

1. LEG 164 OVERVIEW¹

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ABSTRACT

Ocean Drilling Program (ODP) Leg 164 was the first dedicated academic effort to investigate naturally occurring marine gas hydrates. The entire leg was spent using the currently available tools and techniques that are relevant to characterizing gas hydrate and gas-bearing sediments. The shipboard and shore-based investigations that are reported in the ODP Leg 164 *Initial Reports* volume, this ODP *Scientific Results* volume, and the outside literature are the lasting achievements of this leg. Here, we briefly summarize some of the clearest accomplishments of the leg, along with the original objectives. Also included is a brief discussion of the operational shortcomings of this leg.

DRILLING STRATEGY

In November and December 1995, Ocean Drilling Program (ODP) Leg 164 targeted the Blake Ridge gas hydrate field and adjacent Carolina Rise (Paull, Matsumoto, Wallace et al., 1996). The Blake Ridge is a continental rise contourite deposit that has a crest that extends to the southeast perpendicular to the general trend of the North American Continental Margin (Mountain and Tucholke, 1985). The area is associated with an extensive and well-developed bottom simulating reflector (BSR) (Fig. 1), covering about 26,000 km² (Dillon and Paull, 1983). Previous drilling by the Deep Sea Drilling Project had indicated that gas hydrates occurred in this region (e.g., Kvenvolden and Barnard, 1983).

The program consisted of drilling a transect of deep sites (Sites 994, 995, and 997) on the Blake Ridge, extending down through the zone where gas hydrates are stable and into the sedimentary section below. These sites provide an opportunity to study the in situ characteristics of gas hydrates and gas hydrate-bearing sediments and to document the nature of BSRs (Fig. 2). Because of the ephemeral nature of gas hydrates, emphasis was placed on proxy sampling and downhole tool measurements that allowed reconstruction of the in situ conditions associated with the gas hydrates. Thus, the decision was made to emphasize running in situ data-collecting tools in each hole, at the expense of increased core recovery.

Short holes (50–67 m) were also drilled at four sites (Sites 991, 992, 993, and 996) on the Carolina Rise where diapirism has disturbed the gas hydrate-bearing sediment section. The objective was to investigate physical properties and gas migration at these disturbed sites. Sites 991, 992, and 993 were located within the slide scar associated with a major Pleistocene age slide that surrounds a diapir (Popenoe et al., 1993). Site 996 was located along a fault trace on the crest of another diapir that is surrounded by a distinct BSR (Paull et al., 1995).

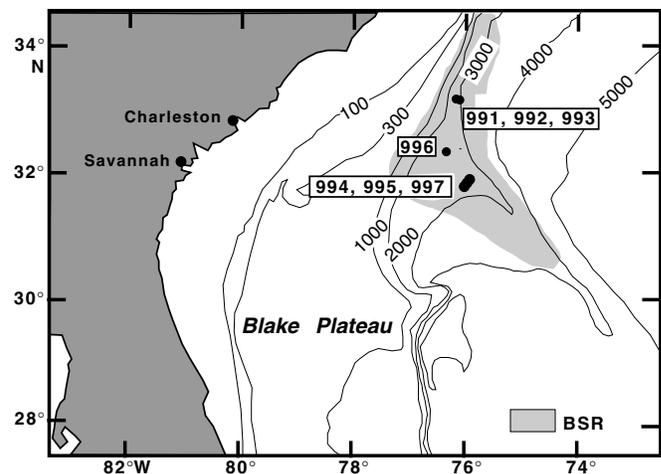


Figure 1. Map showing location of ODP Leg 164 Sites with respect to the regional BSR (Dillon and Paull, 1983).

BASIC SHIPBOARD RESULTS

Deep Holes on Blake Ridge Transect

Sites 994, 995, and 997 were drilled to 700–750 mbsf on the Blake Ridge within the same stratigraphic units. These three sites form a 10-km-long transect that extends from the ridge flank, where there is no BSR, to the ridge crest where there is a very strong BSR (Figs. 1, 2). The holes extended through the base of gas hydrate stability (~450 mbsf) and 250–300 m into the underlying sediments.

Sediment Characteristics

Most of the sediments recovered during Leg 164 accumulated during the Pliocene and Miocene (Okada, Chap. 33, this volume) at very rapid rates (up to 350 m/m.y.). The sediments were deposited by the south-flowing Western Boundary Undercurrent that sweeps southward along the Atlantic Margin (Shipboard Scientific Party, 1972; Gradstein and Sheridan, 1983). The stratigraphic sequence is composed of lithologically rather homogeneous, nanofossil-rich clays and claystones and variable amounts of opaline silica. Intersite and downhole variation in sediment physical properties and lithology was minimal. The lithologic similarity allows the distribution of gas

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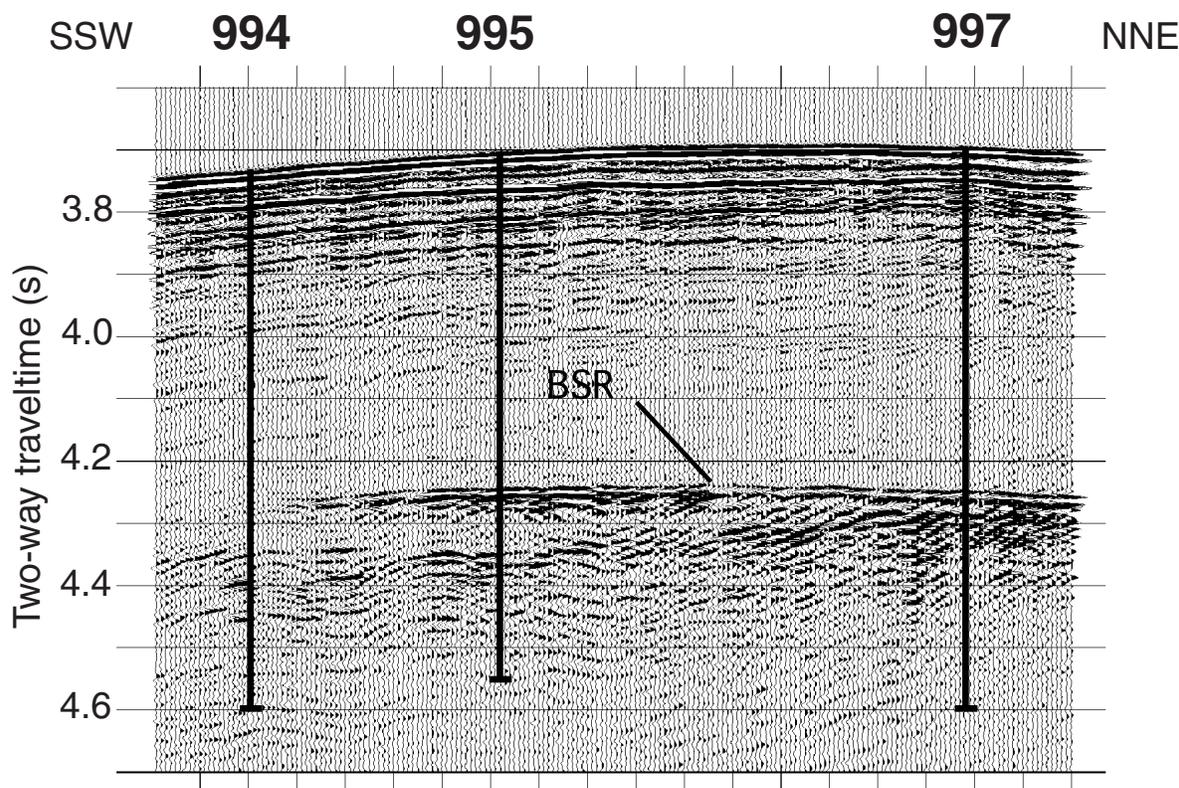


Figure 2. Seismic reflection profile through Sites 994, 995, and 997 showing relationship of drill holes to the BSR.

hydrate and the origins of the BSR (~450 mbsf) to be studied without the complication of lithologic factors. The sediments typically contain between 0.5% and 1.5% organic carbon, enough to generate significant quantities of microbial methane.

Sediment Gases

The cored sediments were very gassy and experienced vigorous expansion during recovery. Sediments frequently extruded from the liners as the cores arrived on deck. Sediment recovery between ~190 and 480 mbsf tended to be low (averaging ~50%). The gas is predominately methane (~99%) with secondary amounts of carbon dioxide, and only trace amounts of ethane and other hydrocarbon gases.

Gas Hydrate Samples

Recovered gas hydrate occurred as nodules and veins. The largest sample was a >30-cm-long piece of massive gas hydrate from Site 997 on the Blake Ridge (Fig. 3). Decomposing gas hydrates yielded gas that was ~99% methane and ~1% carbon dioxide. Volumetric ratios of the evolved gas and water for these hydrate samples ranged from 130 to 160, which is a stoichiometric ratio that suggests at least 70% cage filling of Structure I methane gas hydrates (Sloan, 1990). The most commonly observed hydrate occurrences were associated with thin (~1 mm) veins of white hydrate, which could be seen on the surfaces of quickly opened cores from Site 996 on the Blake Ridge Diapir.

Pore-Water Chloride

Measurements of interstitial water chloride concentrations from high-resolution sampling provided quantitative estimates of the minimum amounts of in situ gas hydrate in individual samples. During

gas hydrate formation, water and methane removal leave residual pore waters increasingly saline. Over time, locally elevated chloride concentrations associated with gas hydrate formation diffuse away. When sediment-hosted gas hydrates decompose during drilling and core recovery, they release water and gas back into the pore space, freshening the pore waters. Pore-water profiles from Sites 994, 995, and 997 trend to fresher values to depths of ~200 mbsf. From ~200 mbsf to the depth of the BSR (~450 mbsf), pore-water chloride concentrations are highly variable and characterized by local, anomalously fresh values (Fig. 4). Beneath ~450 mbsf, the chloride values are nearly constant. Departures from base-line chloride values can be used to calculate the minimum amount of gas hydrate that occurs in the samples. Shipboard calculations of the amount of gas hydrate that decomposed in individual samples were quite variable, but most samples had 1%–2% gas hydrate filling the total sediment volume and some ranged up to 14% within the zone from 200 to 450 mbsf. Nearly as much gas hydrate was inferred to occur at Site 994, which was not associated with a BSR, as at Sites 995 and 997, where a well-developed BSR is identified.

Well-Log Data

An extensive suite of logs was run at each deep site. Well logs show distinct zones of higher velocity and electrical resistivity that are coincident with zones where chloride anomalies indicate the presence of gas hydrates (Fig. 5). Shipboard physical properties data (e.g., porosity, grain density, water content, etc.) do not explain these variations. Thus, it is inferred that the log parameters are related to properties that are lost during core recovery (e.g., free gas and gas hydrate). Calculations of the amount of gas hydrate needed to produce these offsets are consistent with predictions from the chloride data. Below 450 mbsf, sediment velocities are equal to or less than seawater (1500 m/s), indicating the presence of free gas.



Figure 3. Photograph of a nearly pure piece of gas hydrate (Section 164-997A-42X-3; 331 mbsf) that is ~5 cm × 14 cm in size, white colored, and coated by greenish gray drilling slurry. Note the bubbles within the slurry.

In Situ Gas Sampling

A pressure core sampler (PCS) was used with unprecedented success (Dickens et al., 1997). The device takes a small sediment core (42 mm diameter, up to 0.86 m long) from the bottom of the bore hole and seals the core into a pressure housing so that recovery occurs under in situ pressure. Thus, PCS cores contain all their original gases until they are opened to the atmosphere. PCS cores recovered from Sites 995 and 997 produced between 0.8 and 46 L of methane per liter of pore space (Dickens et al., Chaps. 11 and 43, both this volume). Gas volumes captured by the PCS often grossly exceeded (~10 times) the concentration needed for gas saturation under surface conditions (Fig. 6). Such observations make it easy to understand why the other cores expanded so dramatically during recovery. Above the base of gas hydrate stability, the excess gas was presumably supplied from dissociation of gas hydrates that would have occupied up to 8% of the sediment volume. The excess gas that was captured at and beneath the base of gas hydrate stability demonstrates that free gas is associated with the BSR and occurs intermittently throughout the sedimentary section below. In fact, the volume of free gas trapped in sediments beneath the base of gas hydrate stability rivals the amounts stored as gas hydrate. Dickens et al. (1977) used the measured amount of gas and the known regional distribution of the BSR (Dillon and Paull, 1983) to estimate that ~35 Gt of methane carbon is stored in the Blake Ridge (15 Gt are in gas hydrate, 5 Gt dissolved in pore water, and 15 in free gas).

Vertical Seismic Profiles

The velocity structure of the sediments and the precise depth of the BSR were determined with vertical seismic reflection profiles (Holbrook et al., 1996; Fig. 7). The velocities of sediments overlying

the BSR only reached ~1850 m/s, consistent with the presence of a few percent gas hydrate. However, velocities as low as ~1400 m/s were measured beneath the BSR at Site 997, indicating the presence of free gas.

In Situ Temperatures

More than nine in situ temperature measurements establish the temperature gradient to depths of up to 415 mbsf at each site (Ruppel, 1997). Extrapolation of these thermal gradients to depths that correspond with the BSR allows the experimentally predicted gas hydrate phase boundaries (assuming hydrostatic pressure) to be determined. The predicted temperatures are 0.5°C to 2.9°C colder than experimental data predict the base of gas hydrate stability would be.

Core Recovery Temperatures

Many cores came up surprisingly cold and some cores were partially frozen. The cool temperatures measured in the zone where gas hydrates (200–450 mbsf) were common are interpreted to be an artifact of the recent decomposition of gas hydrates and the cooling associated with the expansion of escaping gas. Gas hydrate dissociation is endothermic and thus cools the surrounding sediments. However, surprisingly cold temperatures were also measured on freshly recovered cores from Site 997 below the gas hydrate-bearing zone. These low temperatures are attributed to cooling associated with the expansion of escaping gas bubbles.

Diapir Sites

Short holes (50–67 mbsf) were drilled on the flanks and crest of the Cape Fear Diapir (Sites 991, 992, and 993) and the Blake Ridge

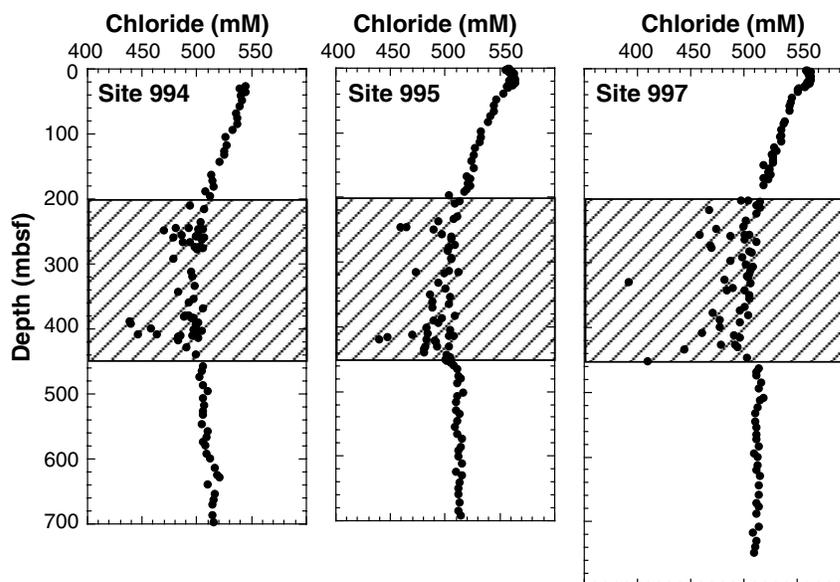


Figure 4. Plots of interstitial water chloride values measured at Sites 994, 995, and 997. Hatched areas indicate zone where gas hydrates are common.

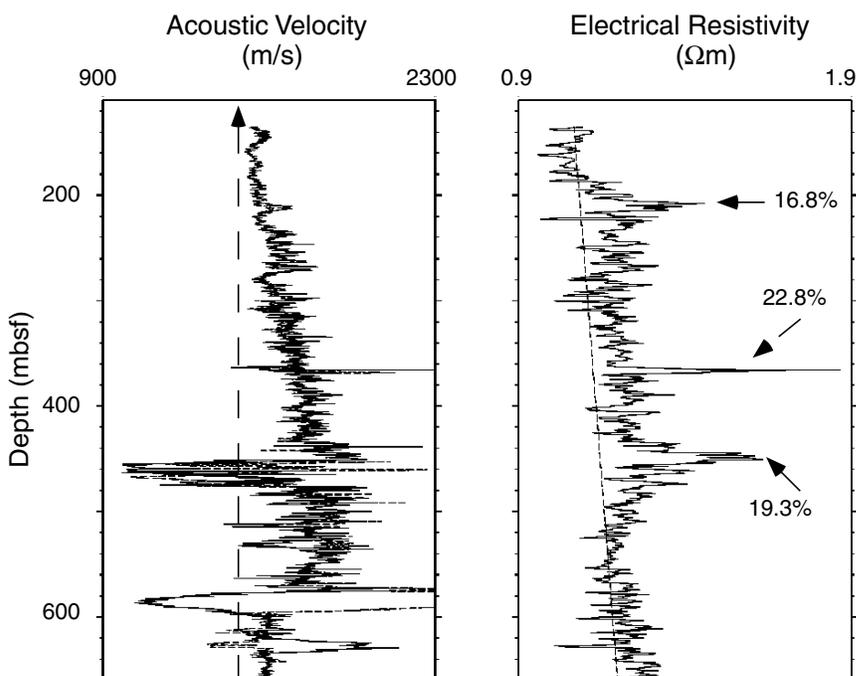


Figure 5. Plot illustrating acoustic velocity log (left) and resistivity log data (right) from ODP Hole 997B. Dashed line on acoustic log indicates seawater velocities (i.e., 1500 m/s). Also shown is the projection of resistivity trend used to calculate “potential” gas hydrate amounts by shipboard scientists (see Collett and Ladd, Chap. 19, this volume; Lee, Chap. 20, this volume). Arrows indicate log peaks associated with greater calculated amounts of gas hydrate.

Diapir (Site 996). Increases in salinity observed at these sites suggest that salt cores exist in the diapirs at depth.

Slide Scar

Sites 991, 992, and 993 all lay within the scar of the Cape Fear Slide. A thin veneer (2.05 m) of Holocene material covered the slide scar at Site 991, but older materials were exposed at the seafloor at Sites 992 and 993. The sediments from Sites 991 and 992 were strongly deformed.

Seafloor Gas Venting

Site 996 is located where gas-rich plumes occur in the water column above a pockmarked seafloor associated with active chemosynthetic biological communities (Paull et al., 1995). Beneath these

sea-floor features, a small fault extends downward toward the BSR, suggesting that fluid migration is associated with gas hydrate-bearing sediment below. Gas hydrates were common in cores from the uppermost sediment column.

The shallow cores (>20 mbsf) evolved enough hydrogen sulfide to saturate hand-held sensors (>100 ppm). Because hydrogen sulfide concentrations decrease with depth and are not elevated at other sites in the region, the hydrogen sulfide is believed to be produced locally from sulfate via anaerobic methane oxidation (Whiticar and Faber, 1986) near the seafloor. Thus, the methane supplied from below and sulfate derived from seawater react to produce hydrogen sulfide within the surface sediments. Pervasively cemented carbonate horizons and fossil seep communities were found in the subsurface. Thus, seepage appears to have occurred at least intermittently at this site throughout the Pleistocene.

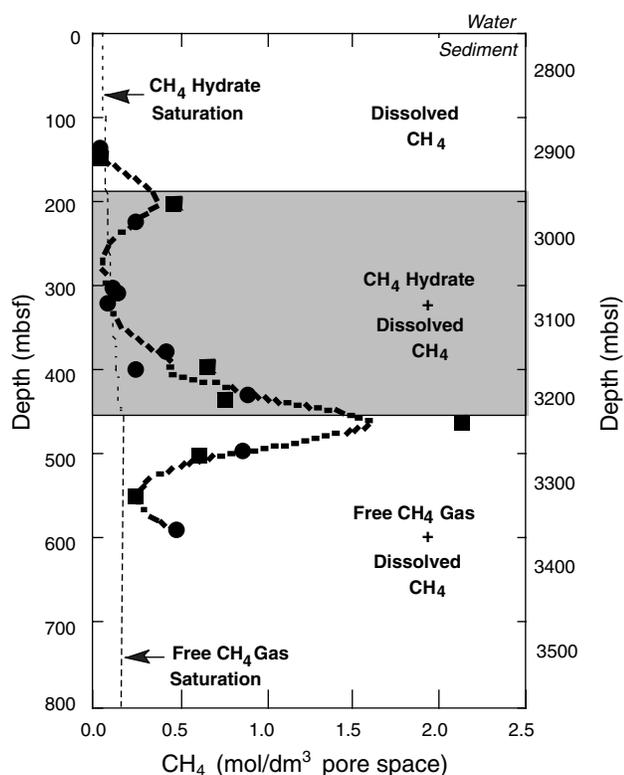


Figure 6. In situ methane quantities at Sites 995 (circles) and 997 (squares) shown with respect to water depth (mbsl) and sediment depth (mbsf). Methane hydrate occurs in sediment from 190 to 450 mbsf, whereas free methane gas occurs in sediment below 450 mbsf. In situ methane quantities (mol/dm^3 pore space) indicate the total volume of gas released from the PCS (Dickens et al., Chaps. 11 and 43, both this volume). A smoothed curve through all in situ methane quantities (bold), a saturation curve (dashed line) for methane in seawater with methane hydrate, or in seawater with free methane gas, is shown.

COMPARISON BETWEEN THE STATED OBJECTIVES AND RESULTS OF THE LEG

Each drilling leg that is being considered by the ODP is outlined in a Drilling Prospectus that is circulated through the ODP community. The Prospectus documents the major objectives and a strategy to achieve the objective. Below, each of the 12 original objectives of Leg 164 are listed with a statement about what was accomplished toward meeting that objective.

1. Assessing the amounts of gas trapped in extensively hydrated sediments.

The traditional methods of core description do not work for estimating the amounts of gas hydrate because gas hydrates are unstable under surface conditions. Thus, estimates of the amounts of gas hydrate were made using the following proxy techniques. Shipboard estimates based on conservative calculations using the chloride values indicated up to 14% of the sediment volume of some samples and on average 1.3%, 1.8%, and 2.4% of the sediment volume above 450 mbsf was filled with gas hydrate at Sites 994, 995, and 997, respectively. The oxygen isotopic composition (based on a newly determined fractionation factor between water and gas hydrate) predict that 3%–6% of the sediment volume between 200 and 450 mbsf at Sites 994, 995, and 997 was occupied by gas hydrate (Matsumoto and Borowski, Chap. 6, this volume). Gas volumes from the PCS samples

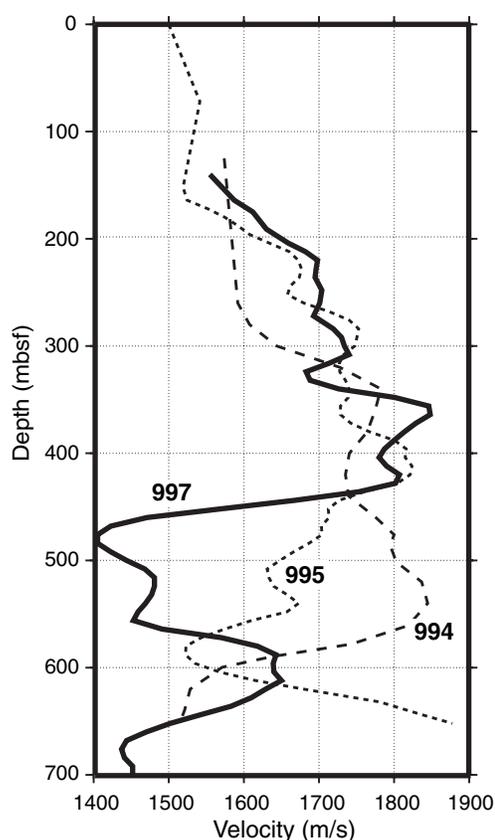


Figure 7. Velocity profiles obtained with vertical seismic experiments conducted at Sites 994, 995, and 997 (Holbrook et al., 1996).

required that individual samples contained between 0% and 9% gas hydrate (Dickens et al., 1997). Calculations based on downhole resistivity log data indicate that 1%–11% of the bulk sediment volume was occupied by gas hydrate (Collett and Ladd, Chap. 19, this volume). Calculations based on downhole velocity log data indicate that either 12.1% (using porosity values from the bulk density) or 3.8% (using core-derived porosity) of the bulk sediment was gas hydrate filled (Lee, Chap. 20, this volume). Data from a shear-wave sonic tool indicates that 5%–10% of the pore space was occupied by gas hydrates (Guerin et al., in press). Seismic velocity data from the vertical seismic profiles suggest that at least 2% of the sediment volume is occupied by gas hydrate (Holbrook et al., 1996). The various techniques used to make these estimates operate on variable spatial scales and are based on simple assumptions. Nevertheless, the assumptions are fundamentally different between the techniques. However, the estimated values using the various techniques are broadly consistent and indicate that on average a few percent of the sediment volume was filled with gas hydrate, with some zones having higher concentrations.

Whereas the chloride data clearly indicated that the top of an extensive zone of gas hydrate extended between ~200 and 450 mbsf at Sites 994, 995, and 997, different interpretations of the chloride data produce different total amounts and distribution of the gas hydrate. The shipboard estimates were based on the departures in the chloride values from a baseline that was fitted to the measured values. However, this interpretation does not account for the occurrence of chloride values lower than seawater throughout most of the cored sedimentary section. Other ways of fitting and modeling the pore-water Cl^- values will produce higher estimates of the gas hydrate amounts (Paull and Ussler, 1997; Egeberg and Dickens, 1999). Egeberg and

Dickens (1999) have modeled the data with respect to distribution of gas hydrate and predict that the top of the gas hydrate-bearing zone extends to ~40 mbsf. In their model, the gas hydrate formation starts within ~15 m of the base of sulfate reduction, where the dissolved methane concentrations in the pore waters are still only a few millimoles/liter (Hoelher et al., Chap. 8, this volume).

Comparisons between the amounts of gas recovered from the PCS (Dickens et al., 1997 and Chaps. 11 and 43, both this volume) and the traditional ODP headspace gas measurements (Kvenvolden and Lorenson, Chap. 3, this volume) indicate that headspace gas measurements can grossly underestimate in situ gas concentrations, especially where the concentration exceeds surface saturation values. The Leg 164 PCS data may be the first accurate measurements of gas concentrations in gas-rich marine sediments drilled by ODP (Dickens et al., 1997 and Chap. 11, this volume).

2. Contributing to an understanding of the lateral variability in the extent of gas hydrate development.

The measured variations in the lithology, physical properties, pore-water geochemistry, and downhole logs measurements among Sites 994, 995, and 997 were subtle. Estimates of the amount of gas hydrate that occurred in Site 994 (which was not associated with a BSR) and at two sites with BSRs (Sites 995 and 997), did not differ by more than a factor of two (Collett and Ladd, Chap. 19, this volume; Lee, Chap. 20, this volume). Lateral variations in the velocity fields, based on new amplitude vs. offset and acoustic tomographic analyses of multichannel profiles near the Blake Ridge drilling transect show limited lateral variations across an even longer transect (Tinivella and Lodolo, Chap. 28, this volume).

3. Refining the understanding of the relationship between bottom-simulating reflectors and gas hydrate development.

The bottom-simulating reflectors (BSRs) in the seismic reflection data from Sites 995 and 997 are associated with free gas in the underlying sediments (Holbrook et al., 1996; Collett and Ladd, Chap. 19, this volume; Lee, Chap. 20, this volume; Tinivella and Lodolo, Chap. 28, this volume). Most of the gas hydrate that was inferred to occur during Leg 164 was not near the depths associated with the BSR, but rather dispersed throughout at least the overlying ~250-m-thick interval.

4. Investigating the distribution and in situ fabric of gas hydrates within sediments.

Collectively, the inferred occurrences of gas hydrate indicated that it occurs either as (1) dispersed within the pores of fine-grained sediments without obviously disturbing the sediment structure or (2) massive hydrate within large cavities that are perhaps fractures and faults.

The distribution of the fine-grained gas hydrate within these lithologically uniform-appearing sediments (Balsam and Damuth, Chap. 31, this volume) was surprisingly heterogeneous. Data from diverse sources (e.g., visual observations of gas hydrate, core temperatures, chloride values, well logs) show that the amount of gas hydrate varies on scales of centimeters to meters. Visually obvious lithologic explanations were not seen during the shipboard core descriptions to explain the variations in gas hydrate amount; similarly, shore-based geochemical studies of the sediment chemistries have not revealed obvious explanations for these variations either (Watanabe et al., Chap. 15, this volume, Lu et al., Chap. 14, this volume). However, detailed grain-size analyses suggest that the samples with low chloride values, and thus increased amounts of gas hydrate, typically were slightly coarser grained (Ginsburg et al., Chap. 24, this volume).

On a larger scale, two zones lying between 185 and 260 mbsf and 380 and 450 mbsf contained distinctly more gas hydrate. Whereas methane recycling near the base of gas hydrate stability can easily ex-

plain the higher concentrations in the lower zone, the upper concentration zone is more difficult to explain if the lithologies were truly uniform. However, detailed studies of the lithology indicate increased abundance of siliceous microfossils in the upper zone (Kraemer et al., Chap. 23, this volume; Ikeda et al., Chap. 35, this volume). Kraemer et al. (Chap. 23, this volume) suggests that the relatively large and round pores may provide appropriate nucleation sites for gas hydrate formation.

5. Establishing the changes in the physical properties associated with gas hydrate formation and decomposition in continental margin sediments.

Shipboard physical properties measurements only show a slow progressive change in the sediment characteristics that are associated with compaction. However, the distinct variations in well-log responses suggest the in situ properties of the hydrate-bearing materials are distinct. Most of the models used to calculate amounts of gas hydrate assumed that the gas hydrate was passively filling the sediment pores or coating the grains (Guerin et al., in press) rather than preferentially cementing the grain contacts together.

6. Determining whether the gas captured in gas hydrates is produced locally or has migrated in from elsewhere.

The chemical and isotopic composition of the gases evolved from gas hydrate collected as the PCS degassed or sampled from the cores samples (Lorenson and Collett, Chap. 4, this volume; Matsumoto et al., Chap. 2, this volume; Paull et al., Chap. 7, this volume) indicate that the gases are primarily microbially produced via CO₂ reduction. Wehner et al. (Chap. 5, this volume) infer that traces of ethane and propane found in the absorbed gases indicate migration from below.

Although small in comparison with the near-surface population, substantial bacterial populations were measured throughout the sections (Wellsbury et al., 1997; Wellsbury et al., Chap. 36, this volume). Moreover, the concentrations of acetate increase at depths that are approximately coincident with the base of gas hydrate stability. Acetate is a substrate that is known to support substantial communities of methane-producing bacteria, but is usually depleted in marine sediments after just a few meters of burial. However, on the Blake Ridge, acetate reappears as a significant component in the pore water at ~350 mbsf, its concentration continues to increase to the bottom of the holes, and concentrations of up to 17 mM are reported at 728 mbsf (Wellsbury et al., 1997; Egeberg and Barth, 1998). Wellsbury et al. (1997) infers that these bacteria are actively turning over the existing acetate. However, models of the isotopic composition of the recovered gases and the known fractionation effects suggest that the majority of the methane and dissolved carbon dioxide were not locally produced (Paull et al., Chap. 7, this volume). The models indicate that the majority of the gas has migrated into the system from elsewhere.

Models of the observed changes in the pore-water chemistry (e.g., Egeberg and Barth, 1998; Egeberg and Dickens, 1999) suggest that there is a slow upward migration of pore water (~0.2 m/k.y). These models are further supported by the Cl⁻ isotope data (Hesse et al., Chap. 12, this volume).

Egeberg and Dickens (1999) also present pore-water bromide concentrations that exceed 3 mM, which is among the highest values ever recorded for a deep-sea sediment. Because organic matter decomposition is the only source of increased Br, and the Br concentrations are significantly higher than can be produced from in situ organic matter decomposition, they infer that there is a flux of Br from another area where there is considerable organic matter decomposition.

Over the Blake Ridge Diapir, the upward migration of gas is clearly focused along a high-angle fault system that forms a conduit to bring gas to the seafloor. Whereas regional seismic data indicate that faults that extend to the seafloor are unusual, high-angle faults that extend from the BSR to near the seafloor are very common. Woods

et al. (unpubl. data) infer that these common high-angle structures may be acting as important conduits for the vertical transport of pore water and gas.

7. Investigating the role of gas hydrates in the formation of authigenic carbonate nodules.

Authigenic carbonates with relatively depleted $\delta^{13}\text{C}$ values occur from ~20 mbsf downward to ~180 mbsf at Sites 994, 995, and 997 (Pierre et al., Chap. 13, this volume; Rodriguez et al., Chap. 30, this volume). The onset of isotopically light carbonates is coincident with the base of sulfate reduction (Borowski et al., Chap. 9, this volume; Hoelher et al., Chap. 8, this volume; Rodriguez et al., Chap. 30, this volume). Distinct seepage-related diagenetic carbonates were also identified at Site 996, where methane is escaping to the seafloor along the fault conduits (Naehr et al., Chap. 29, this volume). Authigenic carbonate precipitation is also promoted by increased alkalinity associated with anaerobic methane oxidation (Borowski et al., Chap. 9, this volume).

Authigenic siderite is commonly associated with gas hydrate-bearing sediments (Matsumoto, 1989). Previously it was inferred that the formation of siderite occurred in association with gas hydrate decomposition at the base of the gas hydrate stability zone. However, the occurrence of siderite in these sites starts at about 180 mbsf, above the level of distinct gas hydrate (Pierre et al., Chap. 13, this volume; Rodriguez et al., Chap. 30, this volume) and well above the base of gas hydrate stability.

8. Refining our understanding of chemical and isotopic composition of gas hydrates.

The methane to ethane ratios (typically >1,000) and isotopic ratios ($\delta^{13}\text{C}$ of methane <-60‰ Peedee belemnite [PDB]; Fig. 8) of the gases recovered from the cores indicate that the gas is largely of microbial origin (Paull et al., Chap. 7, this volume). The isotopic compositions of the methane recovered from gas hydrate samples (-66‰ to -70‰ PDB and -201‰ to -206‰ standard mean ocean water [SMOW]) are essentially indistinguishable from the isotopic composition of the surrounding interstitial methane (Lorenson and Collett, Chap. 4, this volume, Paull et al., Chap. 7, this volume, Matsumoto et al., Chap. 2, this volume). However, the oxygen isotopic composition of the water ranged from 2.67‰ to 3.52‰, which is 3.5‰–4.0‰ heavier than the ambient interstitial waters (Matsumoto et al., Chap. 2, this volume).

The isotopic composition of the gas samples from the PCS showed significantly more scatter in values than the core gases from a similar depth (Paull et al., Chap. 7, this volume). However, the volume weighted averages for the total gas from a single PCS core is the same as that from adjacent free gas and headspace samples (Wallace et al., Chap. 10, this volume). This indicates that there is no isotopic fractionation of methane during core recovery despite considerable gas loss (upwards of 99.9%). The cause of the increased scatter for individual gas samples from a single PCS core remains unclear.

Measurements of the noble gas composition were attempted (Dickens and Kennedy, Chap. 16, this volume). The objective was to determine whether significant fractionation of noble gases and enrichment of xenon occurs during gas hydrate formation. All specimens of gas hydrate from Leg 164 that were analyzed are enriched in xenon relative to noble gas ratios in air and air-saturated seawater. However, the experiments were far from conclusive because of significant contamination.

9. Determining the gas composition, hydration number, and crystal structure of natural gas hydrates.

The gas that filled the hydrates was primarily methane with an isotopic composition that indicates that it was produced via CO_2 reduction (Matsumoto et al., Chap. 2, this volume, Paull et al., Chap. 7,

this volume). Samples of gas hydrate that were recovered from the cored sediments yielded volumetric water to gas ratios that indicate that a minimum of 71% of the potential gas-bearing cages and, after corrections for potential contamination, suggested that probably most hydrate cages are gas filled (Lorenson and Collett, Chap. 4, this volume). Nuclear magnetic resonance measurements and X-ray diffraction analysis confirm the high cage occupancy and indicate that both the large and the small cages were filled with methane (Matsumoto et al., Chap. 2, this volume).

10. Determining the role of gas hydrates in stimulating or modifying fluid circulation.

Active fluid flow was demonstrated to be occurring on the top of the Blake Ridge Diapir at Site 996. Apparently, faults form conduits for advective degassing of methane associated with gas hydrate-related reservoirs on the Blake Ridge. The isotopic compositions of methane captured within sediments at <50 mbsf at this vent are consistent with the isotopic composition of methane sampled from the gas hydrate- and free-gas-bearing zones below ~150 mbsf at Deep Sea Drilling Project Site 533 (Brooks et al., 1983; Galimov and Kvenvolden, 1983) and on ODP Leg 164 (Paull et al., Chap. 7, this volume).

Models of the pore-water chemical gradients at Site 997 (Egeberg and Dickens, 1999) suggest that there is slow upward migration of pore water (~0.2 m/k.y.). However, the extent to which the gas hydrates themselves alter sediment properties and effect the patterns of fluid flow was not resolved. Similarly, the effect of the free gas in the sediments below the base of gas hydrate stability is unknown. The occurrence of pore waters that are significantly fresher than seawater throughout the sedimentary section will also increase the buoyancy of the pore waters.

11. Investigating the potential connection between major slumps and the breakdown of gas hydrate.

A direct connection between gas hydrate decomposition and slumping was not generated. However, physical properties of cores that came from depth on the Blake Ridge are significantly undercompacted. One explanation for this undercompaction is that the presence of free gas and gas hydrate in the sediments prevents normal compaction from occurring (Winters, Chap. 40, this volume).

12. Establishing the influence of the Carolina Rise Diapirs on the gas hydrates as well as the origin of the diapirs themselves.

The pore-water chloride profiles over the diapirs increase down core, suggesting that these are salt-cored diapirs. However, little was learned about the effects that the diapirs exert on the gas hydrate.

LEG POSTMORTEM

Because progress was made toward most of the leg's objectives, Leg 164 has to be viewed as very successful. However, with any large operation there are inevitably a few shortcomings, which we outline here.

Obtaining unequivocal data on the chemical composition of in situ pore-water values is critical for making assessments of gas hydrate composition. Amounts of gas hydrate can be calculated very accurately if the true in situ values are known. Although numerous attempts were made to sample the in situ pore waters using two ODP tools (water sampling temperature probe and the Fisseler Water Sampler), all the samples were seriously contaminated and of little or no value.

Site 994 was located less than a kilometer to the south of an area that displays a well-developed BSR. The site was intended as a background site. However, Site 994 was very similar to Sites 995 and 997,

and contained similar amounts of gas and gas hydrate. However, the lack of a BSR is believed to indicate that there was insufficient gas to saturate the pore waters immediately beneath the base of the gas hydrate stability zone at Site 994. Whereas Site 994 provided very important information concerning the nature of the BSR and gas hydrate distribution, it does not serve as a gas-hydrate-free reference site.

Direct measurements of the amounts of gas and gas hydrate(?) that occur within the upper 200 m of the seafloor were not obtained. Thus, a major ambiguity exists about the nature of the top of the gas hydrate-bearing zone. Unfortunately, appropriate techniques to make these measurements have yet to be developed.

Leg 164 was designed to make a static description of a gas hydrate deposit. However, it is increasingly clear that these are dynamic reservoirs. Establishing the rates at which these deposits evolve is a major challenge for future gas hydrate researchers.

CONCLUSION

Providing an assessment of the amount and distribution of gas and gas hydrate that occurred in Blake Ridge sediments was the most important accomplishment of Leg 164. Estimates made using diverse and independent techniques converge to show that gas hydrates occupy ~1% to 10% of the sediment volume in a zone that is at least ~250-m thick on the Blake Ridge. Site 994, a site without a BSR, contains nearly as much gas hydrate as those sites with a BSR. Apparently the BSR in this area occurs when gas saturation is achieved at the base of the gas hydrate stability field. The volume of free gas that occurs beneath the base of gas hydrate stability in this region rivals the amounts stored in the overlying section.

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