OCEAN DRILLING PROGRAM

LEG 204 SCIENTIFIC PROSPECTUS

DRILLING GAS HYDRATES ON HYDRATE RIDGE, CASCADIA CONTINENTAL MARGIN

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This Scientific Prospectus is based on precruise JOIDES panel discussions and scientific input from the designated Co-chief Scientists on behalf of the drilling proponents. The operational plans within reflect JOIDES Planning Committee and thematic panel priorities. During the course of the cruise, actual site operations may indicate to the Co-chief Scientists and the Operations Manager that it would be scientifically or operationally advantageous to amend the plan detailed in this prospectus. It should be understood that any proposed changes to the plan presented here are contingent upon the approval of the Director of the Ocean Drilling Program in consultation with the Science and Operations Committees (successors to the Planning Committee) and the Pollution Prevention and Safety Panel.

ABSTRACT

During Ocean Drilling Program (ODP) Leg 204, we will drill a transect of sites through the gas hydrate stability zone on the southern part of Hydrate Ridge on the Cascadia accretionary margin offshore Oregon. Massive hydrates are present at the seafloor there, and high-resolution threedimensional seismic data indicate a complicated subsurface plumbing system. The transect will cover two distinctly different sedimentary and tectonic environments—the older sediments of the uplifted accretionary complex and the younger, well-stratified sediments of an adjacent rapidly filling slope basin. Leg objectives include (1) comparing the source region for gas and the physical and chemical mechanisms of hydrate formation between accretionary ridge and slope basin settings; (2) calibrating estimates of hydrate and underlying free gas concentrations determined with geophysical remote sensing techniques; (3) testing, using geochemical tracers, physical properties measurements, and microstructural analysis, whether variations in bottom-simulating reflector (BSR) and sub-BSR reflectivity observed in seismic data result from tectonically induced hydrate destabilization; (4) developing an understanding of the geochemical effects of hydrate formation in order to identify paleoproxies for methane release that can be used to integrate the geologic data into climate models; (5) determining the porosity and shear strength of hydrate-bearing and underlying sediments in order to evaluate the relationship between hydrates, fluid flow, and slope stability; and (6) quantifying the distribution of methanogenic and methanotropic bacteria in the sediments in order to evaluate their contribution to hydrate formation and destruction and related sediment diagenesis. To achieve these objectives, the first part of Leg 204 will be dedicated to logging while drilling (LWD) to identify regions of rapid change in physical properties prior to coring. This should permit us to optimize use of time-consuming special tools to measure in situ temperature and pressure and to retrieve cores at in situ pressure. Cores will be immediately scanned with an infrared device to detect cold spots indicative of dissociating hydrate prior to the standard sampling and analysis protocols commonly used in ODP operations. The leg also includes a two-ship seismic program with the Ewing to acquire offset vertical seismic profiles and other seismic data.

INTRODUCTION

Gas hydrate is an icelike 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 >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 (e.g., 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 the following:

- 1. How are hydrates and underlying free gas distributed vertically and horizontally in the sediment?
- 2. What controls their distribution (i.e., the sources of gas, fluid migration, and the physical chemistry of hydrate formation)?
- 3. What are the effects of this distribution on the mechanical properties of the seafloor?
- 4. How can hydrate and gas distribution be mapped regionally using remote-sensing geophysical techniques?
- 5. How does hydrate respond to changes in pressure and temperature resulting from tectonic and oceanographic perturbation?
- 6. How can we use the isotopic record as a proxy for past tectonic and climate changes?

In addition, the question of whether the hydrate system harbors a rich biosphere 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.

The Ocean Drilling Program (ODP) has a critical role to play in addressing the above questions because it provides the only means of directly sampling gas hydrates and underlying sediments containing free gas. Hydrates have been sampled during several ODP cruises. Leg 164 to the Blake Ridge was the first (and, to date, 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 will be to acquire samples under pressure using the ODP pressure core system (PCS) and the recently developed hydrate autoclave coring equipment (HYACE, HYACINTH) (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 and pressure (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 will frequently deploy tools to measure in situ temperature and pressure, especially in zones where logging-while-drilling (LWD) data indicate 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 have also incorporated an extensive suite of downhole and two-ship seismic experiments into our drilling plan.

BACKGROUND

Geologic 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 ~4.5 cm/yr (Fig. F1A). Sediment on the subducting plate contains large volumes of sandy and silty turbidites. At present, most of this sediment appears to be accreted to the continental margin, either by offscraping at the deformation front or by being underplated beneath the accretionary complex some tens of kilometers east of the deformation front (MacKay et al., 1992; MacKay, 1995) (Fig. F2).

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 yr ago (Kulm et al., 1986). It is characterized by a northern peak having a minimum depth of ~600 m and a southern peak with a depth of ~800 m (Fig. F1B). Hydrate Ridge appears to be capped by hydrate, as indicated by a nearly ubiquitous and strong bottom-simulating reflector (BSR) (Trehu et al., 1999).

A regional two-dimensional (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 to drill Site 892 (ODP Leg 194 Scientific Party, 1993). At this site, massive H₂S-rich hydrates were recovered from 2 to 19 meters below seafloor (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 (VSPs) 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 and in seafloor gas hydrates elsewhere 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 per year, which have generated an extensive database of swath bathymetry, deep-towed side-scan, and seafloor observations and samples collected via

submersible and remotely operated vehicle (Suess and Bohrmann, 1997; Torres et al., 1998, 1999; Bohrmann et al., 2002; Linke and Suess, 2001). In addition, a high-resolution three-dimensional (3-D) seismic survey was recently conducted in the immediate region of planned drilling (Trehu and Bangs, 2001).

Seafloor Observations from Southern Hydrate Ridge

Side-scan 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., 1988; 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 side-scan data indicate that the pinnacle is located in the center of a buried carbonate apron with a diameter of ~250 m (Johnson and Goldfinger, unpubl. data). Authigenic carbonates on the Cascadia margin form from methane oxidation in the sediments and discharge of isotopically light dissolved inorganic carbon at the seafloor and into the ocean. The relative absence of carbonate on the southern summit of Hydrate Ridge is thought to indicate that this hydrate/gas system is younger than that on the northern summit, providing a spatial proxy for temporal evolution of this hydrate-bearing accretionary ridge (Trehu et al., 1999). This interpretation is supported by U-Th dating of recovered carbonates (Teichert et al., 2001), which indicates that the pinnacle is <10,000 yr old, whereas the carbonate carapace on northern Hydrate Ridge is >100,000 yr 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 >50 kg of massive hydrate was recovered in a television-guided grab sample (Bohrmann et al., 1998). The samples show dense interfingering of gas hydrate with soft sediment (Fig. F3A). 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) (Fig. F4B) to massive (Suess et al., 2001). Thin sections show a structure in which gas bubbles have been filled with hydrate (Fig. F3C). Wet bulk densities of 80 hydrate samples measured on board the *Sonne* range from 0.35 to 7.5 g/cm³. Pore space was estimated from the change in sample volume before and after compression to ~160 bar (Bohrmann et al., 2000). 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 Borhmann, 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 (Figs. F1B, 3D). Because the seafloor at all three sites is well within the hydrate stability zone (Fig. F3E), 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; Rehder et al., unpubl. data). 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 dissolves in the ocean rather than reaching the atmosphere.

High-Resolution Three-Dimensional Seismic Data

Two 2-D multichannel seismic profiles across southern Hydrate Ridge acquired in 1989 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 m apart spanning the region between the two southern lines from the 1989 survey (Fig. F1C). Shots from two generator-injector (GI) guns fired simultaneously were recorded on the Lamont-Doherty Earth Observatory portable 600-m-long, 48-channel towed streamer and on an array of 21 UTIG four-component ocean bottom seismometers (OBSs). The locations of the ship and the streamer were determined via differential Global Positioning System (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.

Figure F5 shows east-west line 230 from the data volume. The data have been 3-D prestack time migrated and then converted to depth using velocities from a 3-D *P*-wave velocity model derived from tomographic inversion of first arrivals recorded on the OBSs (Arsenault et al., 2001). The profile is coincident with line 2 from the 1989 site survey (Fig. F2A). Locations of several of the planned drill sites are also shown as are boundaries between an upper facies of folded and uplifted sediments that unconformably overlies a stratigraphic sequence in which seismic layering is less pronounced. This facies in turn overlies a low-frequency, incoherent zone interpreted to be highly deformed accretionary complex material.

The data show considerable stratigraphic and structural complexity both above and below the BSR. Certain reflective horizons are anomalously bright, and these amplitude anomalies are consistent for hundreds of meters. In particular, we point out the event labeled "A" on Figure F5. This reflection has an amplitude that is ~10 times greater than that of adjacent stratigraphic events and two times greater than that of the BSR. Relative true-amplitude seismic sections illustrating characteristics of reflection A and of overlying actively venting features near the southern summit of Hydrate Ridge are shown in Figure F4A, F4B, F4C, and F4D. Locations of sections are shown on the side-scan map to illustrate the relationship between reflection A and seafloor venting. A north-south slice through the data volume indicates that this bright, negatively polarized stratigraphic horizon is continuous with the bright "spot" immediately underlying the BSR beneath the summit (Fig. F4D).

We speculate that this surface transports methane-rich fluids toward the summit of southern Hydrate Ridge and predict that variations in stratigraphic permeability favored fluid flow along this horizon, which may be an unconformity. We further speculate that diagenetic reactions have resulted in a feedback effect, enhancing flow along this surface. These speculations will be tested during Leg 204 by drilling at proposed Sites HR3a, HR4a, and HR4c.

Chaotic bright reflectivity is observed just beneath the seafloor at the summit (line 300; Fig. F4B). This reflectivity pattern is observed only at the summit and is almost exactly coincident with the "tongue" of intermediate-strength seafloor reflectivity northeast of the "pinnacle" observed in deeptowed side-scan data. This pattern also underlies the acoustic "bubble" plume that was observed each time the southern summit was crossed during the seismic data acquisition cruise. We speculate that this pattern indicates the depth extent of massive hydrate, and we will test this speculation by drilling at proposed Site HR4b. Whereas it appears that reflection A is a primary source of fluids for the summit vents, the mechanism whereby methane migrates to the seafloor is not imaged in the seismic data. We speculate that the region between reflection A and the seafloor is broken by small faults that are not well resolved in the seismic data but that permit methane-rich fluids to rise vertically from reflection A to the seafloor.

Complicated reflectivity patterns are also observed east of the southern Hydrate Ridge axis and are associated with an active secondary anticline (anticline A in Fig. F5). The "double BSR" originally identified on line 2 from the 1989 site survey (labeled C in Fig. F5) shallows to the south and merges with the BSR along 3-D line 274. It is continuous with a package of bright, regionally extensive reflections that cut across the BSR (labeled B and B' in Figs. F4 and F5). Although these reflections are very strong, they are "ringy," and polarity cannot be unambiguously determined, unlike for the BSR and for reflection A. They are also pervasively faulted, with offsets consistent with tensional cracking in response to uplift and folding. Their amplitude does not change abruptly as they cross the BSR, although there is a slight increase in amplitude as depth decreases. The lack of change in amplitude of reflection B as it crosses the BSR suggests that the high reflectivity is not a result of free gas beneath the BSR, which should form hydrate on entering the hydrate stability zone, thus changing the reflectivity. We speculate that reflection C is an unconformity at the base of an uplifted and deformed slope basin, within which the BSR is relatively weak. We further speculate that permeability of the slope basin sediments is generally low, that sedimentary horizons marked by reflections B and B' have higher permeability than adjacent strata, and that fluids rising through the accretionary complex migrate along the unconformity until they reach the B and B' horizons. The high amplitude of these reflections may result from carbonate formation along this horizon as a result of fluid flow. Proposed Sites HR1a and HR1b target the bright reflection pair B below and above the BSR. Proposed Site HR1c targets reflection C.

The BSR is anomalously shallow in the saddle between axis of Hydrate Ridge and anticline A (Fig. F5). If one assumes that seafloor temperature, sediment velocity between the seafloor and the BSR, and fluid and gas composition are known, the apparent thermal gradient can be calculated from observed BSR depth (e.g., Zwart et al., 1996). Beneath Hydrate Ridge, the depth of the BSR is generally consistent with a temperature gradient of 0.06° C/m, assuming an average velocity between the seafloor and BSR of 1.6 km/s, as determined from OBS data, and a seafloor temperature of 4° C at 800 m and 3° C at 1200 m, as indicated by hydrographic data. A BSR uplift of ~20 m, implying a temperature gradient of ~0.07°C/m, is suggested in the saddle between anticline A and the crest of Hydrate Ridge with the same assumptions. However, if reflections B and B' are caused by carbonates in the hydrate stability zone, then average velocity may be higher and the inferred temperature

gradient may be lower. Assuming an average velocity of 1.80 km/s above the BSR almost eliminates the apparent thermal gradient anomaly. A slightly lower temperature gradient is suggested for the slope basin to the east, suggesting fluid flow toward Hydrate Ridge, although this may also be, in part, due to lateral variations in sediment velocity. Leg 204 will provide critical constraints for decreasing the uncertainty in deriving constraints on fluid flow from observations of BSR depth.

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). Microorganisms are at the base of the food chain in these communities. Recent work suggests the complex complementary relationships between sulfate reducing, methanogenic, and methanotrophic microorganisms in hydrate-bearing sediments (e.g., Parkes et al., 2000; Boetius et al., 2000). These microorganisms 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 record and record of the history of past fluid flow and hydrate formation and dissociation (e.g., 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 and Borowski et al. (1996), who showed that steep sulfate gradients and shallow depths to sulfate-methane interface are a consequence of the increased influence of AMO, but 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 nonhydrate-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 in 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 timescales (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" that extended downward to 295 mbsf during the last glaciation.

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, 1983), which indicates a sedimentation rate of 120 cm/k.y. 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 (Fig. F2A) may be a significant source of methane for hydrate beneath Hydrate Ridge (Hyndman and Davis, 1992). Leg 204 will test the hypothesis that the distribution, texture, and chemistry of hydrate and related pore fluids beneath Hydrate Ridge differ from those of 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 (e.g., Paull et al., 1994; Rempel and Buffett, 1998; 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. The mechanisms whereby the gas is isolated from water, thus delaying hydrate formation as it passes through the stability zone, remains enigmatic. Drilling through these massive hydrate deposits will provide evidence on the extent of their distribution and texture, the composition of related pore waters, and their association with structural features.

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 H₂S 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 δ^{13} C, and thus the isotopic signal might reveal episodes of CH₄ venting in the past (Wefer and al., 1994; Dickens et al., 1995, 1997; Kennett et al., 1996; Torres et al., unpubl. data). Analyses of the isotopic composition of the pore fluids in Leg 204 cores, where fluid flow rate and mechanisms are expected to vary among the sites, will provide the framework needed to unravel the history of hydrate formation and destabilization recorded in the O and C isotopes in benthic foraminifers and authigenic carbonate phases.

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 toward estimating the global abundance of hydrate and evaluating its 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 will drill through hydrates in a variety of settings with different seismic characteristics and measure the physical properties of the hydrate stability and underlying free gas zones through downhole logging and a series of nested seismic experiments. The geophysical data will be referenced to direct observations of cores to address this fundamental objective of current hydrate studies.

Hydrates and Slope Stability

The possible relationship between hydrates and slope failure is presently poorly understood. On one hand, hydrates may stabilize slopes by cementing 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, Matsumoto, Wallace, et al., 1996) and have discussed how such slope instability might release massive amounts of methane into the ocean (Paull, Matsumoto, Wallace, et al., 1996; Nisbet and Piper, 1998). Leg 204 will provide critical information for testing the hypothesis that the presence of hydrate leads to instability of the underlying material by constraining mechanical and hydrological properties.

Biological Communities Associated with Hydrate and Underlying Free Gas Zones

Microorganisms play 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 to address during Leg 204 include the following: 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 pore water chemistry and texture, and vice-versa?

DRILLING STRATEGY

To test the hypotheses discussed above, we propose six primary drill sites (HR1a, HR2alt, HR3a, HR4a, HR4b, and HR4), extending to depths of 60–700 mbsf (Table T1, T2). Six alternate sites (HR1b, HR5a, HR6, HR1c, HR2, and HR2altB) were identified that will be drilled if problems are encountered at the primary sites or if time allows (Table 3). Locations of the sites are overlain on a map showing seafloor topography in Figure F1C.

The leg will start with a dedicated LWD effort. To recover the section prior to LWD, proposed Site HR1a will be cored to 350 mbsf depth. We will then employ LWD at proposed Sites HR1a (to 350 mbsf), HR3a (to 350 mbsf), HR2a (to 350 mbsf), and HR4a (to 100 mbsf), HR4b (to 60 mbsf), and HR4c (to 240 mbsf) (Table 2). If time allows, alternative proposed Sites HR1b, HR1c, HR5, and HR6 will also be drilled with the LWD (Table 3). The cruise includes a scheduled port stop to offload the LWD equipment and personnel.

Following this port call, we will continue coring operations. At each site, we will core with the advanced piston corer (APC). After APC refusal, we will core with the extended core barrel (XCB) and then the rotary core barrel (RCB) as necessary (Table 2). Two cored holes are planned for each site. Because of the ephemeral nature of gas hydrate, the drilling plan emphasizes downhole measurements and in situ sampling strategies. These include extensive use of the ODP and HYACE/HYACINTH systems to acquire cores under in situ pressure and tools such as the Davis-Villinger temperature probe (DVTP) to measure in situ temperature and pressure. This strategy should allow reconstruction of the distribution and concentration of gas hydrate and free gas stored in the sediment.

A novel aspect of this leg will be the use of infrared thermal imaging to scan each core (at least those from within and near the hydrate stability zone) immediately as it is brought on board. Because hydrate dissociation is a strongly endothermic process, cold spots thus detected should permit us to quickly identify portions of the core containing both massive and disseminated hydrate. Multiple scans may permit calculation of the original amount of hydrate present based on the change in temperature with time.

We will record pressure and acceleration at the bit during some of the APC drilling using the drill string acceleration tool to provide information on the time and intensity of impact of the APC. During this time, OBSs will be deployed nearby by the *Ewing* to record "background" seismic noise. We will test whether the APC generates a detectable signal on the OBS. If so, we will collect reverse-VSP data, with the APC acting as a downhole source. This source has the potential to excite shear waves, whereas the conventional air gun/water gun sources generate only *P*-waves.

LOGGING STRATEGY

Logging While Drilling

State-of-the-art LWD tools will be deployed to 350 mbsf at proposed Sites HR2alt and HR3a and to total depth (TD) at other sites to obtain high-quality porosity and density (ADN) logs, various resistivity measurements (including oriented resistivity images similar to Formation MicroScanner [FMS] images but with 360° coverage of the borehole wall), and gamma radiation (resistivity at the bit [RAB]). The RAB images should be particularly interesting and will be potentially useful for pinpointing gas hydrate–bearing zones. In addition to directly addressing the leg objectives, the information retrieved through logging while drilling will be critical for planning subsequent leg

activities, such as locating intervals where the pressure core sampler (PCS) and HYACE tools might be used as well as positioning of stations for VSP experiments.

Wireline Logging

Wireline logging and VSP experiments will be performed at three proposed sites, HR1a, HR2alt, and HR3a. Proposed Site HR1a will be cored and logged to 350 mbsf, and proposed Sites HR2alt and HR3a will be cored and logged to 650 and 700 mbsf, respectively. The standard wireline triple combination (triple combo) and FMS-sonic tool strings will be deployed, as well as the threecomponent well seismic tool (WST-3) to record the vertical and offset VSP experiments. Acousticvelocity logs (along with the VSPs) are critical in determining the velocity structure associated with the BSR. Depth-to-seismic ties will also be accomplished by means of synthetic seismograms computed from density and sonic logs. This correlation can be made using standard logs to measure the density, porosity, and compressional velocity of the sediments. Both P-wave and S-wave velocity measurements will be made using the standard dipole sonic imager (DSI) tool. Sediment permeability may be estimated using temperature gradients and heat flow changes by running temperature, porosity, and resistivity (dual induction tool [DIT]) logs. The dual laterolog (DLL) would only need to be used in the unlikely event that the bulk resistivity is extremely high. Previously measured resistivities at nearby Site 889 and Site 890 were <1.0 and <2.5 Ω m, respectively, and therefore the standard dual induction resistivity (DITE) tool should provide adequate results. Highresolution FMS images will compliment the RAB images and may indicate thin beds and fractures in hydrated sediments (e.g., sediment fabric).

The VSPs will be coupled with walkaway shooting. Results from an offset VSP would also show velocity changes below hydrates, particularly if free gas is present. Walkaway shooting will provide a unique understanding of the lateral variations in the acoustic structure (both V_P and V_S) that are in turn related to the extent, fabric, and distribution of gas hydrates.

SAMPLING STRATEGY

Generally, traditional sampling procedures, as discussed in detail on the ODP World Wide Web site (http://www-odp.tamu.edu/publications/policy.html), will be followed. This includes maintaining a minimum permanent archive that consists of half of each core. Distribution of samples from the other half will be determined by the Sample Allocation Committee after discussion with all members of the shipboard and shore-based scientific parties.

Exceptions to this standard procedure will be employed in some intervals containing hydrates or features related to hydrate dynamics for which splitting the core to retain an archive half would destroy the material of interest. This includes samples acquired by HYACE or PCS and samples for microbiological analysis. For microbiological analysis, sample handling procedures developed for Leg 201, the first ODP leg dedicated to microbiology, will be followed (http://www-odp.tamu.edu/publications/prosp/201_prs/201toc.html), with possible modifications based on experience gained during Leg 201. HYACE cores will be retained temporarily in the HYACE laboratory transfer chamber for further testing. Selected hydrate-bearing samples obtained through both pressure coring and conventional coring may also be preserved in liquid nitrogen, in freezers at -80° C, or in pressure chambers.

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TABLE CAPTIONS

Table 1. Summary table of sites for Leg 204 updated after the Pollution Prevention and Safety Panel meeting of 3–4 December 2001. All sites are approved as listed.

Table 2. Time estimates for Leg 204: primary and secondary sites.

Table 3. Leg 204 alternate sites.

FIGURE CAPTIONS

Figure F1. A. Map of the Cascadia subduction zone. The box shows the location of the topographic map shown in B. **B.** Bathymetric map of the Cascadia accretionary prism in the vicinity of Hydrate Ridge. NHR = north Hydrate Ridge summit, SHR = south Hydrate Ridge summit; SEK = Southeast Knoll. Locations of the 3-D seismic survey and the 2-D seismic profiles shown in Figure F2 are also indicated. **C.** Bathymetric map of southern Hydrate Ridge. Locations of the planned drill sites are also shown (solid circles = primary sites, open circles = alternate sites). EM300 bathymetric data are from Clague et al. (2001).

Figure F2. A. Seismic profile across the northern part of the 3-D seismic survey (1989 line 2). The frontal thrust, décollement surface, ocean basement, and approximate outline of the area shown in Figure 4 are marked. This profile is tentatively interpreted to show stepping down of the décollement and underplating of subducted sediments beneath Hydrate Ridge. **B.** Line 1 from the 1989 survey, which crosses Hydrate Ridge just south of the 3-D survey. Relatively gentle folding of sediments on the western flank of Hydrate Ridge suggest that vergence of the deformation front has recently changed from landward to seaward. A possible step in oceanic basement is also shown. Oceanic basement is ~7 km beneath the summit of Hydrate Ridge. SP = shotpoint, BSR = bottom-simulating reflector.

Figure F3. A. Massive hydrate from the summit of southern Hydrate Ridge. **B.** Porous hydrate from the summit of southern Hydrate Ridge (from Suess et al., 2001). **C.** Thin section of macroscopically massive hydrate showing porous structure (from Bohrmann et al., 1998). The thin section measures ~6 cm across. **D.** Acoustic "bubble" plumes from three sites on the Oregon margin (see Fig. F1B), recorded by a Seabeam 2000 12-kHz echo sounder. **E.** Phase diagram for methane hydrate in seawater. The depths of the northern and southern summits of Hydrate Ridge, the measured temperature gradient at Site 892, and the temperature-depth profile from a concentration/temperature/depth (CTD) cast on northern Hydrate Ridge are also shown. Hydrate should be stable at the seafloor and in the water column to a depth of ~450 m over Hydrate Ridge.

Figure F4. A–D. Seismic slices from the 3-D seismic data that illustrate the characteristics of reflection A. **E-H.** Slices that illustrate reflections B, B', and C. **I.** The locations of these profiles are shown on the map, which has topographic contours overlain on deep-towed side-scan data (Johnson and Goldfinger, unpubl. data). Note the bright spot southwest of the summit. It probably defines the extent of a buried apron of carbonates that surrounds the carbonate "pinnacle" that was discovered during Alvin dives in 1999. This carbonate structure sits in a moat and rises ~50 m above the surrounding seafloor (C). Its shadow appears in the side-scan data as a black spot within the bright spot. Dives show abundant vent fauna in cracks on the pinnacle, indicating aqueous fluid flow, but no bubbles have been observed. In the seismic data, this feature is characterized by blanking of underlying seismic reflections. A "tongue" of intermediate-strength seafloor reflectivity northeast of the pinnacle probably delimits the region of massive hydrate at the seafloor and appears in the seismic data as a region of bright, chaotic reflectivity (B). All bubbles observed on southern Hydrate Ridge via submersible or 12-kHz echo sounder emanate from this summit region. Reflection pair B, B', and C are associated with anticline A (Fig. F5) on the eastern flank but are not associated with any reflectivity anomalies on the seafloor. J. Predicted and observed BSR depths along line 230. Fine lines show predicted bottom-simulating reflector (BSR) depths for different assumed temperature gradients. The lower of the two solid lines is for an assumed seafloor temperature of 4°C; the upper fine line is for a seafloor temperature that decreases linearly from 4° to 3°C as depth increases from 800 to 1200 m, as indicated by hydrographic data (Trehu et al., 1995). The thick dashed line is calculated from line 230 assuming a constant average velocity between the seafloor and the BSR of 1.6 km/s. A temperature gradient of ~0.7°C/km is suggested for the saddle between the axis of the ridge and anticline A; a gradient of 0.055°C/km is suggested for the slope basin. Open symbols show effects of uncertainties in average velocity. A velocity of 1.8 km/s above the BSR removes the apparent thermal anomaly at a water depth of 860-900 m; a velocity of 1.5 km/s removes the anomaly for water depths >1020 m. This figure illustrates the difficulty of resolving small differences in apparent temperature gradient from the BSR data in this region.

Figure F5. An east-west slice through the 3-D data volume, converted to depth using a 3-D velocity model determined through tomographic inversion of first arrivals recorded on OBSs (Arsenault et al., 2001). Sites to be drilled during Leg 204 are shown. Primary Site HR2alt is in a similar setting as HR2altB, which has been approved by the Pollution Prevention and Safety Panel as a backup site in case we encounter difficulties at proposed Site HR2alt. The BSR and reflectivity of underlying strata are brighter at proposed Site HR2alt than at HR2altB. The solid green line marks the boundary between low-amplitude, low-frequency, chaotic reflectivity, interpreted to be highly deformed sediments of the accretionary complex, and overlying reflective strata. This boundary corresponds to a rapid increase in velocity from <1.8 to >2.0 km/s. The dashed green line delimits a zone of intermediate reflectivity. Reflections marked A, B, B', and C and anticlines A and B are discussed in the text. VE = vertical exaggeration.

Table 1. Summary of PPSP-approved Leg 204 sites.

Site	Priority	Line seismic grid	Trace seismic grid	X UTM	Y UTM	Latitude (°N)	Longitude (°W)	Water depth (m)	Penetratior (mbsf)
HR1a	1	230	465	331775	4939164	44.586159	125.119213	890	350
HR1b	2	230	365	330531	4939185	44.586056	125.134881	850	150
HR1c	2	230	538	332678	4939392	44.588421	125.107920	970	260
HR2	2	300	742	335207	4937321	44.57037	125.075417	1200	620
HR2alt	1	300	750	335304	4937312	44.57031	125.074193	1210	620
HR2altB	2	230	800	335964	4939039	44.586001	125.066437	1200	650
HR3a	1	230	278	329453	4939224	44.586152	125.148464	870	700
HR4a	1	308	272	329321	4937277	44.568605	125.149480	794	100
HR4b	1	300	283	329471	4937471	44.570386	125.147657	780	60
HR4c	1	268	268	329294	4938281	44.577631	125.150153	830	240
HR5a	2	230	625	333791	4939105	44.586096	125.093815	1035	260
HR6	2	283	250	329065	4937903	44.574176	125.152910	830	60

Table 2. Planned Leg 204 operations and time estimates.

San Francisco HR1a								` , ,	(days)
HR1a		37.45° 122.27°	NA	Starting port for Leg 204 (leg begins w/1st line ashore) (Note: load all Anadril LWD, Hyacinth, and PCS tools) Transit ~448 nmi to Site HR1a @ 10.5 kt	5.0	1.8			
	976	44.586159°	350	Hole A: APC to ~150 mbsf, XCB to ~350 mbsf; Adara, DVTP			2.3		
		125.119213°		Hole B: drill LWD hole to 350 mbsf Transit ~1.2 nmi to Site HR3a @ 10.5 kt		0.1	1.5		3.8
HR3a	893	44.586152° 125.148464°	700	Hole A: drill LWD hole to 350 mbsf			1.4		1.4
HR2alt	1221	44.57031°	620	Transit ~3.3 nmi to Site HR2alt @ 10.5 kt Hole A: drill LWD hole to 350 mbsf		0.1	1.6		
		125.074193°		Transit ~3.2 nmi to Site HR4a @ 10.5 kt		0.1			1.6
HR4a	773	44.568605° 125.149480°	100	Hole A: drill LWD hole to 100 mbsf			0.9		0.9
HR4b	803	44.570386°	60	Transit ~0.1 nmi to Site HR4b @ 10.5 kt Hole A: drill LWD hole to 60 mbsf		0.1	0.8		0.7
TIKAD	003	125.147657°	00	Transit ~0.4 nmi to Site HR4c @ 10.5 kt		0.1	0.0		0.8
HR4c	795	44.577631°	240	Hole A: drill LWD hole to 240 mbsf		0.1	1.2		1.2
storia		125.150153° 46.12°	NA	Transit ~124 nmi to Astoria @ 10.5 kt Mid-leg port call: offload LWD tools	0.4	0.6			1.2
HR2alt	1221	123.50° 44.57031°	620	(estimate 12-hr port call—daylight only) Transit ~126 nmi to Site HR2alt @ 10.5 kt Hole B: APC to ~150 mbsf, XCB to ~500 mbsf;		0.6	3.1		
TINZUIC	1221	125.074193°	020	Adara, DVTP Hole C: APC to ~150 mbsf, XCB to ~500 mbsf;			3.7		6.8
				PCS, Hyacinth Transit ~3.2 nmi to Site HR4a @ 10.5 kt		0.1			
HR4a	773	44.568605°	100	Hole B: APC to ~100 mbsf; Adara			0.7		
		125.149480°		Hole C: APC to ~100 mbsf; PCS, Hyacinth		0.1	1.1		1.8
HR3a	893	44.586152°	700	Transit ~1.1 nmi to Site HR3a @ 10.5 kt Hole B: APC to ~150 mbsf, XCB to 500 mbsf; DVTP		0.1	2.9		
		125.148464°		Hole C: APC to ~150 mbsf, XCB to 500 mbsf; PCS, Hyacinth			3.4		
				Hole D: drill to ~490 mbsf, RCB to 700 mbsf; MBR			3.5	2.5	
				(WL log—triple combo/FMS-sonic/VSP/offset) Transit ~1.2 nmi to Site HR1a @ 10.5 kt		0.1			12.3
HR1a	976	44.586159°	350	Hole C: APC to ~150 mbsf, XCB to ~350 mbsf; PCS, Hyacinth			3.2	2.5	
		125.119213°		(WL log—triple combo/FMS-sonic/VSP/offset) Transit ~2.1 nmi to Site HR2alt @ 10.5 kt		0.1			5.7
HR2alt	1221	44.57031°	620	Hole D: drill to ~490 mbsf, RCB to 620 mbsf; MBR			3.5	2.5	
		125.074193°		(WL log—triple combo/FMS-sonic/VSP/offset) Transit ~3.1 nmi to Site HR4b @ 10.5 kt		0.1			6.0
HR4b	803	44.570386°	60	Hole B: APC to ~60 mbsf; Adara			0.6		
		125.147657°		Hole C: APC to ~60 mbsf; PCS, Hyacinth			0.9		1.5
HR4c	795	44.577631°	240	Transit ~0.4 nmi to Site HR4c @ 10.5 kt Hole B: APC to ~150 mbsf, XCB to 240 mbsf; DVTP		0.1	1.3		
		125.150153°		Hole C: APC to ~150 mbsf, XCB to 240 mbsf; PCS, Hyacinth			2.2		3.5
an Diego		32.45° 117.10°	NA	Transit ~819 nmi to San Diego @ 10.5 kt Ending port for Leg 203 (leg officially ends with 1st line ashore)		3.4			
ubtotal:					5.4	7.5	39.6	7.5	47.1

Table 3. Leg 204 alternate sites.

Site	Water depth (m)	Latitude (°N) Longitude (°W)	PPSP- approved penetration (mbsf)	Operations description	Coring and LWD (days)	Total Site (days)
HR5	1046	44.586096°	260	Hole A: Drill LWD hole to 260 mbsf	1.2	
		125.093815°		Hole B: APC to ~150 mbsf, XCB to ~260 mbsf; Adara, DVTP	1.5	
				Hole C: APC to ~150 mbsf, XCB to ~260 mbsf; PCS, Hyacinth	2.4	5.1
HR6	861	44.574176°	60	Hole A: Drill LWD hole to 60 mbsf	0.8	
		125.152910°		Hole B: APC to ~60 mbsf; Adara	0.6	
				Hole C: APC to ~60 mbsf; PCS, Hyacinth	1.7	3.1
HR1b	931	44.586056°	150	Hole A: Drill LWD hole to 150 mbsf	1.0	
		125.119213°		Hole B: APC to ~130 mbsf, XCB to ~150 mbsf; Adara, DVTP	0.9	
				Hole C: APC to ~130 mbsf, XCB/PCS to ~150 mbsf; Hyacinth	1.7	3.6