texas A&M Research Foundation (TAMRF). Additional small tasks that arose during the course of the research were included under these three primary tasks in consultation with the DOE-NETL Program Manager.

Dr. Frank R. Rack presented the results of both phases of the cooperative agreement between JOI and DOE-NETL in Morgantown, WV on October 20, 2006. The slides used for this presentation are included in this report as Appendix A.

Research continues on both ODP Leg 204 and IODP Expedition 311 samples and data. Publications submitted by shipboard and shore-based participants of these two expeditions are published online as they are accepted, and links to publications in journals and books are provided whenever possible on either the ODP or IODP Publications websites, as described below.

The *Proceedings of the ODP, Scientific Results, 204*, are available at URL: [http://www-odp.tamu.edu/publications/204_SR/204TOC.HTM].

The *Proceedings of the IODP, Expedition 311*, are available at URL: [<http://iodp.tamu.edu/publications/proceedings.html>].

Additional scientific contributions from both of these expeditions will continue to be produced. A summary of the current citation listings for ODP Leg 204 and IODP Expedition 311 is provided in this report as Appendix B.

The participants of IODP Expedition 311 are listed in Appendix C.

Appendix D contains the JOI Final Technical Report for Phase 1 of this cooperative agreement, as presented to DOE-NETL in April 2004.

All tasks outlined in the original statement of work were accomplished except for the deployment and use of the X-ray CT system under Subtask 2-2, which was cancelled due to scheduling conflicts. This reduction in scope provided resources that were applied to other activities to support the overall project. Post-expedition analysis of results and report writing will continue beyond this reporting period, however, all field deployments associated with this project have been successfully concluded as of this writing.

Joint Oceanographic Institutions and Dr. Frank Rack would like to thank all of the participants of ODP Leg 204 and IODP Expedition 311, as well as William Gwilliam the DOE-NETL Program Manager responsible for this cooperative agreement, for their contributions to this project over these many years.

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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-McClelland 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

APPENDIX A

FINAL PRESENTATION TO DOE-NETL IN OCTOBER 2006

DOE - National Energy Technology Laboratory
Morgantown, WV
October 20, 2006

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

Cooperative Agreement DE-FC26-01NT41329

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Funding has been provided by NSF and the international partners for ODP and IODP, IODP-MI, and through a JOI cooperative agreement with DOE-NETL aimed at characterizing methane hydrates using tools deployed on the R/V JOIDES Resolution.



SCIENTIFIC OCEAN DRILLING VESSELS

D/V Glomar Challenger
Deep Sea Drilling Project
(1968-1983)

R/V JOIDES Resolution
Ocean Drilling Program
(1985-2003)



Image courtesy of Roy Davis
Deep Sea Drilling Project
Scripps Institution of Oceanography



Image courtesy of John Beck
Ocean Drilling Program
Texas A&M University

ODP/IODP INVESTIGATIONS OF MARINE METHANE HYDRATE



Hydrate image courtesy of
Dr. Gary Klinkhammer
(Oregon State University)



Hydrate image from ODP Leg 164,
Blake Plateau and Carolina Rise

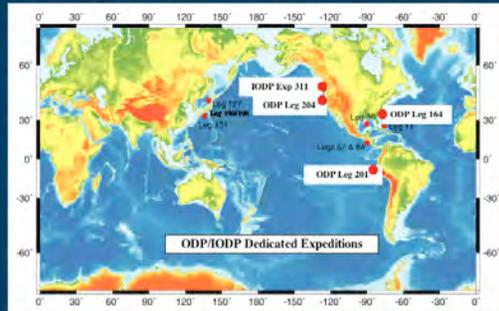
DSDP/ODP Methane Hydrate Research: Accomplishments (1970-1990)

- 1970 - 1st BSR drilled, **DSDP Leg 11: Blake Ridge** (offshore Carolinas)
- 1979 - hydrate samples observed in core, **DSDP Leg 86: W. Mexican Margin**
- 1979 - hydrate samples preserved in LN₂, **DSDP Leg 87: Guatemala Margin**
- 1980 - 1st use of the Pressure Core Barrel (PCB), **DSDP Leg 78: Blake Ridge**
- 1982 - 1.5 m-long massive hydrate sample recovered, **DSDP Leg 84: Guatemala Margin** (used in cooperative federal hydrate research program)
- 1983 - Microbiology & hydrates, **DSDP Leg 90: Gulf of Mexico**
- 1986 - Hydrates in slope sediments; 1st scientific use of the wireline Pressure Core Sampler (PCS): **ODP Leg 112: Peru Margin**
- 1989 - Hydrates in Sea of Japan, **ODP Leg 137: offshore western Japan**
- 1990 - Hydrates in Nankai Trough, **ODP Leg 131: offshore eastern Japan**

ODP/IODP Methane Hydrate Research: Accomplishments (1991-2005)

- 1992 - Drilled through BSR (installed CORK), **Leg 146: offshore Cascadia Margin** (Vancouver Island to Oregon - N. Hydrate Ridge)
- 1995 - 1st dedicated hydrate expedition, **Leg 180: Blake Ridge** (offshore Carolinas) - using geophysical data and drilling to test models
- 1997 - LWD data from hydrate-bearing sediments, **Leg 170: Costa Rican Margin** (ground-truth and modeling of geophysical data)
- 2000-2001 - accretionary prism, LWD, advanced CORK installations in a region with gas hydrates, **Legs 190 and 190: Nankai Trough** (offshore Japan)
- 2002 - 1st dedicated microbiology expedition, **Leg 201: Peru Margin** (investigating interrelationships between hydrates and microbiology)
- 2002 - 2nd dedicated hydrate expedition, **Leg 204: southern Hydrate Ridge** (offshore Oregon); additional funds provided by NSF, DOE/NETL, USGS, European Commission (HYACINTH project).
- 2005 - 3rd dedicated hydrate expedition, **IODP Expedition 311: Cascadia Margin** (offshore Vancouver Island); additional funds provided by DOE/NETL.

SCIENTIFIC DRILLING FOR METHANE HYDRATE



JOI/ODP Proposal to U.S. DOE/NETL "Methane Hydrates" Solicitation



NETL awarded \$ 1,438,202 (including cost-share) in Phase 1 of this cooperative agreement, entitled: "In-Situ Sampling and Characterization of Naturally Occurring Marine Methane Hydrate Using the D/V JOIDES Resolution".

Tasks 1-7: Upgrade the ODP Pressure Core Sampler (PCS), PCS gas manifold, and ODP memory tools (DVTP, DVTP-P, APC-methane, APC-T tools) for use on Legs 201 and 204.

Acquire equipment to characterize methane hydrates (e.g., G/GI Seismic Gun, Infrared Thermal Imaging System); modify the FUGRO piezoprobe tool for use with the ODP bottom hole assembly (BHA). Geriatrics Study on Leg 204.



Joint Oceanographic Institutions, Inc. / Ocean Drilling Program



JOI Cooperative Agreement with DOE/National Energy Technology Lab



Deliverable: Task 1.1 - Preliminary Evaluation of Existing Pressure/Temperature Coring Systems (October 2001).

Report available online at DOE/NETL website.
<http://NETL.CERTREC.COM>
Login: NETL
Password: ARCHIVE
Go to Bottom of List (\$2.4 MB file)
[HYD_00037_2001.PDF](#)

739 page summary of information available about four existing pressure coring systems synthesized from Technical Notes, JOIDES meeting minutes, Web Pages, and other information sources.



Joint Oceanographic Institutions, Inc. / Ocean Drilling Program



JOI Cooperative Agreement with DOE-NETL, Phase 2

Objective: Provide enhanced coring and measurement capabilities on the R/V JOIDES Resolution for IODP Expedition 311 a dedicated hydrate cruise to the Cascadia Continental Margin off Vancouver Island, Canada so that hydrate deposits in this region are well characterized.

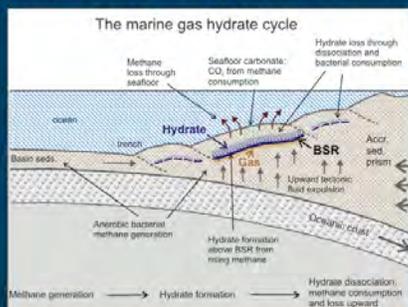
Task 1: Management and Oversight of Phase 2 Award (\$500K)

Task 2: Mobilize and deploy the HYA CINTH pressure coring systems and associated core logging subsystems for IODP Expedition 311 with adequate engineering and technical support; deploy X-ray linear scanner; work with TAMU technical staff to provide an enhanced infrared thermal imaging track for core measurements on the catwalk.

Task 3: Procure, outfit and deploy a refrigerated van to house pressure core logging equipment and degassing equipment.



THE MARINE GAS HYDRATE CYCLE



Expedition 311 Scientists, 2005, IODP Expedition 311 Preliminary Report. (doi:10.2204/iodp.pr.311.2005); Figure after Hyndman and Davis, 1992.

Hydrate distribution in sediment

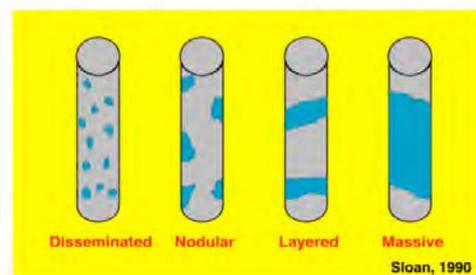


Figure courtesy of Dr. Timothy Collett (USGS) and the National Research Council of Canada

ODP LEG 204 - HYDRATE RIDGE, OFFSHORE OREGON: A METHANE HYDRATE NATURAL LABORATORY

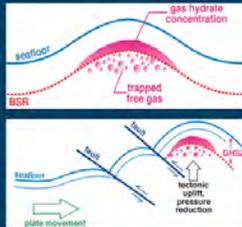
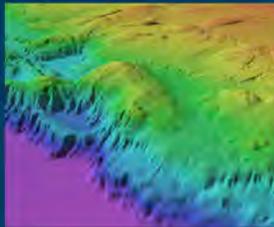


Figure courtesy of Dr. Chris Goldfinger (Oregon State University)
From Trehu, Bohrmann, Rack, et al., 2002, ODP Leg 204 Preliminary Report

Figures courtesy of Dr. Bill Dillon (USGS, retired) and Hydrate Energy International (HEI)

ODP Leg 204 - Hydrate Ridge, Offshore Oregon

Objectives for ODP Leg 204

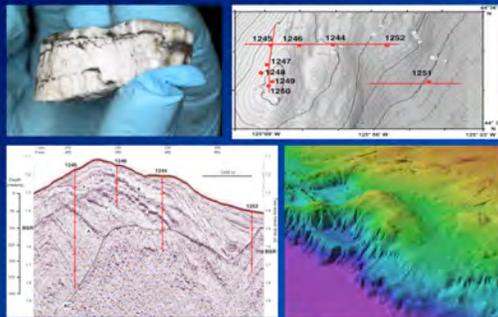
- (1) Compare the source region for gas and the physical and chemical mechanisms of hydrate formation between accretionary ridge and slope basin settings.
- (2) Calibrate estimates of hydrate and underlying free gas concentrations determined with geophysical remote sensing techniques.
- (3) Test, using geochemical tracers, physical properties measurements, and microstructural analysis, whether variations in bottom-simulating reflector (BSR) and sub-BSR reflectivity observed in seismic data result from tectonically induced hydrate destabilization.

Objectives for ODP Leg 204

- (4) Develop an understanding of the geochemical effects of hydrate formation in order to identify paleoproxies for methane release that can be used to integrate the geologic data into climate models.
- (5) Determine the porosity and shear strength of hydrate-bearing and underlying sediments in order to evaluate the relationships among hydrates, fluid flow and slope stability.
- (6) Quantify the distribution of methanogenic and methanotropic bacteria in the sediments in order to evaluate their contribution to hydrate formation and destruction, and to sediment diagenesis.

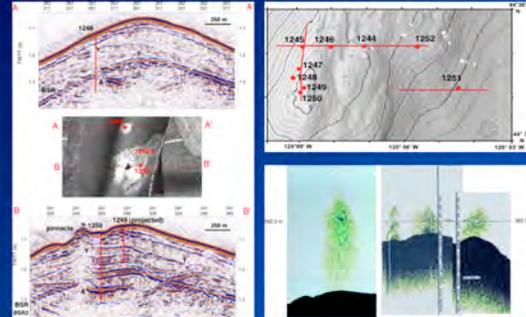


Hydrate Ridge, Offshore Oregon - ODP Leg 204



Trehu, Bohrmann, Rack, et al., 2002, ODP Leg 204 Preliminary Report

Hydrate Ridge, Offshore Oregon - ODP Leg 204

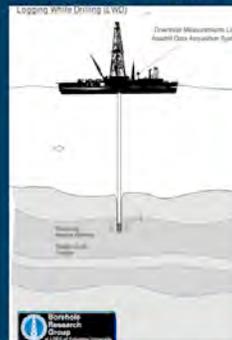


Trehu, Bohrmann, Rack, et al., 2002, ODP Leg 204 Preliminary Report

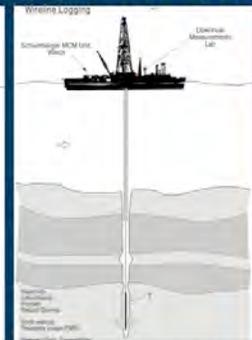
ODP Leg 204 Operational Summary

- 50.4 days (88.3%) was spent **operating**; 6.7 days (11.7%) were spent in port and/or in transit to/from Hydrate Ridge.
- Overall, **9 Sites** were drilled/cored, with **45 Holes** and **3068.3 meters of sediment was recovered** (83.5% core recovery).
- **Water depths** of sites ranged from **788.5 mbrf to 1228.0 mbrf**.
- **Penetration depths** varied from **9.5 mbsf to 540.3 mbsf**.
- 8 of 9 sites were drilled using **LWD** tools (resistivity-at-bit, NMR, density/neutron).
- ODP Leg 204 **characterized gas hydrate using indirect evidence** (e.g., increased electrical resistivities and p-wave velocities on downhole logs, low-salinity pore water anomalies, infrared thermal anomalies (low temp.), decreases in void gas C1/C2 ratios) **and through direct sampling and preservation of hydrate**.

Logging While Drilling (LWD)



Conventional Wireline Logging



Images courtesy of Lamont-Doherty Earth Observatory, Borehole Research Group

Logging While Drilling and Downhole Logging Measurements

RAB – Resistivity at Bit
ADN – Azimuthal Density Neutron

The RAB and ADN tools provide the following information while drilling:

- 360° oriented azimuthal resistivity images of the borehole wall
- Early detection of invasion by borehole fluids into the formation
- A gamma-ray detector for lithology characterization.
- 360° oriented azimuthal density image of the borehole wall
- Acquires formation porosity and photoelectric effect data continuously
- Can be connected in-line with other LWD tools

RAB vs. FMS

Comparison of LWD Resistivity at the Bit (RAB) tool and wireline electrical imaging tool measurements of dense fracturing in consolidated sediments.

- Resolution RAB = 150 mm FMS = 5 mm
- Borehole contact RAB = full 360° FMS = 4 pads
- Conveyance RAB = drill pipe FMS = wireline

Resistivity While Coring (RAB-C)

Resistivity While Coring System - (RAB-C)
Modified RAB and MDCB

- Resistivity at Bit (RAB) tool generates FMS-like resistivity images while drilling.
- RAB-C system will incorporate CDP tool to collect core while generating resistivity images.

Drilling Tools

HYDROCARBON MONITORING OF CORES: ODP LEG 204 - HYDRATE RIDGE

EXTRACTION OF SEDIMENT PORE WATER

Images courtesy of Dr. Walter Borowski

ODP Leg 204 Specialty Tool Deployments

Extensive use of specialty tools to characterize subsurface temperature and pressure (*in situ*) conditions, included:

- 81 out of 81 successful runs with the **APC-Temperature Tool**.
- 8 out of 8 successful runs with the **Davis-Villinger Temperature Probe (DVTP)**.
- 16 out of 16 successful runs with the **Davis-Villinger Temperature Probe with Pressure (DVTP-P)**.
- **Fugro Piezoprobe** tool was tested from the R/V **JOIDES Resolution** to measure *in situ* pore pressure dissipation.
- 107 out of 110 successful runs with the **APC-methane Tool**, which includes Temperature, Pressure, and Conductivity using sensors in the APC piston head (time series measurements).

Downhole Temperature Measurements

APC-Temperature Tool in APC Cutting Shoe



Davis-Villinger Temperature Probe (DVTP and DVTP-P)

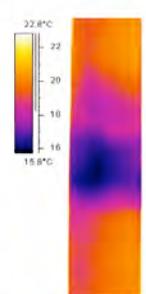


The DVTP-P provides in situ pore pressure measurements, in addition to measurements of formation temperature.




FLIR ThermoCam SC2000 IR-TIS - ODP Leg 201 First Thermal Image of Hydrate Sample - Site 1230

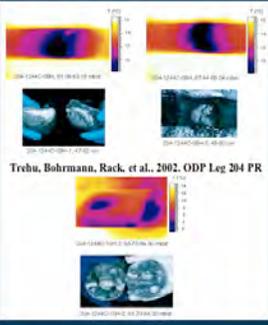




D'Hondt, Jørgensen, Miller, et al., 2002. ODP Leg 201 Prel. Rept.

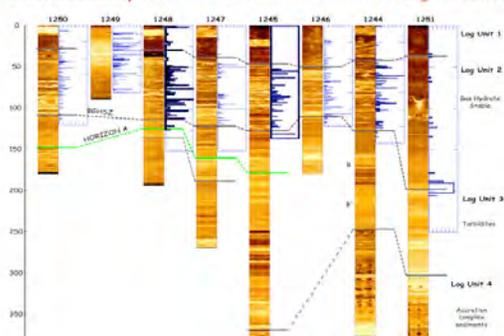
INFRARED THERMAL IMAGING OF CORES TO ASSESS THE DISTRIBUTION OF METHANE HYDRATE: ODP LEG 204 - HYDRATE RIDGE



Trehu, Bohrmann, Rack, et al., 2002. ODP Leg 204 PR

LWD Resistivity Data and Thermal Anomalies at Leg 204 Sites



Trehu, Bohrmann, Rack, et al., 2002. ODP Leg 204 Prel. Rept.

Pressure Coring Tools used on ODP Leg 204

ODP standard tool

- **Pressure Core Sampler (PCS):** 30 out of 39 runs were successful (recovered core under pressure). One PCS core contained 95 liters of methane from a ~1 meter-long core.

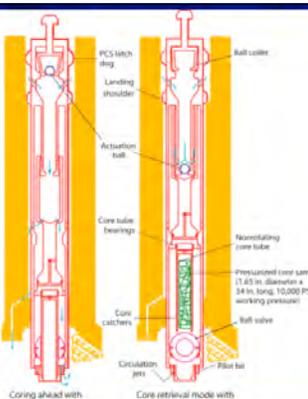
HYACINTH tools (under development)

- **Fugro Pressure Corer (FPC):** 2 out of 10 runs were successful.
- **HYACE Rotary Corer (HRC):** 4 out of 8 runs were successful.

Pressurized cores recovered with the HYACINTH FPC and HRC, were transferred under pressure to a logging chamber, and were logged (gamma density measurements) using a multi-sensor core logger-vertical (MSCL-V) system. One HRC core contained 105 liters of methane from a ~1 meter-long core.

Pressure Core Sampler (PCS)





Coring ahead with ball valve open Core retrieval mode with sample chamber closed

Hydrate Core Samples Preserved in Liquid-Nitrogen at ODP Gulf Coast Repository, College Station, TX

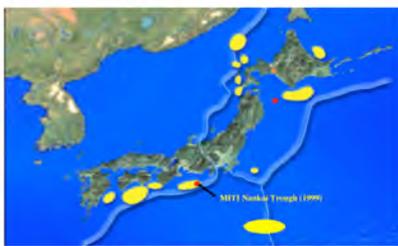


Interdisciplinary Collaborative Expeditions for Years of Hydrate Observation and Perturbation Experiments (ICEY HOPE)

Proposal to use the D/V *JOIDES Resolution* (including shipboard laboratories, sampling, logging and downhole measurement tools) during “windows of opportunity” that occurred when the ship went off contract with ODP/IODP.

Focus on basic research to reduce uncertainties and improve our understanding about the role of natural gas hydrates (e.g., global carbon cycle, climate change, seafloor stability, resource potential, ocean observing systems, time series to examine dynamics of physical and biogeochemical processes).

Potential Methane Hydrate Prospects Offshore Japan



Figures courtesy of Dr. Yasuhiko Ichikawa (Japan National Oil Corporation)



Joint Oceanographic Institutions / Methane Hydrate Research



Integrated Ocean Drilling Program (IODP) (2003 through 2013, and beyond)



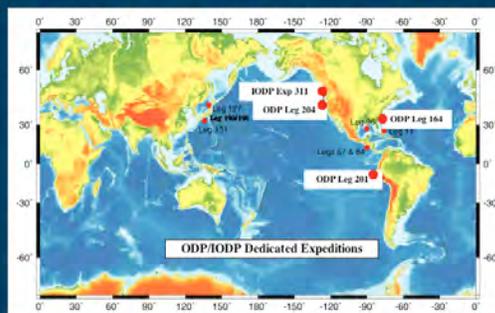
Center for Deep Earth Exploration (CDEX); JAMSTEC

U.S. Implementing Organization (USIO); JOI Alliance

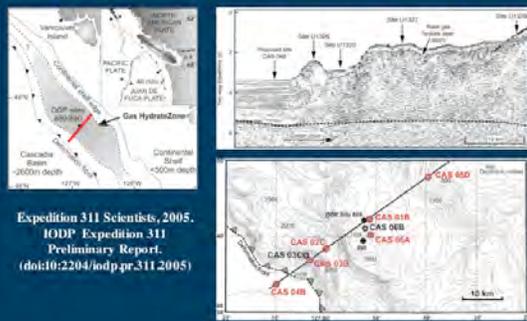
European Consortium for Ocean Research Drilling (ECORD) Science Operator (ESO)

Science Operations Funding from U.S.-NSF, Japan-MEXT, Europe-EMA/ECORD, and China-MOST through IODP Management International (IODP-MI)

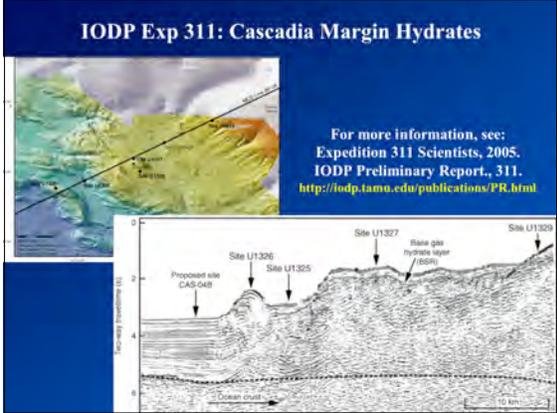
SCIENTIFIC DRILLING FOR METHANE HYDRATE



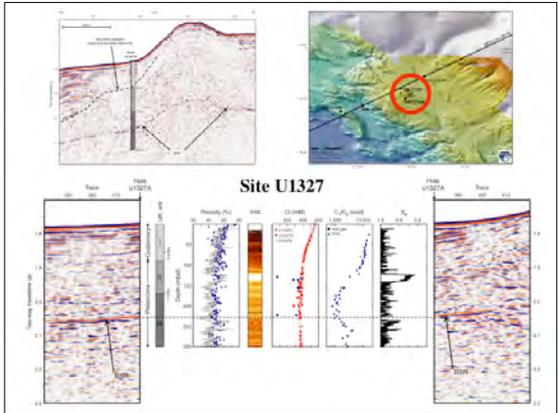
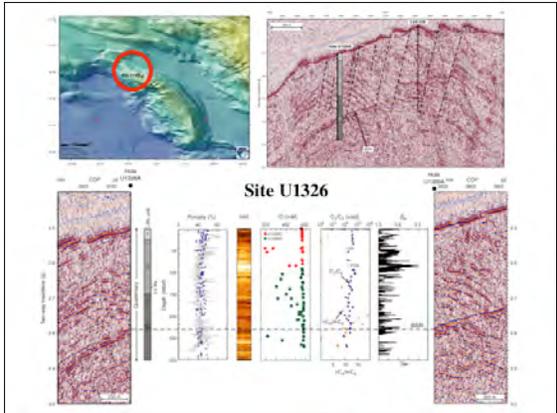
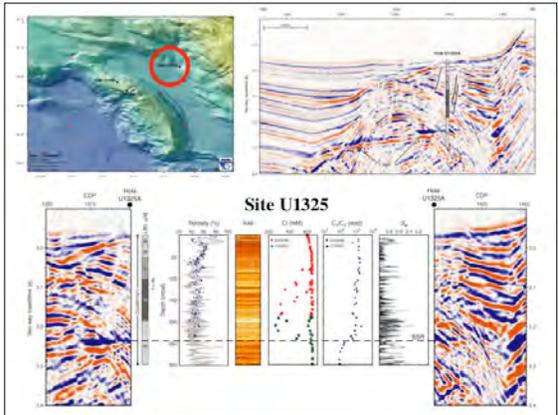
IODP EXPEDITION 311 - CASCADIA MARGIN: THE 2ND METHANE HYDRATE NATURAL LABORATORY

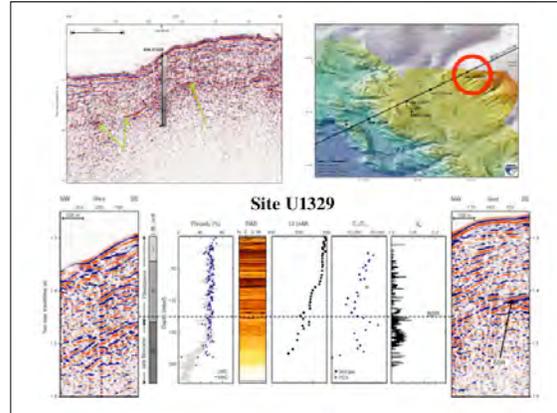
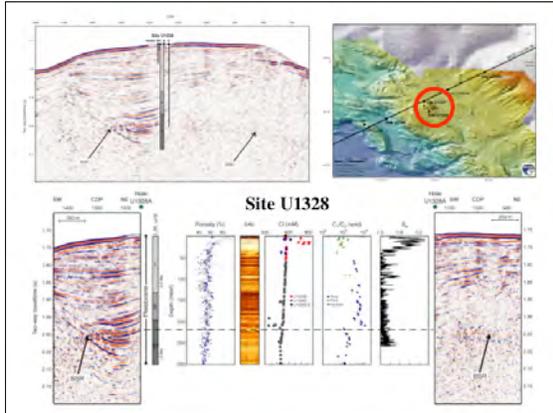


Expedition 311 Scientists, 2005. IODP Expedition 311 Preliminary Report. (doi:10.2204/iodp.pr.311.2005)



- ### IODP Expedition 311 Operational Summary
- Out of 62 days, **37 days (60%)** were spent **operating on site**.
 - Overall, **5 Sites** were drilled/cored, with **23 Holes** and **1218.2 meters of sediment was recovered** (75.4% core recovery) in 223 cores, and another 2810.3 meters were drilled.
 - **Water depths** of sites ranged from **945.5 mbsl to 2201.1 mbsl**.
 - **Penetration depths** varied from **1.5 mbsf to 1209.5 mbsf**.
 - 5 sites were drilled using **LWD/MWD** tools (annular-pressure-while-drilling [APWD], resistivity-at-the-bit [RAB], and NMR).
 - **The transect of sites represent the evolution of gas hydrate across the margin**, from the earliest occurrence on the westernmost accreted ridge (Site U1326) to its final stage at the eastward limit of gas hydrate occurrence (Site U1329).





Pressure Coring Tools used on IODP Exp. 311

IODP standard tool

- **Pressure Core Sampler (PCS):** 16 out of 24 runs were successful (recovered core under pressure); **pressurized cores were logged** using a multi-sensor core logger-vertical (MSCL-V) system.

HYACINTH tools

- **Fugro Pressure Corer (FPC):** 2 out of 9 runs were successful.
- **HYACE Rotary Corer (HRC):** 4 out of 10 runs were successful.

Pressurized cores recovered with the HYACINTH FPC and HRC, were transferred **under pressure** to a logging chamber and were logged (gamma density, p-wave velocity) using a multi-sensor core logger-pressure (MSCL-P) system and an X-ray linear scanner.

Pressure Core Sampler (PCS)

FPC AND HRC PRESSURE CORING SYSTEMS

Images courtesy of Dr. Peter Schultheiss and the HYACINTH Project Partners (EU)

CONTROLLING TEMPERATURE IN PRESSURE CORES USING ICE IMMEDIATELY AFTER RECOVERY

Image courtesy of Drs. Peter Schultheiss and Melanie Holland

**REFRIGERATED CONTAINER VANS USED FOR PCS
PRESSURE CORE LOGGING AND MICROBIAL
SAMPLING: IODP EXPEDITION 311**

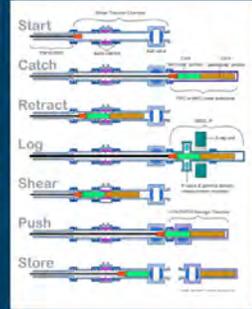


Images courtesy of Brad Julson (IODP-USIO Science Services, TAMU)

**HYACINTH PRESSURE CORE TRANSFER AND
PRESSURE CORE LOGGING PROCESS:
IODP EXPEDITION 311**



Images courtesy of Dr. Peter Schultheiss and the HYACINTH Project Partners (EU)



**X-RAY LINEAR SCANNING OF CORES:
IODP EXPEDITION 311**



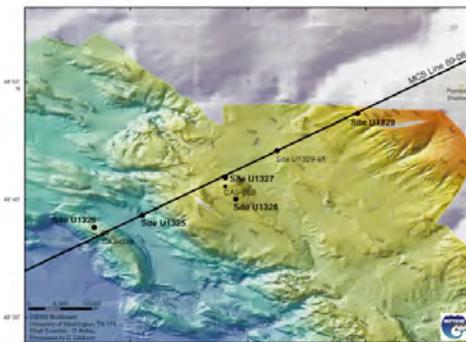
Image courtesy of Dr. Barry Freifeld (LBNL)

**NON-INVASIVE MEASUREMENTS OF PRESSURE
CORES AND GAS SAMPLING IN REFRIGERATED VANS**

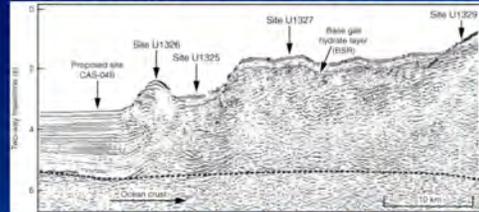


Images courtesy of Drs. Peter Schultheiss and Melanie Holland

IODP Expedition 311 Site Locations

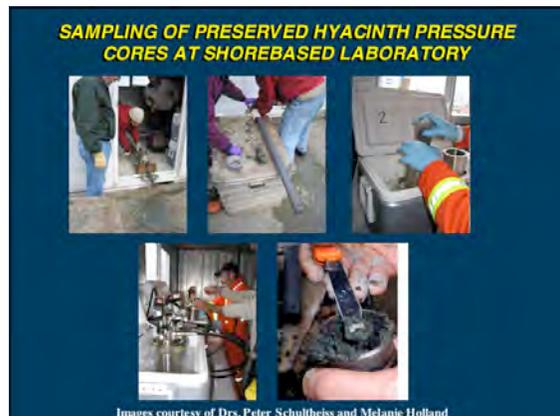
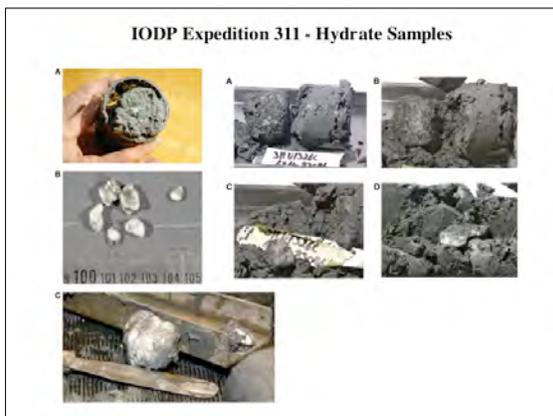
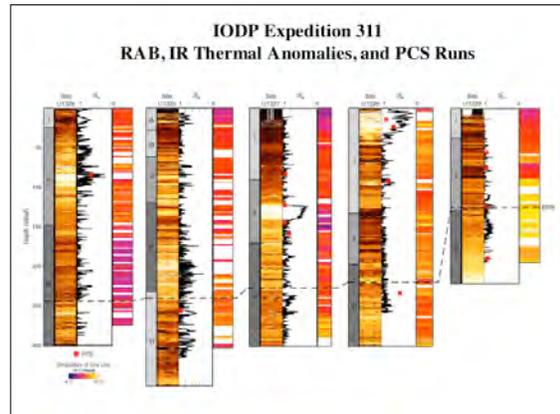
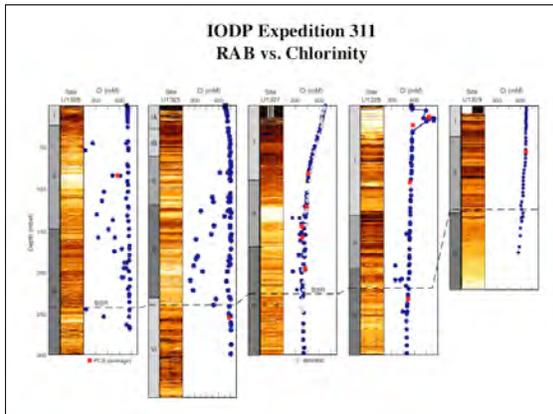


Pressure Coring Results from IODP Expedition 311



Pressure Coring Results (X:T = held pressure X times out of Total # of deployments; average percent recovery for total deployments).

Sites:	U1326	U1325	U1327	U1328	U1329
PCS	1:1; 26%	1:3; 77%	5:8; 86%	5:6; 62%	4:6; 80%
FPC	1:1; 15%	0:2; 9%	1:2; 66%	0:3; 59%	0:1; 100%
HRC	0:1; 0%	0:2; 14%	3:4; 97%	0:2; 0%	1:1; 100%



SUMMARY AND CONCLUSIONS

The outcomes from ODP Legs 201 and 204, and IODP Expedition 311 have demonstrated that the R/V JOIDES Resolution is an ideal platform for characterizing, sampling, and preserving marine methane hydrate using the suite of downhole tools, techniques, and measurement systems that were provided on these expeditions.

Rapid innovation and incorporation of "lessons-learned" was essential to the success of these expeditions. Effective partnerships were demonstrated among engineering and scientific disciplines, which provided solutions to operational and logistical challenges in real-time. Clearly-designated lines of authority and well documented procedures ensured safety at all times, and led to the preservation of high-quality hydrate samples stored in liquid nitrogen and pressure vessels. Experiences are widely shared and contributed to the transfer of knowledge and technology to industry related projects in the Gulf of Mexico, Alaska, offshore Japan and offshore India, among others.

Thank you for listening!

QUESTIONS?

FOR FURTHER INFORMATION:
<http://www.iodp.org>
<http://www.iodp-usio.org>
<http://iodp.tamu.edu/publications/>
http://www-odp.tamu.edu/publications/204_SR/204sr.html

APPENDIX B

LIST OF CURRENT PUBLICATIONS FOR
ODP LEG 204 AND IODP EXPEDITION 311

Leg-Related Citations*

Initial Reports Scientific Results Journals/Books Conferences

Leg 204

Initial Reports volume citation

Tréhu, A.M, Bohrmann, G., Rack, F.R., Torres, M.E., et al., 2003. *Proc. ODP, Init. Repts.*, 204: College Station, TX (Ocean Drilling Program). [doi:10.2973/odp.proc.ir.204.2003](https://doi.org/10.2973/odp.proc.ir.204.2003)

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[Initial Reports](#) [Scientific Results](#) [Journals/Books](#) [Conferences](#)

Scientific Results volume citation

Tréhu, A.M., Bohrmann, G., Torres, M.E., and Colwell, F.S. (Eds.), 2006. *Proc. ODP, Sci. Results*, 204: College Station, TX (Ocean Drilling Program). [doi:10.2973/odp.proc.sr.204.2006](https://doi.org/10.2973/odp.proc.sr.204.2006)

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PROCEEDINGS OF THE INTEGRATED OCEAN DRILLING PROGRAM VOLUME 311



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APPENDIX D

JOI FINAL TECHNICAL REPORT – PHASE 1