

DOE/MC/21181-T3



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DOE/MC/21181--T3

PROGRESS REPORT:

DE92 017657

EVALUATION OF THE GEOLOGICAL RELATIONSHIPS TO GAS HYDRATE FORMATION AND STABILITY

Period: June 16 through September 30, 1988

U.S. Department of Energy (DOE)
Morgantown Energy Technology Center (METC)
Contract No. DE-AC21-84MC21181

By Jan Krason and Pat Finley (303) 356-4065

PERSONNEL

During the reporting period the following staff were involved with the project: Dr. Jan Krason (Principal Investigator/Project Manager) and Mr. Patrick Finley (Geologist-Geochemist).

OBJECTIVES

1. Assess status of research completed as of the Stop Work Order of 22 August, 1987, and determine the most efficient strategy for completion of the project.
2. Reassemble research team following one-year hiatus.
3. Initiate work on gas hydrate research following one-year hiatus due to lack of funds.
4. Prepare materials for the 1988 Peer Review and deliver an oral presentation in Kansas City, Missouri.

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ACCOMPLISHMENTS

1. Assessed status of research completed and developed timetable for completion of project work.
2. Began research on the remaining gas hydrate study regions
3. Prepared material and presented discussion on project for the 1988 Peer Review Meeting.

DISCUSSION

Geoexplorers International, Inc. was authorized to continue work on Contract No. DE-AC21-84MC21181, *Evaluation of Geologic Relationships to Gas Hydrate Formation and Stability* on 16 June, 1988.

Much work has gone into restarting the research which was abruptly halted in September, 1987 by a Stop Work Order from DOE. Since the order demanded that all work stop immediately, much vital research was dropped in mid-course. We have been able to establish the status of the research as of the time of order, and have begun to go forward from there. It must be emphasized that the one-year hiatus has had a devastating impact on our efficiency of generating the Basin Analysis reports. The systematic methodology, sequencing of personnel, and vital overlap of responsibilities and tasks among the geoscientists and technicians at Geoexplorers International, Inc. which contributed to our impressive output of technical reports since the projects inception have been disturbed by the interruption in funding by DOE.

The DOE-mandated hiatus in research and subsequent funding arrangements have also decimated our professional research team. Resumption of funding by DOE was contingent on Geoexplorers International, Inc. agreeing to only be reimbursed for 50% of expenditures up to mandated ceiling. Any expenses in finishing the project in excess of the DOE-mandated ceiling were to be borne entirely by Geoexplorers International, Inc., in spite of the fact that the original contract is a Cost-Plus agreement rather than a Fixed-Price agreement. The lack of adequate funding has forced Geoexplorers International, Inc. to furlough a valuable member of the original research team, Marek Ciesnik. Mr. Ciesnik was involved in the project from its inception and was co-author of five Basin Analysis volumes and the major critical review of Gas Hydrates in Russian Literature. Mr. Ciesnik's expertise and accumulated experience in gas hydrate research will be missed.

The skeleton research crew that remains deployed on the gas hydrate project is forced by current funding levels to perform technician duties, further limiting our efficiency. Most typing and all drafting for the project is now being done by the principal investigators. While these scientists are fully capable of these tasks, this arrangement substantially slows the progress on the remaining study regions.

Dr. Krason and Mr. Finley participated in the 1988 Peer Review session in Kansas City, Missouri. Substantial amounts of time were expended in preparing the extensive documentation required by the DOE peer review procedures.

In spite of the efforts that were put into the peer review, we have not received any constructive response on the presentation or the reviewers comments. This is in contrast to the 1985 Peer Review meeting for which, the contractor-prepared documentation was subsequently distributed in a published proceedings volume. In 1985 the rankings of the review panel members were distributed to the participants, with the participants being given a chance to respond to the comments. This procedure was very constructive in permitting contractors to identify and adjust for perceived strengths and weaknesses in their project performance. While it is certain that DOE has some legitimate reasons for their secrecy in the 1988 matter, we suggest that the reviews could be of more use if widely distributed rather than being held as proprietary by high-ranking DOE officials. The great expenditure of funds effort for the Peer Review would perhaps be more effective for all concerned if some measure of "Glasnost" prevailed the DOE Office of Program Analysis.

Since the extensive documentation which we prepared for the Peer Review has not been made available to the DOE-METC personnel overseeing this project, we are including that documentation in this progress report. The specifications for the documentation required that it stress the broad results of the whole project rather than specific technical issues. Thus, the orientation of the peer review documentation is similar to that of our final report. Given the severe limitations on available funds for preparation of the final report, we intend to include a large part of the included material directly into the final report. For these reasons and to facilitate DOE review of the final report we are requesting that any changes in the included material which are needed before inclusion into the final report be brought to our attention immediately. If no response or required revision is received from DOE-METC, we will assume that the material has been thoroughly reviewed and accepted in its entirety.

NEW PERIOD OBJECTIVES

1. Complete and submit draft of Beaufort Sea report.
2. Type and edit Nankai Trough report.
3. Begin research on Timor Trough.

DISCLAIMER

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PEER REVIEW DOCUMENTATION

EVALUATION OF GEOLOGICAL RELATIONSHIPS TO GAS HYDRATE FORMATION AND STABILITY

Principal Investigator:

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Key Personnel:

Jan Krason	Project Manager/Geologist	25% of Full Time
Patrick Finley	Geologist/Geochemist	Full Time (6/85 - 8/87)
Marek Ciesnik	Geologist	Full Time (11/84 - 8/87)
Ian Ridley	Sr. Geologist	Full Time (11/84 - 5/85)
Bernard Rudloff	Geologist	Full Time (4/85 - 10/85)

Curriculum Vitae for the above personnel are supplied in the attached Appendix.

Technical Staff:

Magaret Krason	Draftsperson	Full Time (11/84 - 3/87)
B. Joan Gross	Typist	Sub-Contract

Project Output:

INTRODUCTION

Gas hydrates are a potential gas resource which may supplement U.S. energy supplies in the future. Research into the formation and stability of gas hydrates and applicable recovery technology is necessary to define and quantify this resource.

Understanding of the geological environments controlling gas hydrate occurrence is fundamental to their eventual exploitation. Much of the current knowledge of natural gas hydrate occurrence was obtained indirectly. Geophysical and geological data collected for purposes other than gas hydrate study indicated

gas hydrate presence. Thorough review and analysis of all available geological data is necessary to assess the regional extent of known gas hydrate occurrences. The systematic study of geological environments of identified gas hydrate occurrences provides the basic data to determine the relationships of geological environments to gas hydrate formation and stability.

OBJECTIVES

Determination of the relationships of geological environments of gas hydrate formation and stability is one of the major tasks of the research project performed by Geoeplorers International, Inc. for the U.S. Department of Energy, Morgantown Energy Technology Center (DOE-METC). Assessment of the gas resource potential of gas hydrates at twenty-four offshore and five onshore sites is an ultimate study objective.

PROJECT DESCRIPTION

The project investigates the relationship of geological environments on gas hydrate formation and stability by basin analysis of gas hydrate sites. Basin analyses are performed on 24 offshore locations with direct or indirect evidence of gas hydrates. The gas hydrate sites included in this study, located in various parts of the world, have been pre-designated by DOE-METC (Figure 1). Extensive geological investigations are conducted for each study region comprising one or more gas hydrate locations. Sediment composition, provenance, and depositional history are documented for each study region. Structural development of the sedimentary basin is determined using drilling results and seismic reflection profiles. Potential for generation of biogenic methane and conventional thermogenic hydrocarbons is assessed by analysis of existing geochemical data and by thermal modeling. All available seismic data, both published and unpublished, are examined for evidence of gas hydrates. Bottom simulating reflectors (BSRs) and other seismic anomalies are mapped. Drilling evidence of possible gas hydrates is reviewed. Based on the limited available information, conditional assessments of gas resources are derived. Quantities of gas contained both in the gas hydrate and possibly trapped beneath the gas hydrate stability zone are estimated.

ACCOMPLISHMENTS

Detailed results of ten regional basin analysis studies of gas hydrate locations have been published by DOE-METC (Figure 1). Five of these study regions are located on passive continental margins: offshore of Newfoundland and Labrador, Canada (Krason and Rudloff, 1985), the Baltimore Canyon Trough (Krason and Ridley, 1985a) and Blake-Bahama Outer Ridge (Krason and Ridley, 1985b) offshore of the eastern United States, the western Gulf of Mexico (Krason et al., 1985), and the Black Sea (Ciesnik and Krason, 1987). Five of the regions for which

the results have been published in detail are on active continental margins: the Colombia Basin (Finley and Krason, 1986a) on the Caribbean margin of South and Central America, the Panama Basin (Krason and Ciesnik, 1986a), the Middle America Trench (Finley and Krason, 1986b), offshore of northern California (Krason and Ciesnik, 1986b), and the Aleutian Trench and Bering Sea (Krason and Ciesnik, 1987) all on the Pacific Margins of North and Central America. Results from these studies were summarized at DOE contractors meetings in 1985 (Krason and Ridley, 1985c), 1986 (Krason et al., 1986), and 1987 (Krason et al., 1987).

Reports presenting the detailed results of basin analyses of two study regions were near completion when execution of the contract was interrupted in 1987: the Beaufort Sea offshore of the north slope of Alaska (Finley and Krason, 1988) and the Nankai Trough offshore of Japan (Ciesnik and Krason, 1988). Completion of work on these regions and on the Timor Trough is projected if work on the contract is resumed.

Work on three additional gas hydrate locations--offshore of New Zealand on the Tonga Trench, offshore of Oman in the Makran accretionary complex, and offshore of southwestern Africa--has been suspended. Future research on five onshore gas hydrate locations is also under consideration (Figure 1).

The products of our research are extensive and voluminous. To acquaint the reviewers with the nature of our work we have included the full text of one representative regional report on the Middle America Trench (Finley and Krason, 1986b) under a separate cover.

It would clearly be unreasonable to suggest that the panel members for the peer review examine all of our lengthy reports in full. Thus, brief summaries of the major points of 12 of the basin analysis reports are included in this document:

OFFSHORE NEWFOUNDLAND AND LABRADOR

The continental margin offshore eastern Canada was selected as a gas hydrate study site based on a published report of a bottom simulating reflector (BSR) on a seismic profile from north of the Flemish Knoll (Taylor et al., 1979; Figure 2). Neither the seismic line nor its exact location have been publicly released. The only other mention in the literature of gas hydrates in the offshore Newfoundland and Labrador study region was the statement by Judge (1980) that hydrates "have been detected offshore in the Grand Banks."

The Newfoundland continental margin, consisting of the Grand Banks and adjacent areas, is characterized by a Cretaceous-Quaternary sedimentary section up to 2,000 m thick unconformably overlying separate basins of Triassic-Jurassic marine rocks. The isolated subbasins reach 14,000 m in sediment thickness and contain mature shales with proven source rock potential. The Cretaceous-Quaternary section contains some thermally immature organic-rich strata. The surficial sediments of the Grand Banks are dominated by glacial drift. The continental slope seaward of the Grand Banks is thought to be draped with fine-grained glacial debris. The organic content of these sediments is not well

documented. Faults, diapirs, and associated fractures in the Grand Banks area may enhance permeability sufficiently to allow deep sourced thermogenic gas to migrate to the gas hydrate stability zone.

Because of low ocean water temperatures over the Grand Banks, gas hydrates may be stable at shallower than expected water depths. The Grand Banks is overlain by less than 200 m of water. Gas hydrates are not generally considered to be stable beneath such shallow water. Computer modeling suggests that due to the cold sea water over the Grand Banks, biogenic gas hydrates may be stable beneath water as shallow as 156 m assuming a 2.0°C/100 m geothermal gradient (Figure 3). Thermogenic gas hydrates would be stable at water depths as shallow as 75 m under similar conditions.

A lack of drilling results and quality seismic sections limits the confidence of assessment of gas hydrate potential on the Newfoundland continental margin. Thermogenic gas hydrates may exist where structural deformation permits migration of gas from mature pre-Cretaceous source beds. Biogenic gas hydrates may exist on the adjacent continental slope and rise where sufficient organic matter is present.

The geology of the East Newfoundland Basin (Figure 2) is similar to that of the Grand Banks. A Carboniferous-Jurassic sedimentary section is strongly faulted and of sufficient thermal maturity for dry gas generation. The Cretaceous to Holocene section ranges from 7,000 m near shore to 2,000 m in the center of the basin. Landward, the Cretaceous rocks become marginally mature, but the Cenozoic section remains immature. Diapirism and faulting is limited in the Cretaceous through Holocene section reducing the probability of migration of thermogenic gas to the gas hydrate stability zone.

The BSR reported by Taylor et al. (1979) is inferred to be located on the south margin of the East Newfoundland Basin (Figure 2). Water depths throughout the area are sufficient for gas hydrate formation. Gas generative potential of shallow sediments is undetermined.

The Labrador continental shelf and slope are covered by thick Cenozoic marine deposits covering thin block-faulted Paleozoic and Mesozoic marine rocks. Commercial natural gas production has been obtained from structural traps in Tertiary sandstones. Gas-prone Type III organic matter is predominant throughout the sedimentary section.

Bacterial methane generation was documented from Pleistocene muds in the Labrador continental slope (Figure 2). Piston cores from 500 m water depth recovered glacial mud with low organic carbon content which released large quantities of biogenic methane resulting in expansion cracks in the sediment. The volume of gas and the depth of the overlying water suggest that the gas may have been in hydrate form. If such sedimentary environments are widespread on the Labrador shelf and continental slope, gas hydrates may occur frequently in the area.

Although largely unexplored, the Labrador Sea has potential for gas hydrates. Cores from the Labrador Sea indicate that terrestrial hemipelagic sediments and turbidites have accumulated under anaerobic conditions. These sediments contain undetermined amounts of gas-prone Type III organic matter and thus may be capable of generating biogenic gas. We have located a possible BSR in a seismic section of turbidite sediments from the Labrador Sea (Figure 2). The

depth of the anomalous reflector (0.53 sec subbottom) suggests that it may represent a gas hydrate horizon.

Potential exists for gas hydrate deposits in the Offshore Newfoundland and Labrador study region. Direct evidence of gas hydrates is lacking, but cold water temperatures, mature thermogenic source rocks, proven petroleum potential, documented bacterial methanogenesis, and indirect seismic evidence suggest that gas hydrates may be present in a variety of geological environments offshore of eastern Canada.

BALTIMORE CANYON TROUGH

Selection of the Baltimore Canyon Trough for study was based on a report of seismic evidence of gas hydrates beneath the continental margin of the eastern United States by Tucholke et al. (1977). The Baltimore Canyon Trough study region includes 84,000 km² of the Atlantic continental margin offshore of the states of New Jersey, Maryland, and North Carolina.

The eastern U.S. Continental Margin within the study region experienced an early period of pre- and syn-rifting sedimentation and a period of tectonically driven sedimentation during Middle through Late Triassic and Early Jurassic, which was followed by an uninterrupted, prolonged period of tectonic quiescence and steady thermal subsidence. These conditions led to accumulation of a very thick sequence of deltaic to shallow marine sediments, deposited during Triassic through Tertiary time. The focus of sedimentation was within the Baltimore Canyon Trough, which has accumulated almost 15,000 m of clastic sediment within its deepest part beneath the present continental shelf (Figure 4). A prominent carbonate buildup can be recognized on seismic lines beneath the present upper continental slope and represents the position of the Jurassic and Early Cretaceous shelf edge which subsequently moved landward. The Mesozoic development of a large deltaic complex behind the carbonate shelf edge was replaced in the Tertiary by open oceanic conditions, but deltaic sedimentation was reestablished in the Miocene as a series of prograding clastic wedges. Throughout the evolution of the margin, fine-grained sediments were deposited on the continental slope and rise and were occasionally interbedded with turbidites due to lower sea level during the Tertiary and Quaternary. During late Tertiary through Quaternary time, a dominant fraction of the sedimentary clastic input was channeled toward the shelf edge, which prograded fairly rapidly over the remnants of Late Cretaceous to early Tertiary paleoshelf edge. The inherent instability of the clastic apron led to widespread gravity failure and redeposition of a large amount of sand, silt, and mud (up to 3,000 m thick) over the lower continental slope by turbidity currents and slumping.

Although the continental shelf areas in the study region have been extensively drilled commercially and are thus well understood, these shallow areas have limited potential for gas hydrates. The entire continental shelf is under less than 100 m of water. This area is not conducive for gas hydrate formation and preservation because temperatures are too high and pressures are too low. The continental slope and upper continental rise (200 m to 3,500 m below sea level)

have more potential for hydrate accumulation, but less data are available for assessment.

Gas hydrates have been inferred to occur beneath the present continental margin, based upon the widespread occurrence of BSRs on seismic profiles. In the Baltimore Canyon Trough study region, gas hydrate occurrences are documented seismically from the lower continental slope and upper continental rise, at 2,000 to 3,600 m of oceanic water. Occurrences of gas hydrates are implied from the presence of bottom simulating reflectors (BSRs). Three classes of BSRs, differing in continuity and strength of the reflection, are recognized in the study region. Strong, continuous reflectors are identified on sections from areas between the Hudson and Wilmington canyons. To the northeast and southwest of this area, more diffuse and discontinuous BSRs predominate. The areal extent of BSRs is approximately 30,000 km².

The distribution of gas hydrates may also be affected by the widespread sediment instability on the continental slope and rise which resulted in mass movement of sediment into deeper water. The evolutionary history indicates that the gas hydrate zone and underlying gassy sediments are probably fine-grained argillaceous lithologies which may show a wide range of compaction. The potential for more porous sediments exists near the shelf slope break and along those parts of the continental rise containing deep-water turbidite fans. Gas hydrates may also occur within the Hatteras Outer Ridge, based upon an evolutionary history similar to the Blake Outer Ridge. The critical parameter in this instance is probably the organic matter mass accumulation rate during the development of the ridge.

Rapid changes in sediment thickness caused by widespread submarine erosion, slumping, and turbidite deposition may help explain the discontinuity observed in some BSRs. When sediments are rapidly added or removed from an area by these processes, the thermal regime of the area is altered. The disturbed thermal regime reequilibrates to one stable for the new sediment load. The adjustment of heat flow and geothermal gradient displaces the zone of gas hydrate stability vertically. The vertical shift of gas hydrate stability zones could possibly result in isolated pockets of massive and nodular hydrates with different seismic properties than the surrounding disseminated gas hydrates.

The organic contents of sediment samples from the study region are marginally sufficient for biogenic methane generation. A notable exception is an organic-rich Miocene age sediment layer which may serve as a source for biogenic methane.

Calculated organic and clastic sediment mass accumulation rates for areas throughout the study region likewise suggest organic carbon levels which are marginally sufficient for biogenic methane generation, with the possible exception of the Hatteras Outer Ridge, where richer conditions may exist.

Maturity models of the region suggest that thermogenic sources for methane in gas hydrates are unlikely. Depths of mature source beds are such that extensive vertical migration would be necessary for accumulation in the gas hydrate stability zone. Evidence suggests a dominantly biogenic source of gas for gas hydrates in this region.

Estimates of the areal extent of gas hydrates in the study region range from 30,000 km² to 50,000 km² based on seismic evidence from areas overlain by 2,000 to

3,600 m of water. Assuming that gas hydrates occupy all of the sedimentary pore volume, a gas hydrate zone one meter thick may contain up to 21 trillion cubic feet (TCF) or $2.9 \times 10^{11} \text{ m}^3$ at 0°C and one atmosphere pressure for the area underlain by BSRs.

Gas may be trapped in pore spaces below the lower limit of the gas hydrate stability zone. The thermal reequilibration of the sediments in response to sedimentation may produce relief on the lower surface of the gas hydrate zone. This relief may provide closure necessary for accumulation of gas beneath the impermeable gas hydrate. Such a reservoir beneath a gas hydrate seal with an area of one km^2 and six meters of closure could contain 3 MMCF of gas or 10^5 m^3 .

BLAKE-BAHAMA OUTER RIDGE

The Blake-Bahama Outer Ridge was selected as a gas hydrate study region based on both seismic and drilling evidence of gas hydrates. Bottom simulating reflectors (BSRs) interpreted to mark the base of the gas hydrate stability zone were reported from the Blake-Bahama Outer Ridge by Markel et al. (1970), Lancelot and Ewing (1972), Tucholke et al. (1977), and Paull and Dillon (1981). Samples of gas hydrates were recovered from cores from the Deep Sea Drilling Project (DSDP) Site 533 on Blake Outer Ridge (Kvenvolden and Barnard, 1983).

The Blake-Bahama Outer Ridge study region is located on the Atlantic continental margin offshore of the southeastern United States (Figure 4). The study region covers $190,000 \text{ km}^2$ including the Blake Plateau, Blake Spur, Blake-Bahama Outer Ridge. Water depths in the study region range from 400 m to 5,400 m.

The passive Atlantic continental margin of the United States was developed from the Triassic rifting of North America from northern Africa. The margin is underlain by pre-rift and syn-rift terrigenous sediment accumulations truncated by a regional post-rift unconformity. Above the unconformity, thick accumulations of Cenozoic and Mesozoic marine sediments occur in a series of elongate basins aligned parallel to the continental margin. One such basin with over 10,000 m of sediment accumulation occurs in the Blake-Bahama Outer Ridge study region beneath the Blake Plateau. The basin is developed seaward of the present continental shelf and is not depositionally related to modern sediment accumulation patterns of the continental margin.

The Blake-Bahama Outer Ridge is an elongate bathymetric high extending to the southeast from the continental slope at a water depth of 3,000 to 4,000 m. The 550 km long ridge is a composite of two separate features: the Blake Ridge with a local seafloor relief of up to 2,900 m, and the Bahama ridge to the south with only 500 m of relief. The Blake-Bahama Outer Ridge is a constructional sedimentation feature developed on the continental slope and continental rise. It thus represents a focus of very rapid, localized sedimentation in contrast to the more uniform sedimentation patterns elsewhere on the margin. Seismic stratigraphy indicates that the Blake-Bahama Outer Ridge is younger than a 34 m.y. (million year old) unconformity (Sheridan et al., 1983). The exact age of the initiation of ridge deposition is uncertain, but has been related to a change in ocean currents and/or sediment supply. The present form of the Blake-Bahama Outer Ridge is a result of

the interaction of the Western Boundary Undercurrent and the Florida current (Sheridan et al., 1983). Sediment is transported from the north by the Western Boundary Undercurrent and from the south by the Florida current. The sediment is dumped at the interface of the currents and is contoured by the stronger Western Boundary Undercurrent.

The sediments of the Blake-Bahama Outer Ridge were cored on DSDP Legs 11 and 76. The three locations drilled on Leg 11 cored up to 620 m of Miocene to Holocene hemipelagic mud. On Leg 76, 400 m of Pliocene to Holocene methane-rich clay, having increasing carbonate content with depth, was cored.

A very high-amplitude reflector which parallels the sea floor at 0.6 sec. subbottom was noted in early single-channel seismic lines of the Blake-Bahama Outer Ridge (Markel et al., 1970). Subsequent multichannel lines showed that the reflector cut across bedding planes (Tucholke et al., 1977). Stoll (1971) showed that the high seismic velocity of sediments with interstitial methane hydrates could result in a seismic impedance decrease and thus a negative-phase reflection at the base of the gas hydrate stability zone. Dillon and Paull (1983) demonstrated that such a seismic velocity decrease occurs on seismic lines from the Blake-Bahama Outer Ridge at a subbottom depth of 500 to 600 m corresponding to the bottom simulating reflector (BSR). Based on measured thermal gradients and bottom water temperatures, the pressure and temperature conditions at the BSR correspond to the gas hydrate phase boundary. Based on these factors and the similarity of the Blake-Bahama Outer Ridge BSR to other gas hydrate reflector from elsewhere (Shipley et al., 1979) seismic data from the Blake-Bahama Outer Ridge study region indirectly indicate the presence of gas hydrates in the sediments.

Gas hydrates may have existed at the locations of holes drilled on the Blake-Bahama Outer Ridge early in the Deep Sea Drilling Project. Sediment from Leg 11, Sites 102, 103, and 104 were anomalously methane rich. The gas from Sites 102 and 104 was composed of methane and carbon dioxide with a methane isotopic signature characteristic of microbial methanogenesis (Claypool et al., 1974). No hydrates were observed in the cores; however, drilling on Leg 11 was conducted in 1970, before shipboard scientists were aware that gas hydrates may be present. The depth corresponding to the seismic anomaly was penetrated at Site 102. An increase in sediment induration and carbonate content corresponded to the probable depth of the BSR (Lancelot and Ewing, 1972), but no change in gas composition or concentration was noted. However, Paull and Dillon (1981) suggested that none of the holes on DSDP Leg 11 penetrated to the depth of the BSR due to an underestimation of seismic velocities by DSDP scientists.

Gas hydrate crystals were recovered from DSDP Site 533 on the Blake-Bahama Outer Ridge (Kvenvolden and Barnard, 1983). One sample of sediment containing visible gas hydrates was recovered from a depth of 238 m. Disrupted gassy sediment samples between 152 and 240 m suggested that gas hydrates may have also occurred in this interval, but dissociated during recovery of the cores. Using carbon isotopes, Galimov and Kvenvolden (1983) demonstrated that the methane in the sediment samples and the gas hydrate from Site 533 was biogenic.

Rapid sedimentation during the Miocene and Pliocene which formed the bathymetric feature also favored eventual formation of gas hydrate in the Blake-Bahama Outer Ridge study region. Sediment mass accumulation rates of up to 29

mg/cm²/yr and organic matter accumulation rates up to 0.38 mg/cm²/yr resulted in a short residence time for the sediment in the zone of oxidative degradation. Sediment rapidly entered the sulfate reduction and anaerobic methanogenesis zones before much of the sedimentary organic matter could decompose by oxidation. Excellent preservation of organic material resulted in efficient methanogenesis. Methane in excess of that soluble in pore water under hydrate-forming pressure and temperature conditions formed hydrate at Blake-Bahama Outer Ridge.

Mass-balance calculations using measured total organic content of the sediments at Site 533 and reasonable estimates of methane generation efficiency suggest that gas hydrates probably occupy 5% to 10% of the pore space of the Pliocene section.

Areas of the Blake-Bahama Outer Ridge with the least distinct BSRs correspond with areas of sediment erosion. Rapid erosion of sediment results in a downward shift of the base of the gas hydrate stability zone. Any free gas immediately beneath the gas hydrate stability zone would be incorporated into gas hydrates as the base of the zone migrated downward in the sediments. Many investigators contend that the reflectivity of a BSR is dependent on the presence of free gas beneath the gas hydrate stability zone (Stoll, 1971; Paull and Dillon, 1981). The areas of the Blake-Bahama Outer Ridge with faint BSRs due to rapid sediment erosion may thus indicate areas with less free gas beneath the base of the gas hydrate stability zone, but the faint BSRs do not necessarily indicate less extensive gas hydrate presence within the stability zone.

Depending on the assumptions used to assess the potential gas resource in gas hydrates in the Blake-Bahama Outer Ridge study region, up to 66 TCF ($1.9 \times 10^{12} \text{ m}^3$) of methane may exist in hydrate form. Based on the available geological evidence, 7 TCF ($2 \times 10^{11} \text{ m}^3$) is the most probable estimate for the quantity of methane trapped in hydrate form in the Blake-Bahama Outer Ridge study region.

WESTERN GULF OF MEXICO

The western Gulf of Mexico was selected as a study region based on recovery of gas hydrates from the continental slope offshore of Louisiana (Brooks and Bryant, 1985), and bottom simulating reflectors on three seismic lines from the continental slope of Mexico (Buffler et al., 1979; Hedberg, 1980).

The study region includes the entire Gulf of Mexico west of 88° W longitude, an area of approximately 940,000 km² (Figure 5). Nearly 20% of the study region is underlain by water of insufficient depth to stabilize gas hydrates. This huge region is subdivided into three general geologic provinces, the deep central Gulf of Mexico, the northwestern margin of the Gulf of Mexico, and the western margin of the Gulf of Mexico.

The deep central Gulf of Mexico is floored by crust of debatable origin. Isolated Triassic red-bed sequences on the crust are overlain by extensive Jurassic evaporite deposits. Subsidence and return of deep marine conditions led to the deposition of deep marine clastics and foraminiferal ooze. Increased sediment influx in the Tertiary and Quaternary, and glacially induced sea level fluctuations resulted

in an increase in sedimentation rate and a shift to turbidite deposition on the abyssal plain.

The geology of the northwestern margin of the Gulf of Mexico is dominated by salt diapirism and heavy Cenozoic sedimentation. Cretaceous carbonate platforms were covered with thick sediments from Tertiary orogenies. In response to this sediment loading, which was accelerated in the Quaternary, vertical and lateral flow of salt was initiated, which deformed the sediments and resulted in the characteristic structure and hummocky sea floor topography of the area. Pleistocene sedimentation from the Mississippi River further blanketed the continental slope and produced a submarine fan.

The western margin of the Gulf of Mexico is characterized by gravity induced detachment folds along the Mexican continental slope and salt diapirs in the south. Sliding along a shale decollement zone produced large, regular north trending folds on the continental slope offshore of northwestern Mexico. Southeast of these folds, an area of diapiric structures, the Campeche Knolls, document extensive salt mobilization.

Thermogenic gas hydrates were recovered from the northwestern margin of the Gulf of Mexico. Indirect evidence from Deep Sea Drilling Project Site 88 suggests that thermogenic gas hydrates occur on diapirs in the Campeche Knolls (Figure 5). Burial history reconstructions indicate that hydrocarbons in these gas hydrate deposits must have migrated at least 2,000 to 3,000 m vertically. Their association with salt structures appears to be related to the structural migrational pathways that diapirism provided. The presence of ethane through butane in the migrated thermogenic gas stabilizes these gas hydrates relative to methane hydrates, but saline pore waters due to solution of diapirs destabilize thermogenic gas hydrates.

Biogenic gas hydrates were recovered from the northwestern margin, and are inferred to have been drilled from abyssal plain turbidites in the deep central Gulf of Mexico at Deep Sea Drilling Project Sites 89, 90, and 91 (Figure 5). Sedimentary organic matter appears to have been preserved by rapid sedimentation throughout the region. Total organic carbon content of the sediments varies from 0.2% to 3%. Large amounts of biogenic methane were generated in the deep central Gulf area from sediments with less than the accepted lower threshold of organic carbon content for microbial methanogenesis. Biogenic gas hydrates occur in a wide range of lithologies, and may show an association with volcanic detritus in host sediments. Probable gas hydrate locations in the Gulf of Mexico generally do not display the decrease in pore water salinity with depth which is often associated with gas hydrates.

By thorough examination of all available seismic data we have identified BSRs on over 24 seismic lines from the Mexican continental margin. Bottom simulating reflectors (BSRs) cover approximately 5,000 km² in anticlines offshore of the Mexican coast between Tampico and Veracruz (Figure 6). The BSRs are found in water depths of 1,200 to 2,700 m and at 400 - 600 m subbottom. Dense spacing of seismic lines permits determination of the areal extent of some BSRs and the structural closure beneath these BSRs. Some well defined BSRs can be traced between as many as six seismic sections over distances of up to 80 km. Concentration of the BSRs in anticlines is consistent with the interpretation of free

gas beneath the hydrate zone increasing the amplitude of the hydrate reflection. Thus it is likely that gas hydrates exist in adjacent areas where BSRs are not evident due to a lack of underlying free gas.

Possible gas hydrate resources beneath the western Gulf of Mexico are substantial. Gas hydrates have been cored from shallow to moderate ocean depths (500 to 1,200 m) on the northwestern continental margin. Gas hydrate presence has been inferred in cores from 3,000 to 3,700 m ocean depths in the central and southwestern portions of the study region. Extensive BSRs are found at water depths of 1,500 m to 2,700 m in the southwestern margin of the western Gulf of Mexico region where structural disturbance of the sediments permits their recognition. Extrapolation of geological conditions present at these sites indicates that gas hydrates probably exist in many additional locations throughout the western Gulf of Mexico.

Given the very large data gaps on areal extent, vertical distribution, and degree of pore occupancy of gas hydrates in the Gulf of Mexico, estimates of gas contained in hydrates and as free gas beneath hydrates are speculative. However, reasonable assumptions of these parameters permit estimates of in-place gas volumes at standard conditions: deep central Gulf of Mexico, 1,500 TCF (4.4×10^{13} m³); northwestern margin, 1,200 TCF (3.5×10^{13} m³); western margin, 1,200 TCF (3.5×10^{13} m³).

Gas possibly trapped beneath gas hydrates is calculated only for the 5,000 km² area covered by BSRs. Estimates range from 7 to 350 TCF (2×10^{11} to 1×10^{13} m³) with a most probable figure of 100 TCF (3×10^{12} m³).

Several aspects of the geology of the western Gulf of Mexico are well suited to gas hydrate formation and stabilization. Sediment influx from the Mississippi, Rio Grande, and numerous Mexican rivers imparted adequate amounts of terrestrial, gas-prone organic matter to the deeper parts of the Gulf. Rapid sedimentation, especially during the late Tertiary and the Quaternary, enhanced preservation of the organic matter. Structural disturbance in the form of diapirism, growth and thrust faulting, and decollement folding resulted in migrational conduits from deep thermogenic source beds and zones of efficient microbial methanogenesis to the cool sediments of the gas hydrate stability zone.

COLOMBIA BASIN

The interrelationships of geologic environments and gas hydrates were investigated in the southwestern Caribbean region. Diverse geologic features and abundant indirect evidence of gas hydrates make the Colombia Basin an ideal region for gas hydrate study.

The study region is located north of Panama and Colombia and southwest of Hispanola (Figure 7). The Colombia Basin is bounded to the south by the continental margins of Panama and Colombia. The Nicaragua Rise, South Haitian Borderland, and Beata Ridge border the Colombia Basin to the northwest, north, and east respectively. These bordering uplifts were included in the study region to better evaluate the Colombia Basin itself.

The Colombia Basin consists of deep abyssal plains and two large submarine fans. The continental margins are structurally deformed and resemble convergent plate boundaries. The Nicaragua Rise and Beata Ridge are block-faulted, uplifted terranes.

Shallow coring has indicated that the fan, abyssal plain, and continental margin are covered with turbidites and hemipelagic sediments. Pelagic carbonates cover the Nicaragua Rise, Beata Ridge, and small uplifts on the abyssal plain. Cores of deeply buried sediments have been recovered only from the pelagic areas, but suggest that the turbidites and hemipelagic sediments which cover most of the study region are rich in organic matter and may have high gas generative potential. Seismic stratigraphic interpretations have confirmed the great extent of these possibly organic-rich turbidites.

The study region has experienced considerable structural deformation which has continued to the present. The deformed belts which make up the continental margins show compressive features in seismic profiles, but must also have sustained some strike-slip motion.

In the Colombia Basin study region, gas hydrates are strongly indicated by unusually distinct BSRs in deformed sediments in the lower continental slopes offshore of Panama and Colombia. Selection of this study region was based on two seismic lines described by Shipley et al. in 1979. Subsequently these lines were published by Lu and McMillen (1983). Three additional seismic lines from the study region with BSRs identified were published by Ladd et al. (1984). In the course of this study we have greatly enlarged the collection of seismic lines showing BSRs. From the five lines with BSRs known at the outset of this study, at least 23 seismic lines with probable BSRs are now identified (Figure 7). Furthermore, we would suspect that most, if not all, of the five additional seismic lines crossing the marginal deformed belts from the CT1 series, which are still held as proprietary by the University of Texas Institute for Geophysics will show BSRs. One of the significant findings of this regional study is a BSR in undeformed abyssal plain sediments. This tends to strengthen our inference of a thick, areally extensive gas hydrate deposit in a similar abyssal setting in the western Gulf of Mexico.

The wealth of BSRs in this region has allowed detailed comparisons of the depths of occurrence of BSRs with theoretical models. These comparisons suggest that changes in geothermal gradient and/or pressure gradient exists across the convergent margins. These findings may eventually be of use in elucidating the differing tectonic regimes present along the marginal deformed belt, once control is obtained by drilling.

Geothermal gradients over the continental margins vary from 3.1 to 5.1° C/100 m based on the subbottom depths of BSRs and reported bottom water temperatures. Gas hydrates composed of biogenic methane should be stable to a minimum water depth of about 580 m. Gas hydrates composed of typical thermogenic natural gas should be stable under water deeper than 300 - 400 m in the Colombia Basin.

Deeply buried rocks of the abyssal plain near the continental margin of Colombia are thermally mature with respect to oil and gas generation. If migration paths exist, the gas hydrates of the marginal deformed belt offshore of Colombia

may contain thermogenic gas. Sediments offshore of Panama appear to be too thin to have achieved thermal maturity.

Of the many geological environments examined in the Colombia Basin study region, only the abyssal plain and deformed margin hold high potential for economic gas hydrate deposits. Nicaragua Rise and Beata Ridge have neither seismic nor drilling evidence of gas generative potential necessary for gas hydrate formation. The abyssal plain turbidites have proven high gas generation potential. The lack of sea floor relief over most of the abyssal plain precludes detection of seismic evidence of gas hydrates. The marginal deformed belt displays widespread seismic evidence of gas hydrates, but little direct evidence of gas generative potential of the sediments exists. The sediments in the gas hydrate stability zone of the deformed continental margin are mainly accreted and deformed abyssal turbidites which by analogy should have gas generative potential. Additionally, the sediment pile beneath the deformed margin is very thick. If the accretionary process has been operating for a sufficiently long time, these thick marginal sections may have attained thermal maturity and thus be capable of augmenting shallow biogenic gas in the hydrate stability zone with migrated thermogenic gas. The compressional features of the marginal deformed belts have resulted in substantial sea floor relief which creates very favorable conditions for relief at the base of the gas hydrate stability zone. Thus large anticlinal traps beneath an impermeable gas hydrate interval may be formed in the accretionary complexes of the marginal deformed belts. This possibility of unconventionally trapped free gas combined with the extensive areal continuity of BSRs, relatively shallow water depths (1,600 - 3,800 m), and the proximity to onshore production facilities indicate that the marginal deformed belts offshore of Panama and Colombia is the most favorable area of the study region for eventual economic development of the gas hydrate resource.

The Colombia Basin appears to be a major gas hydrate province which can serve as a model for the assessment of less well studied regions. The abundant seismic evidence can be linked with the extreme gassiness of terrigenous sediments from DSDP Site 154 to suggest that gas hydrates may be widespread. The available seismic coverage over the margins is considerable. The proportion of seismic lines which display BSRs is large. The occurrence of BSRs appears to be more widespread in the Colombia Basin study region than at any other convergent margin currently being investigated. Whereas large quantities of gas hydrates have been identified in areas of the Middle America Trench which are devoid of BSRs, Colombia Basin margin seismic lines show demonstrably extensive BSRs. Although verification must await drilling, it is possible that the high degree of BSR development in the Colombia Basin study region indicates that gas is migrating to the hydrate stability zone from below. Other convergent margins with fewer BSRs, but with other evidence of gas hydrates, may represent scenarios wherein the gas becomes trapped in hydrates as it is generated without significant migration.

PANAMA BASIN

Selection of the Panama Basin for gas hydrate study was based on information by Shipley et al. (1979) who reported the presence of bottom simulating

reflectors (BSRs) on the Pacific continental margin of Panama (Figure 8). Most of the available seismic surveys of the Panama Basin utilized single channel methods which do not resolve the BSRs as well as the multichannel seismic lines discussed by Shipley et al. (1979). Basin analysis focused on factors controlling gas hydrates enabled us to suggest that BSRs may be quite common in the areas of the Pacific continental slopes and upper rises of Panama, Colombia, and Ecuador.

The coverage of the Panama Basin with drilled wells is poor, imposing further constraints on the study. Nonetheless, the analysis of presently available data allowed the formation of the following conclusions and gas hydrate stability in the Panama Basin:

- Thickness of sediments in the Panama Basin ranges from 0 to over 2,000 m. In most parts of the basin the thickness of sedimentary sequences does not exceed 600 m.
- Sedimentary sequences of DSDP sites display great deal of similarity. Pelagic carbonate sediment prevails. More terrigenous material can be expected in areas of continental shelf and slopes.
- While the typical value of heat flow in the Panama Basin is high ($>2\text{HFU}$), the geothermal regimes within the basin are diverse. The geothermal gradients vary from $2^\circ\text{C}/100\text{m}$ to $5^\circ\text{C}/100\text{m}$.
- Bottom sea temperatures in Eastern Panama Basin display uniform average values of 4.5°C at water depths below 1,000 m.
- The entire Panama Basin is characterized by unusually high biological production which is a favorable factor for biogenic methane generation.
- The conditions needed for maintenance of reducing conditions are probably reached only in the areas where the highest biological production is combined with higher rates of sedimentation (exceeding $45\text{-}50\text{ m/m.y.}$). Such conditions are likely to exist in continental slopes and in the vicinity of elevated areas (ridges).
- Due to the relatively low temperatures to which sediments are exposed, most of the preserved organic matter is immature for thermal hydrocarbon generation. Biogenic methane generation is prevalent in supplying hydrocarbon gas for the gas hydrate.
- The identified BSRs represent only a fraction of possibly existing anomalous reflectors related to gas hydrates in the continental margins of Panama, Colombia and Ecuador.
- The analysis of identified BSRs suggests they represent the base of the gas hydrate zone.
- Estimated resources of hydrocarbon gas accumulated in the hypothetical hydrate zone of the continental margin within the Panama Basin show value of 6.8 TCF ($2 \times 10^{11}\text{ m}^3$) per 1 m of thickness of sediment saturated with gas hydrates. In the maximum possible 300 m thick hydrate zone the gas resource can amount to 2,040 TCF ($6 \times 10^{13}\text{ m}^3$).

MIDDLE AMERICA TRENCH

Geological factors controlling the formation, stability, and distribution of gas hydrates were investigated by basin analysis of the Middle America Trench region. Geological, geophysical, and geochemical data from the region were assembled and critically evaluated to develop consistent interpretations of the relationships of

geological environments and gas hydrates. Preliminary estimates of the regional extent of the gas hydrates were derived.

The Middle America Trench study region comprises the continental shelf, continental slope, trench, and abyssal plain offshore of the Pacific coasts of Mexico, Guatemala, El Salvador, Honduras, Nicaragua, and Costa Rica. Subduction of the Pacific Ocean crust beneath Mexico and Central America has formed Middle America Trench and controlled the topography, structure, and sedimentation patterns of the study region.

The Middle America Trench is a product of the interaction of four lithospheric plates. The oceanic Cocos and Rivera Plates which are separated by a transform boundary are subducting beneath the North America and Caribbean Plates which are also in strike-slip contact. The complex interaction has produced strikingly different geological structure and topography of the trench and continental margins north and south of the Cocos-North America-Caribbean triple junction.

The trench north of the triple junction offshore of Mexico truncates onshore structures obliquely, producing a relatively shallow trench with a compressionally deformed continental slope and a very narrow continental shelf. The continental margin along the northern segment of the trench has been actively growing since Miocene time by accretion of trench sediments scraped from the subducting plate to the foot of the continental slope.

South of the triple junction, the trench parallels onshore geological features and is relatively deep. The continental slope is more gently dipping and regular. A broad continental shelf is underlain by a deep forearc basin. Although the structure of the continental margin south of the triple junction is well documented only in one area, it appears to be very different from the structure of the margin to the north. The continental slope is composed of metamorphic and ultramafic igneous rocks overlain by a thin veneer of sediments. In contrast to the northern segment, trench sediments are not accreted to the margin, but are entirely subducted.

Continental slope sediments in the study region are principally organic-rich mud and mudstone with abundant volcanic ash. Limestones and permeable beds of coarse-grained ash and sand from trench and canyon floor settings are minor constituents of the sedimentary sections.

Abundant organic matter in continental slope sediments indicates a high potential for microbial methane generation. The thin accumulations of sediments preclude thermal maturation of the organic matter. Sediments which have been subducted or accreted to the margin may be thermally mature as may sediments in the deep forearc basins landward of the southern segment of the trench. Hydrocarbons recovered from metamorphic basement rocks offshore of Guatemala may have been generated from any of these sources or by abiogenic processes.

Gas hydrates were identified from sediments cored from the continental slope of the Middle America Trench. Hydrate presence was confirmed by the quantity of gas released upon dissociation, low core temperatures, and physical properties. Recovered samples ranged from interstitial crystals, to fracture-filling chunks, to one core of massive gas hydrate. Based on these recoveries the Middle America Trench study region presents the greatest quantity of direct information available on the geological environments of offshore gas hydrates.

Gas hydrates were recovered at three widely separated areas of the Middle America Trench study region. The Deep Sea Drilling Project (DSDP) proved the existence of gas hydrates offshore of Acapulco, Mexico; San Jose, Guatemala; and the Nicoya Peninsula of Costa Rica. In each instance methane was the dominant component of the hydrates with minor amounts of carbon dioxide and heavier hydrocarbons. All occurrences are best categorized as resulting from bacterial methanogenesis, but unusual isotopic signatures indicate the possibility of thermogenic or abiogenic sources.

Offshore of Mexico gas hydrates were recovered as loose volcanic sediment cemented by interstitial gas hydrates. Additionally, chunks of gas hydrate were recovered from fractures. Frozen material which was not positively identified as gas hydrate was also recovered. Abundant hydrocarbon gas was found in cores with no gas hydrates.

Offshore of Costa Rica, a gas hydrate was recovered from a single drill hole. The material was associated with both fractures and volcanic ash.

Offshore of Guatemala, gas hydrates were drilled in the lower and upper continental slopes. The lower slope location produced nodular samples from a sandy volcanic ash layer. On the upper slope gas hydrates were recovered as chunks apparently formed in fractures at DSDP Sites 497 and 568. These recoveries were restricted to 360 and 405 m depths respectively, even though geochemistry suggested that hydrates should have been found at shallower intervals. At Site 570, a full range of hydrate types, including interstitial, fracture-filling, and massive gas hydrates were recovered.

Seismic evidence indicates that gas hydrates are probably widespread throughout the study region. Bottom simulating reflectors (BSRs) are found in high quality seismic lines of the continental slope. Limited seismic coverage restricts mapping of BSR distribution to a few small areas. However, parts of the study region between areas surveyed probably also have abundant BSRs. A previously unreported area of abundant BSRs offshore of Mexico was discovered in this study.

Decreases in the chloride content and increases in O_2 content of pore water with depth is evident at some drill holes in the Middle America Trench study region. This pattern has been attributed to gas hydrate presence (Hesse and Harrison, 1981; Hesse et al., 1985). Detailed analysis of the data suggests that only a portion of the observed chemical anomalies can be attributed to gas hydrate dissociation.

The massive gas hydrate recovered at Site 570 may require unusual geological conditions to form. One published model of massive gas hydrate formation involves trapping methane by a lithological seal concurrent with rapid Tertiary uplift (Kvenvolden et al., 1984; Kvenvolden and Claypool, 1985). Another theory holds that massive gas hydrate formed in open space and permeable fractures in and adjacent to a fault (Mathews and von Huene, 1985). The available geological and geochemical evidence supports the fault-controlled model.

Presence of permeable lithologies and abundant hydrocarbon supplies appear to control gas hydrate occurrences in the Middle America Trench study region. Sedimentation rate has no direct influence. There is evidence that structural deformation may enhance gas hydrate formation, but no clear link can be proven.

Estimates of gas resources in gas hydrates in the study region are speculative. Seismic evidence indicates widespread gas hydrate layers at the base of the gas hydrate stability zone. Lack of penetration of the base of the stability zone precludes accurate estimation of the degree of gas hydrate development. Drilling above the base of the hydrate stability zone indicates that gas hydrates do not occur regularly. However, the abundant gas hydrates at Site 570 indicate that some areas of the study region have thicknesses and concentrations of gas hydrates that may have economic value in the future.

NORTHERN CALIFORNIA

Northern offshore of California is one of twenty-four localities worldwide with presumed gas hydrate occurrence. The evidence for gas hydrate presence in this region is based entirely on seismic data which revealed widespread bottom simulating reflectors (BSRs) underlying the continental margin of north of the Mendocino Fracture Zone (Field and Kvenvolden, 1985).

Among the geological factors which are directly responsible for presence or absence of the gas hydrates, the following were reviewed:

- o tectonic position of the region
- o sedimentary environments
- o structural deformation
- o shale diapirism
- o hydrocarbon generation and migration These factors determine three major conditions necessary for gas hydrate occurrence:
- o thermal regime in the hydrate formation zone (HFZ)
- o pressure conditions
- o hydrocarbon gas supply to the HFZ

Major regional tectonic differences between the areas north and south of the Mendocino Fracture Zone seem to favor gas hydrate formation in the north while precluding hydrate occurrence south of the fracture zone. The Mendocino Fracture Zone is the northwestern extension of the San Andreas fault. It divides the California continental margin into two segments: one characterized by active subduction of the Gorda plate, the other by right-lateral movement of the Pacific plate. This feature appears to have a direct bearing on the different geothermal regimes in the two areas. As has been shown in the model developed by Lachenbruch and Sass (1980), heat flow is lower in continental margins with active subduction. Other geologic factors seem to be fairly uniform throughout the area, and play only a modifying role in gas hydrate distribution.

Possible gas resources in the area north of the Mendocino Fracture Zone were assessed to be 1 TCF per 1 m of hydrate-bearing sediment thickness; the average thickness of the HFZ is approximately 200 m.

BLACK SEA

The Black Sea is located in extreme southeastern Europe between two prominent Alpien mountain ranges, the Crimea and the Caucasus ranges on the north and the Pontic Mountains on the south. The total area of this, the world's largest enclosed marine basin is approximately 432,000 km².

The Black Sea region is one of the few locations worldwide where the presence of gas hydrates was directly confirmed in recovered cores (Yefremova and Zhizhchenko, 1972). According to these authors, gas hydrates were found at the Black Sea station 116, at 6.4 to 8.1 m subbottom depth. The water depth at the station was reported to be 1,950 m. Unfortunately, neither the precise location of the site nor more geological or geochemical data were published. Makogon (1974) also wrote about "frost-like hydrate crystals observed on broken surfaces of cores from the Black Sea.

In the mid-1970s, a variety of investigations were conducted in the Black Sea during cruises of Atlantis II (1974) and Glomar Challenger (1975). Although none of these investigations was specifically designed for gas hydrate research, they provided important data related to geological environments in the basin. Knowledge of these conditions is crucial for the delineation of the areas favorable for gas hydrate formation, as well as the areas where gas hydrate occurrence cannot be anticipated. Analysis of the Black Sea basin strongly suggests that where temperatures and pressures are within the gas hydrate stability range, hydrate distribution is most likely controlled by methane concentrations. Modeling indicates favorable temperature-pressure conditions in the Black Sea beneath approximately 900 m sea depth. The lower boundary of the gas hydrate stability zone may extend from 0 to 323 m subbottom depth at water column depths of 900 to 2,000 m respectively.

All geological expeditions to the Black Sea have revealed substantial amounts of hydrocarbon gases escaping from recovered cores. Geochemical analyses of these gases have invariably shown a biogenic provenance. Indeed, the Black Sea is widely known for extensive biogenic methanogenesis. Sea water stratification effectively prevents water exchange between the upper and lower layers. The lack of water-mixing processes establishes a thick chemical reducing zone which enables the sinking organic matter to be preserved to a significant degree. The well preserved organic matter results in high rates of microbial methanogenesis. The typical succession of bacterial environments described by Claypool and Kaplan (1974) is easily discernible in the water and sediment column of the Black Sea. Reducing conditions usually occur at 150 to 200 m water depth. It has been estimated that the main source of the organic matter supplied to the Black Sea (90 to 95%) is unicellular algae. Only 10% of the total organic matter is delivered to the basin in detrital form by rivers. Yet, despite very favorable conditions for biogenic methanogenesis, the pore water in the nearbottom sediments of the western Black Sea was found largely undersaturated with methane. Assuming the accuracy of the measurements of methane content in sediments presented by Ivanov (1984), average methane concentrations are far below those needed for gas hydrate generation and stabilization (Claypool and Kaplan, 1974). Therefore, gas hydrate formation in the Black Sea region is conceivable in those

areas of higher concentrations of methane, which perhaps coincides with rock formations with increased porosity and permeability. Such areas probably are patchy in character throughout the basin. Identification of hydrate-prone areas requires more data on sedimentation and lithology of the sedimentary units of the basin.

Bottom simulating reflectors (BSRs) commonly used to identify lower boundaries of the gas hydrate stability zone were not conclusively identified in the Black Sea. This is largely due to sediment stratification being predominantly parallel to the sea floor throughout the entire basin.

With the assumption that the zone favorable for gas hydrates in the Black Sea extends over 1% of the area delineated by the 900 m isobath, the estimated resources of hydrocarbon gas in gas hydrates amounts to $2 \times 10^{10} \text{ m}^3$ (0.7 TCF) per 1 m of hydrated sediment thickness.

BERING SEA AND ALEUTIAN TRENCH

Four major areas with suggested presence of gas hydrates were examined in this study. Two of these areas, the Navarin and the Norton basins, are located within the Bering Sea shelf, whereas the remaining two areas of the Atka Basin in the central Aleutian Trench system and eastern Aleutian Trench represent a huge region of the Aleutian Trench-Arch system. All four areas are geologically diverse and complex.

Thorough study of publicly available literature and seismic data enabled us to identify the gas hydrate-related BSRs only in the upper and middle continental slopes in the west flanks of the Navarin Basin and in the eastern Aleutian Trench-Arc sedimentary complex. Bottom simulating reflectors are often difficult to discern, particularly under the structural conditions of the Navarin and Norton basins. The identified BSRs are mostly relatively weak and discontinuous reflectors. Under thermal and pressure conditions favorable for gas hydrate formation, the relative scarcity of the BSRs can be attributed to insufficient gas supply to the potential gas hydrate zone. Basin analysis suggests limited biogenic hydrocarbon generation in the four areas studied. Migration of thermogenic gases is probably limited due to the widespread diagenetic processes in diatomaceous strata, which resulted in the formation of low-permeability diagenetic horizons. The gas hydrate-related BSRs are located in the areas of increased biogenic methanogenesis, with nearby faults possibly acting as the pathways for thermogenic hydrocarbons.

The potential of gas hydrates in the Norton Basin, reported by Kvenvolden and Barnard (1983) from personal communication with Mousseau, is questionable. Anomalous seismic reflectors caused by gas hydrates would be extremely difficult to recognize in the area due to structural conditions. Shallow water, relatively high water temperature, high geothermal gradients, and overall low concentration of methane in pore water do not create a favorable gas hydrate-hosting environment. Patchy and irregular gas hydrate zones could be potentially related to the remnants of permafrost preserved from the Pleistocene epoch and locally increased amounts of biogenically and thermogenically derived hydrocarbons.

Navarin Basin

The Navarin Basin consists of three northwest-trending subbasins with sedimentary sequences of 3,658 m to 4,573 m. The prevailing lithologies of the Navarin Basin are marine sediments deposited in middle bathyal to inner neritic zones. Faults which may act as migration paths for thermogenic hydrocarbons strike northwest and mostly occur on the continental slope and in outermost shelf areas. Rate of sedimentation in the Navarin Basin ranges from 100 to 350 m/m.y. which is favorable for biogenic methanogenesis.

The hydrocarbon gases in the sediments of Navarin Basin appear to be mostly of biogenic origin. Thermogenic hydrocarbons have also been found. The COST 1 exploratory well recorded organic carbon values from below 0.5 percent to 2 percent. Thermal maturity at the COST well was recorded at 3,600 m. Traps for migrating hydrocarbons potentially occur most likely in deeper sedimentary sections in the central part of the basin as well as in pinching-out strata of the basin western flanks of the basin.

The upper and middle continental slope appear to be the most favorable gas hydrate formation. Favorable factors include increased biogenic methanogenesis, thermogenic hydrocarbons, high rates of sedimentation, and favorable thermal and pressure conditions.

Norton Basin

Norton Basin constitutes a broad downwarped area within the northwestern Bering Sea shelf. The basin is composed of two subbasins, the St. Lawrence and Stuart, divided by the Yukon horst. Norton Basin is filled with up to 3,800 m of Tertiary sediments which outcrop on the basin flanks. Mudstones and siltstones interbedded with sandstones, shales, and coal are major lithological components of Norton Basin. The upper 200 to 300 m of sediments are horizontally stratified without any major tectonic deformations.

Total organic carbon in Norton Basin ranges from 0.8 percent to 2.0 percent. Extremely high values of TOC (reaching 50 percent) coincide with horizons containing coal. Kerogen analyses indicate the presence of Type III kerogen with poor hydrocarbon generation potential. Only the deepest parts of the basin have conditions favorable for generation of thermogenic hydrocarbon gases. The available geochemical data suggest that most of the hydrocarbons in nearbottom sediments are thermogenic. Biogenic processes are only locally active and modify the geochemical characteristics of the hydrocarbons in sediment.

Shallow sea-water column ranging from 0 to 25 m over the entire basin is unfavorable for gas hydrate formation because of excessively high sea-floor temperatures and low confining pressures.

Atka Basin

In the vicinity of DSDP Sites 186 and 187, where the seismic evidence on gas hydrate presence was found, the sedimentary pile consists mainly of silty clays and to

a lesser extent volcanic ash and silty sands. Organic carbon in sediments of the accretionary complex in the vicinity of Atka Basin averages less than 0.5 percent. The high rate of sedimentation in Atka Basin, reaching 180 m/m.y., is a favorable element in prevention of organic matter oxidation. Analyses of hydrocarbons in cored sediments show mostly biogenic origin.

Despite the favorable thermal and pressure conditions for gas hydrate formation in Atka Basin, the seismic evidence of their presence is patchy. Insufficient gas supply to the potential gas hydrate zone may be a key factor.

Eastern Aleutian Trench-Arc

Continental slope lithologies of this area consist of clayey silt and sands interbedded with volcanic ash. Total organic carbon values in the sediments range from traces to 0.8 percent, averaging 0.6 percent. The average geothermal gradient within the eastern Aleutian Trench-Arc complex is 2.8°C/100 m.

As there is no direct evidence on gas hydrate presence in the area, review of 2,500 km high resolution seismic lines did not reveal conspicuous bottom simulating reflectors (BSRs). Only weak and discontinuous BSRs were identified in the middle continental slope east of Kodiak Island.

BEAUFORT SEA

The Beaufort Sea is the southern part of the Arctic Ocean offshore of the North Slope of Alaska, and the Yukon and Mackenzie districts of Canada. The Beaufort Sea study region extends northward from the Arctic coasts of Alaska and Canada between Point Barrow, Alaska on the west to Cape Beaufort, Canada on the east. The northern boundary of the Beaufort Sea study region is at 73°N longitude. The study region comprises broad continental shelves, slopes, and rises, and the Arctic abyssal plain.

Early Cretaceous rifting and subsequent uplift of the Brooks Range in Alaska controlled the present structure and stratigraphy of the Beaufort Sea study region. Rifting and sea floor spreading in Neocomian time created the present Canada Basin and the passive continental margin of the Beaufort Sea (Grantz et al., 1979). Uplift of the Brooks range by thrusting in the Cretaceous and early Tertiary provided vast quantities of sediments which were deposited over the ancestral rifts and prograded seaward to construct the sedimentary prism underlying the present continental shelf, slope and rise of the study region. Most of the sediments underlying the Beaufort Sea study region are terrigenous clastic detritus from the uplift of the Brooks Range and associated structures. Older sedimentary rocks are limited to the nearshore areas of the continental shelf where water depths are very shallow.

The sediments of arctic Alaska and northwest Canada can be grouped into three distinctive sequences deposited in different tectonic settings. The oldest identified sedimentary rocks of the region are the pre-Mississippian Franklinian sequence. Rocks of the Franklinian sequence were deposited in a geosynclinal

environment between Cambrian and Devonian time. The Franklinian sediments were lithified, deformed, and uplifted between Late Devonian and Early Mississippian time; the resulting erosion surface has been recognized throughout the Arctic region and is termed the Arctic platform. The platform subsided slightly and remained stable from Early Mississippian time to Late Jurassic-Early Cretaceous time. Upon this surface, thick accumulations of shelf clastics and carbonates comprising the Ellesmerian sequence were deposited. Northern source for Ellesmerian sediments is assumed based on depositional features of the rocks. Uplift of the northern source of the Ellesmerian sediments in Jurassic time created an extensive regional angular unconformity in the sediments. The Ellesmerian sequence was eroded to a wedge edge and stripped from the northernmost parts of the Arctic platform which underlie the present outer continental shelf. Rifting and sea-floor spreading the source terrain to the north throughout Late Jurassic and Early Cretaceous time produce the passive margin. The uplift of the Brooks Range to the south and post-rifting subsidence to the north resulted in a reversal in the direction of sediment transport. Orogenic sediments of the Brookian sequence filled the foreland Colville Trough, overtopped the bordering Barrow Arch, and produced a northward prograding sedimentary wedge which underlies the present outer continental shelf and slope.

The composition and thermal history of the Brookian sequence strata beneath the outer continental shelf and slope of the Beaufort Sea study region is not known directly. Proximity to the huge hydrocarbon accumulations at Prudhoe Bay and in the Canadian Mackenzie Delta indicates that rich, mature sources exist in the study region. Due to a lack of deep sea test holes, thermal maturity and hydrocarbon generation potential estimates are obtained by extrapolation of onshore and nearshore trends and by thermal modeling. These analyses show that the source rocks for the Prudhoe Bay accumulation are not present over much of the study region. Tertiary sediments equivalent to the sources of the giant Mackenzie Delta oil fields require burial to 4,000 m to attain maturity. Thus, gas hydrate formation from thermogenic gas requires large scale vertical migration from source beds to the gas hydrate stability zone. Adequate organic carbon content and rapid sedimentation of the tertiary shelf and slope sediments of the Beaufort Sea indicate a good potential for microbial methanogenesis.

Abundant bottom simulating reflectors (BSRs), interpreted to mark the lower limit of the gas hydrate stability zone, occur in seismic profiles from offshore of northern Alaska. Grantz et al. (1976) reported strong bottom simulating reflectors on single channel seismic profiles from the continental slope and rise north of Alaska. Subsequent multichannel seismic sections also showed abundant BSRs beneath the slope and rise (Grantz et al., 1979). Additionally, enhanced-amplitude reflectors parallel with bedding planes were noted from the upper slope. These were also presumed to be caused by gas hydrates. Seismic evidence of gas seeps has been noted in restricted areas of the continental shelf.

The large suite of single channel and multichannel seismic lines in the Beaufort Sea study region has allowed us to map the distribution of BSRs and to analyze the relationships between BSR depths and geologic structures. Bottom simulating reflectors are common on the continental slope northwest of Prudhoe Bay which is dominated by normal faulting and mass wasting. Bottom simulating

reflectors are likewise abundant on the outer continental shelf and continental slope northeast of Prudhoe Bay with widespread shale diapirism. Just offshore of Prudhoe Bay a 50 km stretch of the continental slope is devoid of BSRs.

Seismic lines from offshore of the North Slope document that the base of the gas hydrate stability zone is a prime locus for slope failure. Both single channel and multichannel seismic lines indicate that incompetent gassy sediment beneath the gas hydrate stability zone regularly fails and the overlying hydrate-bound sediment slides downslope.

Contrary to the trend predicted by MacLeod (1982), BSRs overlying shale diapirs in the Beaufort Sea study region decrease in subbottom depth relative to BSRs elsewhere on the slope. Modeling indicates geothermal gradients over the diapirs averaging 5.5 to 6°C/100 m compared to typical slope gradients of 4.2°C/100 m. The heat flow over the shale diapirs increases regularly to the east.

Computer models and evidence from exploratory drillholes suggest that gas hydrates are present beneath subsea permafrost on the Beaufort continental shelf. Permafrost was formed in the sediments of the present continental shelf while the shelf was subaerially exposed during the Pleistocene. Subsequent inundation by the Beaufort Sea warmed the surface of the continental shelf, melting most of the permafrost. Seismic, drilling, and electromagnetic data indicate that isolated areas of subsea permafrost still exist beneath the Beaufort continental shelf. Modeling indicates that relict permafrost stabilizes hydrates in underlying sediments. Permafrost at subbottom depths greater than 200 m stabilizes methane hydrate sufficiently that gas hydrates may exist beneath the permafrost as far landward as the coastline of the Beaufort Sea. Sediment intervals having high resistivity and seismic velocity and low permeability were penetrated during exploratory drilling on the Beaufort continental shelf offshore of Canada. These unusual intervals located beneath relict permafrost released large quantities of mud gas. The gassy zones were interpreted to contain gas hydrates (Weaver and Stewart, 1983).

The abundant seismic evidence of gas hydrates in the Beaufort Sea study region is consistent with highly efficient biogenic methane formation. The seismic lines from the Beaufort Sea present the best evidence to date of substantial accumulations of free gas within traps beneath the base of the gas hydrate stability zone. The Beaufort Sea study region contains vast potential resources of gas in and beneath the widespread gas hydrate zones.

DISCUSSION

The preceding summaries of regional basin analyses document that potentially economic accumulations of gas hydrates can be formed in both active and passive margin settings. The principal requirement for gas hydrate formation in either setting is abundant methane. Passive margin sediments with high sedimentation rates and sufficient sedimentary organic carbon can generate large quantities of biogenic methane for hydrate formation. Similarly, active margin locations near a terrigenous sediment source can also have high methane generation potential due to rapid burial of adequate amounts of sedimentary organic matter. Many active margins with evidence of gas hydrate presence correspond to areas

subject to upwelling. Upwelling currents can enhance methane generation by increasing primary productivity and thus sedimentary organic carbon.

Structural deformation of the marginal sediments at both active and passive sites can enhance gas hydrate formation by providing pathways for migration of both biogenic and thermogenic gas to the shallow gas hydrate stability zone. Additionally, conventional hydrocarbon traps may initially concentrate sufficient amounts of hydrocarbons for subsequent gas hydrate formation. Based on studies completed and released thus far, diapirs of salt or shale appear to enhance gas hydrate formation along passive margins, whereas typical normal faulting appears to have little influence. On active margins, correlation of gas hydrate evidence with imbricate thrust fault zones on the continental slope is apparent. Strike-slip faulting in conjunction with pure compressional thrusting further increases the likelihood of gas hydrate presence on an active margin. The few instances of diapirism on active margins likewise show a possible connection with gas hydrates. Results from regional studies of other active margin gas hydrate locations currently in progress (Figure 1) or soon to be published address additional influences of active margin geodynamics on gas hydrate formation and stability.

In addition to the basin analysis and assessment of gas hydrates in the above mentioned regions, we have also completed a very extensive study and published a separate report entitled "Gas Hydrates in the Russian Literature" (Krasov and Ciesnik, 1986b). Our report includes a large amount of the most up-to-date information presented for the first time in English. The fact that many Russian authors consider gas hydrates as an enormous energy resource is particularly noteworthy. However, Russian research programs have been mostly oriented toward the engineering aspects of gas hydrates. Geological environments of gas hydrate formation have not been sufficiently documented. Gas hydrate occurrences in offshore areas are not often represented in Russian literature.

FUTURE WORK

To achieve the objectives of this project it is important that the systematic study of the remaining gas hydrate locations (Figure 1) be completed. The basin analysis approach and the format of our reports are very well suited to the project objectives and will be applied to the few remaining gas hydrate locations.

The final report will summarize the major findings from our regional studies and present our conclusions on the geological factors which control gas hydrate formation and stability. Based on these conclusions we will recommend further research concerning gas hydrates as:

- o Potential unconventional energy sources
- o Pathfinders for conventional oil and gas deposits

- o Aids in interpreting the thermal and tectonic history of offshore regions

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Impact on Energy Problems:

This project relates directly to the mission of the Department of Energy. Fundamental research on a major potential unconventional energy resource is clearly a principal role for the Department of Energy.

Our research indicates that the quantities of gas contained in gas hydrates worldwide are enormous. The potential gas resources in and beneath gas hydrates located in the Exclusive Economic Zone of the United States are considerable.

Much of our work involves collection and critical review of diverse types of geoscientific data. The deep water beneath which gas hydrates occur in offshore sediments dictates that generating new empirical data on gas hydrate occurrences would require large expenditures to fund a research vessel and staff. A large amount of data relevant to gas hydrate formation and stability has already been collected during the last three decades of marine exploration. To obtain and use these data to better understand the potential hydrate resource is certainly a more prudent use of scarce research funds than randomly searching the ocean-bottom sediments for gas hydrates. By consideration of the information which we have assembled on the relationships of geology and gas hydrates, future research programs involving surveying and drilling for hydrates can be planned in a more cost-effective manner. To paraphrase, it is sensible to determine what the existing information can tell us about gas hydrates before generating expensive and possibly redundant new data.

Prior to the release of our basin analysis series, knowledge of gas hydrates in offshore settings was limited to isolated literature citations of anomalous geochemical or geophysical data. By integrating the methods of basin analysis, and exhaustive review of all publically available data on each region we have often been able to tie up loose ends in the literature which may be related to gas hydrate presence. The combination of the new evidence of gas hydrate presence which we have developed at many locations, and our stress on putting all data in a geological context has allowed us to derive independent assessments of gas hydrate resource potential. For example, our findings indicate a vastly greater potential of large gas hydrate occurrences in the Gulf of Mexico (Krason et al., 1985) than previously recognized, while we have concluded that gas hydrate presence in the sediments of the Middle American Trench is a small fraction of previously published estimates.

Our work bears not only on the scale of the potential hydrate resource, but also on relevant exploration methodologies. Often workers whose experience is limited to only a certain region or scientific discipline have proposed innovative geochemical or geophysical techniques to detect hydrates. Our work has shown that many of these potentially powerful methods are limited in applicability to specific locations, or may have little to do with hydrate presence. Our review of proposed formation processes for economically-attractive massive hydrate deposits has determined that the deposits may be more common than originally believed, and that well-developed exploration strategies from conventional hydrocarbon exploration may be applicable to locating the most productive areas.

The Basin Analysis reports which we have generated in the course of our research on gas hydrates indirectly relates to the mission of the DOE to investigate conventional fossil energy sources. Our approach in studying a region to determine gas hydrate potential is very similar to that employed by energy companies in the initial phases of exploration of a frontier region. If widely distributed and announced, our reports could be used as a concise background document on the geology and hydrocarbon potential of a region, to increase the exploration efficiency of U.S. firms.

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