

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

TECHNICAL PROGRESS REPORT #4

Type of Report: Quarterly

Reporting Period Start Date: July 1, 2002

Reporting Period End Date: September 30, 2002

Principal Authors: Dr. Frank R. Rack, Dr. Gerhard Bohrmann, Dr.
Anne Trehu, Michael Storms, Derryl Schroeder, and the
ODP Leg 204 Shipboard Scientific Party

Date Report Issued: November 2002

COOPERATIVE AGREEMENT DE-FC26-01NT41329

Frank R. Rack (Joint Oceanographic Institutions; 1755 Massachusetts Ave.,
NW; Suite 700; Washington, DC, 20036; Tel: (202) 232-3900, ext. 216;
Email: frack@joiscience.org);

Gerhard Bohrmann (GEOMAR, Christian-Albrechts Universitat zu Kiel,
Wischhofstrasse 1-3, Gebaude 4, Kiel 24148, Germany)

Anne M. Trehu (College of Oceanic and Atmospheric Sciences, Oregon
State University, Corvallis OR 97331-5503, USA)

Michael Storms and Derryl Schroeder (Ocean Drilling Program; 1000
Discovery Drive; TAMU Research Park; College Station, TX 77845);

ODP Leg 204 Shipboard Scientific Party* (see attached list of participants
provided at the end of this report)

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness or any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily reflect those of the United States Government or any agency thereof.

The international Ocean Drilling Program is managed by Joint Oceanographic Institutions, Inc., under contract with the U.S. National Science Foundation. Funding for the program is provided by the following agencies:

**Australia/Canada/Chinese Taipei/Korea Consortium for Ocean Drilling
Deutsche Forschungsgemeinschaft (Federal Republic of Germany)
Institut National des Sciences de l'Univers-Centre National de la Recherche Scientifique (INSU-CNRS; France)
Ocean Research Institute of the University of Tokyo (Japan)
National Science Foundation (United States)
Natural Environment Research Council (United Kingdom)
European Science Foundation Consortium for Ocean Drilling (Belgium, Denmark, Finland, Iceland, Ireland, Italy, The Netherlands, Norway, Portugal, Spain, Sweden, and Switzerland)
Marine High-Technology Bureau of the State Science and Technology Commissions of the People's Republic of China**

Any opinions, findings, and conclusions or recommendations expressed in this report are those of the author(s) and do not necessarily reflect the views of the National Science Foundation, the participating agencies, Joint Oceanographic Institutions, Inc., Texas A&M University, or Texas A&M Research Foundation.

ABSTRACT

The primary accomplishment of the JOI Cooperative Agreement with DOE/NETL in this quarter was the deployment of tools and measurement systems on ODP Leg 204 to study hydrate deposits on Hydrate Ridge, offshore Oregon from July through September, 2002.

During Leg 204, we cored and logged 9 sites on the Oregon continental margin to determine the distribution and concentration of gas hydrates in an accretionary ridge and adjacent slope basin, investigate the mechanisms that transport methane and other gases into the gas hydrate stability zone (GHSZ), and obtain constraints on physical properties of hydrates in situ. A 3D seismic survey conducted in 2000 provided images of potential subsurface fluid conduits and indicated the position of the GHSZ throughout the survey region. After coring the first site, we acquired Logging-While-Drilling (LWD) data at all but one site to provide an overview of downhole physical properties. The LWD data confirmed the general position of key seismic stratigraphic horizons and yielded an initial estimate of hydrate concentration through the proxy of in situ electrical resistivity. These records proved to be of great value in planning subsequent coring. The second new hydrate proxy to be tested was infrared thermal imaging of cores on the catwalk as rapidly as possible after retrieval. The thermal images were used to identify hydrate samples and to map estimate the distribution and texture of hydrate within the cores. Geochemical analyses of interstitial waters and of headspace and void gases provide additional information on the distribution and concentration of hydrate within the stability zone, the origin and pathway of fluids into and through the GHSZ, and the rates at which the process of gas hydrate formation is occurring. Bio- and lithostratigraphic description of cores, measurement of physical properties, and in situ pressure core sampling and thermal measurements complement the data set, providing ground-truth tests of inferred physical and sedimentological properties.

Among the most interesting preliminary results are: 1) the discovery that gas hydrates are distributed through a broad depth range within the GHSZ and that different physical and chemical proxies for hydrate distribution and concentration give generally consistent results; 2) evidence for the importance of sediment properties for controlling the migration of fluids in the accretionary complex; 3) geochemical indications that the gas hydrate system at Hydrate Ridge contains significant concentrations of higher order hydrocarbons and that fractionation and mixing signals will provide important constraints on gas hydrate dynamics; and 4) the discovery of very high chlorinity values that extend for at least 10 mbsf near the summit, indicating that hydrate formation here must be very rapid.

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

TABLE OF CONTENTS

Disclaimer	2
Abstract	3
Table of Contents	4
Introduction	5
Executive Summary	6
Experimental	8
Results and Discussion	17
Conclusion	32
References	34
List of Acronyms and Abbreviations	36
List of ODP Leg 204 Shipboard Scientific Party Members	37

INTRODUCTION

DOE/NETL funding was used by JOI/ODP to upgrade or modify many of the existing downhole tools onboard the D/V JOIDES *Resolution* so that they could be used to better characterize methane hydrates on ODP Leg 204, on Hydrate Ridge.

During ODP Leg 204, several newly modified downhole tools were deployed to better characterize the subsurface lithologies and environments hosting microbial populations and gas hydrates. Methane hydrates were sampled in cores recovered from several sites drilled during the cruise and routine use of an infrared thermal imaging system confirmed the validity of this method for locating hydrate recovered in cores from the identification of their thermal anomaly.

The ODP Pressure Core System (PCS) was deployed 39 times during ODP Leg 204 and successfully retrieved cores from a broad range of sediment depths along Hydrate Ridge. The PCS gas manifold was used in conjunction with the PCS throughout ODP Leg 204 to measure the total volume and composition of gases recovered in sediment cores, many of which contained methane hydrate.

Solid pieces of gas hydrate were recovered from many discrete intervals during the leg. Infrared camera core temperature measurements as well as chemical and physical property data suggest the occurrence of gas hydrate above the GHSZ.

The HYACE/HYACINTH Fugro Pressure Corer (FPC) and HYACE Rotary Corer (HRC) were deployed 8 times and 10 times respectively on ODP Leg 204 with demonstrated success in recovering pressurized cores and logging them under pressure using a GEOTEK vertical multi-sensor core logger. Much was learned about the operation of these tools with shipboard systems on the D/V JOIDES *Resolution*.

The DVTP, DVTP-P, APC-methane, and APC-Temperature tools (ODP memory tools) were used extensively and successfully during ODP Leg 204 aboard the D/V JOIDES *Resolution*. These systems provided a strong operational capability for characterizing the in situ properties of methane hydrates in subsurface environments on Hydrate Ridge during ODP Leg 204.

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

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

EXECUTIVE SUMMARY

The primary accomplishments of the JOI Cooperative Agreement with DOE/NETL in this quarter was the deployment of tools and measurement systems for use on ODP Leg 204, which studied hydrate deposits on Hydrate Ridge, offshore Oregon.

An automated track-mounted infrared-thermal imaging system (IR-TIS) was deployed for the first time on ODP Leg 204. This system was used to identify methane hydrate intervals in the recovered cores. The initial results of these experiments are presented in this report.

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

The PCS was deployed 39 times during ODP Leg 204 and successfully retrieved cores from a broad range of sediment depths along Hydrate Ridge on the Oregon margin. The PCS gas manifold was used in conjunction with the Pressure Core Sampler (PCS) throughout ODP Leg 204 to measure the total volume and composition of gases recovered in sediment cores associated with methane hydrates.

The FUGRO Pressure Corer (FPC) and HYACE Rotary Corer (HRC), two of the HYACE/HYACINTH pressure coring tools, were also deployed on the D/V JOIDES *Resolution* during ODP Legs 204 to field-test these coring systems at several sites located offshore Oregon. The field-testing of these tools provides a corollary benefit to DOE/NETL at no cost to this project. The testing of these tools on the D/V JOIDES *Resolution* was negotiated as part of a cooperative agreement between JOI/ODP and the HYACINTH partners.

The DVTP, DVTP-P, APC-methane, and APC-Temperature tools (ODP memory tools) were used extensively during ODP Leg 204. The data obtained from the successful deployments of these tools is still being evaluated by the scientists and engineers involved in this testing; however, preliminary results will be presented in this report.

Two core logging chambers (ODP-LC) that were fabricated for use on ODP Leg 204. These chambers were able to accept standard ODP APC/XCB core sections in their existing core liners and allowed them to be re-pressurized and logged to collect gamma ray attenuation (bulk density) and compressional-wave acoustic velocity measurements. These measurements were made using a vertical multi-sensor (pressure) core logging (MSCL-V) system that was deployed on Leg 204. These chambers allowed physical properties data to be collected on hydrate cores recovered using conventional coring

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

techniques and re-pressurized. These data will be compared with similar properties measured on cores recovered at in-situ pressures by the HYACINTH corers to evaluate the similarities and/or differences among data collected using these two approaches.

Leg 204 scientists and LDEO logging engineers defined the specifics of LWD and VSP experiments planned for ODP Leg 204 (Task 5.0). Tool modifications were made to create a LWD Resistivity-at-the-Bit with Coring (RAB-C) tool, which was deployed on ODP Leg 204. This tool resulted from the integration of the ODP motor-driven core barrel (MDCB) inner core tube with the Schlumberger/Anadrill RAB landing sub.

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

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

This report will present an overview of the preliminary results obtained from tool and instrument deployments on ODP Leg 204, as well as providing a brief discussion of the laboratory analyses of the recovered cores.

EXPERIMENTAL

INTRODUCTION

Gas hydrate is an ice-like substance that contains methane or other low molecular weight gases in a lattice of water molecules. Methane hydrates are stable under the temperature and pressure conditions generally found in the Arctic and near the seafloor at water depths greater than 500 m. They are quite common beneath the slope of both active and passive continental margins, where methane originates from the decomposition of organic matter. International interest in this material has increased considerably in the past several years because of increasing recognition that the large volumes of gas stored in these structures represent a significant fraction of the global methane budget and may therefore be a potential energy resource for the future (see review by Kvenvolden and Lorenson, 2001). Several authors have also suggested that sudden, widespread dissociation of subseafloor gas hydrates in response to changing environmental conditions may have had a significant effect on past climate (eg. Revelle, 1983; Nisbet, 1990; Paull et al., 1991; Katz et al., 1999; Dickens, 2001). These effects remain speculative, as the volume of gas stored in the gas hydrate reservoir and its behavior during changing environmental conditions are currently poorly constrained.

In order to evaluate the economic potential of hydrates, their role as a natural hazard, and their impact on climate, we need to know:

- How are hydrates and underlying free gas distributed vertically and horizontally in the sediment?
- What controls their distribution (i.e. the sources of gas, fluid migration, and the physical chemistry of hydrate formation)?
- What are the effects of this distribution on the mechanical properties of the seafloor?
- How can hydrate and gas distribution be mapped regionally using remote sensing geophysical techniques?
- How does hydrate respond to changes in pressure and temperature resulting from tectonic and oceanographic perturbation?
- How can we use the isotopic record as a proxy for past tectonic and climate changes?
- Does the hydrate system harbor a rich biosphere? This question is of broad interest, particularly given the recent recognition that the biosphere extends deeper into the earth and that it has a larger impact on the geologic record than previously thought.

ODP has a critical role to play in addressing the above questions because it provides the only means available to the international academic community of directly sampling gas hydrates and underlying sediments beneath the oceans. Hydrates have been sampled during several ODP cruises. Leg 164 to the Blake Ridge was the first (and, prior to Leg

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

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

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

Drilling results to date also suggest that there are other factors controlling the depth to which gas hydrates are stable in addition to temperature, pressure and methane solubility (e.g. Ruppel, 1997) and that hydrate may persist in a metastable state outside the stability field (Guerrin et al., 1999; Buffett and Zatsepina, 1999). To address these outstanding issues, we had frequent deployments of tools to measure in situ temperature and pressure, especially in zones where logging-while-drilling (LWD) data indicated rapid changes in the physical properties of the sediments.

Because of the recognition that estimation of hydrate and free gas concentrations using geophysical remote sensing techniques is more complicated than previously thought (e.g. MacKay et al., 1994; Holbrook et al., 1996), we also conducted an extensive suite of downhole and two-ship seismic experiments.

Geological and Geophysical Setting

Hydrate Ridge is a 25 km long and 15 km wide ridge in the Cascadia accretionary complex, formed as the Juan de Fuca plate subducts obliquely beneath North America at a rate of about 4.5 cm/yr. Sediment on the subducting plate contains large volumes of sandy and silty turbidites. At present, most of this sediment is accreted to the continental margin, either by offscraping at the deformation front or by underplating beneath the accretionary complex some 10s of kilometers east of the deformation front (MacKay et al., 1992; MacKay, 1995).

Hydrate Ridge has been the site of many geological and geophysical cruises since cold seeps were first discovered on this part of the margin nearly 20 years ago (Kulm et al.,

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

1986). Hydrate Ridge is characterized by a northern peak having a minimum water depth of about 600 m, and a southern peak with a water depth of about 800 m. Hydrate Ridge appears to be capped by hydrate, as indicated by a nearly ubiquitous and strong BSR (Trehu et al., 1999).

A regional 2-D multichannel seismic survey was acquired in 1989 as a site survey for ODP Leg 146, which was designed primarily to study dynamics of fluid flow in accretionary complexes. The location where an upward deflection of the BSR is cut by a fault on the northern summit of Hydrate ridge was selected for ODP Site 892 (ODP Leg 146 Scientific Party, 1993). At this site, massive H₂S-rich hydrates were recovered from 2-19 mbsf (Kastner et al., 1995). No hydrate was recovered from near the BSR, but geochemical pore water and temperature anomalies suggested the presence of disseminated hydrate in the pore space to 68 mbsf (Kastner et al., 1995; Hovland et al., 1995). Vertical seismic profiles (VSP) indicated the presence of free gas for at least 20 m beneath the gas hydrate stability zone (MacKay et al., 1994). Trehu and Flueh (2001) argue, based on seismic velocities and attenuation, that free gas is present for 500-600 m beneath the BSR at Site 892. Methane at Site 892 is primarily of biogenic origin (Kvenvolden, 1995), but higher order hydrocarbons of thermogenic origin are also present (Hovland et al., 1995; Schluter et al., 1998).

Since 1996, there have been several cruises/year, which have generated an extensive database of swath bathymetry, deep-towed sidescan, and seafloor observations and samples collected via submersible and remotely operated vehicle (Suess and Bohrmann, 1997; Torres et al., 1998, 1999; Bohrmann et al., 2000; Linke and Suess, 2001). In addition, a high-resolution 3-D seismic survey was conducted in 2000 as a site survey for Leg 204 (Trehu and Bangs, 2001; Trehu et al., 2002). Those data provide a framework for interpreting the Leg 204 results.

Seafloor Observations of Southern Hydrate Ridge

Sidescan data, seafloor camera tows, and diving with manned and remotely operated submersibles demonstrated the presence of extensive massive carbonate pavement on the northern summit of Hydrate Ridge (Carson et al., 1994; Clague et al., 2001, Sample and Kopf, 1995; Bohrmann et al., 1998; Greinert et al., 2001). Until recently, massive authigenic carbonate pavement was thought to be absent on the southern summit of Hydrate Ridge. During Alvin dives in 1999, however, a 50 m high carbonate "pinnacle" was discovered 250 m southwest of the summit (Torres et al., 1999). Deep-towed sidescan data indicate that the pinnacle is located in the center of a buried carbonate apron with a diameter of ~250 meters. Authigenic carbonates on the Cascadia margin form from methane oxidation within the sediments and discharge of isotopically light dissolved inorganic carbon at seafloor. The relative absence of carbonate on the southern summit of Hydrate Ridge was interpreted to indicate that this hydrate/gas system is younger than that on the northern summit, providing a spatial proxy for temporal evolution of hydrate-bearing accretionary ridges (Trehu et al., 1999). This interpretation

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

is supported by U-Th dating of recovered carbonates (Teichert et al., 2001), which indicates that the pinnacle is <12,000 years old whereas the carbonate carapace on northern Hydrate Ridge is > 100,000 years old.

One especially interesting feature of southern Hydrate Ridge is the abundance of massive hydrate at the seafloor near its summit. This was first discovered in 1996, when over 50 kg of massive hydrate were recovered in a TV-guided grab sample (Bohrmann et al., 1998). The samples show dense interfingering of gas hydrate with soft sediment. In most cases, pure white hydrate occurs in layers several millimeters to several centimeters thick. Host sediment is often present as small clasts within the pure gas hydrate matrix. On a macroscopic scale, the fabric varies from highly porous (with pores of up to 5 cm in diameter) to massive (Suess et al., 2001). Thin sections show a structure in which gas bubbles have been filled with hydrate. Wet bulk densities of 80 hydrate samples measured on board R/V Sonne range from 0.35 g/cm³ to 7.5 g/cm³. Pore space was estimated from the change in sample volume before and after compression to approximately 160 bar (Bohrmann et al., 2002). The samples show high variability in pore volumes ranging from 10-70 vol.%, and the values are negatively correlated with sample density. From this correlation, the end-member density at zero porosity was estimated to be ~0.81 g/cm³. This value is lower than the theoretical density of pure methane hydrate (0.91 g/cm³). Field-emission scanning electron microscopy indicates that this is due to submicron porosity of the massive hydrate (Techmer et al. 2001).

The low bulk density of the natural methane hydrates from Hydrate Ridge results in a strong positive buoyancy force, implying that the hydrate remains on the seafloor only because of the shear strength of the host sediment. Unusual seafloor topography observed on southern Hydrate Ridge during ALVIN and ROPOS surveys, which is characterized by mounds and depressions with a wavelength of a few meters, may result from spontaneous breaking off of hydrate from the seafloor. This may be an important mechanism for transporting methane from the seafloor to the atmosphere.

Vigorous streams of methane bubbles have been observed emanating from vents on the seafloor on the northern and southern peaks of Hydrate Ridge (Suess and Bohrmann, 1997; Suess et al., 1999; Torres et al., 1998, 1999) as well as from a similar, but smaller, reflective high in the accretionary complex known as SE Knoll. Because the seafloor at all three sites is well within the hydrate stability zone, the presence of methane bubbles beneath and at the seafloor suggests rapid transport of methane to the seafloor from sediments beneath the hydrate stability zone. Because seawater is undersaturated in methane, their persistence in the water column suggests that they are protected by a thin coating of hydrate (Suess et al., 2001). Disappearance of the acoustic "bubble" plumes at 450-500 m below the sea surface (near the top of the hydrate stability zone) suggests that the hydrate shell dissociates and that most of the methane in the bubble plumes is dissolved in the ocean rather than reaching the atmosphere.

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

Biological communities associated with hydrate and geochemical implications

Communities of tube worms, bacterial mats, clams and other fauna are associated with seafloor hydrates and methane vents on Hydrate Ridge and elsewhere (e.g. Kulm et al., 1986; MacDonald et al., 1989; Suess et al., 1999, 2001; Sassen et al., 2001). Micro-organisms are at the base of the food chain in these communities. Recent work suggests the complex complementary relationships between sulfate reducing, methanogenic, and methanotrophic micro-organisms in hydrate-bearing sediments (e.g. Parkes et al., 2000; Boetius et al., 2000). These micro-organisms must be playing an important role in methane formation and oxidation and are therefore a critical component of the hydrate system. Identification of these organisms and determination of their abundances, spatial variability and rates of activities is just beginning.

Particularly interesting are recently discovered organisms that play a critical role in anaerobic methane oxidation (AMO), which is the process forming the carbonates that remain in the geologic and record of the history of past fluid flow and hydrate formation and dissociation (eg. Sample and Kopf, 1995; Bohrmann et al., 1998; Greinert et al., 2001). Very high rates of AMO have been measured in sediment overlying massive gas hydrates on southern Hydrate Ridge (Boetius et al., 2000), and attributed to structured aggregates consisting of a central cluster of methanotropic archaea coated by sulfate reducing bacteria. That microbes oxidize methane by utilizing sulfate in the absence of oxygen was long suspected by geochemists, based on interstitial sulfate and methane gradients. Borowski et al. (1996) showed that steep sulfate gradients and shallow depths to the sulfate-methane interface are a consequence of the increased influence of AMO, and Boetius et al. (2000) were the first to observe the microorganisms that presumably catalyze anaerobic methane oxidation. These bacterial aggregates appear to be abundant in sediments of Hydrate Ridge and mediate AMO when enough sulfate is available.

Analysis of sulfide minerals provides a possible opportunity to reconstruct past biological activity because most of the reduced sulfide produced during bacterial sulfate reduction in non-hydrate-bearing sediments is ultimately sequestered in various iron phases, which usually involve multiple steps terminating in the formation of sedimentary pyrite. In the Cascadia margin, the sequestering of sulfide into the clathrate structure (e.g. Kastner et al., 1995, Bohrmann et al., 1998) essentially removes it from further reaction with ferrous iron complexation. There is a wealth of information on the significance of iron-sulfide interactions within marine sediments (e.g. Berner, 1970, and many others). The burial of this mineral phase contributes significantly to the oxygen level of the atmosphere, the sulfate concentration in seawater, and the pH of the oceans over geologic time scales (e.g. Garrels and Perry, 1974; Holland, 1978; Boudreau and Canfield, 1993). Another significant effect of H₂S sequestering by hydrates is the development of anomalous intervals of high greigite content at the intervals in which gas hydrates were recovered or were inferred to exist (Housen and Musgrave, 1996). Based on the rock magnetic properties at Site 889, Housen and Musgrave (1996) identified the presence of a "fossil gas hydrate zone" which extended downwards to 295 mbsf during the last glaciation.

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

High-resolution 3-D seismic data

Two 2-D multichannel seismic profiles acquired in 1989 across southern Hydrate Ridge suggested a complicated subsurface plumbing system related to the presence of hydrate and free gas. Prior to a 3-D high-resolution seismic survey in 2000 (Trehu and Bangs, 2001), the relationship between subsurface reflections and the summit vents was not known because no profiles crossed the summit. The 3-D survey comprised 81 profiles spaced 50 meters apart and covered the southern summit of Hydrate Ridge and the western edge of the adjacent slope basin. Shots from 2 GI guns fired simultaneously were recorded on the Lamont portable 600-m-long, 48-channel towed streamer and on an array of 21 UTIG 4-component ocean bottom seismometers. The locations of the ship and of the streamer were determined via differential GPS and four compasses, respectively, and 3-D fold was monitored during the cruise to identify locations where additional data were needed. Excellent data quality was obtained in spite of strong winds and high seas. The data contain frequencies up to ~250 Hz, providing considerable stratigraphic and structural resolution.

SCIENTIFIC OBJECTIVES

Stratigraphic and structural controls on hydrate development:

The structural and stratigraphic setting of Hydrate Ridge contrasts with that of the adjacent slope basin to the east. Beneath the slope basin, the seismic signature of the hydrate is quite similar to that on the Blake Ridge, with an intermittent BSR and enhancement of stratigraphic reflectivity beneath the BSR (Holbrook et al., 1996). Sedimentation rate in this basin is likely very rapid, based on radiocarbon dating of a core in a neighboring basin just north of Hydrate Ridge (Karlin, 1984), which indicates a sedimentation rate of 120 cm/1000 yr. Sediments in that core are siliceous hemipelagic ooze with calcareous microfossils, and similarity in high frequency energy penetration between the two basins suggests a similar sediment composition. Because of this expected high sedimentation rate and high carbon content in the sediments, we suspect that the source of methane in this setting will be dominantly local, with little or no contribution from subducted sediments. In contrast, fluids migrating upward from underthrust sediments may be a significant source of methane for hydrate beneath Hydrate Ridge (Hyndman and Davis, 1992). Leg 204 tested the hypothesis that the distribution, texture, and chemistry of hydrate and related pore fluids beneath Hydrate Ridge differ from those the slope basin.

Formation of massive hydrate near the seafloor:

The presence of massive hydrate near the seafloor is enigmatic, as most models for hydrate formation in a region of diffuse fluid flow predict a decreasing gradient in hydrate concentration above the BSR (eg. Paull et al., 1994; Rempel and Buffett, 1998;

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

Xu and Ruppel, 1999). Several explanations have been proposed, including formation in the past when the stability boundary was near the seafloor, formation at depth and exposure by erosion (Bohrmann et al., 1998), and transport of methane through the hydrate stability field as free gas isolated from water (Suess et al., 2001). The third explanation is most likely given the observations of vigorous plumes of bubbles at the seafloor and in the water column where the massive hydrates are observed. One objective of Leg 204 was to obtain insight into the mechanisms whereby the gas is isolated from water, thus delaying hydrate formation as it passes through the stability field. In addition, drilling through these massive hydrate deposits provided new constraints on their extent, texture, structural setting, and the chemistry of interstitial waters.

Impact on the geochemical and geological record:

Geochemical consequences of hydrate formation and destabilization include: modification of the isotopic composition of the water in pore fluids; changes in the isotopic composition of the dissolved carbonate species, which is incorporated into carbonate phases; and sequestering of the in situ generated H_2S into the hydrate structure. Isotopic composition of carbonate cements recovered by drilling during Leg 146 were used by Sample and Kopf (1995) to infer the history of fluid flow in this margin as well as the depth of the source of the carbon reservoirs. Bohrmann et al. (1998) have suggested that the stability of the massive gas hydrate deposits on the southern summit of Hydrate Ridge has changed with time, and that carbonate phases associated with the hydrates can be used to document the changes. Benthic foraminifers might also record this decrease in $\delta^{13}C$, and thus the isotopic signal might reveal episodes of CH_4 venting in the past (Wefer and al., 1994; Dickens et al., 1995, 1997; Kennett et al., 1996). One objective of Leg 204 was to determine the isotopic composition of the pore fluids and carbonates associated with hydrate to provide the framework needed to unravel the history of hydrate formation and destabilization recorded in benthic foraminifera and authigenic carbonate phases elsewhere.

Calibration of geophysical estimates of hydrate and gas volumes:

Better calibration of regional estimates of hydrate and free gas volumes based on geophysical mapping and modeling techniques is of critical importance towards estimating the global abundance of hydrate and evaluating their role in climate change and potential for economic exploitation. Recent experience during Legs 146 and 164 has underlined the complexity of this issue. During Leg 204, we drilled through hydrates in a variety of settings with different seismic characteristics and measured the physical properties of the hydrate stability and underlying free gas zones with temperature and pressure probes and through downhole logging and a series of nested seismic experiments, thus providing data to calibrate various techniques for remote sensing of hydrate distribution and concentration.

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

Hydrates and slope stability:

The possible relationship between hydrates and slope failure is presently poorly understood. On the one hand, hydrates may stabilize slopes by cementing sediment grains. On the other hand, if hydrates impede fluid flow, they may weaken the underlying sediment by trapping fluids and free gas. There may be a feedback between these two processes such that the presence of hydrate initially delays slumping, leading to less frequent but larger episodes. Several investigators have noted the possible correlation of hydrates and slope instability (e.g. Booth et al., 1994; Trehu et al., 1995; Paull et al., 1996) and have discussed how such slope instability might release massive amounts of methane into the ocean (Paull et al., 1996; Nisbet and Piper, 1998). One objective of Leg 204 was to determine the mechanical and hydrological properties of hydrate-bearing sediment to better constrain models of slope instability.

Biological communities associated with hydrate and underlying free gas zones:

Micro-organisms playing an important role in both methane formation and oxidation and are therefore a critical component of the hydrate system. Identification of these organisms and determination of their abundances, spatial variability and rates of activities is just beginning. Important questions addressed during Leg 204 included: What impact do these organisms have on the volume of methane produced and oxidized beneath Hydrate Ridge? At what depths are they concentrated? What effect do they have on sediment diagenesis and the development of magnetic minerals? Does the hydrate-related biosphere differ between Hydrate Ridge and the adjacent slope basin? How do microorganisms affect sediment and porewater chemistry and texture, and vice-versa?

DRILLING STRATEGY

To test the hypotheses discussed above, we originally proposed three primary drill sites, extending to depths of 400-700m. Preliminary analysis of the 3-D seismic data confirmed the rationale behind these three sites but led to minor modifications of site locations. It also led to addition of 6 shallow-penetration (<250 m) sites to sample the massive hydrate at the summit and to determine updip changes along subsurface horizons that appeared to be fluid pathways feeding the summit vents. Three of these additional sites were primary sites and three were alternates; all were approved for drilling by PPSP.

The Leg started with a mini-leg dedicated to logging while drilling (LWD). For safety reasons, Site 1a was cored to 350 m depth prior to LWD, thus sampling all seismic facies that were to be drilled. We had approval from PPSP to proceed with LWD at all sites or until the time allocated to LWD was expended if no safety issues were encountered at this site. Our objective was to use the LWD data to determine where to use time consuming special downhole tools prior to coring.

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

Another novel aspect of this Leg use of infrared thermal imaging to systematically scan each core (at least those from within and near the hydrate stability zone) immediately as it was brought on board. Because hydrate dissociation is a strongly endothermic process, cold spots thus detected permitted us to quickly confirm which portions of the core contained massive and disseminated hydrate. Experiments were designed to determine whether the original amount of hydrate present could be determined based on the change in temperature with time.

RESULTS AND DISCUSSION

Site Summary, ODP Site 1244

Introduction:

Site 1244 (proposed site HR1a) is located in 890 meters of water on the eastern flank of Hydrate Ridge ~3 km NE of the southern summit. The 3-D seismic data available from a Leg 204 Site Survey show that the Bottom-Simulating Reflection (BSR), a reflection that cuts across stratigraphic horizons and is generally thought to indicate the presence of free gas at the base of the gas hydrate stability zone (GHSZ), is at a depth of ~125 mbsf at this site. The temperature and pressure at the seafloor at this site are well within the GHSZ, indicating that gas hydrates can exist within the entire stratigraphic section above the BSR if hydrate-forming gases are available in concentrations that exceed their in situ solubility. The 3-D seismic data also indicate that the top of a zone of incoherent seismic reflections that forms the core of Hydrate Ridge is located at a depth of ~300 mbsf at Site 1244. This facies has been interpreted to comprise fractured accretionary complex material. Dipping, faulted, and strongly reflective strata interpreted to be an uplifted and deformed slope basin overlie this facies. An unconformity at ~40 mbsf at this site is correlated with an unconformity observed at 130 mbsf at Site 1251.

The primary drilling objectives at this site were to: (1) determine the distribution and concentrations of gas hydrate within the gas hydrate stability zone; (2) determine the nature of a pair of strong reflections (referred to as B and B') that underlies much of the eastern flank of Hydrate Ridge; (3) determine the composition, structure and fluid regime within the seismically incoherent unit underlying the stratified sediments; and (4) sample the subsurface biosphere associated with these features.

Operations:

Three holes were cored at Site 1244. Hole 1244A was abandoned when the first core overshot and did not record a mudline. Hole 1244B was abandoned at 53.1 mbsf after 6 cores were obtained because the BHA had to be brought to the surface to retrieve a downhole instrument (Fugro piezoprobe) that had become unscrewed from the Schlumberger conductor cable. One APCT measurement was taken at 35.1 mbsf in this hole. Hole 1244C, which comprises 39 cores, began at the seafloor and continued to 333.5 mbsf. Special tools in Hole 1244C included 3 APCT (at 62.5, 81.5 and 110.0 mbsf), 1 DVTP (63.5 mbsf), 1 DVTP-P (150.2 mbsf) and 3 PCS (120, 131, and 142 mbsf) runs. Hole 1244C was abandoned 16.5 m above the target depth of 350 mbsf when hole conditions suggested that a change from XCB to RCB coring would be appropriate. Examination of the core and the initial chemical data from this depth suggested we had reached the deepest target (i.e. the accretionary complex). We thus had fulfilled the PPSP requirement that we core the primary facies that we expected to encounter during Logging While Drilling (LWD) prior to proceeding with LWD at all sites. In addition to

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

resulting in a more efficient and cost-effective cruise plan, acquiring LWD at all sites at the beginning of the Leg enabled us to use the LWD data in concert with the 3-D seismic data to anticipate the nature of horizons prior to drilling and better plan the use of special tools for the rest of the Leg.

Principal Scientific Results:

On the basis of visual observations, smear slides, and correlation with physical property data (especially magnetic susceptibility), the sedimentary sequence can be divided into three primary lithostratigraphic units, with 3 subdivisions in the second unit. Lithostratigraphic Unit I (from the seafloor to 69 mbsf) and Unit II (69-245 mbsf) are both characterized by hemipelagic clay interlayered with turbidites, with thicker, coarser turbidites common in Unit II. Individual turbidites are characterized by sand and silt layers that fine upwards to bioturbated, sulfide-rich silty clay and clay. The turbidites are particularly well developed in the interval from 160-230 mbsf. A 60-cm-thick layer at 216 mbsf that is especially rich in detrital ash shards corresponds to a strong, regional seismic reflection referred to here as reflection B'. The lithology changes to more indurated and fractured claystone interbedded with glauconite-bearing to glauconite-rich silts and sands below 245 mbsf, corresponding to the top of the seismically incoherent zone that we tentatively attribute to the accretionary complex.

Biogenic components vary downcore, with siliceous microfossils dominating. Biostratigraphic boundaries based on diatoms correlate well with lithostratigraphic unit boundaries and with seismic stratigraphic boundaries identified in the 3-D seismic data. Sediments overlying a regional unconformity at ~45 mbsf (approximately the boundary between lithostratigraphic Units I and II) yield diatoms that define a biostratigraphic age of 0.3 Ma. This unconformity is also sampled at Site 1255 at 130 mbsf. Lithostratigraphic Unit III has an age of 2.4-2.7 Ma.

Physical properties data are generally consistent with the lithostratigraphic, biostratigraphic and seismic stratigraphic boundaries. The boundary between lithostratigraphic Units I and II is marked by a localized decrease in wet bulk density. As mentioned in the previous paragraph, the turbidites of lithostratigraphic Unit II are particularly well developed in the interval from 160-230 mbsf. This interval is characterized by high values of whole-core magnetic susceptibility. The widest and strongest magnetic susceptibility peak, at 168 mbsf, correlates with seismic reflection Horizon B. This horizon is also coincident with an increase in wet bulk density. We also note excellent correlation between moisture and density (MAD) measurements on core samples with measurements of density and porosity obtained via LWD.

One novel aspect of Leg 204 is the regular use of both hand-held and track-mounted infrared (IR) cameras to image all cores. Cores from within the GHSZ were imaged several times by the physical properties scientists. The hand-held IR camera proved to be very effective for rapid identification of the location of hydrate specimens within the

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

cores. Gas hydrate samples were recovered as whole rounds in Cores 1244C-8H and 1244C-10H (samples from 63, 68 and 84 mbsf) and preserved detailed shore-based studies. A few pieces were dissociated for chemical analysis (discussed below). In all three cases, the hydrate occurred as layers or nodules several mm to 1.5 cm thick aligned at an angle of 45-60° to the core liner, suggesting formation along steeply dipping fractures.

The track-mounted IR camera imaged the cores systematically, and these records were used to confirm hydrate occurrences spotted by the hand-held cameras, to develop techniques for detecting more subtle signatures of disseminated hydrate, and to track the temporal evolution of the thermal signature of hydrate dissociation. The IR thermal imaging of the cores on the catwalk indicated the presence numerous occurrences of nodular and/or disseminated hydrates extending from ~45 mbsf to the BSR at 124 mbsf. Cl anomalies (discussed in the next paragraph) also indicate that gas hydrate occurs intermittently within this 79-m-thick zone. Moreover, the top and bottom of this zone of direct and indirect hydrate indicators corresponds very closely to a zone of strong and highly variable resistivity in the LWD data (discussed below), confirming that the LWD data are a valuable tool for predicting the occurrence of hydrate in the sediments.

Geochemical analysis of interstitial waters has revealed that depth variations in the concentration of several different chemical species correlate with the hydrate stability zone. The most direct correlation is seen in Cl concentrations. Above the first occurrence of hydrate (from the seafloor to ~45 mbsf), Cl concentration in the pore water is similar to that in seawater. Between 45 mbsf and the BSR at ~125 mbsf, there are numerous low Cl spikes that likely reflect the freshening effect of dissociated hydrate on the interstitial waters. Correlation of Cl data with the IR camera data indicates that the spatial sampling of Cl anomalies is biased, which smoothes estimates of hydrate concentration based on Cl anomalies. Additional work to better quantify this bias is planned for other sites. Never the less, these data can be used to obtain a rough estimate of hydrate concentration if a “no-hydrate” background concentration can be estimated. At Site 1244, Cl concentrations from the BSR to 300 mbsf decrease linearly at a rate of ~0.35 mM/m. This suggests a diffusive gradient between seawater and low Cl fluids in the accretionary complex. The reduced chlorinity at depth may reflect dehydration of clay minerals deeper in the accretionary complex. Considering uncertainties in the background concentration of Cl, we estimate that 2-8% of the pore space is occupied by hydrate, with locally higher and lower concentrations. The Cl concentration profile within the deepest, incoherent seismic facies is approximately constant, suggesting a zone of fluid advection and mixing, consistent with LWD, physical properties, and core observations, all of which suggest a pervasively fractured medium.

The ratio of methane to ethane (C1/C2 ratio) also shows a clear correlation with the presence of hydrate, with step-like decreases in this ratio both at 40 mbsf and at the BSR in gases obtained by the headspace technique and by extracting gas from void space in the cores. This observation will be discussed further in the Site Summary for Site 1255.

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

Slightly lower C1/C2 ratios are observed in gas obtained by dissociating discrete hydrate samples, suggesting some fractionation of C2 into hydrate. The molecular composition of gases released from three successful Pressure Core Samplers (PCS) is similar to that of the headspace gases. It has not yet been determined whether in situ methane concentrations of 57 mM, 62 mM and 95 mM from depths of 120, 131 and 142 mbsf, respectively, are above or below solubility. There are the first in situ gas concentrations obtained from Hydrate Ridge.

Samples were taken to support a range of shore-based microbiological studies, but there are no results to report at this time. Measurements of sulfate concentration in the interstitial waters, which indicate that the boundary between microbial methane consumption and generation is located at 8 mbsf at this site, were used to guide high-resolution sampling for microbiological studies.

Downhole tools employed at this site included 4 APCT runs, 1 DVTP run, 1 DVTPP run and 3 PCS runs. Seven downhole temperature measurements (including the average of waterline temperatures) were used to define a linear temperature gradient of 0.0575 °C/m, similar to the temperature gradient determined at ODP Site 892 during Leg 146. This temperature gradient predicts that the BSR should be at a depth of 135 mbsf, based on the pure methane and seawater stability curve and seismic velocities obtained from a 3-D ocean bottom seismometer survey conducted in 2000 in tandem with the 3-D reflection survey. Resolution of the apparent mismatch of 10 m between the BSR depth determined from the seismic data and that calculated from the observed temperature gradient awaits a more detailed analysis of the uncertainties in the temperature measurements and better constraint on the velocity of the sediments between the BSR and the seafloor, which will be obtained from VSP experiments to be conducted during the second half of Leg 204. The pore pressure dissipation measurement made by the DVTPP follows the expected pattern, but detailed analyses to determine whether in situ pressure departs from hydrostatic pressure awaits post-cruise study. The three PCS deployments were successful, as was discussed in the previous paragraph.

The LWD data obtained at this site are of excellent quality and provide spectacular images of electrical resistivity within the borehole. As mentioned above, high-amplitude, variable resistivity from 40-130 mbsf suggests the presence of hydrate and correlates with other indirect and direct indicators of hydrate presence. Sinusoidal patterns in the resistivity images of the borehole wall suggest that gas hydrate is concentrated in steeply dipping fractures as well as along bedding planes. The data also show strong borehole breakouts, which are indicative of a northeast-southwest oriented axis of least compressive stress.

In summary, Site 1244, which is the first site that was logged and cored during Leg 204, has provided strong evidence that gas hydrates are common within the hydrate stability zone on the Oregon continental margin and that they are a major factor influencing the biogeochemical evolution of the margin. It is also clear that the integration of

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

geophysical remote sensing data such as 3D seismic reflection surveying, Logging While Drilling, and IR thermal scanning provides a reliable “roadmap” to guide further sampling and analysis. Additional work planned at this site includes the acquisition of wireline logging and downhole seismic data.

Site Summary, ODP Site 1245

Introduction:

Site 1245 (proposed site HR3a) is located in 870 meters of water on the western flank of Hydrate Ridge ~3 km NW of the southern summit. The 3-D seismic data available from a Leg 204 Site Survey show that the Bottom-Simulating Reflector (BSR), a reflector that cuts across stratigraphic horizons and is generally thought to indicate the presence of free gas at the base of the gas hydrate stability zone (GHSZ), is at a depth of ~134 mbsf at this site. As at all sites during Leg 204, the temperature and pressure at the seafloor at this site are well within the GHSZ, indicating that gas hydrates can exist within the entire stratigraphic section above the BSR if hydrate-forming gases are available in concentrations that exceed their in situ solubility. A faint reflection that underlies the BSR and is approximately parallel to it has tentatively been interpreted to be a second BSR that may indicate the base of the stability zone of hydrates that include higher hydrocarbons. This site also samples a strong regional seismic reflection, referred to below as Horizon A. Horizon A can be mapped from the northern boundary of the seismic survey, where it clearly follows stratigraphic boundaries, to the summit, where it appears as a “bright spot” beneath the BSR. On its down-dip edge, it appears to lap onto the boundary between coherent folded strata and the seismically incoherent facies interpreted to represent highly deformed sediments of the accretionary complex. It has been interpreted to be a “conduit” that transports fluids from the accretionary complex to the summit. Several unconformities, referred to as Horizons Y and Z, overlie Horizon A and appear to represent discontinuities in sediment accumulation in a slope basin that was formed during growth of an underlying accretionary anticline.

A primary objective at Site 1245 was to determine the distribution, composition and concentration of gas hydrate in the sediments on the western flank of Hydrate Ridge and contrast these parameters with those on the eastern flank of the ridge and in the adjacent slope basin, where the sub-BSR fluid migration pathways inferred from seismic data are distinctly different. Another important objective was to sample sediments and fluids from Horizon A to determine whether this horizon is indeed a conduit supplying methane to form gas hydrate and carbonate on the seafloor at the summit. A third objective was to sample the sedimentary section of the western flank of Hydrate Ridge below the BSR to provide constraints for interpreting variations in BSR strength across the western flank. Site 1245 is also a reference site for a north-south trending transect that extends from Site 1245 to the summit and includes Sites 1247, 1248, 1249 and 1250.

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

Operations:

Hole 1245A (water depth 886.5 m) was drilled to a depth of 380 mbsf without coring on July 18, 2002, to obtain the initial Logging-While-Drilling (LWD) data for this site. We returned to this site from August 6-15, 2002, to core Holes 1245B to 1245E. Hole 1245B was cored to 473.7 mbsf using the APC and XCB. Holes 1245C and 1245D were cored to 201.7 mbsf and 24 mbsf, respectively, for extensive high-resolution geochemical and microbiological sampling. Hole 1245E was drilled to 473.7 mbsf and then cored to 540.3 mbsf using the RCB. Coring in Hole 1245E stopped short of the originally planned depth of 700 mbsf because of deteriorating hole conditions. The hole began to collapse trapping the bottom hole assembly. Fortunately it was not necessary to sever the pipe, although preparations were made to do so. The upper 300 mbsf of Hole 1245E were used for wireline logging. Plans for conventional, offset and walkaway seismic lines were abandoned when the downhole seismometer would not clamp in Hole 1245E and the hole continued to collapse. The APCT was run 8 times, the DVTP was run 3 times, and the PCS was run 5 times in this site. There were also 2 runs each of the HYACINTH HRC and FPC pressure coring devices. Eleven whole-round samples of sediment thought to contain gas hydrate were preserved in liquid nitrogen or in pressure vessels for post-cruise studies.

Principal Scientific Results:

Biostratigraphic observations from the 540 m of core recovered at Site 1245 indicate that the entire 540 m-thick sequence is younger than 1.65 Ma. Distinct changes in sedimentation rate occurred at 55 and 150 mbsf. Sediments deeper than 150 mbsf were deposited from 1.0 to 1.6 Ma at a rate of ~62 cm/kyr, whereas the overlying strata were deposited at a slower rate of 10-23 cm/kyr. Lithostratigraphic analysis indicates that the dominant lithologies are clay with carbonate concretions and foraminifer-rich interlayers in the upper 0-31 mbsf, underlain by diatom-bearing clay and silty clay with frequent sand-rich turbidites containing a few glass-rich layers from 31.5-212.7 mbsf. Included within this deeper sequence is seismic Horizon A, characterized by two thick, ash-rich, sandy layers between 174 and 181 mbsf. Between 212.7 and 419.3 mbsf, nannofossil-rich claystone and silty claystone with glauconite layers and turbidites are seen, underlain by claystone containing thick turbidites and heterogeneous mud clasts.

The precruise 3D seismic reflection site-survey and the LWD data obtained in Hole 1245A provided a "roadmap" that was used to guide the sampling and analysis strategy at this site. The LWD data, which were acquired in the first hole drilled at this site, were processed and available for interpretation for ~4 weeks prior to coring. Data are of excellent quality. The logs show a marked increase in the amplitude and variability of formation resistivity between 48 and 131 mbsf (Log Unit II), which was interpreted to indicate the extent of the zone within which gas hydrates would be found. High resistivity layers are both subhorizontal, indicating accumulation of gas hydrate parallel to bedding, and steeply dipping, indicating that hydrate fills fractures. Archie saturation calculations

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

predict a hydrate concentration of ~10-30% of the pore volume in layers distributed throughout this interval.

The estimated depth distribution of hydrate obtained from the LWD data was confirmed by several other proxies used to infer hydrate distribution as well as by the actual samples of hydrate that were recovered (54 – 129 mbsf). Low chlorinity anomalies are detected in samples of interstitial waters from 55 – 125 mbsf and are interpreted to reflect in situ hydrate concentrations that are generally below 3%, with one anomaly suggesting a concentration of 15%. Low temperature anomalies were observed with the infrared (IR) cameras between 50 and 129 mbsf. Estimates of total in situ methane concentration obtained from a Pressure Core Sampler (PCS) at 57 mbsf indicated a concentration very close to in situ saturation, and a PCS located at 120 mbsf indicated that in situ methane concentration just above the BSR is an order of magnitude greater than saturation at in situ conditions. Two PCS runs below the BSR yielded concentrations slightly below saturation. The consistency between these multiple independent estimates of the depth range of the zone of hydrate occurrence gives us considerable confidence in the validity of these estimates. Models will be investigated post-cruise to relate the depth to the top of hydrate to the depth of the sulfate/methane interface (SMI), observed at ~ 7 mbsf at this site, and to more precisely predict the in situ methane concentration as a function of depth within the hydrate stability zone.

In addition to being used to rapidly identify the temperature range and potential location of hydrate samples in cores on the catwalk, the IR camera was used to estimate the distribution and texture of hydrate downhole. Approximately 80 IR anomalies were identified and classified. In Site 1245B, 75% of the anomalies suggested disseminated hydrate and 25% suggested nodular hydrate; in Site 1245C, 60% of the anomalies suggested disseminated hydrate and 17% suggested nodular hydrate. The IR data were also used to investigate the relationship between IR imaging, chlorinity anomalies in interstitial pore water and hydrate distribution in the core by conducting a controlled experiment on a section of core known to contain hydrate (Section 204-1245C-7H-5), as identified on the catwalk using the IR camera. When the core liner was split and removed, a 2 cm-thick, steeply-dipping layer of hydrate was found. After allowing the hydrate to dissociate for 90 minutes, closely spaced sediment samples were taken near the hydrate, including one sample from where the hydrate had been. The chlorinity anomaly is strongly attenuated 5 cm away from the hydrate sample and has disappeared 10 cm from the hydrate. Since normally only 2 interstitial water samples are taken in each 9.5 m-long core, the chlorinity measurements are spatially biased. Frequent low chlorinity anomalies downcore must indicate extensive distribution of hydrate. Additional comparison and calibration between data sets with different length scales and sensitivity to hydrate concentration should improve our ability to estimate in situ concentrations from such data.

The LWD data provided the first evidence obtained during Leg 204 for the hypothesis that seismic Horizon A is a significant regional feature. At all 4 sites where Horizon A

was crossed during the LWD phase of Leg 204, it is characterized by a very distinctive, strong, double-peaked, low density anomaly (< 1.5 gm/cc compared to 1.85 gm/cc in adjacent sediments) that is ~ 4 m-wide. Coincidence of this LWD density anomaly with the estimated depth of Horizon A in the seismic data provided confirmation that the velocities used for converting the seismic data to depth were accurate enough to predict the depth of target horizons to within a few meters, pending processing of wireline acoustic data. The direct correlation between the low density layers and the thick ash layers mentioned above was confirmed by bulk density and magnetic susceptibility measurements made on the cores.

Another major result of Site 1245 was the discovery of significant concentrations of higher order hydrocarbons beneath the BSR. Methane/ethane (C_1/C_2) ratios in headspace samples reach values < 100 between 130 and 180 mbsf. When combined with the measured in situ temperature gradient (~ 0.055 °C/m) and the observation that the C_1/C_2 anomaly is due entirely to an increase in ethane concentration, the data suggest that thermogenic hydrocarbons are migrating from deeper in the accretionary complex. Lithium anomalies observed in association with Horizon A support this interpretation. In addition to C_2 , enrichments in C_3 and other higher order hydrocarbons were also observed. At Site 1245, the minimum in the C_1/C_2 ratio occurs around 150 mbsf, ~ 30 m above Horizon A. At some of the other sites it is below Horizon A, suggesting a complex relationship between Horizon A, subsurface fluid transport, and the possible formation of hydrates of methane and other hydrate-forming gases.

In summary, Site 1245 provided confirmation that multiple proxies for in situ hydrate occurrence, including electrical resistivity measured downhole, core temperatures measured on the catwalk, and chloride anomalies measured in interstitial waters extracted from sediment samples, are consistent with direct measurements of gas concentration in predicting the distribution and concentration of gas hydrates in the subsurface, although additional analysis is needed to more precisely understand and calibrate these different proxies. It also demonstrated that a distinctive seismic event underlying the BSR and referred to as Horizon A results from the presence of a pair of low-density ash-bearing sand layers that are likely to be fluid conduits. It provided evidence for migration of higher hydrocarbons beneath the gas hydrate stability zone, although determining details of the role of seismic Horizon A in this migration will only be resolved through integration of data from several sites. Finally, it provided important lithostratigraphic and biostratigraphic data for reconstructing the geologic history of this hydrate-bearing system, including the rate at which the system formed and lithologic controls on fluid migration and hydrate distribution.

Site Summary, ODP Site 1246

Introduction:

Site 1246 (proposed site HR1b) is located in 848 meters of water near the crest of Hydrate Ridge ~3 km N of the southern summit. The 3-D seismic data available from a Leg 204 Site Survey show that the Bottom-Simulating Reflector (BSR), a reflector that cuts across stratigraphic horizons and is generally thought to indicate the presence of free gas at the base of the gas hydrate stability zone (GHSZ), is at a depth of ~114 mbsf at this site. This site also samples a pair of bright, regional seismic reflectors, referred to below as horizons B and B', at depths of ~60 and 100 mbsf, respectively. The temperature and pressure at the seafloor at this site are well within the GHSZ, indicating that gas hydrates can exist within the entire stratigraphic section above the BSR if hydrate-forming gases are available in concentrations that exceed their in situ solubility.

The primary objective at Site 1246 was to sample horizons B and B' when they are within the gas hydrate stability zone (GHSZ). By comparing this site to Site 1244, where horizons B and B' are below the GHSZ, we hope to constrain lithologic and hydrologic explanations for the strong reflectivity of these seismic horizons and obtain insights into the processes that transport fluids into and through the GHSZ. A better understanding of the relationships among seismic reflectivity, sediment lithology and physical properties is needed to develop effective strategies to predict hydrate occurrence from seismic and other remote sensing data

Operations:

Hole 1246A was drilled to a depth of 180 mbsf without coring on July 19, 2002, to obtain the initial Logging While Drilling (LWD) data for this site. We returned on August 11, 2002, near the middle of Leg 204 to core Hole 1246B. Sixteen APC cores were obtained, sampling to a depth of 136.7 mbsf with 99% recovery. The APCT was run 5 times; no other special tools were deployed. Only basic sampling was conducted on these cores (headspace and void gas analyses, two whole rounds /core for chemical analysis of interstitial water, basic physical properties measurements, lithostratigraphic and biostratigraphic description). Further analyses will be conducted onshore.

Principal Scientific Results:

The precruise 3D seismic reflection site-survey and the LWD data obtained in Hole 1246A provided a "roadmap" that was used to guide the sampling and analysis strategy at this site. As mentioned above, the seismic data define the link between Sites 1244 and 1246 and suggest approximate depths to Horizons B and B' and the BSR of ~60, 100 and 114 mbsf, respectively. The LWD data, which were acquired in the first hole drilled at this site, were processed and available for interpretation for 3 weeks prior to coring. These logs provided a first look at the probable distribution of hydrate within the GHSZ.

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

Based on the Archie relationships between electrical resistivity and porosity, LWD data suggested that hydrate should occur intermittently between 53 and 109 mbsf. The LWD data also indicate that Horizon B is characterized by relatively high density and resistivity, as was found at Site 1244. Unlike Site 1244, no prominent low density anomaly is found associated with Horizon B' at Site 1246.

Use of the infrared (IR) camera continued, both to rapidly identify gas hydrate through the core liner and to investigate the distribution and texture of hydrate in the cores and visualize the process of dissociation. Temperature anomalies in the IR thermal images suggest the intermittent presence of hydrate from ~15-117 mbsf, a somewhat more extensive depth range than is indicated by other hydrate proxies (see discussion of interstitial waters and LWD). In addition, several of the IR thermal anomalies are correlated with changes in the lithologic and physical properties of the sediments and with anomalies in chemistry of the pore waters. These changes are in turn correlated with seismic Horizon B. Whole rounds of core containing particularly strong IR temperature anomalies, and therefore suspected of containing gas hydrate veins or nodules, were recovered from 66.5, 96.6, and 105.0 mbsf and preserved in liquid nitrogen for detailed shore-based studies. A gas hydrate sample recovered from 109.5 mbsf was divided into two pieces; one piece was allowed to dissociate on board for chemical analysis (discussed below) and the other was preserved

On the basis of visual sediment descriptions, examination of smear slides, and correlation with physical property data (especially magnetic susceptibility), the sedimentary sequence can be divided into two primary lithostratigraphic units. Lithostratigraphic Unit I (from the seafloor to 21.7 mbsf) is a Late Pleistocene to Holocene unit characterized by dark greenish gray diatom and nannofossil-bearing hemipelagic clay. Lithostratigraphic Unit II, which extends to the base of the Hole 1246B, is defined by the onset of graded silt and sand layers, which represent a series of turbidites of varying thicknesses bounded by erosional contacts and separated by periods of bioturbated hemipelagic sedimentation. Layers comprised of >50% sand are found at 62, 71 and 136 mbsf, respectively. The sandy layer at 62 mbsf (found in Core 204-1246B-8H) can be correlated with the base of seismic Horizon B. (Note that the thickness and base of this layer is not defined because whole rounds were taken for microbiology and interstitial water analyses prior to core description). The overlying graded sequence is ~2 m-thick and is gray colored, in sharp contrast to most of the sediment cored during this Leg. The gray color results from a high percentage of quartz grains. This zone contains fewer biogenic components than adjacent strata, suggesting rapid deposition. A similar sequence is found at 56 mbsf in Core 204-1246B-7H, although the base of this upper turbidite sequence contains less sand.

Detailed analysis of physical properties data reveals that the two turbidite sequences that comprise Horizon B are each characterized by a high density and high magnetic susceptibility anomaly and that each layer is ~2.5 m thick. Preliminary synthetic seismograms calculated based on the density log confirm that the resulting double-peaked

density anomaly that extends from 54 to 67 mbsf explains the complicated waveform of seismic Horizon B at this site. The relatively high density probably results from the grain size and packing of the sediments. The source of the high magnetic susceptibility has not yet been identified. A thin (<50 cm-thick), high resistivity anomaly also appears near the base of each of these turbidites, suggesting the presence of hydrate. Low temperatures measured on the catwalk with the IR camera are additional indirect indicators for the presence of gas hydrate in the lowermost coarse-grained portion of each turbidite sequence. A sample thought to contain hydrate was recovered from the base of the lower turbidite (Interval 204-1246B-8H-S04, 25-30cm) and was preserved in liquid nitrogen for post-cruise analysis. Samples of this coarse-grained layer were also taken for interstitial water and microbiology studies.

The correlation between physical properties, lithology and seismic horizon B' at Site 1246, where it occurs a few meters above the BSR, is not clear. A thin (<1 cm-thick) volcanic ash-rich layer is observed at 96 cm depth in section 4 of Core 204-1246B-11H (~95 mbsf). Strong, narrow (<1 m) high resistivity and thermal anomalies indicative of the presence of gas hydrate are observed at 96-97 mbsf in the LWD and IR data, respectively. A sample thought to contain hydrate was recovered in section 5 of Core 204-1246B-11H at this depth. Recovery in Core 204-1246B-11H was 80%, and the primary lithological source of Horizon B' may not have been recovered. Shore-based studies are planned to determine the age and provenance of this ash and to compare it to the ash recovered from Site 1244. The ash data will complement the biostratigraphic ages, which suggest an age of ~0.3 Ma at Horizon B'. Seismic modeling will also provide constraints on the nature of fluids in this horizon. At Site 1244, where Horizon B' is found at 216 mbsf (well below the gas hydrate stability zone), it is associated with a 60 cm-thick layer that is rich in detrital shards of volcanic glass and corresponds to a distinctive low density anomaly in the LWD and shipboard physical properties data. We will test the model that Horizon B' contains free gas at Site 1244 and that the disappearance of the density anomaly at Site 1246 results from formation of gas hydrate.

Geochemical analyses of interstitial waters made during Leg 204 have revealed variations in the concentration of several different chemical species with depth that correlate with the GHSZ. At Site 1246, the most direct correlation is based on chloride concentrations, which show a pattern similar to that observed at most other sites, with the exception of those at the southern summit of Hydrate Ridge. From the seafloor to ~40 mbsf, chloride concentrations are similar to those of seawater suggesting that no hydrate is present. Between 40 mbsf and the BSR at ~114 mbsf, there are numerous low chloride spikes that likely reflect the dilution of porewater by water from dissociated hydrate. The lowest chloride value at this site (~430 mM) is from a sample that fortuitously coincided with the coarse-grained basal zone of the Horizon B turbidite discussed above. Assuming the "no-hydrate" background concentration of chloride that was estimated for Site 1244, the amplitude of this chloride anomaly suggests that 23% of the pore space in this layer is filled by hydrate. Ba, Li and Na are depleted in this interval, and Ca, Mg and Sr are depleted in the overlying sample, located ~3 m higher in the section. The correlation of

interstitial water chemistry with specific horizons defined by lithologic and physical properties suggests that modeling of these chemical data will provide constraints on the origin, evolution and flow rate of fluids that transport methane into and through the GHSZ.

Analyses of the organic chemistry of gases at Site 1246 indicate that processes here are similar to those at Site 1244. The ratio of methane to ethane (C_1/C_2 ratio) shows a step-like decrease at the BSR, which reflects an increase in C_2 beneath the BSR rather than a change in methane concentration. The presence of propane (C_3) below the BSR suggests the upward migration of higher hydrocarbons from below, and the absence of C_3 within the GHSZ (with one exception at ~22 mbsf) indicates that gas above solubility in this zone should be in the form of Structure I rather than Structure II hydrate. The apparent fractionation of C_2 into gas hydrate, which was reported at sites 1244 and 1251 from analyses made of gases obtained from dissociated hydrate samples, is not apparent here. However, this may be an artifact of sampling since only one hydrate sample was available for gas analysis at Site 1246. Because no Pressure Core Sampler (PCS) runs were made at this site, no in situ gas concentration estimates are possible.

The methane/sulfate boundary at Site 1246 falls between 4 and 7 mbsf but is poorly defined due to sparse sampling; it is slightly shallower than at Site 1244, where it is identified at 9 mbsf. Variations in the depth of the methane/sulfate boundary among Leg 204 sites will be compared to variations in depth to the first occurrence of hydrate as part of a postcruise study.

Five downhole temperature measurements were made at Site 1246. The APCT tool that was used showed a short offset -2°C between the 1st and 2nd runs. Correcting for this offset, the data suggest a temperature gradient of $0.049^\circ\text{C}/\text{m}$, which is lower than the gradient of $0.057^\circ\text{C}/\text{m}$ measured at Sites 1244 and 1251. This temperature gradient predicts that the BSR should occur at 150 mbsf, considerably deeper than the observed depth of ~114mbsf. This observation is consistent with results from other sites near the crest of Hydrate Ridge, whereas sites located away from the crest show much less of a difference between measured and predicted temperatures at the BSR.

In summary, the multidisciplinary approach that characterizes ODP has been used to document multiple correlations between geological and geophysical parameters and the presence of gas hydrate at Site 1246. The primary preliminary result is that seismic Horizon B is caused by a pair of high magnetic susceptibility, high density, and low porosity layers ~2.5 m thick and spaced 10 m apart. Sedimentological analysis indicates that each layer is formed by a turbidite sequence with a complicated internal structure indicating deposition, erosion and redeposition. Electrical resistivity, IR temperature and geochemical anomalies are associated with the basal, coarser-grained layers of each of the two turbidites that constitute Horizon B, indicating that hydrates preferentially form here. Indirect and direct indicators of hydrate were also found associated with Horizon B'. Postcruise work is planned to determine the source of the magnetic susceptibility

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

anomaly, and to correlate lithological and physical properties of these horizons between Site 1244 and Site 1246. Additional efforts will be focused on modeling the seismic response of this horizon as it changes from a fluid-rich layer beneath the BSR to a hydrate-bearing layer above it, and to constrain the source and evolution of the fluids using the geochemical data.

Site Summary, ODP Site 1247

Introduction:

Site 1247 (proposed site HR4c) is located in ~845 meters of water on the western flank of Hydrate Ridge ~800 m NW of the southern summit and approximately half way between Site 1245 and the summit. The 3-D seismic data indicate that the seismic stratigraphic setting is similar to that of Site 1245 (see Site 1245 summary). The Bottom-Simulating Reflector (BSR) is at a depth of ~121-124 mbsf at this site. Horizon A is brighter and shallower (~160 mbsf) at Site 1247 than at Site 1245; Horizon Y is also shallower (~60 mbsf) at this site.

A faint, negative-polarity reflection approximately 40 m below the BSR is observed in this region. While the possibility that this event is a source artifact has not been definitively ruled out, an abrupt decrease in the amplitude of Horizon A as it crosses this reflection and approaches the BSR from below suggests that it may be a “second BSR” resulting from the presence of more stable hydrate structures that contain higher order hydrocarbons, as has been suggested for similar features observed elsewhere.

The primary objective at Site 1247 was to sample sediments and fluids from Horizon A approximately half way between Site 1245 and the summit (Site 1249) in order to determine up-dip variations in the physical and chemical characteristics of this horizon and thus understand the role it plays in fluid migration and formation of hydrate on the seafloor at the summit. A second related objective was to investigate the origin of the second “BSR.” Although they are only 75 m apart, the two Holes drilled at this site sample parts of Horizon A with distinctly different seismic characteristics.

Operations:

Hole 1247A (water depth 845 m) was drilled to a depth of 270 mbsf without coring on July 20, 2002, to obtain the initial Logging-While-Drilling (LWD) data for this site. We returned to this site from August 22-24 to core Hole 1245B, which was offset from Hole 1247A by ~75 m to the east. Hole 1245B was cored to 220 mbsf using the APC and XCB. The APCT was run 6 times (including a mudline run to obtain seafloor temperature), the DVTP was run twice, and the PCS was run 3 times in this hole. The HYACINTH HRC and FPC pressure coring devices were not run at this site. Hole 1247B was then logged (triple combo and sonic/FMS). After wireline logging, a vertical and an offset VSP covering the interval of 104-214 mbsf was acquired by alternately

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

shooting from the JOIDES Resolution and the R/V Ewing, which held station ~700 m away. Plans to conduct walk-away VSPs were abandoned when the Schlumberger VSI tool would no longer clamp in the hole.

Samples suspected of containing hydrate based on IR temperature anomalies were recovered from 93 and 113 mbsf and stored temporarily in liquid nitrogen. However, on later inspection, it was discovered that the samples showed textures indicative of hydrate dissociation, and no hydrate was actually preserved.

Principal Scientific Results:

As at Site 1245, biostratigraphic observations from the 220 m of core recovered in Hole 1247B indicate that the entire 540 m-thick sequence is younger than 1.65 Ma. Sediments deeper than ~165 mbsf were deposited at a rapid, but poorly constrained, rate. These strata are correlative with strata yielding a linear sedimentation rate of 62 cm/k.y. at Site 1245. The interval from ~150-165 mbsf, which contains Horizon A, yields a relatively slow sedimentation rate of 4 cm/k.y. based on nannofossils. Overlying strata were deposited at a rate of 9-22 cm/k.y., similar to what is observed at Site 1245.

Lithostratigraphic analysis indicates that the dominant lithologies are clay with authigenic carbonates and foraminifer-rich interlayers in the upper 0-27 mbsf (Lithostratigraphic Unit I), underlain by diatom-bearing clay and silty clay with frequent sand-rich turbidites containing a few glass-rich layers from 27-212.7 mbsf. Lithostratigraphic Unit III (60-220 mbsf) is distinguished from Unit II by an increase in turbidites and biogenic components. Included in Lithostratigraphic Unit II is seismic Horizon A. Unlike at the other sites where Horizon A was sampled and found to correspond to two ash layers, at Site 1247B a soft sediment debris flow bounded by turbidites was found. Because the signature of Horizon A in the LWD data from Hole 1247A, located only 75 meters from Hole 1247B, is very similar to that observed at the Sites 1245, 1248 and 1250, we conclude that the change in amplitude of Horizon A between the two holes at Site 1247 results from a dramatic local change in lithology rather than from processes related to gas hydrates.

As at other sites, the apparent top of the zone of hydrate occurrence as indicated by a variety of different proxies is generally consistent. The onset of high and variable electrical resistivity and of thermal anomalies observed with the infrared (IR) camera on the catwalk are both at ~45 mbsf. High resistivity layers are subhorizontal, indicating accumulation of gas hydrate parallel to bedding, and steeply dipping, indicating that hydrate fills fractures. The onset of low chlorinity anomalies is at ~55 mbsf. The onset of in situ methane oversaturation as projected from headspace and Pressure Core Sampler measurements is ~38 mbsf.

The above proxies are also consistent with similar depths for the base of the gas hydrate stability zone (GHSZ). The deepest IR thermal anomaly is at 118 mbsf. The deepest

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

chlorinity anomaly is at 114 mbsf. A PCS indicating a volume of methane greater than in situ concentration was taken at 123 mbsf. Seismic velocities from the sonic log and the VSP complement these interpretations by clearly resolving a velocity decrease indicative of the presence of free gas beneath 129-134 mbsf.

The significant concentrations of higher order hydrocarbons found beneath the BSR at Site 1245 were also observed at Site 1247. Here, low values of the methane/ethane ratio ($C_1/C_2 < 100$) persist to a slightly deeper depth than at Site 1245 (~220 mbsf, compared to ~180 mbsf at Site 1245). Hole 1247B did not extend deep enough to resolve the deeper increase in C_1/C_2 and then a return to a “normal” C_1/C_2 decrease with depth below 250 mbsf. The relationship between the anomalously low C_1/C_2 ratios and fluid migration along Horizon A remain unclear.

One of the notable results from this site was identification of a new hydrate proxy that has the potential to provide valuable constraints on the dynamics of hydrate formation. It was found that many samples collected from the depth range in which other proxies indicate the presence of hydrate showed ethane enrichment and propane depletion. This was attributed to fractionation of ethane and exclusion of propane (C_3) during the formation of Structure I hydrate. The observed pattern of anomalies, relative to baseline C_1/C_2 and C_1/C_3 concentrations defined by the majority of samples, can be explained by invoking the presence of gas hydrates within those samples that dissociated on recovery.

Another interesting result was that Horizon A shows a low amplitude chlorinity low and methane high in addition to the Li enrichment observed coincident with this horizon at other sites. Given the expectation that Horizon A should be more permeable where it is characterized by coarse-grained, ash-rich layers than where it consists of a clay-rich debris flow, these observations are surprising and have not yet been explained. The Li enrichment is similar in amplitude to that observed at other sites and is clearly associated with Horizon A, thus supporting the interpretation of a stratigraphic horizon that transports fluids from greater depth.

The depth of the sulfate/methane interface (SMI) at this site is well-constrained by high resolution samples and is determined to be at 11 mbsf. Assuming that this depth is entirely controlled by anaerobic methane oxidation, a methane flux of 2.5×10^{-3} mmol $\text{cm}^{-2} \text{yr}^{-1}$ is inferred, which is about 1.4 times greater than at the Blake Ridge and about 30% less than at Site 1251. However, the assumptions on which this estimate is based do not seem to be valid for the entire interval above the SMI, leading to considerable uncertainty in this estimate.

The in situ temperature measurements in Hole 1247B yielded a very precisely defined slope of 0.0524 °C/m (correlation coefficient of 0.999) and did not reveal any sign of a positive temperature anomaly at Horizon A. This observation will be used to place an upper bound on the rate of fluid transport from depth along this horizon that can be compared to rates obtained from the chemical anomalies.

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

In summary, Site 1247 provided further confirmation that multiple proxies for in situ hydrate occurrence are consistent with direct measurements of gas concentration in predicting the distribution and concentration of gas hydrates in the subsurface. These include electrical resistivity and porosity measured downhole via LWD, core temperatures measured on the catwalk, and chloride anomalies measured in interstitial waters extracted from sediment samples. A new proxy – ethane enrichment and propane depletion – was discovered that holds promise for constraining hydrate dynamics. Results from this site also indicate that lateral changes in the amplitude of Horizon A in the interval between the BSR and a faint “second BSR” probably result from lithologic changes rather than from the presence of more stable hydrates of higher order hydrocarbons, as had been speculated, leaving open the question of the origin of this “second BSR.” Finally, the small chlorinity depletion and methane enhancement associated with Horizon A, which is not observed at Sites 1245, 1248 and 1250, leads to the apparently contradictory conclusion that Horizon A is a more active conduit for deeper fluids where it is composed of a clay-rich debris flow than where it is composed of a pair of coarse-grained, ash-rich sandy silt.

Site Summary, ODP Site 1248

Introduction:

Site 1248 (proposed Site HR6) was drilled in 832 m a water depth of ~300 m northwest of the southern Hydrate Ridge summit. This site is located in the middle of a small (~150 m-in-diameter) high-reflectivity spot on the seafloor imaged by a deep-tow sidescan sonar survey. The small spot is located 300 m north of a larger circular high reflectivity patch around the Pinnacle, a well known active carbonate chemoherm. These are the only two locations on southern Hydrate Ridge where high backscatter reflectivity is observed and are interpreted as seafloor manifestations of fluid venting. TV-sled surveys revealed some evidence for the occurrence of scattered authigenic carbonate fragments within the small high-reflectivity patch, which might be responsible for the higher backscatter signal observed in the sidescan sonar data. The 3-D seismic data show attenuation of the underlying stratigraphic reflectivity, similar to what is observed beneath the Pinnacle. Both areas of high backscatter overlie the intersection of seismic Horizon A, a coarse-grained, ash-rich layer that seems to be a fluid migration pathway, and the Bottom-Simulating Reflector (BSR), which indicates the base of the methane hydrate stability zone as confirmed by multiple proxies for hydrate occurrence (see Site 1245 Summary).

The principal objective at Site 1248 was to investigate whether the sediments below the high-reflectivity seafloor spot are contain evidence of active fluid advection within the stratigraphic sequence of Southern Hydrate Ridge and if these fluids are supplied by Horizon A. Furthermore, this site could be a test site to determine whether this inferred

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

incipient venting area may develop into a massive Pinnacle-like carbonate mound on the seafloor.

Operations:

Three holes were drilled at Site 1248. Logging-While-Drilling (LDW) measurements were made in Hole 1248A down to 194 mbsf. Hole 1248B was abandoned at 17 mbsf (Cores 204-1248B-1H to 3H). Coring disturbance due to near-seafloor massive gas hydrate occurrence and a shattered liner during retrieval of Core 204-1248B-3H, caused poor core recovery (44%). At Hole 1248C, which comprises 17 cores, 5 XCB cores were drilled to 48 mbsf followed by 11 APC and 1 XCB cores to 149 mbsf. After poor core recovery of 23% in Cores 204-128C-1X to -5X, recovery increased in Cores 204-1248C-6H through -17X to 90% of the penetration. Temperature measurements were made using 1 DVTP (at 19.2 mbsf), 3 APCT (at 17.86 and 105 mbsf) and 2 DVTP-P (at 105 mbsf and at the bottom of the hole at 149 mbsf) runs.

Principal Scientific Results:

Two lithostratigraphic units were recognized at Site 1248. Unit I, of Holocene to Late Pleistocene age, is characterized by dark-greenish gray diatom-bearing clay and silty clay and extends from the seafloor to 39 mbsf. These fine-grained lithologies are commonly structureless except for sulfide mottles. Lithostratigraphic Unit II (39-149 mbsf), of Middle to Early Pleistocene age, is dominated by homogenous silty clays with varying amounts of biogenic components. Sand silt-sized turbidites are intercalated as minor lithologies throughout this unit.

High concentrations of beige to white volcanic glass shards were observed in the tail of a few turbidites in Core 204-1248C-14H; these are concentrated around 130 mbsf. This depth interval is well correlated with the occurrence of the regional seismic reflector Horizon A, which appears as a high amplitude reflection within the seismic stratigraphic framework of southern Hydrate Ridge. Its regional extent was mapped in the precruise 3-D seismic survey, where it is observed as a reflector dipping away from the southern summit of Hydrate Ridge. A detailed examination of the sediments at Site 1245 revealed that the volcanic ash is a major sedimentary constituent that was also found at the Horizon A level of other sites (Sites 1250 and 1247).

Site 1248 Logging-While-Drilling data clearly show Horizon A as a two-m-thick anomalous interval, characterized by high resistivity and low density values within the depth interval from ~126 mbsf to ~128 mbsf. These results are indicative of a sand layer containing free gas. Physical property measurements on discrete samples of the cores from Site 1248 confirm the low-density character of Horizon A sediments, which is interpreted to be due to the reduced grain density of the ash. The presence of volcanic ash in Horizon A reduces the grain density because amorphous silica particles in the ash have distinctly lower grain densities than other sedimentary components like quartz, feldspar

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

and clay minerals. Sediments from the interval of Horizon A do not show higher porosity values than the surrounding sediments. The distinctly larger grain size of the ash-rich sediments, however, implies a different packing structure and possibly higher permeability in these intervals, which suggests that Horizon A is a potential fluid migration conduit.

Organic geochemistry measurements on gases remaining in cores from Site 1248 reveal high methane contents throughout. In addition to the high methane levels, there is a surprising variation in ethane content with depth. C_1/C_2 is $<1,000$ near the seafloor, increasing to 10,000 near the base of the gas hydrate stability zone (GHSZ), then decreasing sharply below the BSR. In addition to ethane, propane (C_3) is present in relatively high concentrations in the upper 120 mbsf, and is even more abundant in headspace gas below that depth. The gas analyses at Site 1248 reflect the complex mixing of gases from two hydrocarbon sources. Mixed microbial and thermogenic gases occur in the uppermost 40 mbsf followed downhole by an intermediate interval (~ 40 to ~ 100 mbsf) dominated by microbial gas. Mixed microbial and thermogenic gas also occurs in the deepest sediments at Site 1248 (below 100 mbsf), with thermogenic gas possibly being injected at Horizon A at ~ 130 mbsf. The data thus suggest rapid advection of deeper gas to the seafloor, bypassing the lower part of the GHSZ.

Analyses of gases from a few dissociated hydrate samples from the shallow zone above 40 mbsf showed that while methane occupies most of the water cages of the hydrate structure, higher hydrocarbons are also present. Gas hydrates at Site 1248 are probably primarily Structure I hydrate that incorporate ethane molecules within their cage structure. However, in Sample 204-1248C-2H, 0-10 cm, from 7.37 mbsf, a higher concentration of propane than ethane suggests that Hydrate Structure II is present. Although thermogenic Structure II gas hydrates are common in petroleum provinces such as the Gulf of Mexico and the Caspian Sea, this hydrate type was not known from Hydrate Ridge prior to ODP Leg 204.

Interstitial water geochemistry results clearly show the influence of gas hydrate formation at Site 1248. Based on the chloride distribution in the pore water, the presence of hydrate is suggested from the seafloor to the BSR at 115 mbsf. The data indicate 25% gas hydrate content in the pore space of the uppermost 20 mbsf, whereas LDW resistivity data indicate up to 50% occupancy due to gas hydrates. Below 20 mbsf, gas hydrate content calculated from chloride anomalies ranges from 2-5% pore volume saturation. This pattern of chloride distribution is well documented by direct gas hydrate sampling and by the hydrate-related fabrics observed by the sedimentologists at this site. Soupy and mousse-like textures occur predominantly in silty clay and diatom-bearing silty clay after dissociation of hydrates. These were particularly common in the uppermost 20 mbsf. At these depths more massive gas hydrate samples were recovered, whereas further downcore small nuggets and thin veins of hydrate were sampled. The samples were identified by thermal IR data imaging of cores on the catwalk using a hand-held IR camera. Post-acquisition processing of the IR data shows a principal correlation to the

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

pore-volume saturation derived by LDW resistivity logs, the chloride pore water data, and the sedimentological observations of the occurrence of dissociated hydrate layers.

High advective flow rates in the uppermost 20 mbsf of the sediments drilled at Site 1248 are indicated by several findings. Sulfate concentrations were near zero even in the shallowest pore water sample implying a high methane flux from below that feeds microbial anaerobic methane oxidation (AMO). By consuming the near-seafloor sulfate, a consortium of bacteria and *Achaea* is responsible for AMO close to the seafloor during which millimolar quantities of dissolved sulfide are created. High sulfide concentrations were found within the the uppermost core. In addition, authigenic carbonates that were described in the cores are probably caused by higher dissolved carbon dioxide production, which is another result of higher AMO rates. High interstitial alkalinity throughout the cores provides further evidence for carbonate precipitation.

Temperature measurements from downhole tools (3 APCT, 1 DVTP and 2 DVTP-P runs) were used to calculate a temperature gradient of $0.038^{\circ}\text{C}/\text{m}$, considerably lower than expected. However, if 2 outlier measurements are excluded the gradient is $0.055^{\circ}\text{C}/\text{m}$, identical to the gradient determined from 9 measurements at Site 1245. This temperature gradient predicts the base of the GHSZ at 130 mbsf, assuming methane and standard mean seawater for the calculation. This is 15 m deeper than indicated by the seismic and LWD data and is consistent with a general pattern of greater mismatch between measured *in situ* temperature and BSR depth near the summit of Hydrate Ridge, the cause of which has not yet been determined.

In summary, gas hydrate is present throughout the sediment column from the seafloor to the BSR at Site 1248 as documented by IR imaging, LWD data, chloride anomalies in the pore water, analyses of sedimentary fabric and direct sampling of gas hydrates in a couple of intervals. The Holocene to Pleistocene sediments drilled here indicate strong advective fluid flow near the summit of southern Hydrate Ridge. There is abundant hydrate in near-surface sediments and no sulfate in the shallowest interstitial water samples collected at Site 1248, clearly indicating active flow of methane-bearing fluids. Authigenic carbonate formation occurs close to the seafloor, probably induced by anaerobic methane oxidation. The occurrence of authigenic carbonate as well as gas hydrate probably causes the high reflectivity that was mapped during deep-tow sidescan sonar survey of the seafloor. Advective flow is also indicated by the shallow occurrence of thermogenic hydrocarbons mixed with microbial gases. Gases obtained from dissociation of a shallow gas hydrate sample revealed a higher concentration of propane than ethane ($\text{C}_3 > \text{C}_2$) in addition to methane. Such a gas composition should form Structure II hydrate, although we were not able to confirm this on board. Structure II gas hydrate is well known from petroleum basins like the Gulf of Mexico, although this is the first indication of Structure II hydrate along an accretionary margin.

Site Summary, ODP Site 1249

Introduction:

Site 1249 (proposed Site HR4b) was drilled in 778 m of water on the summit of southern Hydrate Ridge. This area is characterized by active gas venting and gas hydrate formation at the seafloor. Vigorous streams of bubbles emanate from the seafloor at the summit and have been observed during submersible and ROV dives and are consistently observed with high-frequency echosounders as plumes in the water column. Outcrops of massive hydrate are also visible on the seafloor. These observations are interpreted to indicate that methane bubbles rising through the sediment column are sometimes trapped to form hydrate near the seafloor and sometimes escape into the water column. In the subsurface, a distinctive pattern of chaotic, strong reflectivity is seen in seismic data to extend to ~30 mbsf beneath the region where the seafloor is anomalously reflective in side-scan data. This pattern has been interpreted to result from lenses of massive hydrate intercalated with sediment. The BSR at this site is estimated based on seismic data to be at 115 mbsf, but coring was only permitted to 90 mbsf at this summit site because of the possibility of trapped gas beneath the BSR.

The primary objective at Site 1249 was to determine the distribution and concentration of hydrate with depth at the summit and obtain constraints on how methane bubbles can coexist with hydrate and porewater within the hydrate stability field.

Operations:

Twelve holes were drilled at Site 1249. Logging-While-Drilling (LDW) measurements were made in Hole 1249A using the same tools as were used at the other sites during this leg. Hole 1249B was drilled using the new RAB-8 LWD and coring system, which permits simultaneous acquisition of core and logging data. For this test, we drilled to 30 mbsf before beginning RAB coring operations; 8 4.5 m-long cores were taken with liners followed by 9 m-long cores without liners until we reached the permitted depth of 90 mbsf. The 90 m-sediment sequence was APC cored in Holes 1249C to 1249F with core recoveries of less than 30% in the uppermost 20 mbsf and increased core recovery up to 70% deeper in the holes. Six holes (Holes 1249G-L) were APC/XCB cored for a special shore-based "geriatrics" study in which several means of preserving gas hydrates for future study will be compared. During this effort 244.3 m of gas hydrate-bearing sediments were cored with 35.12% core recovery and were stored in 40 steel pressure vessels after recovery and repressurized using methane gas and water. Additional samples were stored in liquid nitrogen.

All pressure coring systems available (PCS, HRC and FPC) were used at Site 1249. The ODP Pressure Core Sampler was deployed seven times in Hole 1249C at 33.5, 63.5, and 88.5 mbsf, in Hole 1249E at 9.08 mbsf and Hole 1249F at 13.5, 58.9, 71.4 mbsf. The FPC was used in Hole 1249D at 8 mbsf, in Hole 1249H at 70.4 mbsf and in Hole 1249G at 13.5 mbsf. The HRC was deployed in Holes 1249F and 1249G at 8 and 13.5 mbsf,

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

respectively. Temperature measurements were made using the DVTP (at 30.4 and 90 mbsf) and the APCT (at 16.5, 24.0, 32.5, 37.5, 39.9, 58.9, 70.4, and 90.0 mbsf).

Principal Scientific Results:

Based on visual observations, smear-slide analyses, physical property measurements, seismic stratigraphy and logging data, the sediments at Site 1249 were divided into 3 lithostratigraphic Units. Each of the three units is known from other sites on the western flank of Hydrate Ridge (Sites 1250, 1248, 1247 and 1245), and a good correlation exists between the sites. Due to poor core recovery resulting at least in part from the presence of massive hydrate at Site 1249, lithostratigraphic Units I and II at this site were combined into a single unit, referred to as Unit I-II. This unit, of Holocene to Early Pleistocene age, is composed of clay and silty clay with varying biogenic components and lithology that changes from nannofossil-bearing to diatom-bearing and diatom-rich. Lithostratigraphic Unit III, of Early Pleistocene age, has similar lithologies to Unit I-II. The upper boundary of Unit III with Unit I-II is defined by the occurrence of visible turbidites in the cores, an increase in grain size, a slight increase in calcareous components, and a slight decrease in biogenic opal. The boundary between these lithostratigraphic units, which varies in depth among the holes from 51 to 59 mbsf, is coincident with seismic Horizon Y, which is interpreted to be a regional angular unconformity.

Site 1249 was the site where the highest concentration of gas hydrates was observed, and a large amount of whole-round sampling was conducted. Massive hydrates pieces were recovered in the uppermost two cores. Due to interbedding of layer up to several cm thick of pure gas hydrate layer with soft sediment, cores disturbance was great and most of the original gas hydrate fabrics were probably not preserved. Soupy and mousse-like textures, probably related to gas hydrate presence were observed by the sedimentologists. Soupy textures can result from the dissociation of massive gas hydrate, a process that releases a considerable amount of water into the sediment. Mousse-like textures result from the dissociation of disseminated gas hydrates in fine-grained sediments. Temperature anomaly profiles from the catwalk-track IR camera support this generalized model for gas hydrate distribution. Downhole gas hydrate presence can also be inferred from LWD resistivity data, and the Archie relationship between resistivity and porosity implies gas hydrate saturations in the pore space at Site 1249 that range from 10% to 92%.

Shipboard analysis of downhole temperatures using conventional techniques results in considerable scatter in the data. The data indicate a relatively low temperature gradient of 0.047-0.051 and predict a depth to the base of the gas hydrate stability zone that is 20 m deeper than the BSR. The explanation for this discrepancy has not yet been explained. One possible factor is that thermal conductivities measured on core samples are not representative of in situ thermal conductivity when large concentrations of hydrate are present in situ. Preliminary examination of the data suggests that the raw data recorded by the temperature probes can be inverted to determine in situ thermal conductivity and

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

that the in situ thermal conductivities are indicative of variable, and in some cases large, concentrations of gas hydrate.

Investigations of the interstitial water composition at Site 1249 show the signature of gas hydrate formation in several ways, and these data will be used post-cruise to determine rates of hydrate formation. Pore fluids recovered from the upper 20 mbsf show pronounced enrichment in dissolved chloride concentration. The highest chloride concentration was 1368 mM in a dry-looking sediment. Formation of such a brine is only possible in a system in which the rate of gas hydrate formation exceeds the rate at which excess salts can be removed by diffusion and/or advection. Small negative anomalies below 10 mbsf were also found due to the freshening effect on pore water of hydrate dissociation during recovery. The presence of brines in the upper 20 mbsf is also reflected by the concentration of other dissolved species such as Na^+ , K^+ , Ba^{2+} , Sr^{2+} , and Mg^{2+} because these ions are excluded from the hydrate structure and enriched in the residual pore water. Superimposed on the enrichment due to brine formation is the effect of rapid advection of fluids that have been formed at deeper depth and modified by chemical processes occurring in near-surface sediments.

In comparison to other sites, headspace samples at Site 1249 showed extremely high methane contents. These large quantities of gas can only be caused by the presence of gas hydrate in the headspace samples. Ethane and propane are also present in high concentrations, and enrichment of these gases at shallow depth reflect the presence of migrated thermogenic hydrocarbons. This is consistent with the observations of active gas venting at this location. Gases from several decomposed hydrate specimens were analyzed and showed that some of the hydrates contained propane and butane, suggesting the presence of Structure II hydrate.

In order to determine in situ methane concentrations, PCS cores were successfully obtained at 14, 34 and 72 mbsf. The degassing experiments revealed concentrations from 215.7 to 5,033.9 mM, which are above methane saturation at in situ temperature and pressure conditions, providing additional evidence for the presence of gas hydrates. For the deepest core, at 72 mbsf, a gas hydrate concentration is estimated to be 2.2 % of the pore volume. Shallow samples show higher concentrations of 7-34% and 60-76 % gas hydrate in the pore space at 34 and 14 mbsf, respectively.

One of the highlights of Site 1249 was the success of the new HYACINTH pressure sampling tools at recovering hydrate-bearing cores at in situ pressures. HRC and FPC cores from 14 mbsf (Core 204-1249G-2E and Core 204-1249H-2Y) both recovered high concentrations of gas hydrate. Cores were retrieved and successfully transferred under in situ pressure to a storage chamber and then logged. In multiple gamma density logs, both cores showed a spectacular interlayering of sediments with low-density layers revealing densities slightly lower than 1 g/cm³. Since pure methane hydrate has a density of ~0.92 g/cm³ we interpret these low density layers to be relatively pure hydrate layers. In addition, a low density spike (0.75 g/cm³) in a 8 cm-thick gas hydrate layer indicates the

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

presence of free gas. The presence of free gas within gas hydrate samples had been postulated from the porous structure of seafloor samples from Hydrate Ridge and from gas release observations during TV-grab sampling. A second indicator of free gas came from the HRC core. A small explosion pushed gas hydrate and sediment interlayers out of the liner from two intervals while the core was being transferred from the pressure vessel to liquid nitrogen. This sudden gas release can only be explained by the expansion of small volumes of free gas that existed in situ within the gas hydrate layer.

In summary, Holocene to Early Pleistocene sediments of Lithostratigraphic Units I-II and II at Site 1249 are well correlated with other sites along the western flank of southern Hydrate Ridge. Site 1249 was cored to a depth of 90 mbsf; thus this entire sequence lies within the gas hydrate stability zone and large quantities of gas hydrates were sampled. Unfortunately core recovery at this site was limited because of the presence of massive hydrate close to the seafloor. Rapid growing of massive hydrates in the uppermost 20 mbsf induces a brine formation which leads to chloride values in the interstitial water of up to 1368 mM. This is the greatest chloride enrichment due to hydrate ever found to date. Degassing of the PCS from Core 204-1249F-4P revealed 95 L gas, which is the greatest volume of gas ever measured with the PCS. Based on the methane in situ concentration of 5,034 M from this PCS, the gas hydrate concentration was estimated to be 60-70% of the pore volume. Further highlights were the first density measurements from gas hydrates under in situ conditions using the HYACINTH pressure coring and laboratory transfer systems. These cores showed direct evidence for free gas within gas hydrate layers 13 mbsf on southern Hydrate Ridge. The coexistence of free gas and gas hydrates well within the hydrate stability zone is only possible when no water is available for further hydrate formation.

Site Summary, ODP Site 1250

Introduction:

Site 1250 (proposed Site HR4a) was drilled in 792 m water depth ~100 m west of the southern summit of Hydrate Ridge and ~100 m east of the carbonate chemoherm known as the Pinnacle. On southern Hydrate Ridge, the Pinnacle is the only carbonate mound, whereas at northern Hydrate Ridge several major chemoherms are known. The Pinnacle has near-vertical flanks rising about 40 m above the seafloor and a diameter of ~150 m. The carbon source for formation of the Pinnacle is known to be methane from the very low delta ^{13}C values. Based on $^{230}\text{Th}/^{234}\text{U}$ dating, the Pinnacle seems to have precipitated during the last 12 ka. The Pinnacle is located in the middle of a high-reflectivity patch mapped by a deep-tow sidescan sonar survey, which might be created by scattered carbonates close to the seafloor and/or the shallow occurrence of gas hydrates. Site 1250 lies close to the eastern rim of the high-reflectivity patch. The pre-cruise 3-D seismic reflection survey data show that the high amplitude reflector known as Horizon A meets the BSR just below the Pinnacle.

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

The primary objective at Site 1250 was to sample the sediments, fluids, gases and gas hydrates under the high backscatter reflectivity seafloor. The sediments at Site 1250 were expected to be strongly affected by the upward fluid migration that has resulted in the formation of the Pinnacle chemoherm. In this context understanding the role of Horizon A as a conduit for fluid flow and its interaction with the BSR was of special interest.

Operations:

Five holes were drilled at Site 1250. Logging-While-Drilling operations were conducted in Holes 1250A and 1250B. Because recording of the RAB tool failed during the first run in Hole 1250A due to depleted batteries, the LDW operation was repeated in Hole 1250B. Holes 1250C and 1250D, which were APC/XCB cored down to 148 mbsf and 147 mbsf, respectively, and each comprises 19 cores with average core recoveries of 82% of the total penetration. Hole 1250E, which comprises two cores with 92% core recovery, was drilled for special biogeochemistry sampling. Hole 1250F was APC/XCB cored from 100 to 182 mbsf to extend the depth of sampling. The PCS was deployed two times in Hole 1250C at 71 and 130 mbsf, three times in Hole 1250D at 35, 103 and 135 mbsf and three times in Hole 1250F at 119, 130 and 132 mbsf. HYACINTH autoclave pressure coring tools were deployed in Hole 1250C (FPC at 137.5 mbsf) and 1250D (HRC at 134.2 mbsf). Special tools were used for temperature measurements in Hole 1250C, including 5 APCT runs at 33, 52, 71, 82.5, 92 mbsf and 2 DVTP runs. Temperature measurements in Hole 1250D included 4 APCT runs at 35, 46.5, 65.5, 103.5 mbsf and 2 DVTP runs. Wireline logging was performed in Hole 1250F using separate runs of the Triple Combination Tool (TAP/DITE/HLDT/APS/HNGS/QSST) and the Formation Microscanner-Sonic tool string (FMS/DSI/SGT) down to 180 mbsf. Vertical and offset VSPs were acquired with the JOIDES Resolution and the R/V Ewing (located at an offset of ~700 m) alternating shots. This was followed by walkaway VSPs shot by the R/V Ewing to downhole seismometers clamped at 91, 138 and 172 mbsf.

Principal Scientific Results:

On the basis of visual sediment descriptions, physical property measurements, Logging-While-Drilling data and seismic correlation, the sedimentary sequence at Site 1250 was divided into three lithostratigraphic units. Lithostratigraphic Unit I, of Holocene to Late Pleistocene age, extends from the seafloor to 9.5 mbsf and is mainly composed of dark-greenish gray clay or silty clay, which is generally diatom-bearing or diatom-rich. Lithostratigraphic Unit II (9.5-14 mbsf), of Late Pleistocene age, is principally composed of similar lithologies as Unit I, but these are intercalated with thin silt and fine sand layers which are not found in Unit I. Based on their appearance, these multiple layers of coarser grain-size are clearly single events that have been rapidly deposited from turbidity currents. Lithostratigraphic Unit III, from 14 to 181 mbsf, consists of silty clay that is nanofossil-rich or diatom-rich, with an age range of Late Pleistocene to Early Pliocene.

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

The boundary between Lithostratigraphic Units II and III is correlated with Horizon Y, a seismic reflector that corresponds to a regional stratigraphic unconformity identified in the 3-D seismic data. This boundary is well defined by a 6-m-thick sequence of coarse-grained, high-frequency thin turbidite layers that includes individual sand layers up to 20 cm-thick. Logging-While-Drilling data recorded a high density peak around seismic Horizon Y, which was confirmed by shipboard physical property measurements. Shipboard MST-data reveal, in addition, a large positive excursion of magnetic susceptibility caused by a higher content of magnetic minerals within the sand layers at the boundary between Lithostratigraphic Units II and III.

Lithostratigraphic Unit III at Site 1250 is divided in two Subunits. Subunit IIIA includes several mass wasting deposits, of which a debris-flow layer between 86.5 and 100 mbsf was the most pronounced example. This deposit was characterized by the occurrence of mud clasts up to 5 cm in diameter and several soft sediment deformation features. Subunit IIIB has a distinctly higher abundance of calcareous nannofossils and foraminifers than Subunit IIIA. The boundary between the stratigraphic Subunits IIIA and IIIB is marked by several light-colored ash-rich layers, which are composed of volcanic glass-rich silt to silty volcanic ash, typically a few cm-thick. This ash-rich interval is well defined in the LWD data by a low-density anomaly and corresponds to the regional seismic reflector known as Horizon A. Physical property measurements on discrete samples at Site 1250 revealed low grain densities in this depth interval, which are explained by the low grain density of the amorphous silicate components of the ash. However, this provides only a partial explanation for the low density values and high resistivity values found in the LDW data, and free gas is probably present at Horizon A. The vertical VSP indicates a drop in P-wave velocity associated with this horizon, which also suggests free gas.

Infrared (IR) imaging of the cores at Site 1250 enabled the on-catwalk identification of gas hydrates, and 20 samples were taken which are thought to contain hydrate based on their temperature anomaly. IR-track imaging revealed 40 temperature anomalies between 14 and 109 mbsf in Hole 1250C and 57 anomalies between 6 and 113 mbsf in Hole 1250D. The depth range of the cold temperature anomalies correlates well with the depth distribution of mousse-like and soupy textures observed by the sedimentologists during core description. The lowermost gas hydrate piece was sampled in Hole 1250F at 100.23 mbsf, which is slightly above the base of the GHSZ at 114 mbsf as defined in the P-wave sonic log.

Chloride concentrations in the pore water at Site 1250 document the different geochemical processes linked to the presence of gas hydrates. In the upper 50 mbsf, an enrichment in dissolved chloride shows the in situ effect of rapid and recent gas hydrate formation. Due to hydrate formation, dissolved ions are excluded from the hydrate structure and become enriched in the residual pore fluids. The fact that we observe this enrichment means that the rate of hydrate formation exceeds the rate at which excess salts can be removed by diffusion and/or advection. Below 50 mbsf, the chloride shows a

gently-sloping baseline toward fresher chloride values. Using this baseline curve, the negative chloride anomalies were used to calculate the amount of gas hydrate responsible for the dilution of each sample. The peak amounts are up to 15% gas hydrate filling of the available pore space with average values ranging from 0 to 6%.

The presence of a high concentration of gas hydrate in the uppermost 10 mbsf had been predicted prior to sampling based on a large LWD resistivity peak. To substantiate both these results and the chloride data, a variety of specimens of gas hydrate were collected from the uppermost 35 mbsf. The hydrate samples show a wide range of morphologies, ranging from massive to nodular, and are often embedded in soupy sediments, which are interpreted to result from decomposition of disseminated hydrate and fluidization of the sediment by hydrate water.

Analyses of other elements in the interstitial waters document that Site 1250 is in a seafloor environment that is strongly influenced by seepage. Sulfate concentrations are zero in the shallowest sample because of the upward flux of methane and anaerobic methane oxidation. In addition, alkalinity is anomalously high in the upper tens of meters reflecting fluid advection. Authigenic carbonate formation is documented by discrete carbonate samples close to the seafloor.

Analyses of gas sampled in cores at Site 1250 show high methane content throughout with no decrease close to the seafloor. This is in agreement with the lack of sulfate in the pore water and the high advection rates. Void gas samples show that the ethane content is also relatively high, and there is a hydrocarbon enrichment (C_3 - C_5) close to the seafloor that indicates lateral migration of wet gas hydrocarbons coming from a deeper source. A distinct increase in ethane at 102-107 mbsf, beneath the gas hydrate stability zone, could be due to release of ethane from decomposed gas hydrate. An increase in propane and n-butane is probably due to migration of hydrocarbons from deeper depths.

Migration of fluids from deeper is also indicated by interstitial water geochemistry, which shows increasing lithium concentrations with depth. This is believed to reflect the diagenetic remobilization of lithium deeper in the accretionary wedge. Superimposed on the downhole linear increase in lithium is a peak in the sediments around seismic reflector Horizon A, indicating focused fluid transport along this zone associated with seismic Horizon A.

In order to obtain in situ gas concentrations and to determine whether methane is saturated under in situ conditions, the Pressure Core Sampler (PCS) was deployed successfully five times. Three PCS deployments above the BSR show concentrations clearly above methane saturation, which predicts gas hydrate concentrations of 0.6-2.2% within the pore volume of the cores. Gas concentrations in the PCS from the deployments below the BSR show that, based on the solubility curve, one sample (Core 204-1250F-4P) taken 7.5 m below the BSR had free gas which should approximately occupy 50% of the available pore space. The second sample (Core 204-1250D-18P) from ~24 m below

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

the BSR had a gas concentration below saturation, which would exist as dissolved gas under in situ conditions.

At Site 1250, there were nine APC temperature measurements made. These data were used to calculate a temperature gradient of 0.049°C/m, which is lower than expected and predicts the base of the GHSZ at 138 mbsf, assuming methane and standard mean seawater for the calculation. This is 26 m deeper than the level of the GHSZ indicated by the seismic and LWD data and is consistent with a general pattern of greater mismatch between measured in situ temperature and BSR depth near the summit of Hydrate Ridge. The cause of this discrepancy is yet not known.

In summary, hemipelagic fine-grained sediments interbedded with turbidites at Site 1250 are Quaternary in age (younger than 1.6 Ma) and contain gas hydrates in varying amounts. Based on chloride anomalies in interstitial water samples and on PCS in situ gas concentration measurements and calculations, the concentrations of hydrate are estimated to be between <1% to a few % of the pore space. Much higher concentrations of hydrates near the seafloor are indicated by LWD resistivity data and direct sampling. Positive chloride anomalies in the pore water in the upper 40 mbsf reveal rapid and active formation of gas hydrates during recent times. High methane concentration, no sulfate, high alkalinity and carbonate diagenesis in the uppermost sediments also document high advection rates of fluid migration, similar to what was observed at the other seep-related sites (Site 1248 and Site 1249). The presence of free gas just below the BSR is documented by the concentrations of methane well above in situ solubility found in a PCS core from below the BSR and by sonic log P-wave data.

Site Summary, ODP Site 1251

Introduction:

Site 1251 (proposed Site HR2alt) was drilled in 1216 m water depth, ~5.5 km east of the southern summit of Hydrate Ridge. The site is located in a slope basin where well-stratified sediments were deposited at a rapid rate. Seismic data record a history of deposition, tilting, folding and depositional hiatuses in the basin that is probably related to the evolution of Hydrate Ridge. A strong BSR suggests that the base of the gas hydrate stability zone (GHSZ) is at ~196 mbsf at this site.

The principal objectives at Site 1251 were to: (1) determine the source of water and gases forming gas hydrates in a setting that is characterized by rapid deposition of hemipelagic sediments and mass-wasting deposits, in contrast to the uplifted sediments of the accretionary complex; (2) determine the distribution of gas hydrates in relation to the typical lithological parameters for the basin; (3) test general models for hydrate formation in regions of rapid sediment accumulation that were developed in the Blake Ridge area from results of ODP Leg 164; (4) provide age constraints on the geological history recorded by seismic stratigraphy.

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

Operations:

Six holes were drilled at Site 1251. In Hole 1251A Logging While Drilling (LWD) measurements were made using a variable, but generally low rate of penetration (ROP) in the upper 30 mbsf, followed by an increased ROP of ~50 m/hr from 30 mbsf to the bottom of the hole (at 380 mbsf). The LWD string included the RAB tool, Measurement-while-Drilling (MWD), NRT (NMR-LWD), and Vision Density Neutron (VDN) tools. Hole 1251B was APC cored (Cores 204-1251B-1H through 24H; including PCS deployments at 105 and 154 mbsf, and FPC deployment at 172 mbsf) with an average core recovery of 80.6% down to 194.6 mbsf, where more lithified sediments significantly reduced the penetration of the bit. XCB coring continued down to 445.1 mbsf (Cores 204-1251B-25X through 53X) with an average recovery of 85.5%. In addition to the XCB coring the three pressure coring tools (PCS, FPC, HRC) were used at 291, 330 and 397 mbsf, respectively. Special tools in Hole 1251B included 4 APCT (at 37.6, 66.1, 94.6, and 125.1 mbsf) and 2 DVTP-P (at 156.6 and 293.6 mbsf) runs. Hole 1251C was terminated after 2 cores. At Hole 1251D, which comprises 30 cores, 3 XCB cores were drilled to 26.9 mbsf followed by APC cores to 173.4 mbsf and XCB cores to 226.5 mbsf. Furthermore a series of special tools were deployed in Hole 1251D: 1 APCT (at 173.4 mbsf), 2 DVTP-P (at 175.4, and 198.2 mbsf), 4 PCS (at 46, 77, 173, and 228 mbsf), 1 FPC (at 227 mbsf) and 1 HRC (at 230 mbsf). Holes 1251E and 1251F were each cored by APC to 9.5 mbsf for high density sampling. Hole 1251G was washed to 2.5 mbsf before 1 APC core was taken for special sampling of turbidite layers. The hole was then washed down to 20 mbsf before an additional PCS (at 21 mbsf) was deployed.

Principal scientific results:

Based on the major and minor lithologies and additional criteria like fabric, physical properties, microscopic, chemical and XRD analysis, the hemipelagic strata and turbidite sequences recovered at Site 1251 were divided in three lithostratigraphic units. Lithostratigraphic Unit I, subdivided into three subunits, extends from the seafloor to 130 mbsf and is characterized dominantly by dark greenish gray clay to silty clay ranging from Holocene to Pleistocene age (0 to ~0.3 Ma). Clay and silty clay, some of which is diatom-bearing, is interlayered with several coarse-grained high-frequency turbidites (Subunit IA; 0-23 mbsf). Subunit IB (23-34 mbsf) is characterized by unsorted pebble-sized mudclasts in a clay matrix and a series of soft-sediment deformation fabrics representing a debris flow unit. This unit can be traced regionally based on its chaotic character in seismic reflection records and reaches a maximum thickness of ~70 m in the center of the slope basin. Stratified diatom-bearing silty clays comprise Subunit IC (34-130 mbsf), which shows clear seismic stratification. The base of Subunit IC is defined to correspond to a prominent angular unconformity imaged in the seismic data, although there is no apparent lithologic discontinuity at that boundary.

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

Hemipelagic clays of Middle Pleistocene age, partly enriched in siliceous and calcareous biogenic components, form Lithostratigraphic Unit II (130-300 mbsf). Unit III (300-443 mbsf) consists of partly lithified clays that show a downcore transition to claystones. A distinct enrichment of green glauconite grains in a 120-cm-thick interval on top of Lithostratigraphic Unit III is probably associated with a major unconformity or period of very low sedimentation rate that is defined by biostratigraphic data to have lasted from 1.6 to 1.0 Ma. Between 320-370 mbsf, the sediments contain a greater amount of biogenic opal, which is well documented by smear slide estimates and XRD-analyses. Authigenic carbonates of various morphologies and mineralogical compositions as well as glauconite grains are scattered throughout this unit. Biostratigraphic investigations using diatoms and calcareous nannofossils assign these sediments to an Early Pleistocene and Late Pliocene age including the Pleistocene/Pliocene boundary around 375 mbsf.

Major downcore changes in physical property data are generally in agreement with seismic stratigraphy and lithostratigraphic boundaries. The uppermost sediments of Lithostratigraphic Units I and II are characterized by uniformly increasing bulk density values and follow a standard compaction curve. The generally increasing trend in both bulk densities from MST and in routine density measurements on discrete samples (MAD) is interrupted by a 50-m-thick sediment sequence between 320 and 370 mbsf in which the bulk densities drop significantly to lower values and porosity values increase. This change in physical properties is caused by higher amounts of biogenic opal-A, which is an amorphous silica component of low grain density and high skeleton porosity. Magnetic susceptibility values at Site 1251 are characterized by generally uniformly low values. Various high-amplitude MS peaks are correlated with either turbidites, enrichments of magnetic minerals resulting from low sedimentation rates or with diagenetic iron formation in certain horizons.

Thermal imaging of cores using the infrared (IR) cameras provided the best method of detecting intervals of hydrate occurrence in the cores at Site 1251, especially when the hydrate occurred in disseminated form. Discrete samples of hydrate were not seen in Hole 1251B, although several zones with cold anomalies have been identified. The IR temperature anomalies observed in Hole 1251B were relatively small ($\Delta T = \sim 1-1.5^\circ\text{C}$) compared to an IR temperature anomaly ($\Delta T = \sim 6^\circ\text{C}$) encountered at Hole 1251D between 190-197 mbsf, which coincides with an interval, from which samples thought to contain hydrate (on the basis of IR anomalies) were obtained and preserved in liquid nitrogen. The data thus indicate higher gas hydrate concentration just above the BSR, which agrees with the chloride data obtained from interstitial water measurements (see below). Due to low recovery of this interval, the BSR was not sampled in Hole 1251B. Small thermal anomalies between 40 and 200 mbsf are interpreted to be indicative of disseminated gas hydrate.

Interstitial water geochemistry at Site 1251 focused on hydrate-related changes in chlorinity pattern, changes in fluid composition in relation to dewatering of the sediments and biogeochemical processes within the sediments. Like in other accretionary wedges,

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

the profile of dissolved chloride at Site 1251 decreases downcore from present seawater values close to the seafloor. At Site 1251 the chloride decrease in the interstitial water corresponds to an increase in dissolved lithium, revealing a fluid source from deeper sediments of the accretionary complex. The dissolved chloride distribution at Site 1251 shows only one distinct negative anomaly, seen in several samples taken just above the BSR from around 190-200 mbsf. This is consistent with the IR temperature and visual observations, indicating that hydrate occurs in this interval at Site 1251. Based on the lowest chloride value measured below an estimated background concentration, gas hydrate occupies up to 20% of the pore space in this zone just above the BSR. This finding is in contrast to all other sites drilled during the leg, where repeated excursions to low-chlorinity values record the presence of gas hydrate over much larger depth intervals above the BSR.

A number of different processes control whether methane reaches levels above saturation within the GHSZ. An important process controlling the methane distribution in the sediments at Site 1251 is methane consumption due to anaerobic methane oxidation using sulfate as an oxidant. Methane consumption or methane flux at the sulfate-methane interface (SMI) can be estimated from the sulfate and methane concentration gradients. At Site 1251 over half the sulfate being reduced is due to anaerobic methane oxidation. Sulfate depletion at the SMI at 4.5 mbsf also leads to higher concentrations of dissolved barium below the SMI.

High residual methane concentrations were measured in cores at Site 1251 using the headspace technique. These methane values increased rapidly below the level of sulfate depletion to minimum methane concentrations of 10 mM at a depth of 6 mbsf. In order to obtain more reliable *in-situ* gas concentrations, the Pressure Core Sampler (PCS) was deployed nine times. The PCS deployments revealed methane concentrations between 46.4 to 158.4 mM at depths between 20 and 290 mbsf. The methane concentration at 20 mbsf is compatible with the shallower headspace methane estimates, and provides the gradient from which the methane flux is calculated. Based on measured methane concentrations slightly above solubility, two PCS deployments within the GHSZ (at 45 and 104 mbsf) show evidence for gas above saturation, implying gas hydrate occurrence. Observations below the BSR are ambiguous. A PCS sample from 32 m below the BSR did not show gas concentration above solubility whereas one from 100 m below the BSR did.

Beside methane (C_1), higher hydrocarbons like ethane (C_2) ethylene ($C_2^=$) and propane (C_3) traces were also detected throughout the sequence cored at Site 1251. The composition of gas samples recovered from both expansion voids in the core liner and headspace measurements show a systematic change from high C_1/C_2 ratios above the BSR at a depth of 196 mbsf at Site 1251, to lower ratios below that depth. This order-of-magnitude decrease in the C_1/C_2 ratio is caused by an abrupt increase of ethane rather than by a change in methane concentration. This could be caused by ethane storage in gas hydrates and a recycling process whereby ethane-enriched gas hydrates at the base of the

GHSZ dissociate in response to subsidence of the slope basin and the resulting upward migration of the GHSZ through the sediment column. An alternative mechanism to explain these observations is that the GHSZ is a barrier to C_2 migration. Additional analysis of the gas composition in hydrate samples from Leg 204 should permit us to distinguish between these two mechanisms.

Temperatures measurements obtained with 5 APCT runs and 3 DVTP-P deployments were used to calculate a linear temperature gradient of $0.0575^\circ\text{C}/\text{m}$ at Site 1251, which is very similar to temperature profiles from other sites on Hydrate Ridge. Extrapolating laboratory measurements of gas hydrate stability for pure methane in water of 3.5% salinity, this temperature gradient predicts that the base of the GHSZ is ~ 196 mbsf, in excellent agreement with the calculated BSR depth of ~ 196 mbsf determined from 3D-seismic reflection and OBS-derived seismic velocity data.

The recorded LWD data in the basin sediments east of Hydrate Ridge in Hole 1251A are of high quality. There is minimal reduction in vertical resolution due to the faster penetration rate during the collection of the data. Resistivity and density log variations indicate thin-bedded changes in lithologies throughout the hole below 130 mbsf, which most likely reflects the downhole occurrence of interbedded turbidites that were observed during core description. There is a little direct evidence for the presence of gas hydrate in the LWD-data, except for a suggestion in the resistivity data of hydrate at 90-110 mbsf and again immediately above the BSR. The Archie relation for estimating gas hydrate saturation from the resistivity log data implies gas hydrate saturation up to 18%. The resistivity data also indicate the presence of free gas extending for ~ 100 m below the BSR. Borehole breakouts are well developed below 300 mbsf and indicate an east-west axis of compressive stress.

In summary, drilling at Site 1251 recovered a sequence of well-stratified hemipelagic sediments of the slope basin adjacent to Hydrate Ridge. Major lithostratigraphic units were characterized and are, in most cases, separated by clearly-defined unconformities in the seismic record. Thermal, sedimentological, geophysical and geochemical proxies for hydrate occurrence, as well as direct sampling, were used to document the presence and dynamics of gas hydrates in host sediments younger than 500,000 years old. At this site, significant hydrate accumulations seem to be limited to two intervals, 90-110 mbsf and just above the BSR at 190-200 mbsf. This contrasts with the hydrate distribution at the other sites cored during Leg 204, where hydrate is found throughout most of the hydrate stability zone.

Site Summary, ODP Site 1252

Introduction:

Site 1252 (proposed Site HR5a) was drilled in 1039 m water depth, ~4.5 km east of the southern summit of Hydrate Ridge. The site is located on the western flank of a secondary anticline that is located east of the crest of Hydrate Ridge. The sediments in the core of the anticline appear to be continuous with the "accretionary complex" sediments sampled near the base of Site 1244, ~1.5 km to the west. Although there is an anomalously bright BSR at a depth of ~170 mbsf within the core of the anticline, the BSR disappears abruptly at an apparent stratigraphic boundary within the accretionary complex sequence and does not extend beneath Site 1252. Sediments onlapping the anticline from the west can be correlated with sediments sampled at Site 1251. Horizontal slices through this anticline reveal that it has a small aspect ratio and high symmetry, suggesting that is perhaps better described as a diapir rather than an anticline. It is at the southern end of an alignment of circular structures that resemble huge pockmarks in high resolution bathymetric and seismic data.

The principal objectives at Site 1252 were to: (1) sample the sediments in the core of the anticline to determine whether they are compositionally and biostratigraphically similar to those at the base of Site 1244; (2) determine the structure of these sediments in order to constrain the mode of growth of the anticline/diapir; (3) determine whether hydrates are present near a very strong BSR but at a site where no BSR is present; and (4) provide age constraints on the geological history recorded by seismic stratigraphy.

Operations:

One hole was drilled at Site 1252, comprising 28 cores (14 APC, 14 XCB) and sampling to a depth of 259.8 mbsf. Six runs of the APCT tool to measure in situ temperature were run. This was the only special downhole tool in at this site. This is also the only site at which we did not acquire Logging-While-Drilling data prior to coring. After coring, wireline logging were acquired including one run with the Triple Combination Tool and one run with the sonic/FMS tool. This alternate site was the last site drilled during Leg 204.

Principal scientific results:

Although this site showed evidence for only very limited occurrences of gas hydrate, it was very interesting in that it showed very clear correlations between lithostratigraphic observations, physical properties measurement and wireline logging results throughout. It was the first site to show significant postdepositional carbonate formation beneath the upper 10s of meters.

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

Based on the major and minor lithologies and additional criteria like fabric, physical properties and microscopic analysis, the sediments recovered at Site 1252 were divided in three lithostratigraphic units. Lithostratigraphic Unit I, subdivided into three subunits, extends from the seafloor to 96.5 mbsf and is dominated by dark greenish gray clay to silty clay ranging in age from 0 to ~0.3 Ma. Unit IA is characterized by strong negative density gradient in the MST data which probably results from the onset of gas exsolution at ~7 mbsf. The lower boundary of Unit I is defined by the same unconformity that was sampled at a depth of 130 mbsf at Site 1251. At both sites, this unconformity is clearly seen in seismic data and is compatible with biostratigraphic data, but does not have a striking lithological signature. At Site 1252, it is overlain by an apparent debris flow called Unit ID, the top of which corresponds to a strong anomaly in magnetic susceptibility. Unit ID pinches out just west of Site 1251. In contrast, a debris flow that comprises Unit IB at Site 1251 is not present at Site 1252. Unit IC at both sites is strikingly similar both in its lithologic description and in its seismic reflection character.

Unit II at Site 1252 is a dark green foraminifer-rich silty clay that is intercalated with lighter-colored layers of fine sand and coarse silt turbidite layers. These thin turbidites results in a nearly continuous zone of high magnetic susceptibility. In contrast to Site 1251, where Unit II is approximately 180 m-thick, Unit II at Site 1252 is only about 20 m thick. This is due primarily to the location of this site where Unit II laps onto the west flank of uplifted "accretionary complex" sediments. Units IB/C through Unit II are characterized by a normal increase in density and decrease in porosity with depth that is probably caused by sediment compaction.

The boundary between Unit II and Unit III is marked by a 5 m-thick series of glauconite-rich sands, including a 2 cm-thick layer of almost pure glauconite sand. This is underlain by a layer of authigenic carbonate that required a transition from APC to XCB coring at 125 mbsf. Wireline density, resistivity and chemical (uranium and potassium contents) logs all show very high values over ~6 meters at this depth, consistent with extensive carbonate precipitation that forms concretions and cement. This boundary corresponds closely with the top of the uplifted "accretionary complex" sediments in the core of the anticline/diapir and is referred to as Unit IIIA. It is underlain, from 210 mbsf to the base of the hole at 260 mbsf, by Unit IIIB, distinguished from Unit IIIA by an increase in biogenic opal and a decrease in silt. Biostratigraphic age of Unit III is 1.6 to > 2 Ma.

The density profile of Unit III is unusual. Physical properties measurements (MST gamma logs and MAD bulk density) indicate that the density decreases by 0.2 g/cm³ (from 1.8 g/cm³ to 1.6 g/cm³) over a distance of ~25 m below the carbonate-rich zone and then is variable but with an average value of about 1.7 g/cm³ and no systematic increase until the base of the hole at 260 mbsf. The wireline density logs show similar behavior, with a local increase to nearly 2.0 g/cm³ in the carbonate layers underlain by a nearly constant density of 1.7 g/cm³ with occasional thin (~2 m-thick) low density (~1.5 g/cm³) excursions. This anomalous density profile, similar to but better defined than what was observed in lower part of the section at Sites 1244 and 1251 suggests that

diapirism driven by this density difference should be considered as a possible mechanism contributing to the tectonic evolution of the accretionary prism.

Thermal imaging of cores using the infrared (IR) cameras indicated only very limited hydrate occurrence at Site 1252. Two possible hydrate samples were preserved from depths of 83 (in Unit ID) and 99 mbsf (in Unit II). The chloride concentration in the interstitial pore water and the C1/C2 ratios in void-space gas samples also did not show anomalies indicative of dissociated hydrate, unlike what was observed at other sites (see, for example, discussion of Site 1247). In contrast, Unit IIIA showed several examples of "classic" moussy and soupy texture in cores recovered from above the base of the gas hydrate stability zone. A sample of the soupy sediment was taken for post-cruise chloride analysis.

The chloride profile shows a general decrease with depth similar to that observed at Sites 1244 and 1251 and attributed to diffusion or slow advection of fresher pore waters generated by dewatering of sediments deeper in the accretionary complex. A closer look at the chloride profile suggests segments of different slope that can be roughly correlated with lithologic boundaries, suggesting lithologic control on permeability.

The thermal gradient of 0.059 measured at Site 1252 is similar to the gradients of 0.057 oC/m measured at Site 1251 and 0.058 oC/m measured at Site 1244 and predicts the base of gas hydrate stability at 170 mbsf, consistent with the estimate of 170 mbsf obtained by projecting the BSR observed in the core of the anticline laterally by 200 m.

In summary, Site 1252 provided the best sampling of the older (> 1.65 Ma) sediments that comprise the uppermost part of the seismically incoherent facies referred to as the "accretionary complex." This zone is characterized by a density inversion relative to the base of the overlying slope basins and an anomalous density versus depth profile. This observation suggests that gravitational instability should be considered and modeled as a possible driving force contributing to the evolution of forearc structure here. The data from this site also reinforce previous observations that the accretionary complex is characterized by low chlorinity interstitial waters and is relatively permeable. Although this site yield little direct evidence of gas hydrate, sediment textures and limited IR thermal anomalies indicate that some hydrate was present, even though no BSR is observed at this site.

CONCLUSION

The primary accomplishment of the JOI Cooperative Agreement with DOE/NETL in this quarter was the deployment of tools and measurement systems on ODP Leg 204, to characterize and investigate gas hydrate deposits on Hydrate Ridge, offshore Oregon from July to September 2002.

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

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

Summary of Leg 204 Gas Hydrate Coring

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

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

- Some cores also processed through linear x-ray machine from Lawrence-Berkley NEL

Summary of Leg 204 Special Tools Deployments

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

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

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

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

Eight of the sites were drilled using LWD technology. A developmental logging-while-coring (LWC) system jointly developed by Lamont-Dougherty Earth Observatory

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

(LDEO), Anadrill, and Texas A & M University (TAMU) was also successfully tested using a Resistance-At-Bit (RAB-8) LWD tool. This marked the first time ever that core samples have been recovered simultaneously with LWD data.

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

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

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

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

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

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

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

Leg 204 officially ended at 0900 hours 2 September 2002 with the first line ashore Westcan Terminal B in Victoria, B. C.

REFERENCES

- Berner, R.A., 1970. Sedimentary pyrite formation: an update. *Geochim. Cosmochim. Acta*, 48:605-615.
- Boetius, A., Ravensschlag, K., Schubert, C.J., Rickert, D., Widdel, F., Gieseke, A., Amann, R., Jorgensen, B.B., Witte, U., and Pfannkuche, O., 2000. Microscopic identification of a microbial consortium apparently mediating anaerobic methane oxidation above marine gas hydrate. *Nature*, 407:623-626.
- Bohrmann, G., Greinert, J., Suess, E., and Torres, M., 1998. Authigenic carbonates from Cascadia Subduction Zone and their relation to gas hydrate stability. *Geology*, 26/7:647-650.
- Bohrmann, G., Linke, P., Suess, E., Pfannkuche, O., and Scientific Party, 2000. R/ V SONNE cruise report, SO143 TECFLUX-I-1999. *GEOMAR Rpt.*, 93.
- Bohrmann, G., Suess, E., Rickert, D., Kuhs, W.F., Torres, M., Trehu, A., and Link, P., 2002. Properties of seafloor methane hydrates at Hydrate Ridge, Cascadia margin. *Fourth Int. Conf. Gas Hydrates*, Yokohama, Japan. (Abstract).
- Booth, J.S., Winters, W.J., and Dillon, W.P., 1994. Circumstantial evidence of gas hydrate and slope failure associations on the United States Atlantic continental margin. In Sloan, E.D., Happel, J., and Hantow, M.A. (Eds.), *Int. Conf. Nat. Gas Hydrates*, 7:487-489.
- Borowski, W.S., Paull, C.K., and Ussler, W., III, 1996. Marine pore-water sulfate profiles indicate in situ methane flux from underlying gas hydrate. *Geology*, 24:655-658.
- Boudreau, B.P., and Canfield, D.E., 1993. A comparison of closed and open system models for porewater and calcite saturation state. *Geochim. Cosmochim. Acta*, 57:317-334.
- Buffet, B.A., and Zatsepina, O.Y., 1999. Metastability of gas hydrate. *Geophys. Res. Lett.*, 26:2981-2984.
- Carson, B., Seke, E., Paskevich, V., and Holmes, M.L., 1994. Fluid expulsion sites on the Cascadia accretionary prism: mapping diagenetic deposits with processed GLORIA imagery. *J. Geophys. Res.*, 99:11959-11969.
- Clague, D., Maher, N. and Paull, C.K., 2001. High-resolution multibeam survey of Hydrate Ridge, offshore Oregon. In Paull, C.K., and Dillon, W.P. (Eds), *Natural Gas Hydrates: Occurrence, Distribution, and Detection*. Am. Geophys. Union, Geophys. Monogr. Ser., 124:297-306.
- In-Situ Sampling and Characterization of Naturally Occurring Marine Methane Hydrate Using the D/V JOIDES Resolution.*

Dickens, G.R., Castillo, M.M., and Walker, J.G.C., 1997. A blast of gas in the latest Paleocene: simulating first-order effects of massive dissociation of oceanic methane hydrate. *Geology*, 25:259-262.

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

Dickens, G.R., 2001. Modeling the global carbon cycle with a gas hydrate capacitor: significance for the latest Paleocene thermal maximum. In Paull, C.K., and Dillon, W.P. (Eds), *Natural Gas Hydrates: Occurrence, Distribution, and Detection*. Am. Geophys Union, Geophys. Monogr. Ser., 124:19-40.

Garrels, R.M., and Perry, E.A., 1974. Cycling of carbon, sulfur, and oxygen through geologic time. In Goldberg, E.D. (Ed.), *The Sea* (Vol. 5): *Marine Chemistry: The Sedimentary Cycle*: New York (Wiley), 569-655.

Greinert, J., Bohrmann, G., and Suess, E., 2001. Gas hydrate-associated carbonates and methane-venting at Hydrate Ridge: classification, distribution and origin of authigenic lithologies. In Paull, C.K., and Dillon, W.P. (Eds.), *Natural Gas Hydrates: Occurrence, Distribution, and Detection*. Am. Geophys. Union, Geophys. Monogr. Ser., 124:99-114.

Guerin, G., Goldberg, D., and Meltser, A., 1999. Characterization of in situ elastic properties of gas-hydrate bearing sediments on the Blake Ridge. *J. Geophys. Res.*, 104:17781-17795.

Holbrook, W.S., Hoskins, H., Wood, W.T., Stephen, R.A., Lizzarralde, D., and the Leg 164 Science Party, 1996. Methane gas-hydrate and free gas on the Blake Ridge from vertical seismic profiling. *Science*, 273:1840-1843.

Holland, H.D., 1978. *The Chemistry of the Atmosphere and Oceans*: New York (Wiley).
Housen, B.A., and Musgrave, R.J., 1996. Rock-magnetic signature of gas hydrates in accretionary prism sediments. *Earth Planet. Sci. Lett.*, 139:509-519.

Hovland, M., Lysne, D. and Whiticar, M., 1995. Gas hydrate and sediment gas composition, Hole 892A. In Carson, B., Westbrook, G.K., Musgrave, R.J., and Suess, E. (Eds.), *Proc. ODP, Sci. Results*, 146 (Pt 1): College Station, TX (Ocean Drilling Program), 151-161.

Hyndman, R.D., and Davis, E.E., 1992. A mechanism for the formation of methane hydrate and seafloor bottom-simulating reflectors by vertical fluid expulsion. *J. Geophys. Res.*, 97:7025-7041.

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

Karlin, R., 1983. Paleomagnetism and diagenesis of hemipelagic sediments in the northeast Pacific Ocean and the Gulf of California [Ph.D. dissert.]. Oregon State Univ., Corvallis.

Kastner, M., Sample, J.C., Whiticar, M.J., Hovland, M., Cragg, B.A., and Parkes, J.R., 1995. Geochemical evidence for fluid flow and diagenesis at the Cascadia convergent margin. In Carson, B., Westbrook, G.K., Musgrave, R.J., and Suess, E. (Eds.), *Proc. ODP, Sci. Results*, 146 (Pt 1): College Station, TX (Ocean Drilling Program), 375-384.

Katz, M.E., Pak, D.K., Dickens, G.R., and Miller, K.G., 1999. The source and fate of massive carbon input during the latest Paleocene thermal maximum. *Science*, 286:1531-1533.

Kennett, J., Hendy, I.L., Behl, 1996. First MASTER Workshop on Gas Hydrates, Ghent, Belgium.

Kulm, L.D., Suess, E., Moore, J.C., Carson, B., Lewis, B.T., Ritger, S.D., Kadko, D.C., Thornburg, T.M., Embley, R.W., Rugh, W.D., Massoth, G.J., Langseth, M.G., Cochrane, G.R., and Scamman, R.L., 1986. Oregon subduction zone: venting, fauna, and carbonates. *Science*, 231:561-566.

Kvenvolden, K.A., 1995. A review of the geochemistry of methane in natural gas hydrate. *Org. Geochem.*, 23:997-1008.

Kvenvolden, K.A., and Lorenson, T.D., 2001. The global occurrence of natural gas hydrate. In Paull, C.K., and Dillon, W.P. (Eds.), *Natural Gas Hydrates: Occurrence, Distribution, and Detection*. Am. Geophys. Union, Geophys. Monogr. Ser., 124:3-18.

Linke, P., Suess, E., and Scientific Party, 2001. R/V *SONNE* cruise report, SO148 TECFLUX-II-2000. *GEOMAR Rpt.*, 98.

MacDonald, I.R., Boland, G.S., Baker, J.S., Brooks, J.M., Kennicutt, M.C., II, and Bidigare, R.R., 1989. Gulf of Mexico hydrocarbon seep communities II. Spatial distribution of seep organisms and hydrocarbons at Bush Hill. *Mar. Biol.*, 101:235-247.

MacKay, M.E., 1995. Structural variation and landward vergence at the toe of the Oregon accretionary prism. *Tectonics*, 14:1309-1320.

MacKay, M.E., Moore, G.F., Cochrane, G.R., Moore, J.C., and Kulm, L.D., 1992. Landward vergence and oblique structural trends in the Oregon margin accretionary prism: implications and effect on fluid flow. *Earth Planet. Sci. Lett.*, 109:477-491.

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

MacKay, M.E., Jarrad, R.D., Westbrook, G.K., Hyndman, R.D., and Shipboard Scientific Party, 1994. ODP Leg 146, Origin of BSRs: geophysical evidence from the Cascadia accretionary prism. *Geology*, 22:459-462.

Nisbet, E.G., 1990. The end of the ice age. *Can. J. Earth Sci.*, 27:148-157.

Nisbet, E.G., and Piper, D.J., 1998. Giant submarine landslides. *Nature*, 392:329-330. ODP Leg 146 Scientific Party, 1993. ODP Leg 146 examines fluid flow in Cascadia margin. *Eos*, 74:345-347.

Parkes, R.J., Cragg, B.A., and Wellsbury, P., 2000. Recent studies on bacterial populations and processes in marine sediments: a review. *Hydrogeol. Rev.*, 8:11-28. Paull, C.K., Matsumoto, R., Wallace, P.J., et al., 1996. *Proc. ODP, Init. Repts.*, 164: College Station, TX (Ocean Drilling Program).

Paull, C.K., and Ussler W., III, 2001. History and significance of gas sampling during the DSDP and ODP. In Paull, C.K., and Dillon, W.P. (Eds.), *Natural Gas Hydrates: Occurrence, Distribution, and Detection*. Am. Geophys. Union, Geophys. Monogr. Ser., 124:53-66.

Paull, C.K., Ussler, W., III, and Borowski, W.A., 1994. Sources of biogenic methane to form marine gas-hydrates: in situ production or upward migration? *Ann. N.Y. Acad. Sci.*, 715:392-409.

Paull, C.K., Ussler, W., III, and Dillon, W.P., 1991. Is the extent of glaciation limited by marine gas-hydrates? *Geophys. Res. Lett.*, 18:432-434.

Rempel, A.W., and Buffett, B.A., 1998. Mathematical models of gas hydrate accumulation. In Henriot, J.P., and Mienert, J. (Eds.), *Gas Hydrates; Relevance to World Margin Stability and Climate Change*, Spec. Publ. Geol. Soc. London, 137:63-74.

Revelle, R., 1983. Methane hydrates in continental slope sediments and increasing atmospheric carbon dioxide. In *Changing Climate*: Washington (National Academy Press), 252-261.

Ruppel, C., 1997. Anomalously cold temperatures observed at the base of the gas hydrate stability zone on the U.S. Atlantic passive margin. *Geology*, 25:699-702.

Sample, J.C., and Kopf, A., 1995. Isotope geochemistry of syntectonic carbonate cements and veins from the Oregon Margin: implications for the hydrogeologic evolution of the accretionary wedge. In Carson, B., Westbrook, G.K., Musgrave, R.J., and Suess, E. (Eds.), *Proc. ODP, Sci. Results*, 146 (Pt 1): College Station, TX (Ocean Drilling Program), 137-148.

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

Sassen, R., Sweet, S.T., Milkov, A.V., Defreitas, D.A., Kennicutt, M.C., and Roberts, H.H., 2001. Stability of thermogenic gas hydrate in the Gulf of Mexico: constraints on models of climate change. In Paull, C.K., and Dillon, W.P. (Eds.), *Natural Gas Hydrates: Occurrence, Distribution, and Detection*. Am. Geophys. Union, Geophys. Monogr. Ser., 124:131-144.

Schluter, M., Linke, P., and Suess, E., 1998. Geochemistry of a sealed deep-sea borehole on the Cascadia margin. *Mar. Geol.*, 148:9-20.

Suess, E., and Bohrmann, G., 1997. FS *SONNE* cruise report, SO110:SO-RO (*SONNE-ROPOS*), Victoria-Kodiak-Victoria, July 9-Aug. 19, 1996. *GEOMAR Rpt.*, 59:181.

Suess, E., Torres, M.E., Bohrmann, G., Collier, R.W., Rickert, D., Goldfinger, C., Linke, P., Heuser, A., Sahling, H., Heeschen, K., Jung, C., Nakamura, K., Greinert, J., Pfannkuche, O., Trehu, A., Klinkhammer, G., Whiticar, M.J., Eisenhauer, A., Teichert, B., and Elvert, M., 2001. Sea floor methane hydrates at Hydrate Ridge, Cascadia margin. In Paull, C.K., and Dillon, W.P. (Eds.), *Natural Gas Hydrates: Occurrence, Distribution, and Detection*. Am. Geophysical Union, Geophys. Monogr. Ser., 124:87-98.

Suess, E.M., Torres, M.E., Bohrmann, G., Collier, R.W., Greinert, J., Linke, P., Rehter, G., Trehu, A.M., Wallmann, K., Winckler, G., and Zulegger, E., 1999. Gas hydrate destabilization: enhanced dewatering, benthic material turnover, and large methane plumes at the Cascadia convergent margin. *Earth Planet. Sci. Lett.*, 170:1-15.

Techmer, K.S., Kuhs, W.F., Heinrichs, T., Bohrmann, G., 2001. Scanning electron microscopic investigations on natural and synthetic gas hydrates: new insights into the formation process. *Eos, Trans.*, 82:173. (Abstract).

Teichert, B.M.A., Eisenhauer, A., and Bohrmann, G., 2001. Chemoherm buildups at the Cascadia Margin (Hydrate Ridge) - evidence for long-term fluid flow. *2001 MARGINS Meet.*, Kiel, 208.

Torres, M.E., Bohrmann, G., Brown, K., deAngelis, M., Hammond, D., Klinkhammer, G., McManus, J., Suess, E., and Trehu, A.M., 1999. Geochemical observations on Hydrate Ridge, Cascadia margin, July, 1999. *Oregon State Univ. Data Rpt.* 174, ref. 99-3.

Trehu, A.M., and Bangs, N., 2001. 3-D seismic imaging of an active margin hydrate system, Oregon continental margin, report of cruise TTN112. *Oregon State Univ. Data Rpt.* 182.

Trehu, A.M., and Flueh, E., 2001. Estimating the thickness of the free gas zone beneath Hydrate Ridge, Oregon continental margin, from seismic velocities and attenuation. *J. Geophys. Res.*, 106:2035-2045.

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

Trehu, A.M., Lin, G., Maxwell, E., and Goldfinger, C., 1995. A seismic reflection profile across the Cascadia subduction zone offshore central Oregon: new constraints on methane distribution and crustal structure. *J. Geophys. Res.*, 100:15101-15116.

Trehu, A.M., Torres, M.E., Moore, G.F., Suess, E., and Bohrmann, G., 1999. Temporal and spatial evolution of a gas-hydrate-bearing accretionary ridge on the Oregon continental margin. *Geology*, 27:939-942.

Wefer, G.P., Heinze, M., and Berger, W.H., 1994. Clues to ancient methane release. *Nature*. 369:282.

Xu, W., and Ruppel, C., 1999. Predicting the occurrence, distribution, and evolution of methane gas hydrate in porous marine sediments. *J. Geophys. Res.*, 104:5081-5096.

LIST OF ACRONYMS AND ABBREVIATIONS

AMO	Anaerobic Methane Oxydation
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
FPC	Fugro Pressure Corer
GHSZ	Gas Hydrate Stability Zone
GPS	Global Positioning System
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
MCDB	Motor Driven Core Barrel
MH	Methane Hydrate
mL	Milliliter
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
VSP	Vertical Seismic Profiling
XCB	Extended Core Barrel

List of ODP Leg 204 Shipboard Scientific Party Members

Co-Chief Scientist - Gerhard Bohrmann (GEOMAR, Christian-Albrechts Universitat zu Kiel, Wischhofstrasse 1-3, Gebaude 4, Kiel 24148, Germany)

Co-Chief Scientist - Anne M. Trehu (College of Oceanic and Atmospheric Sciences, Oregon State University, 104 Oceanography Administration Building, Corvallis OR 97331-5503, USA)

ODP Staff Scientist - Frank R. Rack (Joint Oceanographic Institutions, Inc., 1755 Massachusetts Avenue, Northwest, Suite 700, Washington D.C. 20036, USA)

Inorganic Geochemist - Walter S. Borowski (Earth Sciences Department, Eastern Kentucky University, 512 Lancaster Avenue, Roark 103, Richmond KY 40475-3102, USA)

Inorganic Geochemist – Hitoshi Tomaru (Graduate School of Science, University of Tokyo, Science Building 5, 7-3-1 Hong, Bunkyo-ku, Tokyo 113-0033, Japan)

Inorganic Geochemist - Marta E. Torres (College of Oceanic and Atmospheric Sciences, Oregon State University, 104 Oceanography Administration Building, Corvallis OR 97331-5503, USA)

Organic Geochemist - George E. Claypool (8910 West 2nd Avenue, Lakewood CO 80226, USA)

Organic Geochemist – Young-Joo Lee (Petroleum and Marine Resources Research Division, Korea Institute of Geoscience and Mineral Resources (KIGAM), 30 Kajung-Dong, Yusong-Gu, Daejon 305-350, Korea)

Organic Geochemist – Alexei Milkov (Geochemistry and Environmental Research Group, Texas A&M University, 833 Graham Road, College Station, TX 77845, USA)

PCS Scientist - Gerald R. Dickens (Department of Geology and Geophysics, Rice University, 6100 Main Street, Houston, TX 77005-1892, USA)

Logging Scientist - Timothy S. Collett (Branch of Petroleum Geology, U.S. Geological Survey, Denver Federal Center, Box 25046, MS 939, Denver CO 80225, USA)

Logging Scientist – Nathan Bangs (Institute for Geophysics, University of Texas at Austin, 4412 Spicewood Springs Road, Bldg. 600, Austin, TX 78759-8500, USA)

Geophysicist – Martin Vanneste (Department of Geology, Universitetet i Tromso, Dramsveinen 201, 9037 Tromso, Norway)

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

Microbiologist - Melanie Holland (Department of Geologic Sciences, Box 871404, Arizona State University, Tempe, AZ 85287, USA)

Microbiologist – Mark E. Delwiche (Biotechnologies, Idaho National Engineering and Environmental Laboratory, 2525 N. Fremont St., Idaho Falls, ID 83415, USA)

Micropaleontologist (diatoms) – Mahito Watanabe (Geoscience Institute, Geological Survey of Japan, AIST, 1-1-1 Central 7 Higashi, Tsukuba 305-8567, Japan)

Physical Properties Specialist – Char-Shine Liu (Institute of Oceanography, National Taiwan University, P.O. Box 23-13, Taipei 106, Taiwan)

Physical Properties Specialist - Philip E. Long (Environmental Technology Division, Pacific Northwest National Laboratory, PO Box 999, Mail Stop K9-33, Richland WA 99352, USA)

Physical Properties Specialist - Michael Riedel (Geological Survey of Canada, Pacific Geoscience Centre, 9860 West Saanich Road, Sidney, BC V8L 4B2, Canada)

Physical Properties Specialist - Peter Schultheiss (GEOTEK Ltd., 3 Faraday Close, Drayton Fields, Daventry, Northants NN11 5RD, United Kingdom)

Sedimentologist - Eulalia Gracia (Institute of Earth Sciences (Jaume Almera), CSIC, Lluís Sole i Sabaris, 08028 Barcelona, Spain)

Sedimentologist - Joel E. Johnson (College of Oceanic and Atmospheric Sciences, Oregon State University, 104 Oceanography Admin. Bldg, Corvallis OR 97331, USA)

Sedimentologist – Xin Su (Center of Marine Geology, China University of Geosciences, Xueyuan Road 29, Beijing 100083, People's Republic of China)

Sedimentologist - Barbara Teichert (GEOMAR, Christian-Albrechts Universität zu Kiel, Wischhofstrasse 1-3, Kiel 24148, Germany)

Sedimentologist/Structural Geologist - Jill L. Weinberger (Scripps Institution of Oceanography, University of California, San Diego, 9500 Gilman Drive, Mail Code 0208, San Diego CA 92093-0244, USA)

Logging Staff Scientist - David S. Goldberg (Lamont-Doherty Earth Observatory, Borehole Research Group, Columbia University, Route 9W, Palisades NY 10964, USA)

Logging Staff Scientist - Samantha R. Barr (Department of Geology, University of Leicester, University Road, Leicester LE1 7RH, United Kingdom)

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

Logging Staff Scientist - Gilles Guèrin (Lamont-Doherty Earth Observatory, Columbia University, Borehole Research Group, Palisades, NY 10964, USA)

Operations Manager - Michael A. Storms (Ocean Drilling Program, Texas A&M University, 1000 Discovery Drive, College Station TX 77845, USA)

Development Engineer - Derryl Schroeder (Ocean Drilling Program, Texas A&M University, 1000 Discovery Drive, College Station TX 77845, USA)

Development Engineer – Kevin Grigar (Ocean Drilling Program, Texas A&M University, 1000 Discovery Drive, College Station TX 77845, USA)

HYACINTH Engineer- Roeland Baas (Fugro Engineers, 2260 AG Leidschendam, The Netherlands)

HYACINTH Engineer - Floris Tuynder (Fugro Engineers, 2260 AG Leidschendam, The Netherlands)

HYACINTH Engineer - Felix Weise (Institute of Petroleum Engineering, Technical University of Clausthal, Clausthal, Germany)

HYACINTH Engineer - Thjunjoto (Maritime Technik, Technical University of Berlin, Berlin, Germany)

Piezoprobe Engineer – Terry Langsdorf (Fugro-McClelland Engineers, Houston, TX)

Peizoprobe Engineer – Ko-Min Tjok (Fugro-McClelland Engineers, Houston, TX)

Schlumberger Engineer - Kerry Swain (Schlumberger Offshore Services, 369 Tristar Drive, Webster, TX 77598, USA)

Schlumberger Engineer – Herbert Leyton (Schlumberger Offshore Services, USA)

Schlumberger Engineer – Stefan Mrozewski (Schlumberger Offshore Services, USA)

Schlumberger Engineer – Khaled Moudjeber (Schlumberger Offshore Services, USA)

Laboratory Officer - Brad Julson (Ocean Drilling Program, Texas A&M University, 1000 Discovery Drive, College Station, TX 77845-9547, USA)

Assistant Laboratory Officer – Tim Bronk (Ocean Drilling Program, Texas A&M University, 1000 Discovery Drive, College Station, TX 77845-9547, USA)

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

Marine Lab Specialist: Yeoperson - Angie Miller (Ocean Drilling Program, Texas A&M University, 1000 Discovery Drive, College Station, TX 77845-9547, USA)

Marine Lab Specialist Photography - John Beck (Ocean Drilling Program, Texas A&M University, 1000 Discovery Drive, College Station, TX 77845-9547, USA)

Marine Lab Specialist Photography - Roy Davis (Ocean Drilling Program, Texas A&M University, 1000 Discovery Drive, College Station, TX 77845-9547, USA)

Marine Lab Specialist (Temporary) – Jason Deardorf (Ocean Drilling Program, Texas A&M University, 1000 Discovery Drive, College Station, TX 77845-9547, USA)

Marine Lab Specialist: Downhole Tools – Sandy Dillard (Ocean Drilling Program, Texas A&M University, 1000 Discovery Drive, College Station, TX 77845-9547, USA)

Marine Lab Specialist: Chemistry - Dennis Graham (Ocean Drilling Program, Texas A&M University, 1000 Discovery Drive, College Station, TX 77845-9547, USA)

Marine Laboratory Specialist: Curator - Jessica Huckemeyer (Ocean Drilling Program, Texas A&M University, 1000 Discovery Drive, College Station TX 77845, USA)

Marine Computer Specialist - Margaret Hastedt (Ocean Drilling Program, Texas A&M University, 1000 Discovery Drive, College Station TX 77845, USA)

Marine Lab Specialist: Chemistry – Brian Jones (Ocean Drilling Program, Texas A&M University, 1000 Discovery Drive, College Station, TX 77845-9547, USA)

Marine Lab Specialist (Temporary) – Peter Kannberg (Ocean Drilling Program, Texas A&M University, 1000 Discovery Drive, College Station, TX 77845-9547, USA)

Marine Electronics Specialist – Jan Jurie Kotze (Ocean Drilling Program, Texas A&M University, 1000 Discovery Drive, College Station, TX 77845-9547, USA)

Marine Computer Specialist - Erik Moortgat (Ocean Drilling Program, Texas A&M University, 1000 Discovery Drive, College Station TX 77845, USA)

Marine Electronics Specialist – Peter Pretorius (Ocean Drilling Program, Texas A&M University, 1000 Discovery Drive, College Station, TX 77845-9547, USA)

Marine Lab Specialist: Physical Properties – John W.P. Riley (Ocean Drilling Program, Texas A&M University, 1000 Discovery Drive, College Station, TX 77845-9547, USA)

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

Marine Lab Specialist: Underway Geophysics – Johanna Suhonen (Ocean Drilling Program, Texas A&M University, 1000 Discovery Drive, College Station, TX 77845-9547, USA)

Marine Lab Specialist (Temporary) – Paul Teniere (Ocean Drilling Program, Texas A&M University, 1000 Discovery Drive, College Station, TX 77845-9547, USA)

Marine Lab Specialist: X-ray – Robert Wheatley (Ocean Drilling Program, Texas A&M University, 1000 Discovery Drive, College Station, TX 77845-9547, USA)